> plasma in the space between the target and a substrate oriented preferably parallel to the target at the opposite end of a sputtering chamber. The space in which the secondary plasma is generated is bounded by electrically conductive structure that is electrically floating and presents a high impedance to the RF source. This structure is further connected through a low pass filter which provides a low impedance DC path to ground or to some other potential.

(Smolanoff, col. 3, lines 51-64). Therefore, Smolanoff teaches that a secondary plasma created by RF coils is created between the target and the substrate, in addition to the plasma created at the target. Deposition is performed by exposing the substrate to the secondary plasma, not the main plasma adjacent to the sputtering target. Therefore, Smolanoff fails to teach that "a plasma is created by application of the pulsed DC power to the target; and wherein the film is deposited by exposure of the substrate to the plasma," as is recited in claim 1, or "applying pulsed DC power to the target through a filter to create a plasma wherein the substrate is exposed to the plasma to deposit the film," as is recited in claim 20.

Furthermore, although Smolanoff states that the target "can be energized with a DC or pulsed DC source to energize a main plasma," (Smolanoff, col. 3, lines 53-45), Applicants contend that Smolanoff has not enabled utilization of a pulsed DC power source in an environment with RF energy. Smolanoff's may teach an RF filter between the DC source and the target, but provides no description of that filter. It is Applicants' experience that the exposure of a pulsed DC power supply to an RF environment often leads to destruction of the pulsed DC power supply. Smolanoff has enabled utilization of a DC power supply, but not a pulsed DC power supply.

As discussed above, claims 1 and 20 are allowable over Smolanoff. Claims 8 and 10-13, which depend from claim 1, are therefore allowable over Smolanoff for at least the same reasons as is claim 1.

## Claim Rejections under 35 U.S.C. § 103

### *Claims 2-6*

The Examiner has rejected claims 2-6 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of U.S. Patent No. 5,755,938 ("Fukui"). As discussed above, claim 1 is allowable over Smolanoff. Fukui does not cure the defects in the teachings of Smolanoff. Therefore, claims 2-6, which depend from claim 1, are allowable for at least the same reasons as is claim 1.

### *Claims 7 and 9*

The Examiner has further rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Le et al. (2003/0077914) ("Le"). As discussed above, claim 1 is allowable over Smolanoff. Le does not cure the defects in the teachings of Smolanoff. Therefore, claims 7 and 9, which depend from claim 1, are allowable for at least the same reasons as is claim 1.

## Allowable Subject Matter

The Examiner has indicated that claims 14 and 21-24 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. Claims 14 and 21, from which claims 22-24 depend, have been rewritten as suggested by the Examiner.

## Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully request reconsideration and reexamination of this application and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: Linda J. Thayer for 45,681
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 758329165 US**

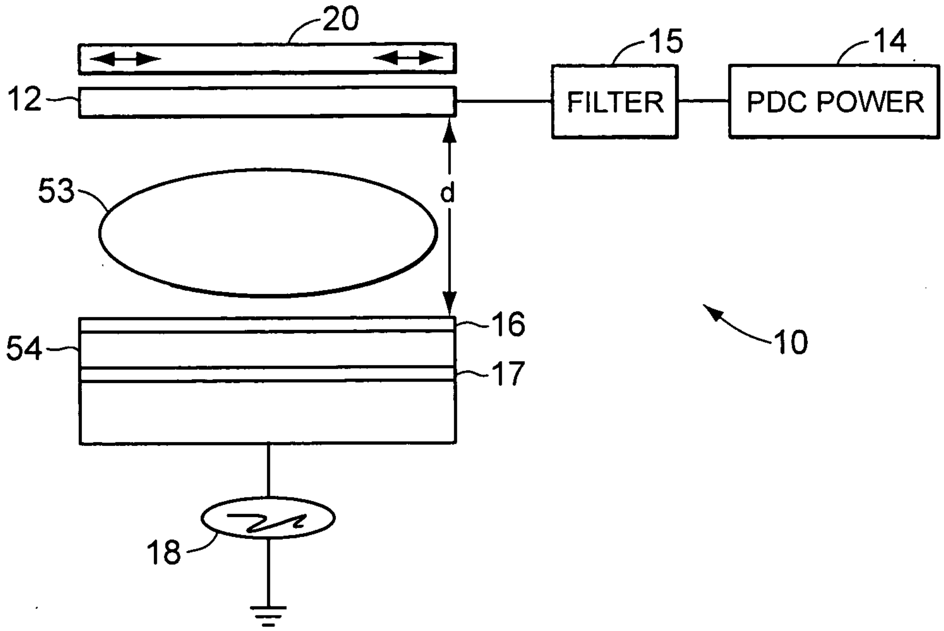
20
15
14
12
FILTER
PDC POWER
53
d
16
54
17
10
18

FIG. 1A

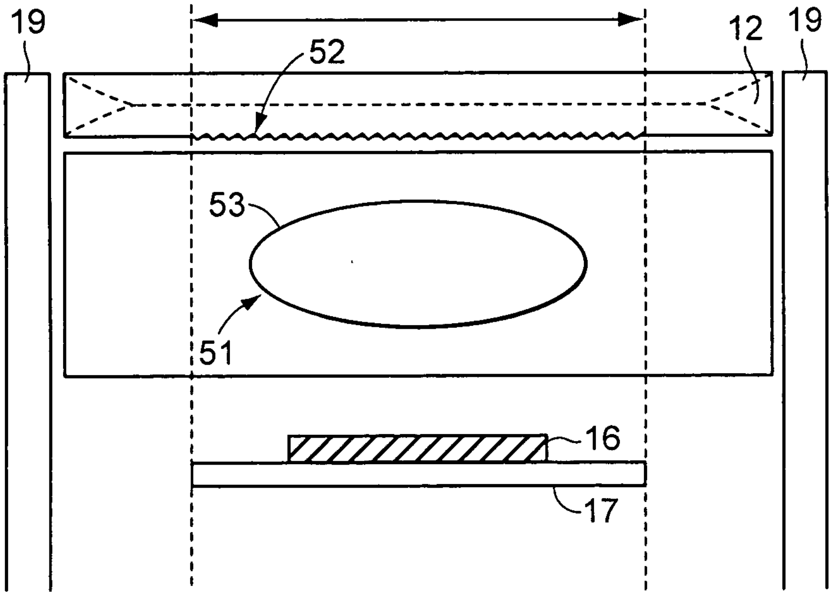
19
12
19
52
53
51
16
17

FIG. 1B

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

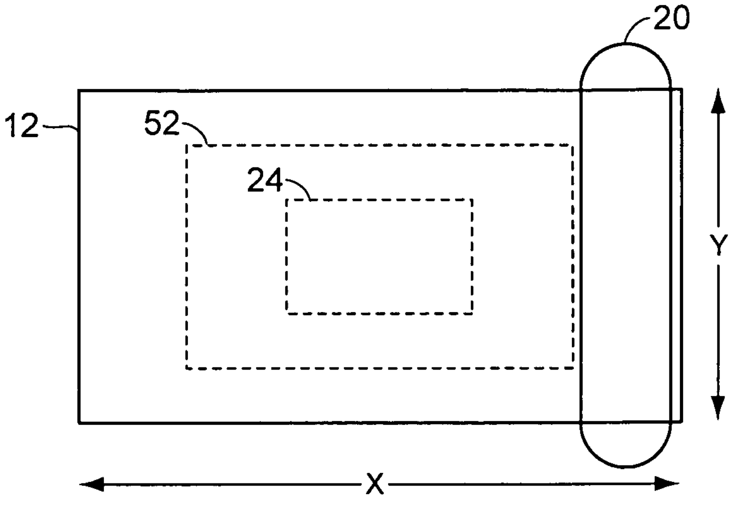

FIG. 2

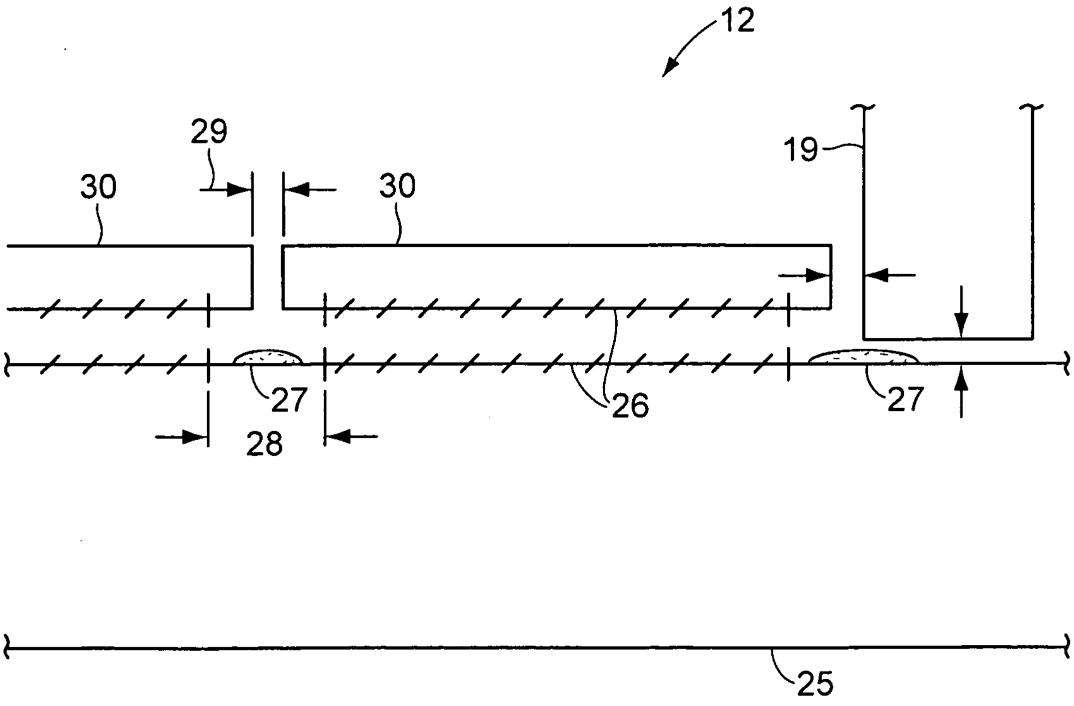

FIG. 3

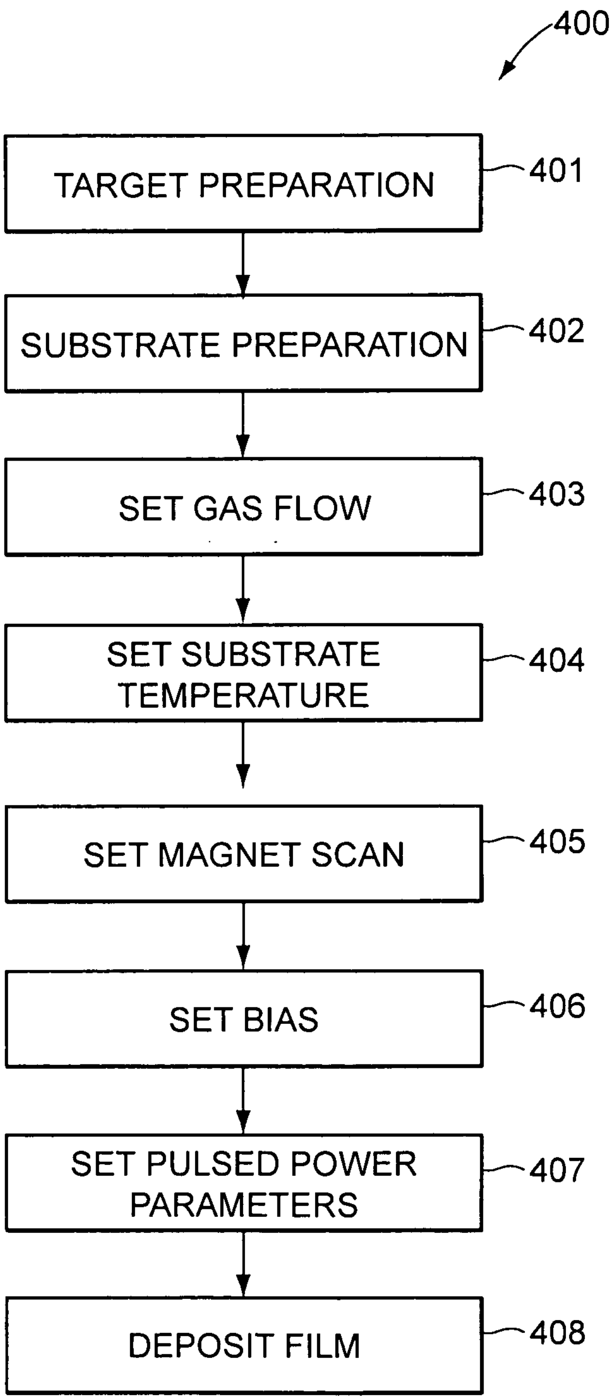
400
TARGET PREPARATION
401
SUBSTRATE PREPARATION
402
SET GAS FLOW
403
SET SUBSTRATE TEMPERATURE
404
SET MAGNET SCAN
405
SET BIAS
406
SET PULSED POWER PARAMETERS
407
DEPOSIT FILM
408

FIG. 4

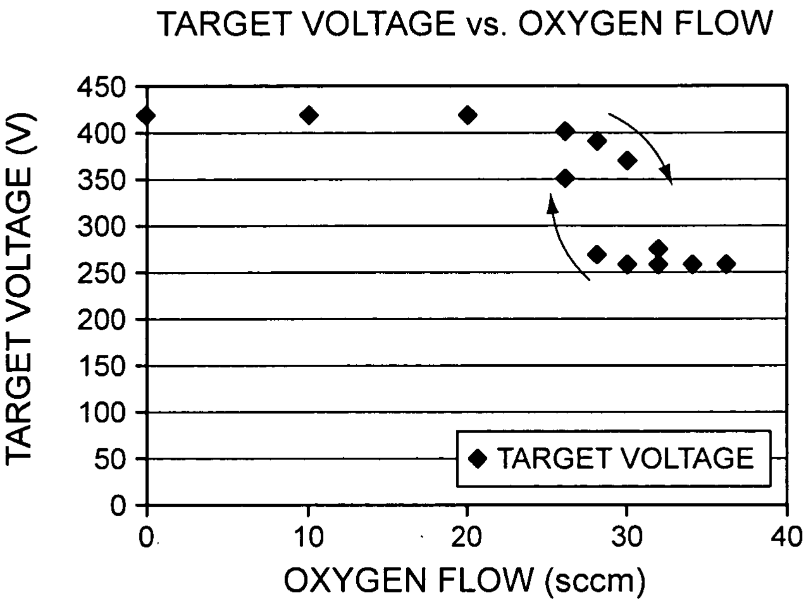
TARGET VOLTAGE vs. OXYGEN FLOW
TARGET VOLTAGE (V)
450
400
350
300
250
200
150
100
50
0
0
10
20
30
40
OXYGEN FLOW (sccm)
◆ TARGET VOLTAGE

FIG. 5

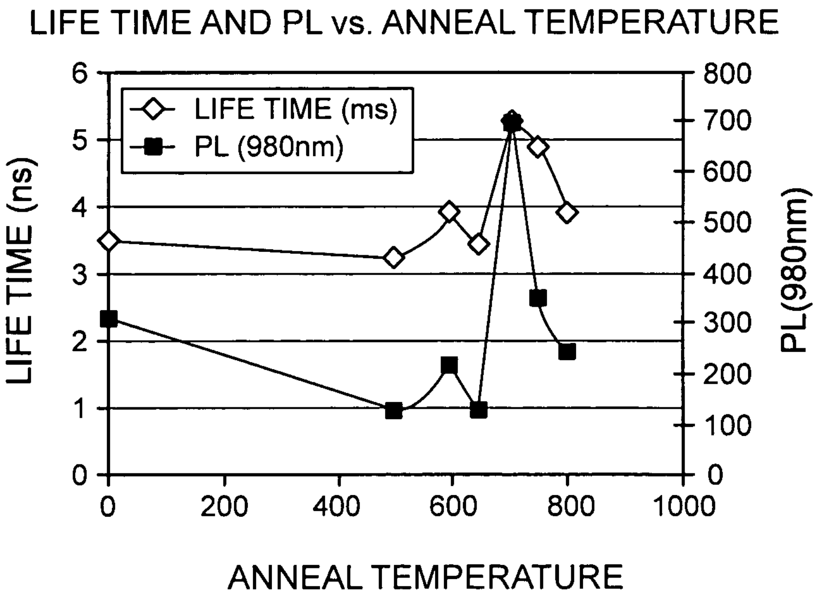
LIFE TIME AND PL vs. ANNEAL TEMPERATURE
LIFE TIME (ns)
6
5
4
3
2
1
0
PL(980nm)
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
ANNEAL TEMPERATURE
◇ LIFE TIME (ms)
■ PL (980nm)

FIG. 6

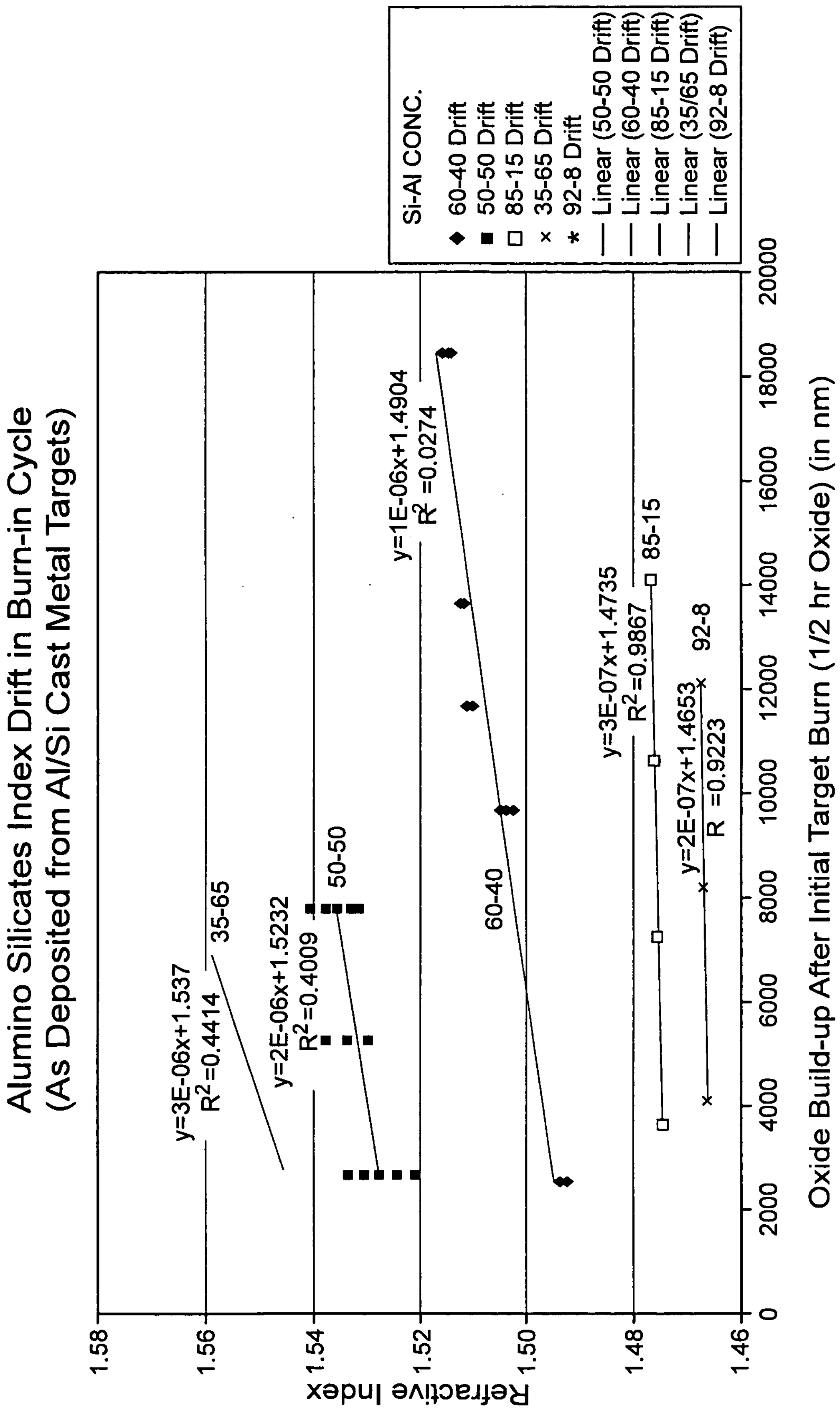
Alumino Silicates Index Drift in Burn-in Cycle
(As Deposited from Al/Si Cast Metal Targets)
Refractive Index
1.58
1.56
1.54
1.52
1.50
1.48
1.46
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
Oxide Build-up After Initial Target Burn (1/2 hr Oxide) (in nm)
y=3E-06x+1.537
$R^2$=0.4414
35-65
y=2E-06x+1.5232
$R^2$=0.4009
50-50
60-40
y=1E-06x+1.4904
$R^2$ =0.0274
y=3E-07x+1.4735
$R^2$=0.9867
85-15
y=2E-07x+1.4653
R =0.9223
92-8
Si-Al CONC.
◆ 60-40 Drift
■ 50-50 Drift
□ 85-15 Drift
× 35-65 Drift
* 92-8 Drift
— Linear (50-50 Drift)
— Linear (60-40 Drift)
— Linear (85-15 Drift)
— Linear (35/65 Drift)
— Linear (92-8 Drift)

FIG. 7

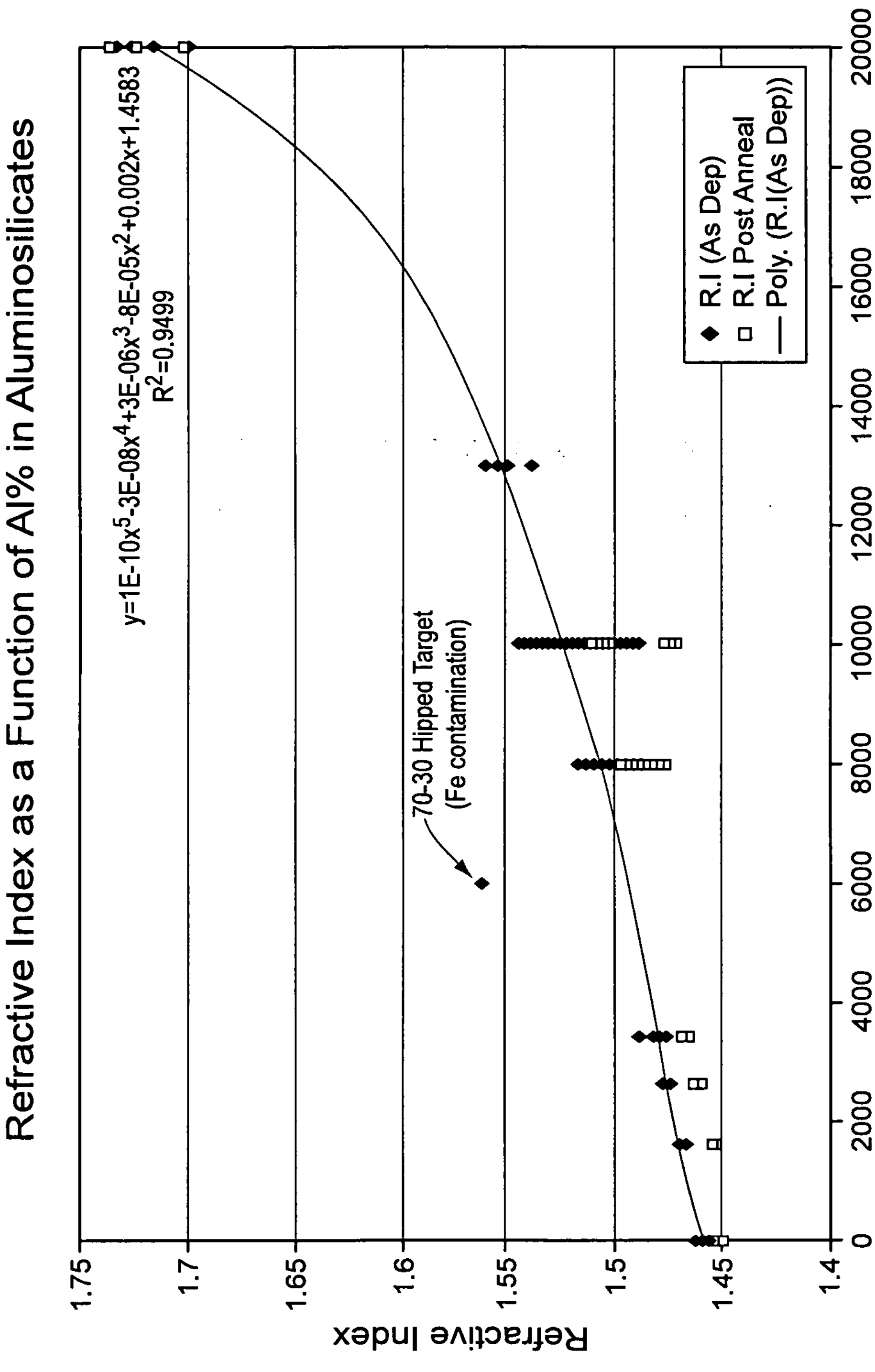
Refractive Index as a Function of Al% in Aluminosilicates
y=1E-10x^5-3E-08x^4+3E-06x^3-8E-05x^2+0.002x+1.4583
R^2=0.9499
70-30 Hipped Target
(Fe contamination)
◆ R.I (As Dep)
□ R.I Post Anneal
— Poly. (R.I(As Dep))
Refractive Index
1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000

FIG. 8

| **Material (Er/Yb/Al/Si)** | **Expected index (Post anneal)** | **Actual index (Post anneal)** | **Process Conditions (Annealed 725c 30min)** |
|---|---|---|---|
| 0.8/0.8/41.4/57 | 1.506 | 1.510 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 1.6/0.5/49/48.9 | 1.526 | 1.528 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/8/92 | 1.452 | 1.456-1.459 | 4.5KW, Ar-30-60,02-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/40/60 | 1.504 | 1.486-1.501 | 3.0-4.5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/50/50 | 1.520 | 1.491-1.503 | 4.0-5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/65/35 | 1.544 | 1.545-1.560 | 4.5-5.5KW, Ar-75-90,0285-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/30/70 | 1.490 | 1.562 (high Fe content) | 5.0KW, Ar-75,02-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 1.5/0/48.5/50 | 1.523 | 1.509-1.513 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |

FIG. 9

| Bias Power (Watts) | DC Power (KW) | Pulsing Freq (KHz) | Reverse Time (µs) | Ar Flow (sccms) | O2 Flow (sccms) | Wafer Position | Target To Wafer Spacing (mm) | Refractive Index Avg (@1550nm) | Refractive Index STD (@1550nm) | Dep Rate (um/Hr) |
|---|---|---|---|---|---|---|---|---|---|---|
| 150 | 4.5 | 200 | 2.2 | 100 | 100 | 1 | 55 | 1.461508 | 0.000535 | 0.957654 |
| 150 | 4.5 | 200 | 2.2 | 100 | 100 | 2 | 55 | 1.462329 | 0.000376 | 0.962581 |
| 400 | 4.5 | 200 | 2.2 | 100 | 100 | 1 | 55 | 1.462774 | 0.000103 | 0.814007 |
| 400 | 4.5 | 200 | 2.2 | 100 | 100 | 2 | 55 | 1.463583 | 0.000095 | 0.824566 |

FIG. 10

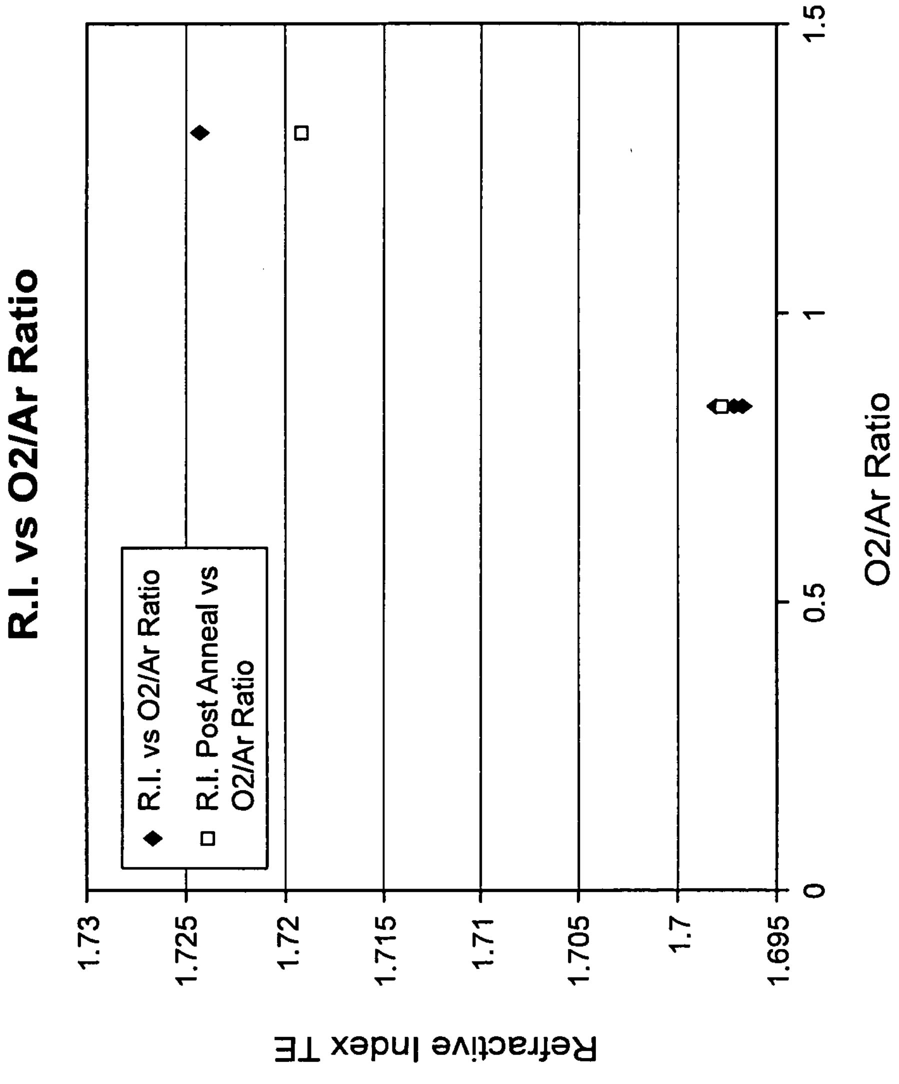
R.I. vs O2/Ar Ratio
◆ R.I. vs O2/Ar Ratio
□ R.I. Post Anneal vs O2/Ar Ratio
Refractive Index TE
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
0.5
1
1.5
O2/Ar Ratio

FIG. 11

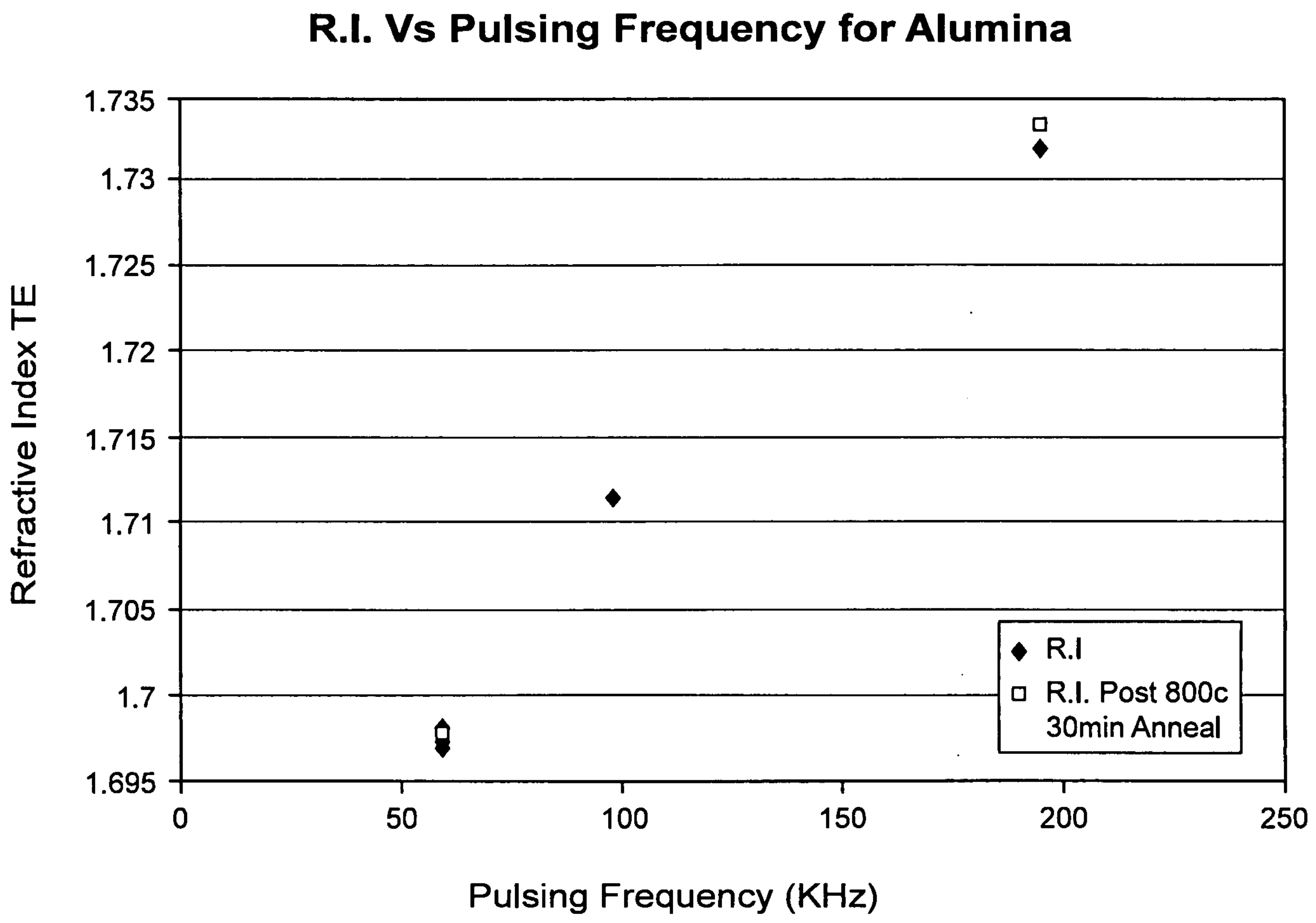
R.I. Vs Pulsing Frequency for Alumina
Refractive Index TE
1.735
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
50
100
150
200
250
Pulsing Frequency (KHz)
◆ R.I
□ R.I. Post 800c 30min Anneal

FIG. 12

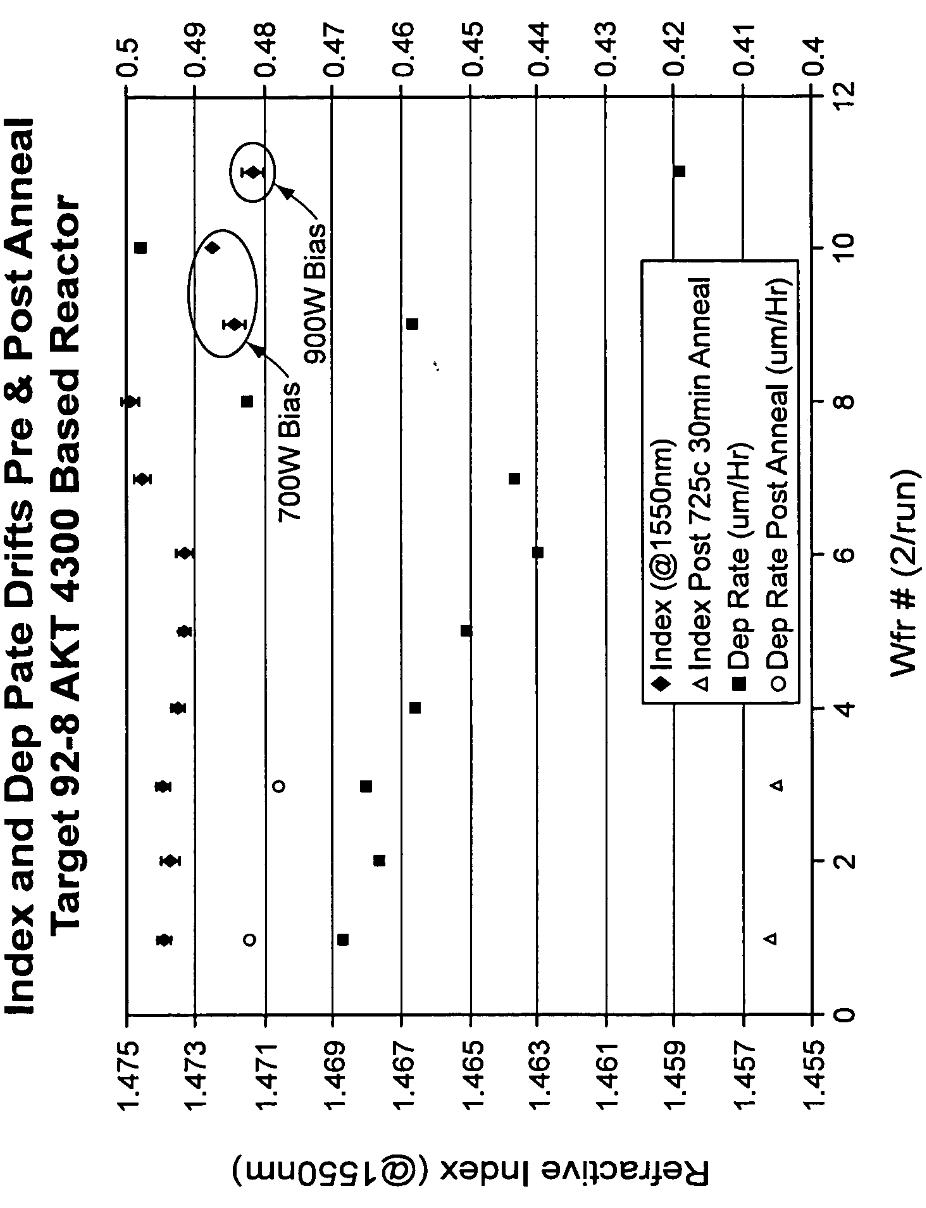
Index and Dep Pate Drifts Pre & Post Anneal
Target 92-8 AKT 4300 Based Reactor
Refractive Index (@1550nm)
1.475
1.473
1.471
1.469
1.467
1.465
1.463
1.461
1.459
1.457
1.455
0.5
0.49
0.48
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.4
0
2
4
6
8
10
12
Wfr # (2/run)
700W Bias
900W Bias
◆ Index (@1550nm)
△ Index Post 725c 30min Anneal
■ Dep Rate (um/Hr)
○ Dep Rate Post Anneal (um/Hr)

FIG. 13

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

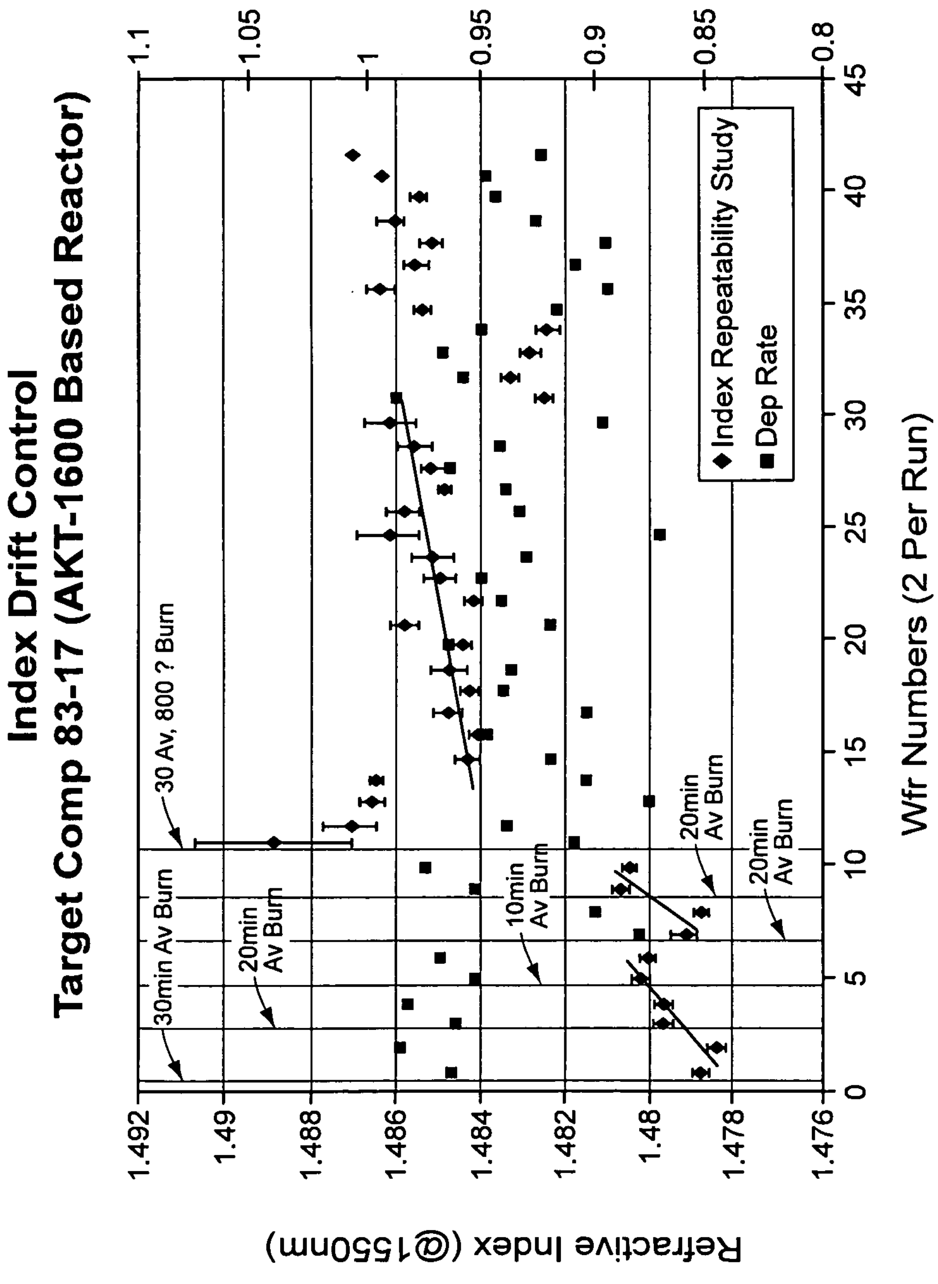

FIG. 14

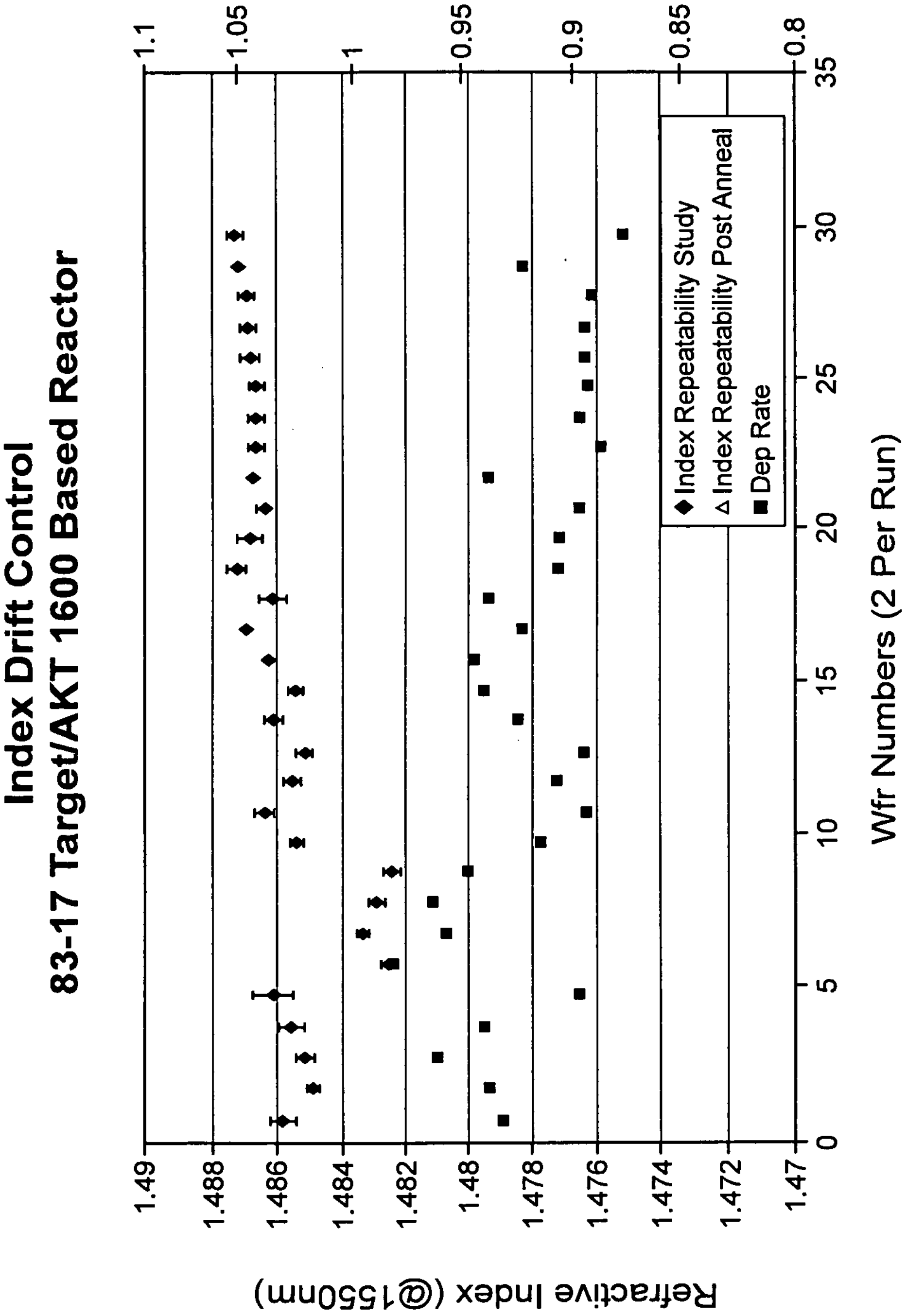
Index Drift Control
83-17 Target/AKT 1600 Based Reactor
Refractive Index (@1550nm)
1.49
1.488
1.486
1.484
1.482
1.48
1.478
1.476
1.474
1.472
1.47
1.1
1.05
1
0.95
0.9
0.85
0.8
0
5
10
15
20
25
30
35
Wfr Numbers (2 Per Run)
◆ Index Repeatability Study
Δ Index Repeatability Post Anneal
■ Dep Rate

FIG. 15

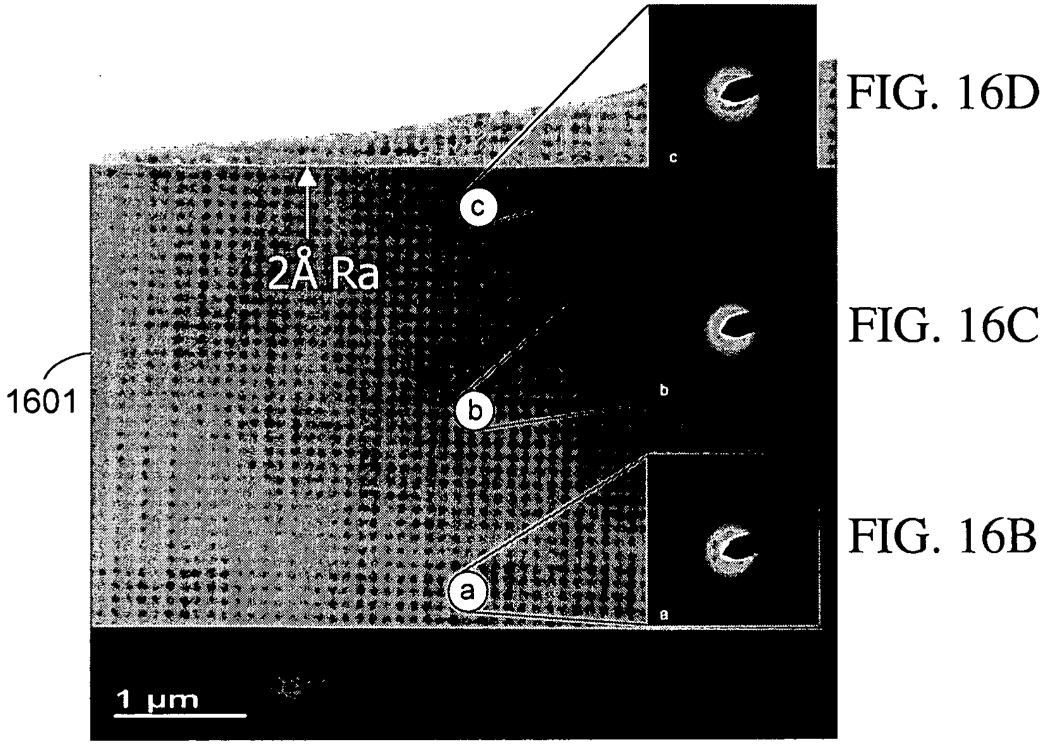

FIG. 16A

SYMMORPHIX PVD ALUMINOSILICATE

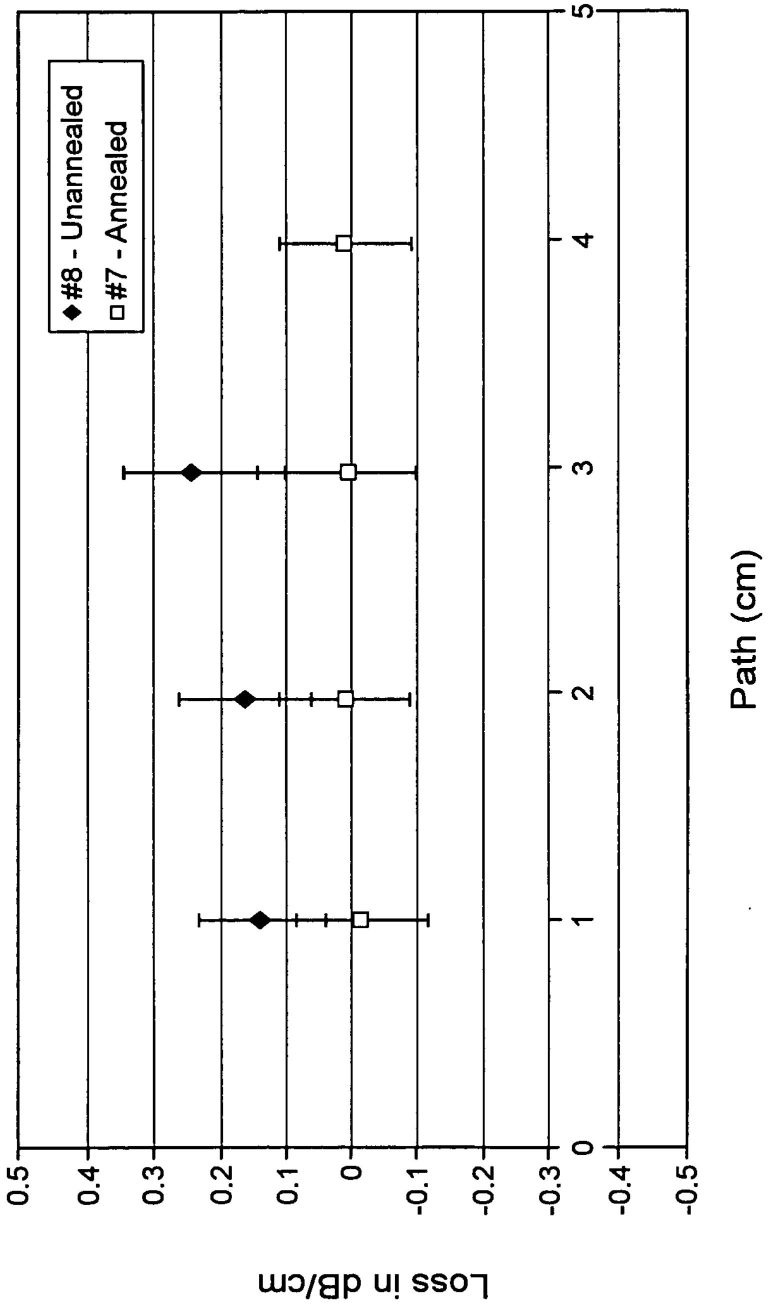
◆ #8 - Unannealed
□ #7 - Annealed
Loss in dB/cm
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
Path (cm)
0
1
2
3
4
5

FIG. 17

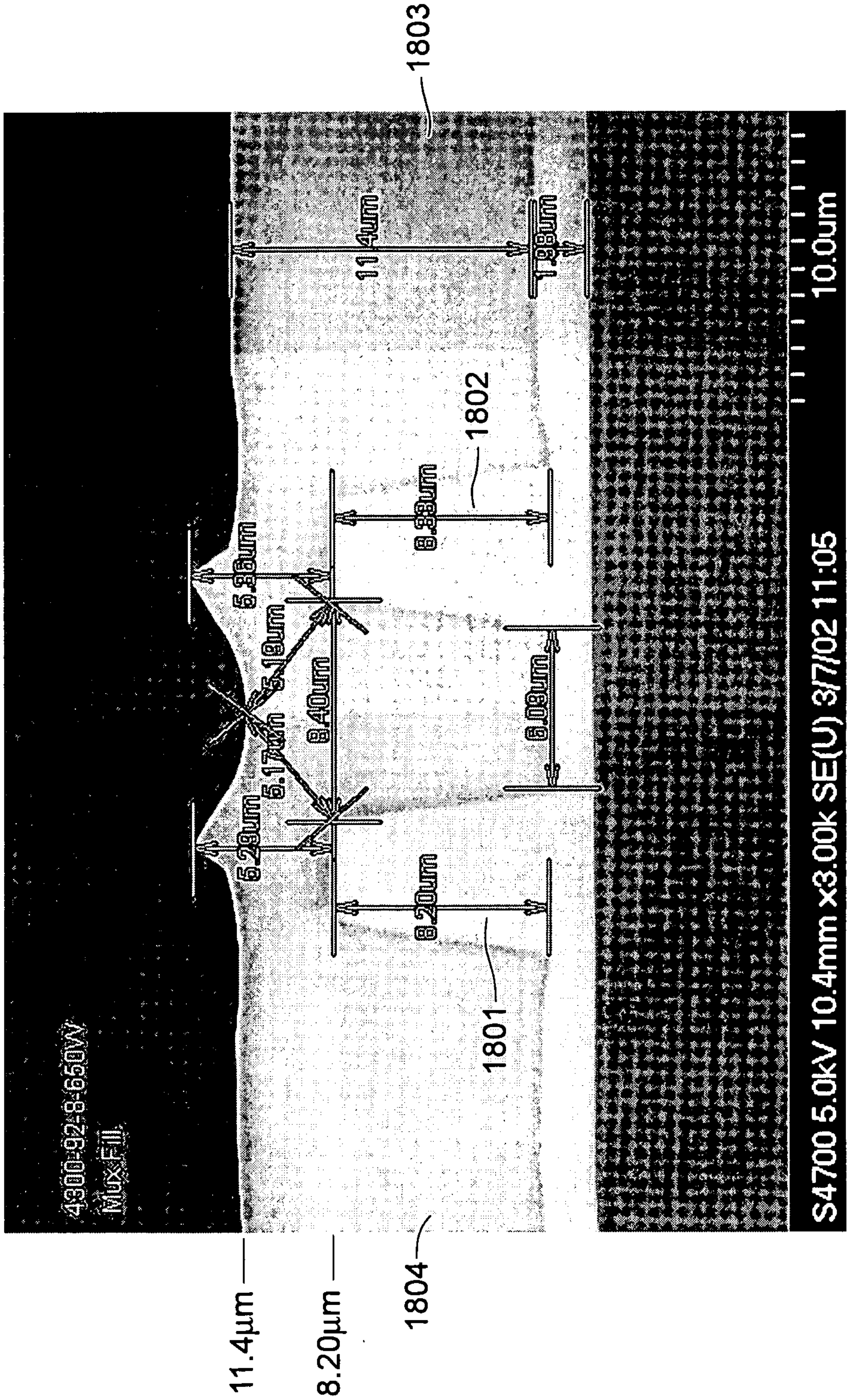
1803
11.4um
1.98um
10.0um
1802
8.33um
5.38um
5.19um
5.17um
8.40um
6.08um
5.29um
8.20um
1801
4300-92-8-650W
Mux Fill
S4700 5.0kV 10.4mm x3.00k SE(U) 3/7/02 11:05
11.4µm
8.20µm
1804

FIG. 18

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

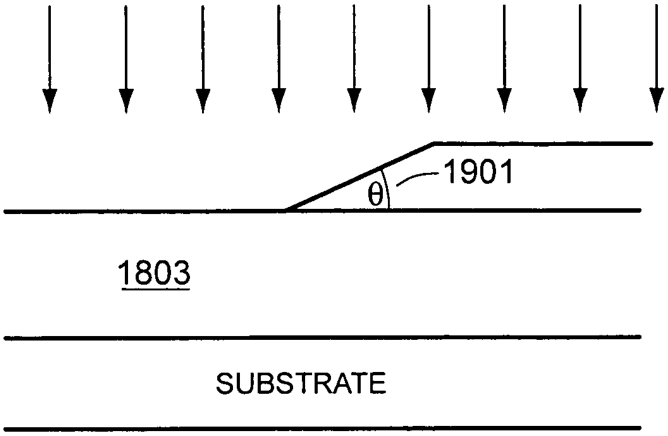

FIG. 19

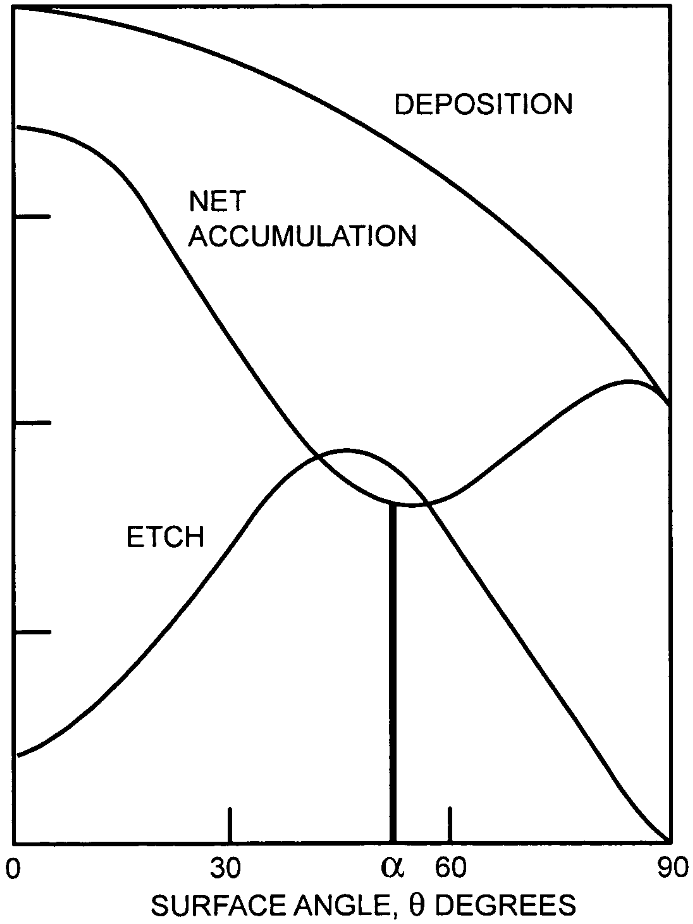

FIG. 20

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

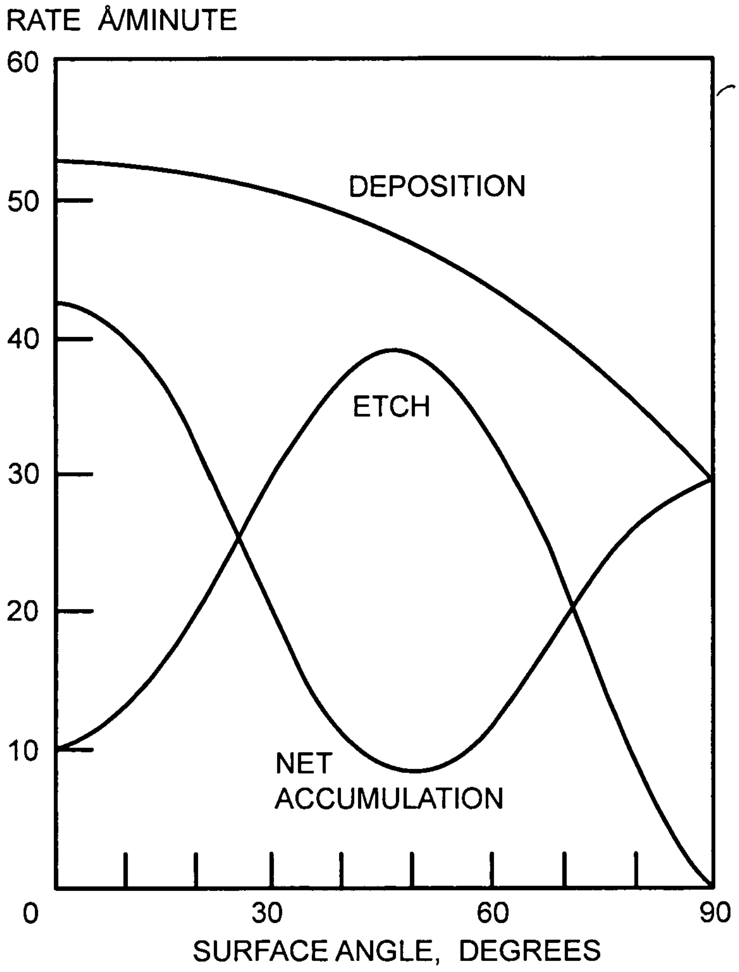

FIG. 21

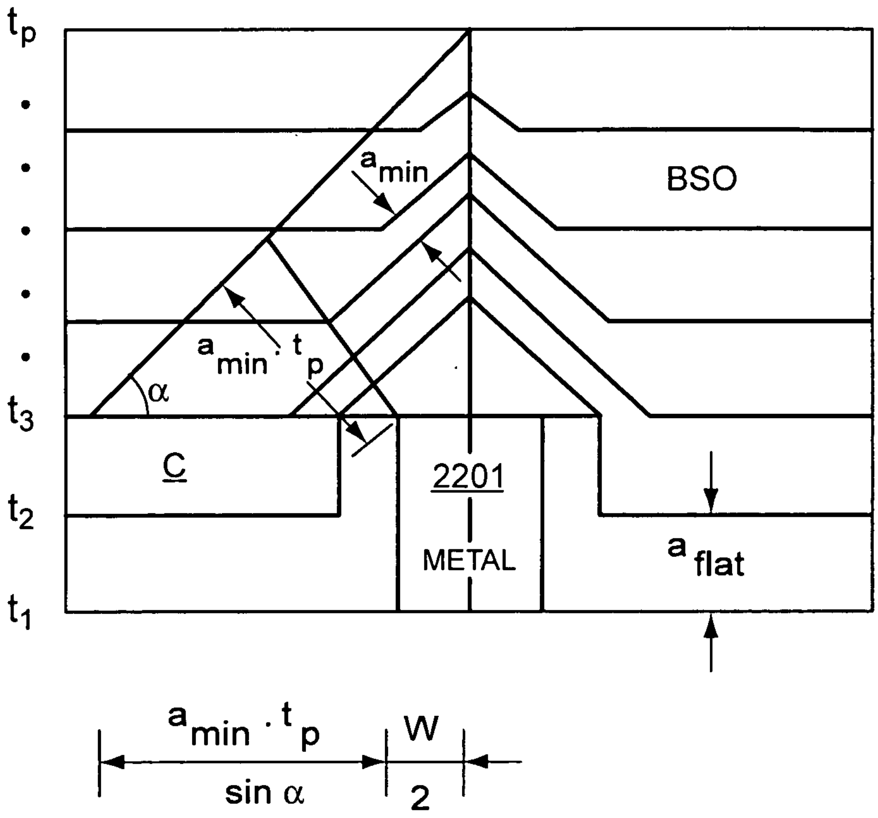
$t_p$
$t_3$
$t_2$
$t_1$
$a_{min}$
BSO
$a_{min} \cdot t_p$
α
C
2201
METAL
$a_{flat}$
$\frac{a_{min} \cdot t_p}{\sin \alpha}$
$\frac{W}{2}$

FIG. 22

REPLACEMENT SHEET
Inventors: Hongmei ZHANG et al.
Application No. 10/101,863
Title: BIASED PULSE DC REACTIVE
SPUTTERING OF OXIDE FILMS

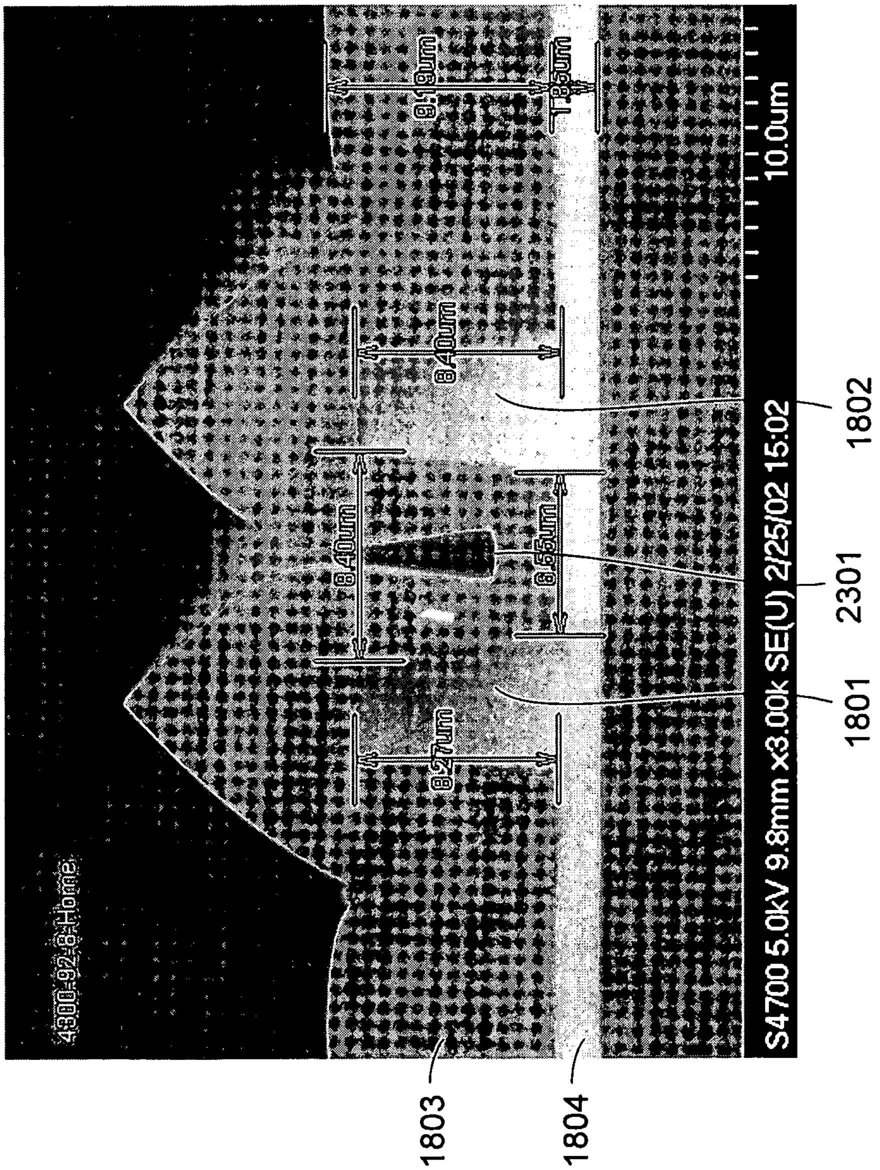

FIG. 23

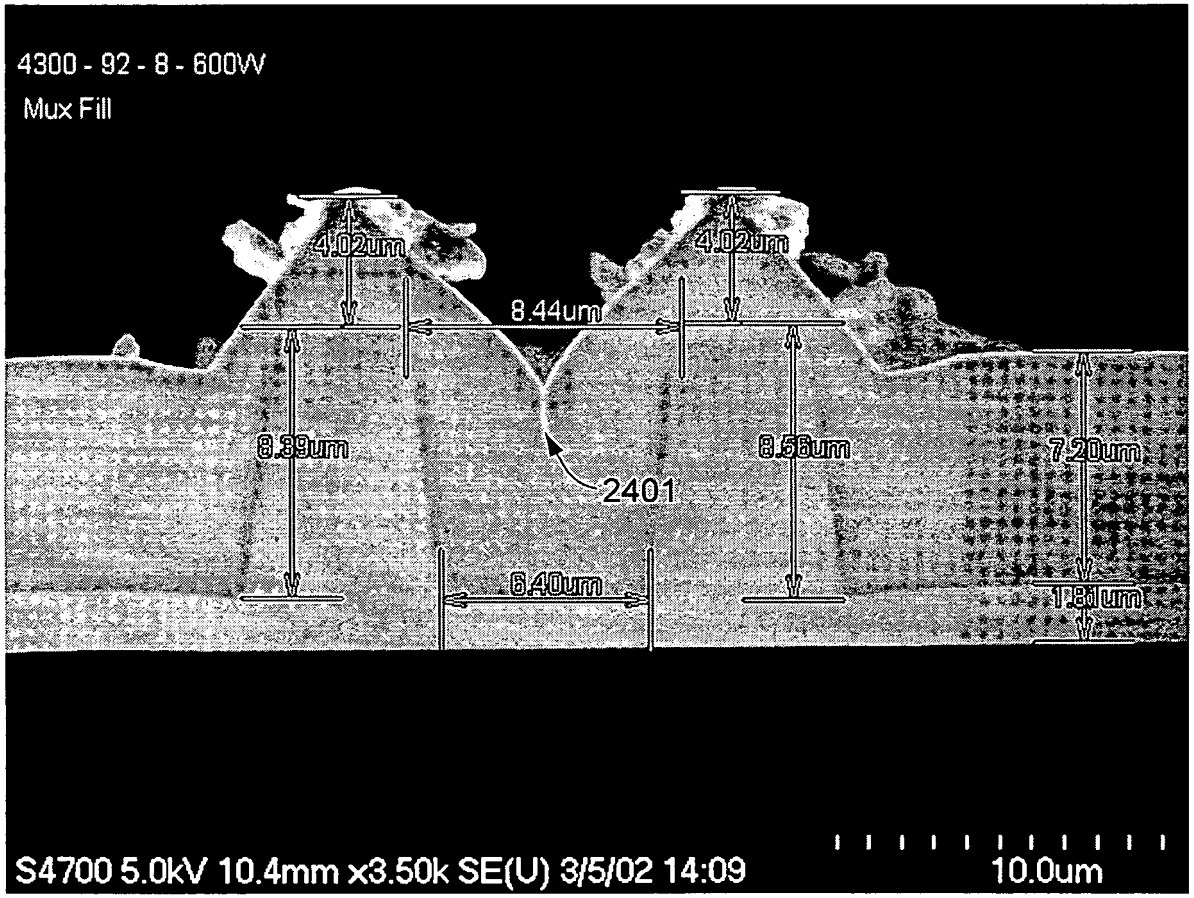
4300 - 92 - 8 - 600W
Mux Fill
4.02um
4.02um
8.44um
8.39um
8.56um
7.20um
2401
6.40um
1.81um
S4700 5.0kV 10.4mm x3.50k SE(U) 3/5/02 14:09
10.0um

FIG. 24

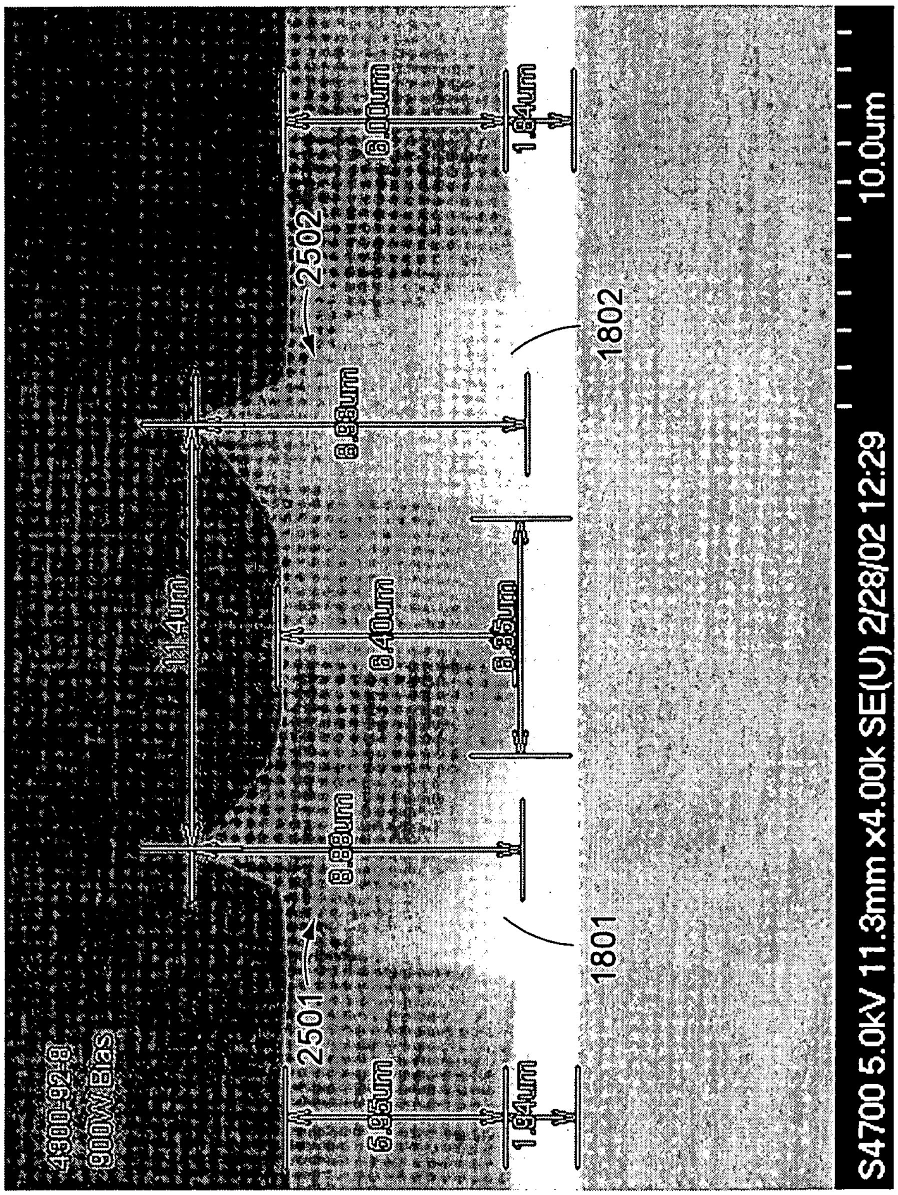
4300-92-8
900W Bias
6.95um
1.94um
2501
1801
8.88um
11.4um
6.40um
8.35um
8.98um
2502
1802
6.00um
1.84um
S4700 5.0kV 11.3mm x4.00k SE(U) 2/28/02 12:29
10.0um

FIG. 25

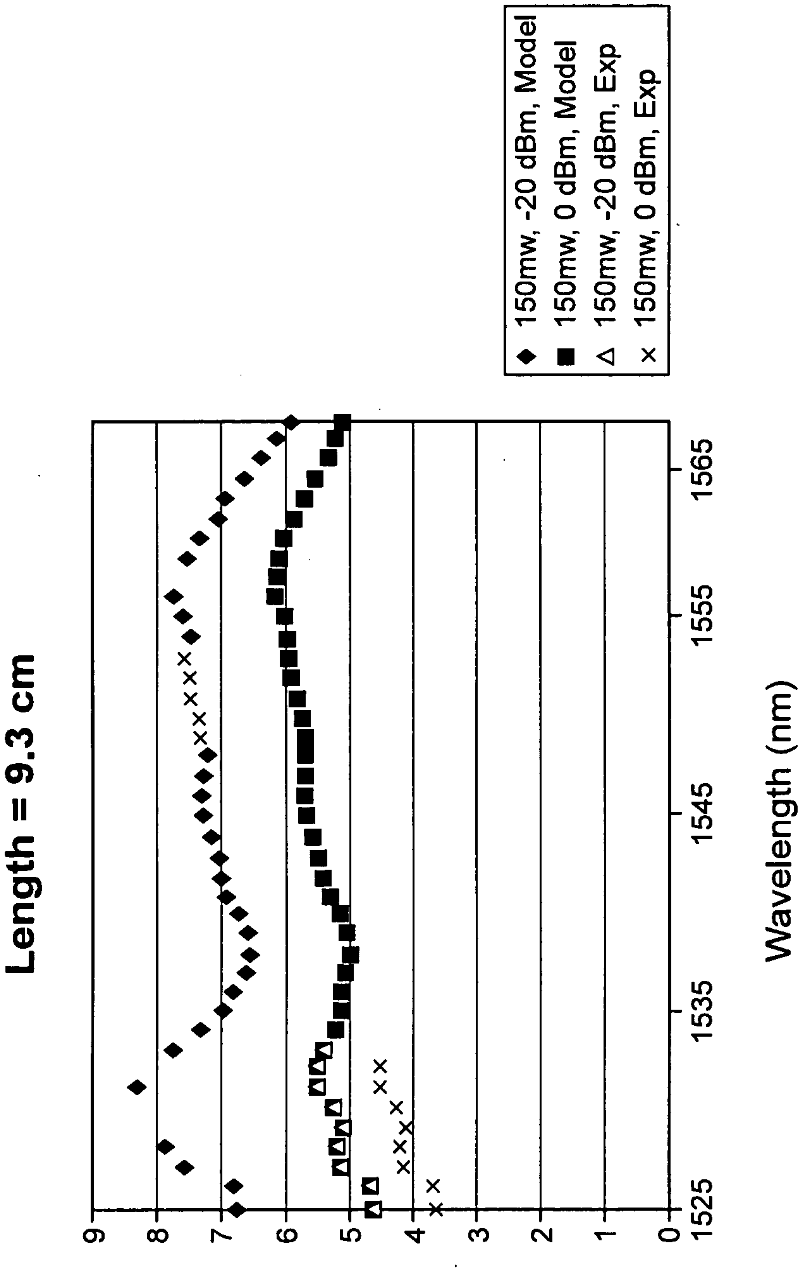
Length = 9.3 cm
Gain (dB)
0
1
2
3
4
5
6
7
8
9
Wavelength (nm)
1525
1535
1545
1555
1565
◆ 150mw, -20 dBm, Model
■ 150mw, 0 dBm, Model
△ 150mw, -20 dBm, Exp
× 150mw, 0 dBm, Exp

FIG. 26

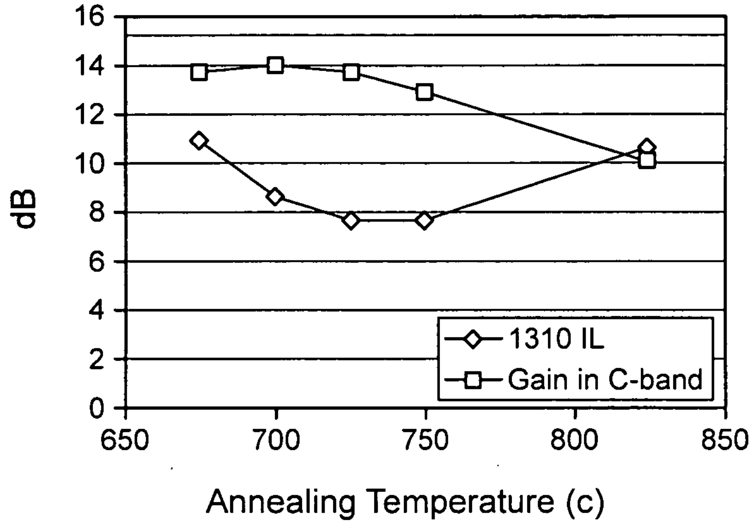
16
14
12
10
8
6
4
2
0
dB
650
700
750
800
850
Annealing Temperature (c)
1310 IL
Gain in C-band

FIG. 27

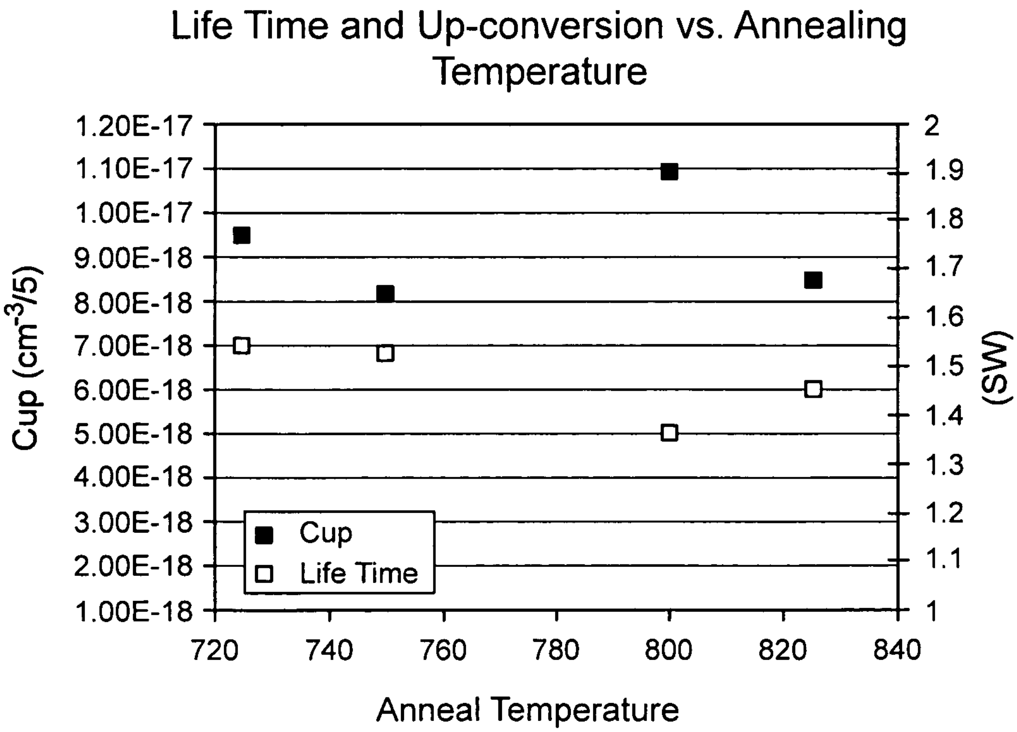
Life Time and Up-conversion vs. Annealing Temperature
1.20E-17
1.10E-17
1.00E-17
9.00E-18
8.00E-18
7.00E-18
6.00E-18
5.00E-18
4.00E-18
3.00E-18
2.00E-18
1.00E-18
Cup (cm^-3/5)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
(SW)
720
740
760
780
800
820
840
Anneal Temperature
Cup
Life Time

FIG. 28

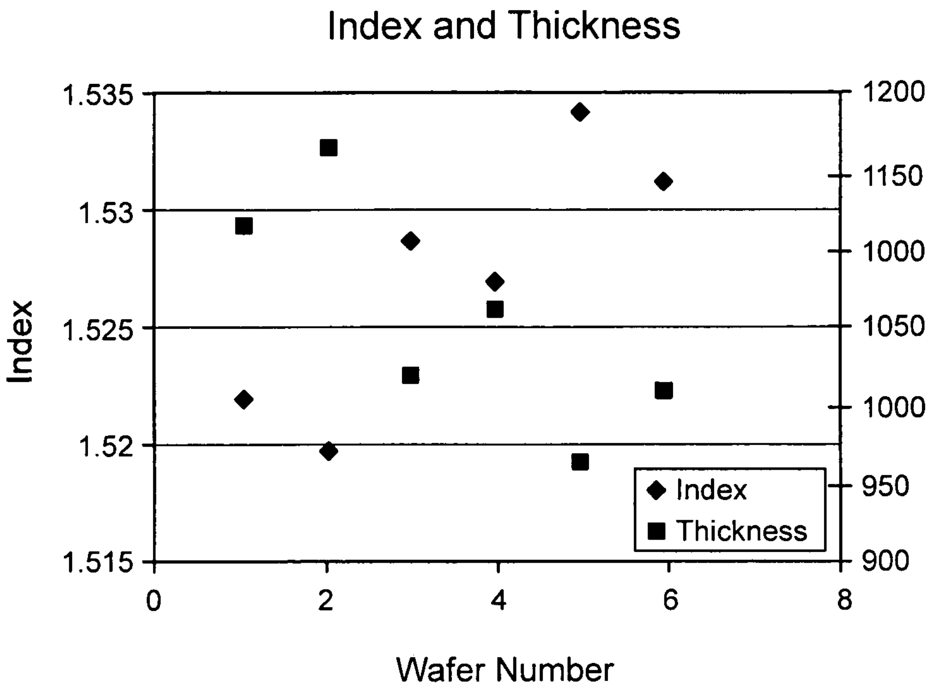
Index and Thickness
1.535
1.53
1.525
1.52
1.515
Index
1200
1150
1000
1050
1000
950
900
0
2
4
6
8
Wafer Number
◆ Index
■ Thickness

FIG. 29

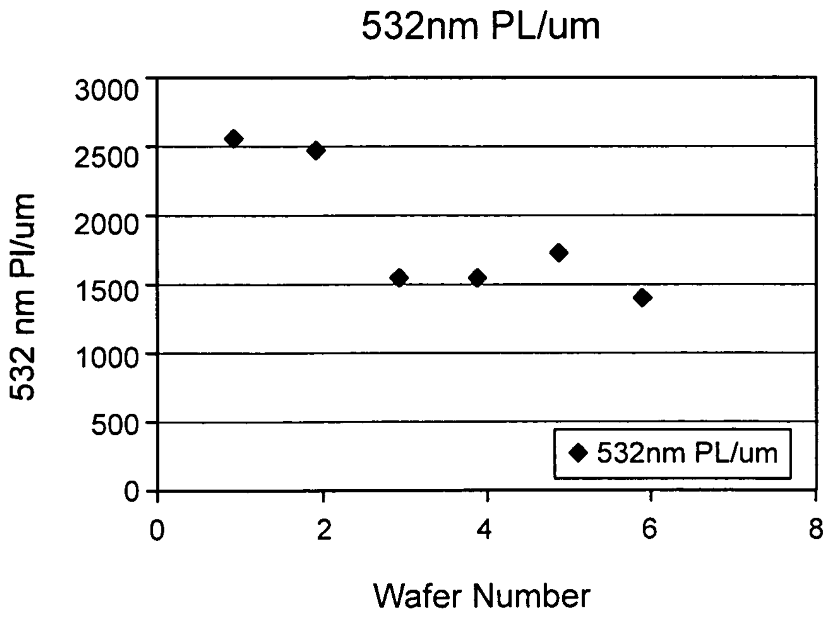
532nm PL/um
3000
2500
2000
1500
1000
500
0
532 nm Pl/um
0
2
4
6
8
Wafer Number
◆ 532nm PL/um

FIG. 30

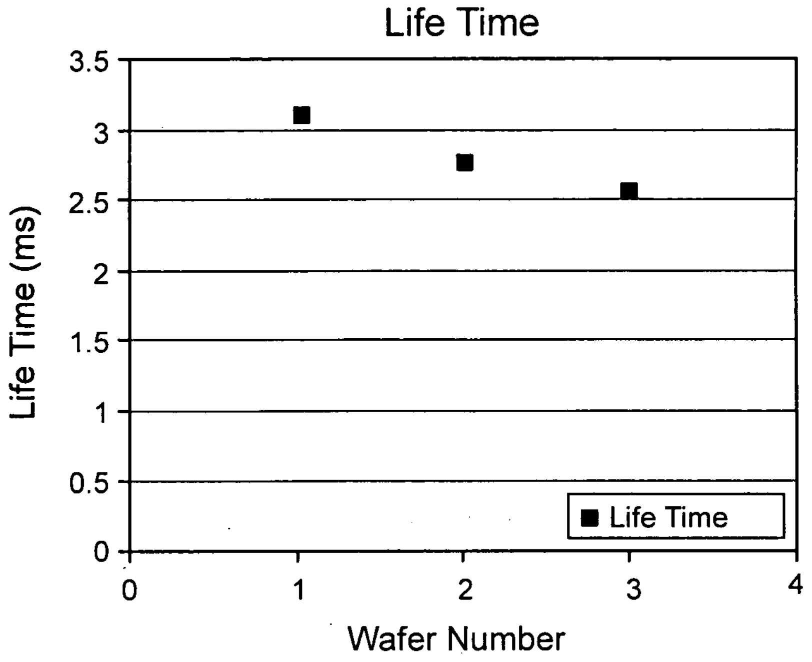
Life Time
Life Time (ms)
3.5
3
2.5
2
1.5
1
0.5
0
0
1
2
3
4
Wafer Number
■ Life Time

FIG. 31

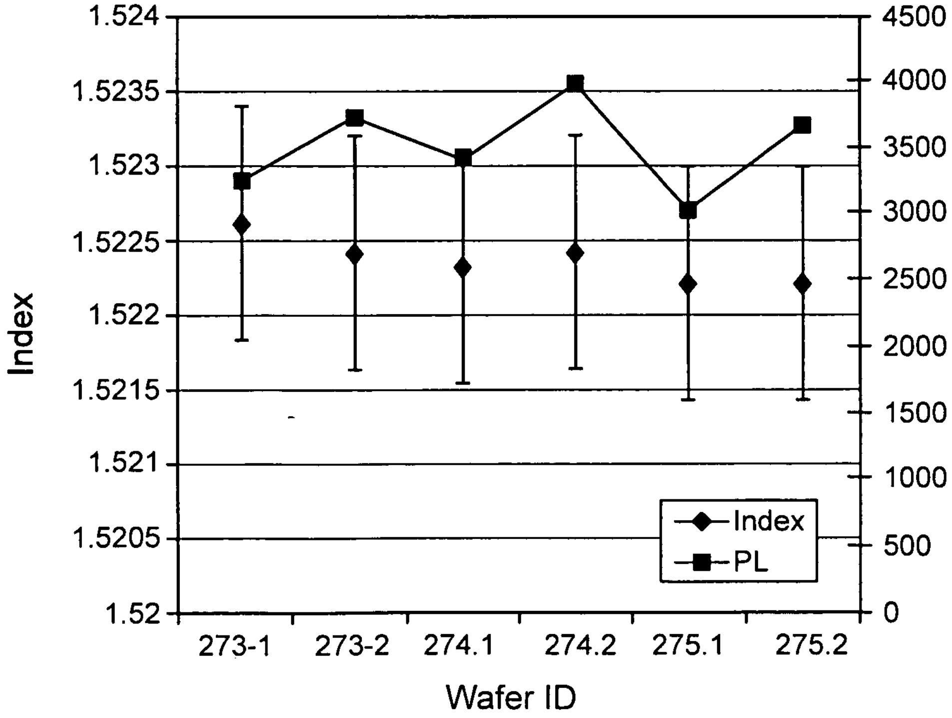
1.524
1.5235
1.523
1.5225
1.522
1.5215
1.521
1.5205
1.52
Index
4500
4000
3500
3000
2500
2000
1500
1000
500
0
273-1
273-2
274.1
274.2
275.1
275.2
Wafer ID
Index
PL

FIG. 32

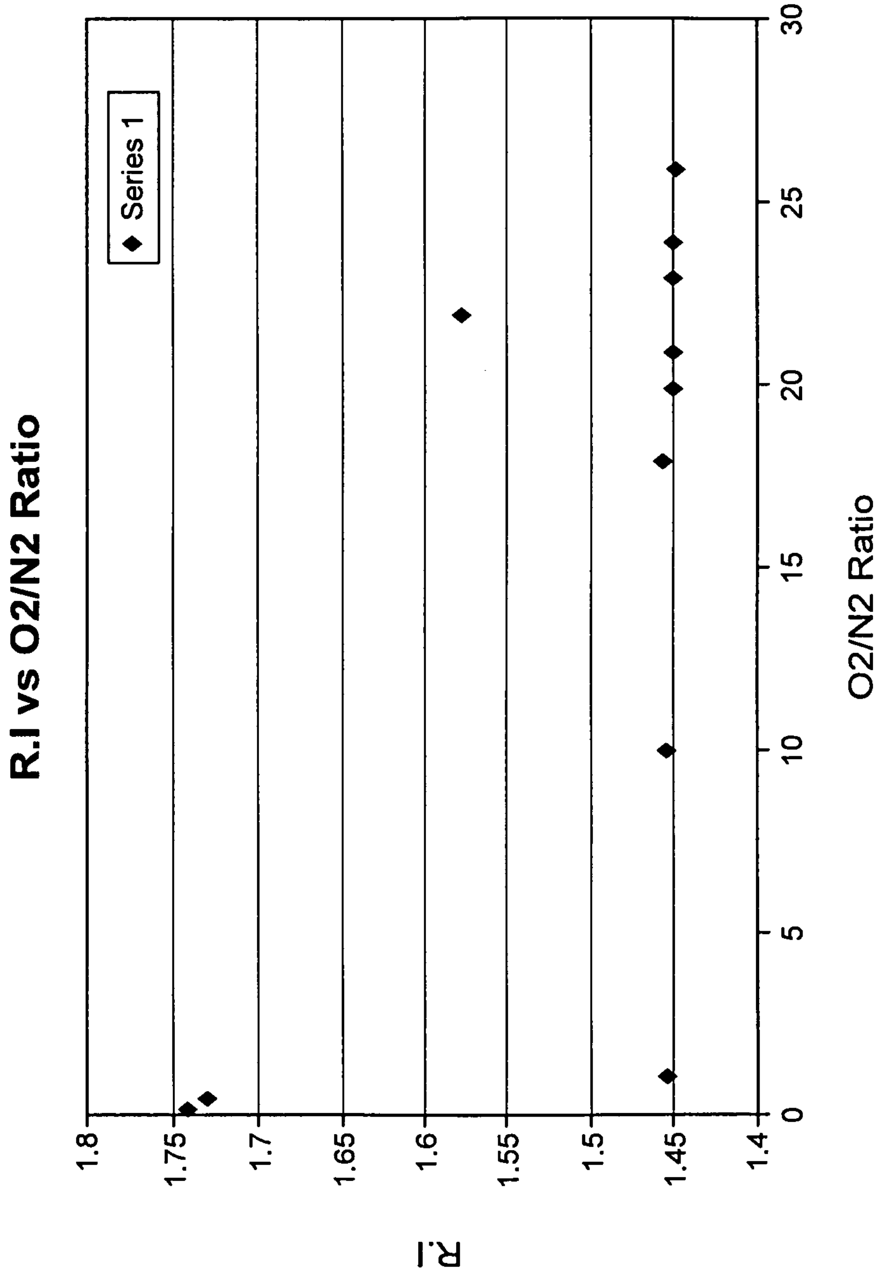
R.I vs O2/N2 Ratio
◆ Series 1
R.I
1.8
1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4
O2/N2 Ratio
0
5
10
15
20
25
30

FIG. 33

OIPE IAP55
DEC 05 2005
PATENT & TRADEMARK OFFICE

OIPE IAP55
DEC 05 2005
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|---|---|---|
| In re Application of: | ) | |
| | ) | |
| ZHANG, Hongmei et al. | ) | Group Art Unit: 2823 |
| | ) | |
| Application No.: 10/101,863 | ) | Examiner: ESTRADA, Michelle |
| | ) | |
| Filed: March 16, 2002 | ) | |
| | ) | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | ) | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## PETITION FOR EXTENSION OF TIME

Applicants petition for a one month extension of time to reply to the Office action of August 4, 2005. The Commissioner is hereby authorized to charge the fee of $120.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: 45,681
for Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EV 758329165 US**

12/08/2005 EAREGAY1 00000041 060916 10101863
01 FC:1251 120.00 DA

OIPE
IAP55
DEC 0 5 2005
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## FOURTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

12/08/2005 EAREGAY1 00000041 060916 10101863
02 FC:1806 180.00 DA

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 5, 2005

By: Linda J. Thayer 45,681
for Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 758329165 US**

OIPE IAP55
DEC 05 2005
PATENT & TRADEMARK OFFICE

| | | | | | |
|---|---|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | **Complete if Known** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT**<br>*(Use as many sheets as necessary)* | | | | *Application Number* | 10/101,863 |
| | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | Hongmei ZHANG |
| | | | | *Art Unit* | 2823 |
| | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of | 1 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | 5,478,456 | 12-26-1995 | Humpal et al. | |
| | | 6,846,765 B2 | 1-25-2005 | Imamura et al. | |
| | | | | | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | DOREY, R.A., "Low temperature micromoulding of functional ceramic devices," Grant summary for GR/S84156/01 for the UK Engineering and Physical Sciences Research Council, 2 pages (2004). | |
| | | HOWSON, R.P., "The reactive sputtering of oxides and nitrides," *Pure & Appl. Chem. 66*(6):1311-1318 (1994). | |
| | | Office Action issued September 21, 2005 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01). | |
| | | Office Action issued on August 8, 2005 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00). | |
| | | Office Action issued on October 3, 2005 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00). | |
| | | Office Action issued on October 19, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |

**EXPRESS MAIL LABEL NO.**
**EV 758329165 US**

| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

# PATENT APPLICATION FEE DETERMINATION RECORD

Effective December 8, 2004

10/101863

## CLAIMS AS FILED - PART I

| | (Column 1) | (Column 2) |
|---|---|---|
| TOTAL CLAIMS | | |
| FOR | NUMBER FILED | NUMBER EXTRA |
| TOTAL CHARGEABLE CLAIMS | minus 20= | * |
| INDEPENDENT CLAIMS | minus 3 = | * |
| MULTIPLE DEPENDENT CLAIM PRESENT | | ☐ |

* If the difference in column 1 is less than zero, enter "0" in column 2

SMALL ENTITY TYPE ☐ OR OTHER THAN SMALL ENTITY

| RATE | FEE | | RATE | FEE |
|---|---|---|---|---|
| BASIC FEE | 150.00 | OR | BASIC FEE | 300.00 |
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |
| TOTAL | | OR | TOTAL | |

## CLAIMS AS AMENDED - PART II

SMALL ENTITY OR OTHER THAN SMALL ENTITY

| AMENDMENT A | (Column 1) | | (Column 2) | (Column 3) |
|---|---|---|---|---|
| 12/05/05 | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total | * 19 | Minus | ** 20 | = |
| Independent | * 4 | Minus | *** 3 | = 1 |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM | | | | ☐ |

| RATE | ADDITIONAL FEE | | RATE | ADDITIONAL FEE |
|---|---|---|---|---|
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | 200.00 |
| +180= | | OR | +360= | |
| TOTAL ADDIT. FEE | | OR | TOTAL ADDIT. FEE | 200.00 |

| AMENDMENT B | (Column 1) | | (Column 2) | (Column 3) |
|---|---|---|---|---|
| | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total | * | Minus | ** | = |
| Independent | * | Minus | *** | = |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM | | | | ☐ |

| RATE | ADDITIONAL FEE | | RATE | ADDITIONAL FEE |
|---|---|---|---|---|
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |
| TOTAL ADDIT. FEE | | OR | TOTAL ADDIT. FEE | |

| AMENDMENT C | (Column 1) | | (Column 2) | (Column 3) |
|---|---|---|---|---|
| | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total | * | Minus | ** | = |
| Independent | * | Minus | *** | = |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM | | | | ☐ |

| RATE | ADDITIONAL FEE | | RATE | ADDITIONAL FEE |
|---|---|---|---|---|
| X$ 25= | | OR | X$50= | |
| X100= | | OR | X200= | |
| +180= | | OR | +360= | |

A

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | M-12245 US | 6938 |

22852 7590 02/14/2006

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| **ART UNIT** | **PAPER NUMBER** |
| 2823 | |

DATE MAILED: 02/14/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 10/03)

| | | | |
|---|---|---|---|
| **Office Action Summary** | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. | |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 | |

***-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --***

### Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

### Status

1)☒ Responsive to communication(s) filed on 05 December 2005.
2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.
3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

### Disposition of Claims

4)☒ Claim(s) 1-14 and 20-24 is/are pending in the application.
4a) Of the above claim(s) _____ is/are withdrawn from consideration.
5)☒ Claim(s) 14 and 21-24 is/are allowed.
6)☒ Claim(s) 1-13 and 20 is/are rejected.
7)☐ Claim(s) _____ is/are objected to.
8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

### Application Papers

9)☐ The specification is objected to by the Examiner.
10)☒ The drawing(s) filed on 05 December 2005 is/are: a)☒ accepted or b)☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

### Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
a)☐ All b)☐ Some * c)☐ None of:
1.☐ Certified copies of the priority documents have been received.
2.☐ Certified copies of the priority documents have been received in Application No. _____.
3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date 12/5/05.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

## DETAILED ACTION

### *Claim Rejections - 35 USC § 102*

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1, 8, 10-13 and 20 are rejected under 35 U.S.C. 102(b) as being anticipated by Smolanoff et al. (6,117,279).

With respect to claim 1, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33).

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claim 12, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claim 13, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claim 20, Smolanoff et al. disclose conditioning a target; preparing the substrate; adjusting the bias power to the substrate; setting the process gas flow; and applying pulsed DC power to the target to deposit the film (Col. 5, line 55-Col. 7, line 50).

## *Claim Rejections - 35 USC § 103*

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 2-6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Fukui et al. (5,755,938).

With respect to claims 2-4 and 6, One of ordinary skill in the art would have been led to the recited temperature, DC power, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, time pulse and bias power are critical. _In re Woodruf_, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With respect to claim 5, Smolanoff et al. do not specifically disclose wherein the filter is a band reject filter at the frequency of the bias power.

Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter (27) at the frequency of the bias power.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fukui et al. to enable the filter type of Smolanoff et al. to be the same according to the teachings of Fukui et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable types of filters for the disclosed filter step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. as applied to claims 1, 8, 10-13 and 20 above, and further in view of Le et al. (2003/0077914).

Smolanoff et al. do not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Leet al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

### *Allowable Subject Matter*

Claims 14 and 21-24 are allowed.

### *Response to Arguments*

Applicant's arguments filed 12/5/05 have been fully considered but they are not persuasive. Applicant argues that deposition is performed by exposing the substrate to the secondary plasma, not the main plasma adjacent to the sputtering target. However, the process of Col. 5- Col. 6 of Smolanoff et al. deposits a thin film on the substrate 15 by exposure to the main plasma (Col. 6, lines 30-33). The additional teachings of the reference, like creating a secondary plasma, do not render invalid the teachings relied on.

Applicant argues that Smolanoff has enabled utilization of a DC power supply, but not a pulsed DC power supply. However, Smolanoff discloses that a pulsed DC power can be used and would work in the process described at Col. 5-Col. 6.

## *Conclusion*

**THIS ACTION IS MADE FINAL.** Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
February 8, 2006

approved
2/8/06

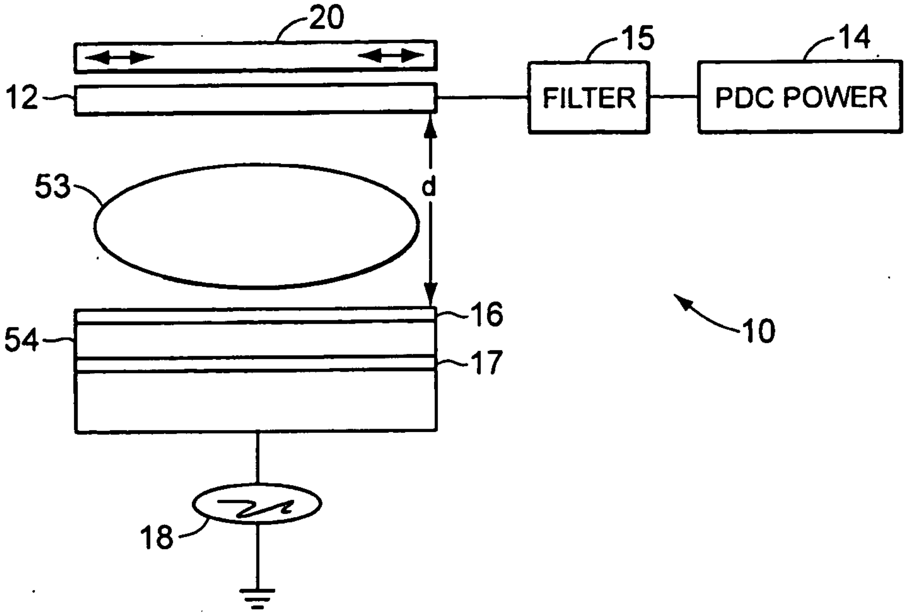

FIG. 1A

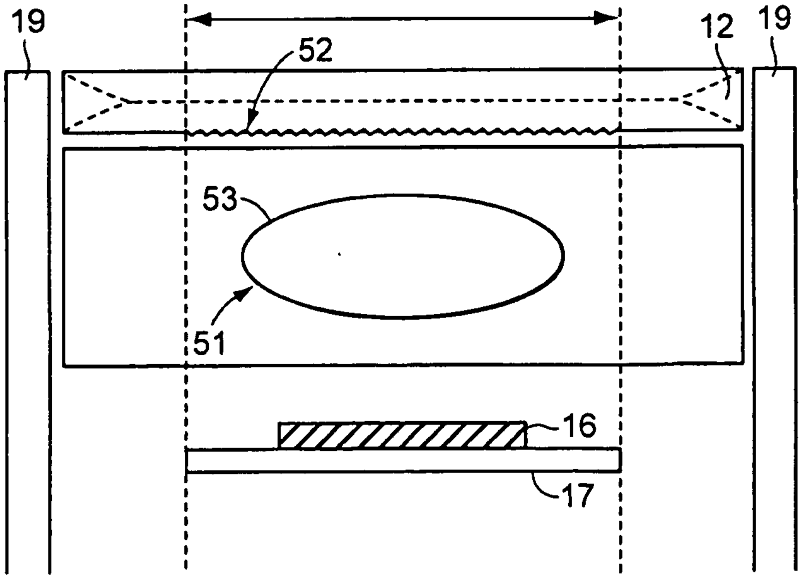

FIG. 1B

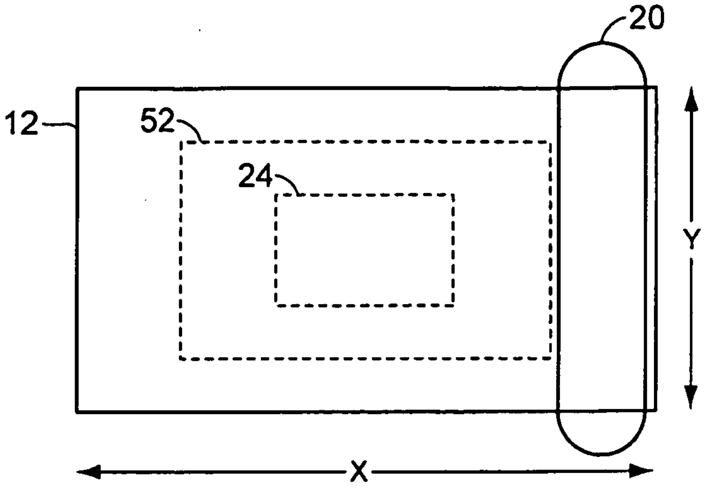

FIG. 2

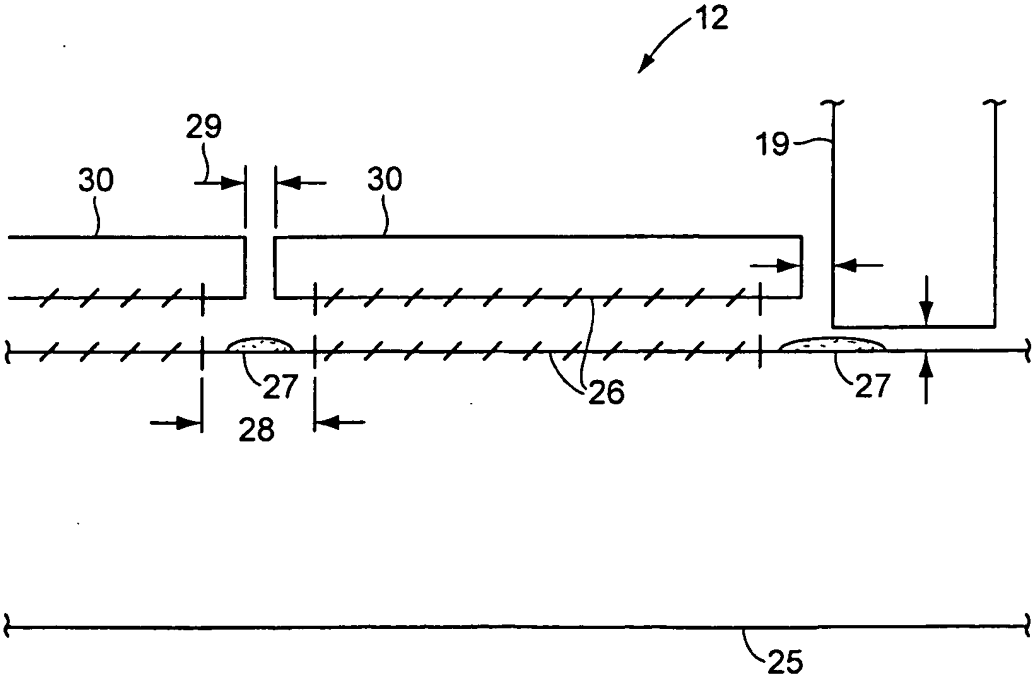

FIG. 3

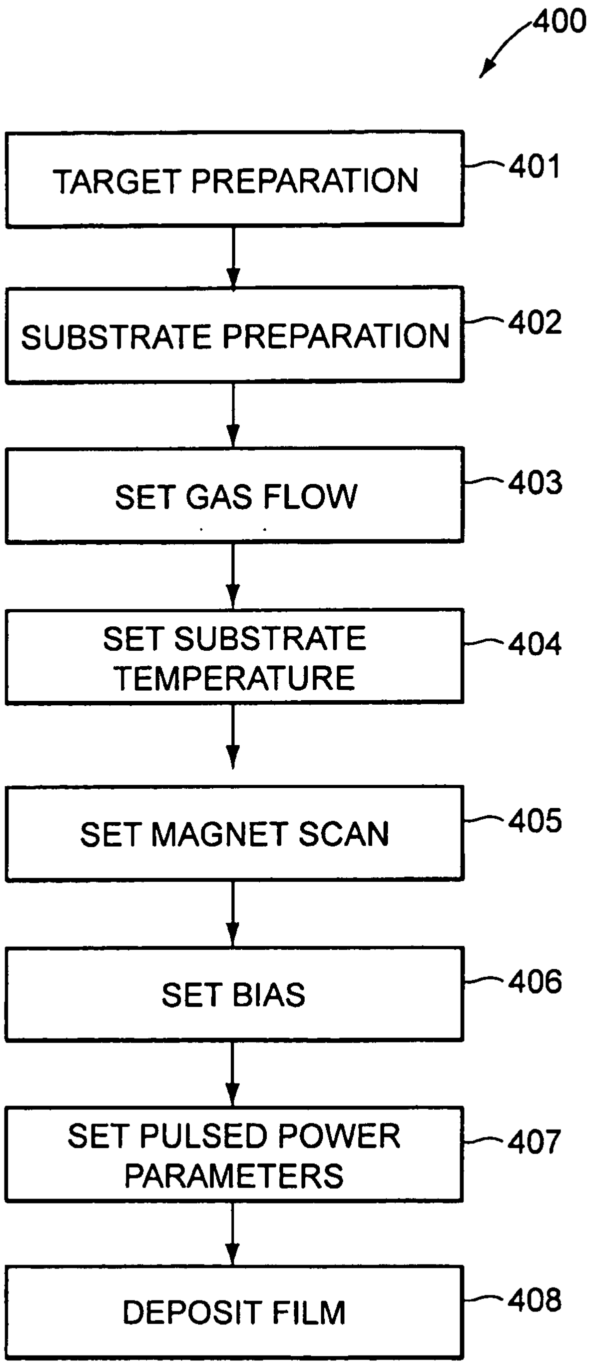
400
TARGET PREPARATION
401
SUBSTRATE PREPARATION
402
SET GAS FLOW
403
SET SUBSTRATE TEMPERATURE
404
SET MAGNET SCAN
405
SET BIAS
406
SET PULSED POWER PARAMETERS
407
DEPOSIT FILM
408

FIG. 4

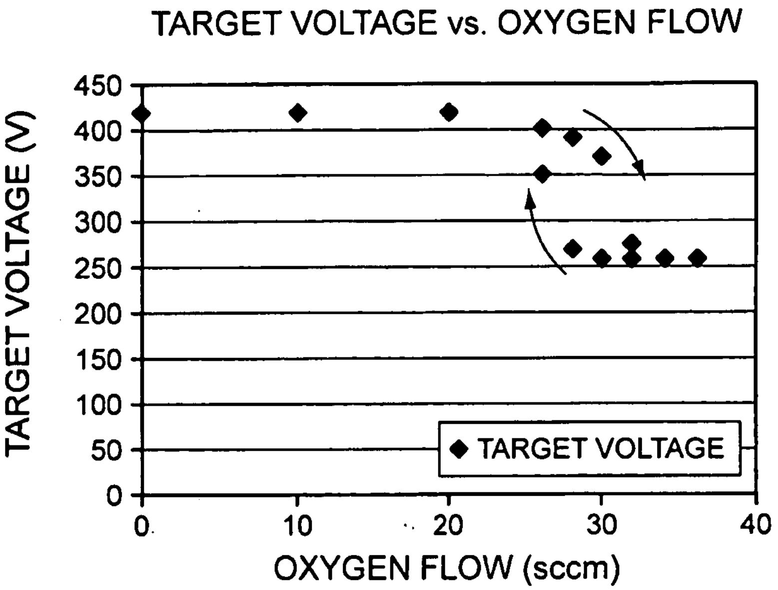
TARGET VOLTAGE vs. OXYGEN FLOW
TARGET VOLTAGE (V)
450
400
350
300
250
200
150
100
50
0
0
10
20
30
40
OXYGEN FLOW (sccm)
◆ TARGET VOLTAGE

FIG. 5

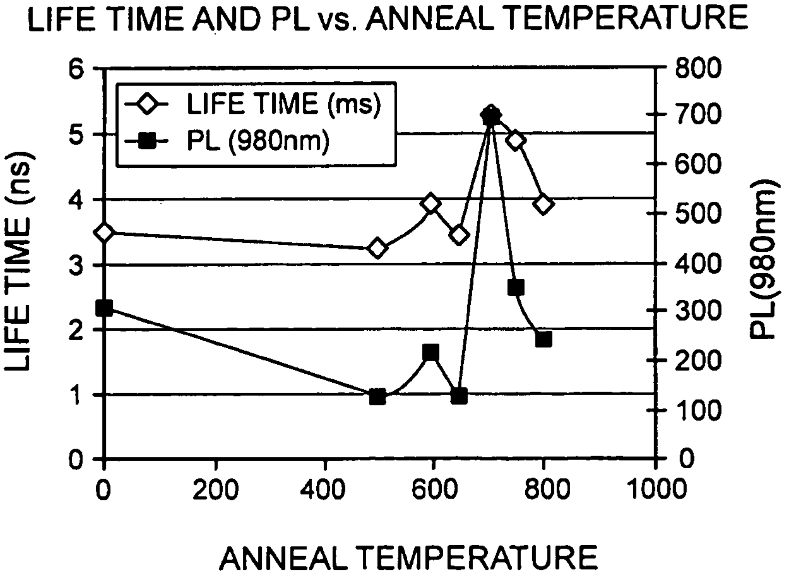
LIFE TIME AND PL vs. ANNEAL TEMPERATURE
LIFE TIME (ns)
6
5
4
3
2
1
0
PL(980nm)
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
ANNEAL TEMPERATURE
LIFE TIME (ms)
PL (980nm)

FIG. 6

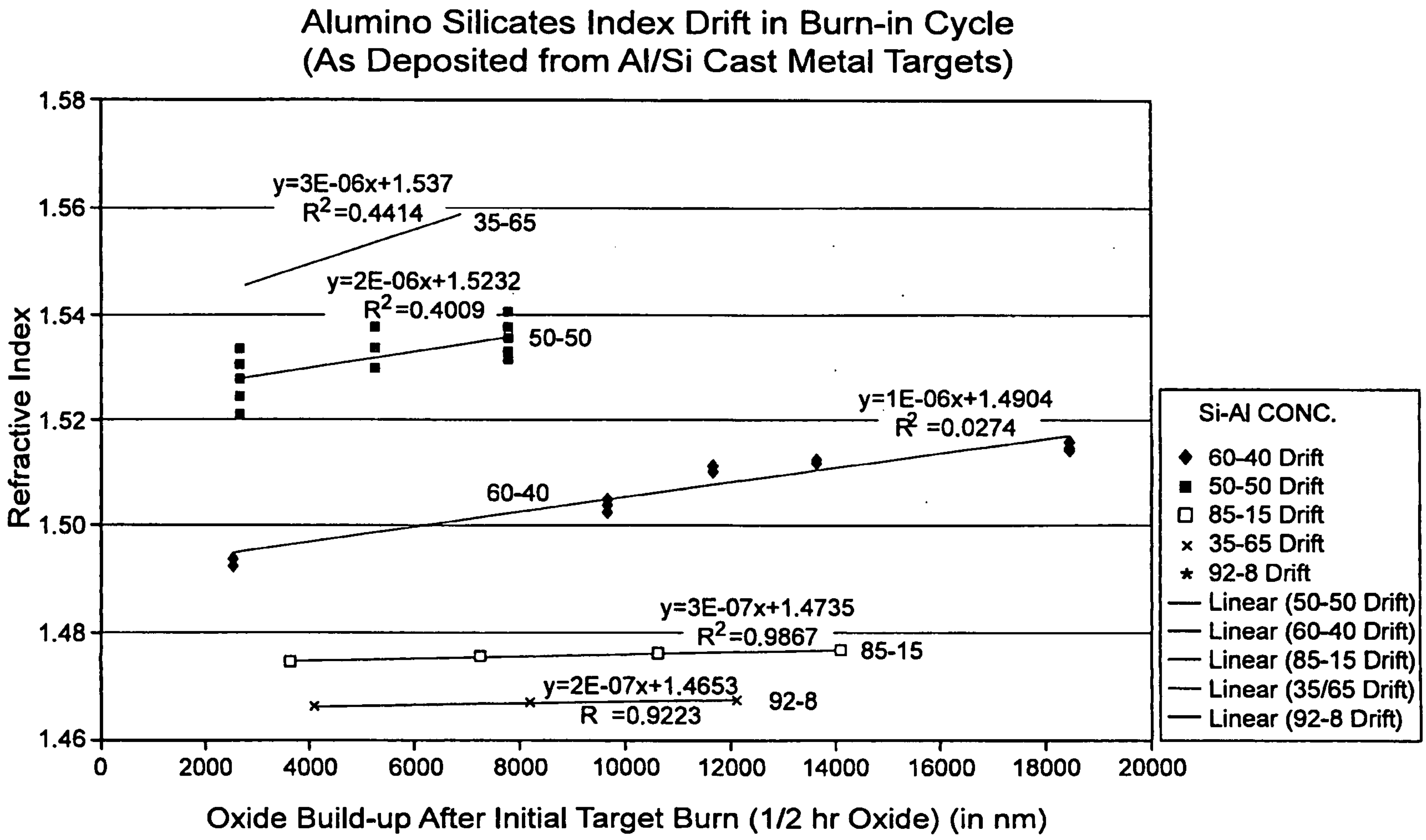
Alumino Silicates Index Drift in Burn-in Cycle
(As Deposited from Al/Si Cast Metal Targets)
Refractive Index
1.58
1.56
1.54
1.52
1.50
1.48
1.46
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
Oxide Build-up After Initial Target Burn (1/2 hr Oxide) (in nm)
y=3E-06x+1.537
R2=0.4414
35-65
y=2E-06x+1.5232
R2=0.4009
50-50
y=1E-06x+1.4904
R2 =0.0274
60-40
y=3E-07x+1.4735
R2=0.9867
85-15
y=2E-07x+1.4653
R =0.9223
92-8
Si-Al CONC.
◆ 60-40 Drift
■ 50-50 Drift
□ 85-15 Drift
× 35-65 Drift
* 92-8 Drift
— Linear (50-50 Drift)
— Linear (60-40 Drift)
— Linear (85-15 Drift)
— Linear (35/65 Drift)
— Linear (92-8 Drift)

FIG. 7

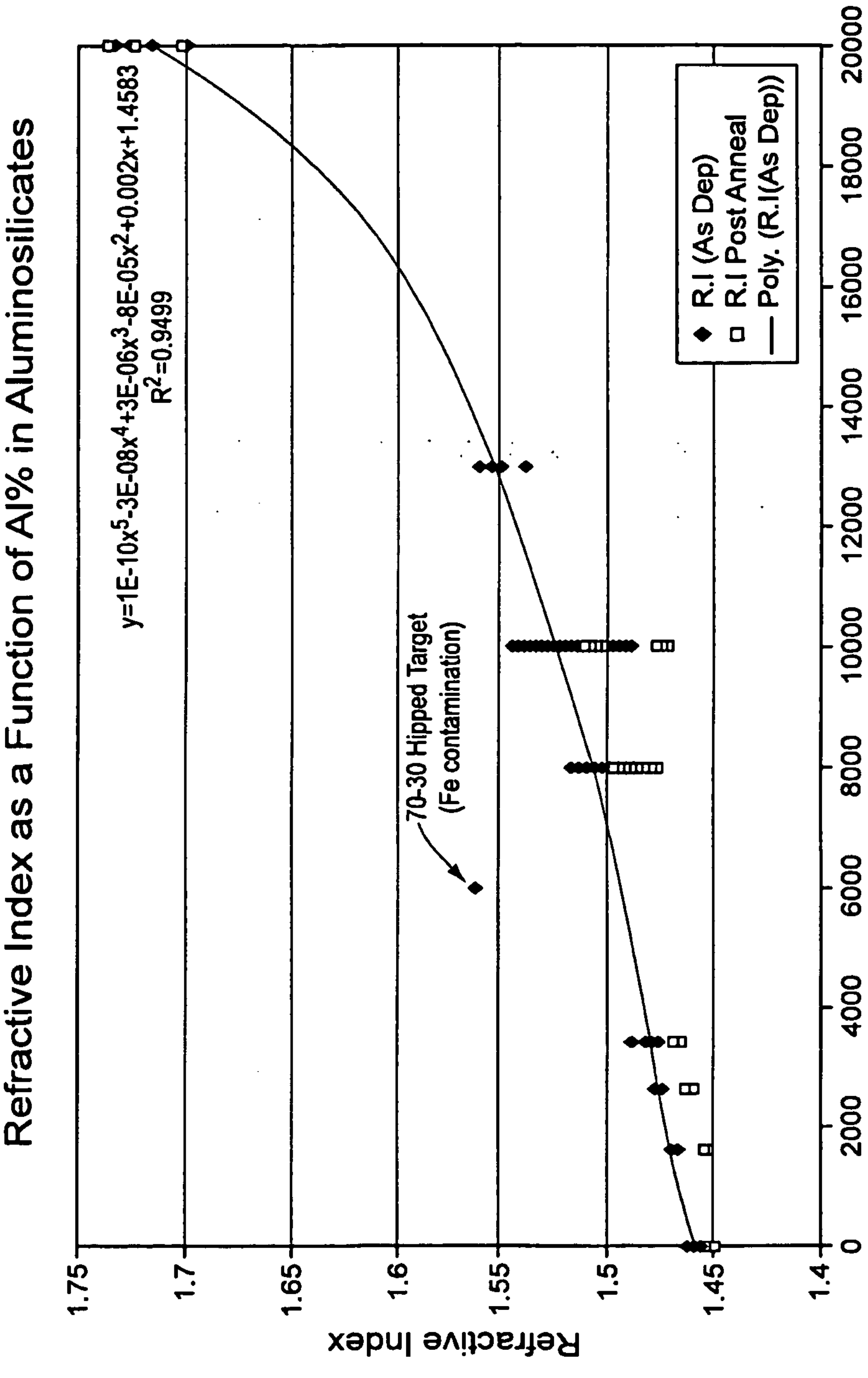
Refractive Index as a Function of Al% in Aluminosilicates
y=1E-10x^5-3E-08x^4+3E-06x^3-8E-05x^2+0.002x+1.4583
R^2=0.9499
70-30 Hipped Target
(Fe contamination)
◆ R.I (As Dep)
□ R.I Post Anneal
— Poly. (R.I(As Dep))
Refractive Index
1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000

FIG. 8

| Material (Er/Yb/Al/Si) | Expected index (Post anneal) | Actual index (Post anneal) | Process Conditions (Annealed 725c 30min) |
|---|---|---|---|
| 0.8/0.8/41.4/57 | 1.506 | 1.510 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 1.6/0.5/49/48.9 | 1.526 | 1.528 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/8/92 | 1.452 | 1.456-1.459 | 4.5KW, Ar-30-60,02-28-44, 120-200Khz, 2.2us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/40/60 | 1.504 | 1.486-1.501 | 3.0-4.5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/50/50 | 1.520 | 1.491-1.503 | 4.0-5KW, Ar-30,02-44, 75-200Khz, 2.2-3.0us, 60-85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/65/35 | 1.544 | 1.545-1.560 | 4.5-5.5KW, Ar-75-90,0285-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 0/0/30/70 | 1.490 | 1.562 (high Fe content) | 5.0KW, Ar-75,02-100, 200Khz, 2.2us, 85mm T-W Space, 4-5mm T-M Space, 0-400W Bias |
| 1.5/0/48.5/50 | 1.523 | 1.509-1.513 | 6KW, Ar-60,02-28sccm, 120Khz, 2.2us, 60mm T-W Space, 4-5mm T-M Space, 0-400W Bias |

FIG. 9

| Bias Power (Watts) | DC Power (KW) | Pulsing Freq (KHz) | Reverse Time (µs) | Ar Flow (sccms) | O2 Flow (sccms) | Wafer Position | Target To Wafer Spacing (mm) | Refractive Index Avg (@1550nm) | Refractive Index STD (@1550nm) | Dep Rate (um/Hr) |
|---|---|---|---|---|---|---|---|---|---|---|
| 150 | 4.5 | 200 | 2.2 | 100 | 100 | 1 | 55 | 1.461508 | 0.000535 | 0.957654 |
| 150 | 4.5 | 200 | 2.2 | 100 | 100 | 2 | 55 | 1.462329 | 0.000376 | 0.962581 |
| 400 | 4.5 | 200 | 2.2 | 100 | 100 | 1 | 55 | 1.462774 | 0.000103 | 0.814007 |
| 400 | 4.5 | 200 | 2.2 | 100 | 100 | 2 | 55 | 1.463583 | 0.000095 | 0.824566 |

FIG. 10

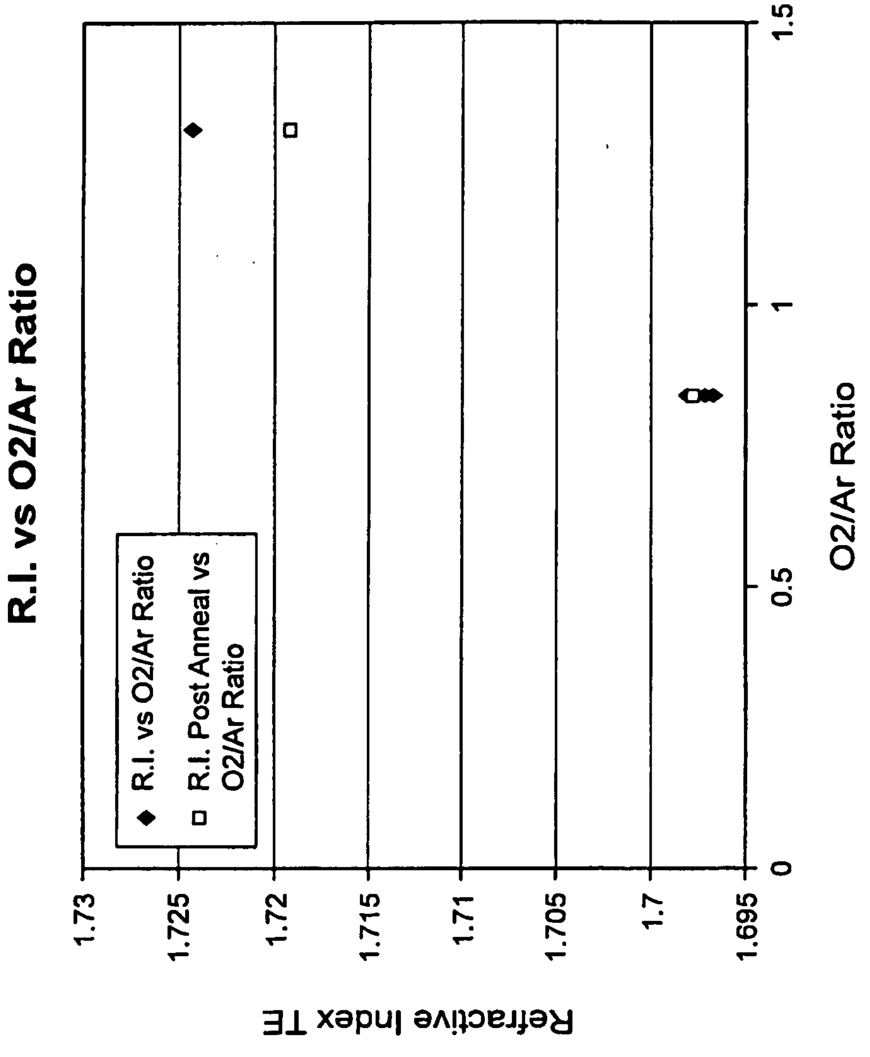
R.I. vs O2/Ar Ratio
◆ R.I. vs O2/Ar Ratio
□ R.I. Post Anneal vs O2/Ar Ratio
Refractive Index TE
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
0
0.5
1
1.5
O2/Ar Ratio

FIG. 11

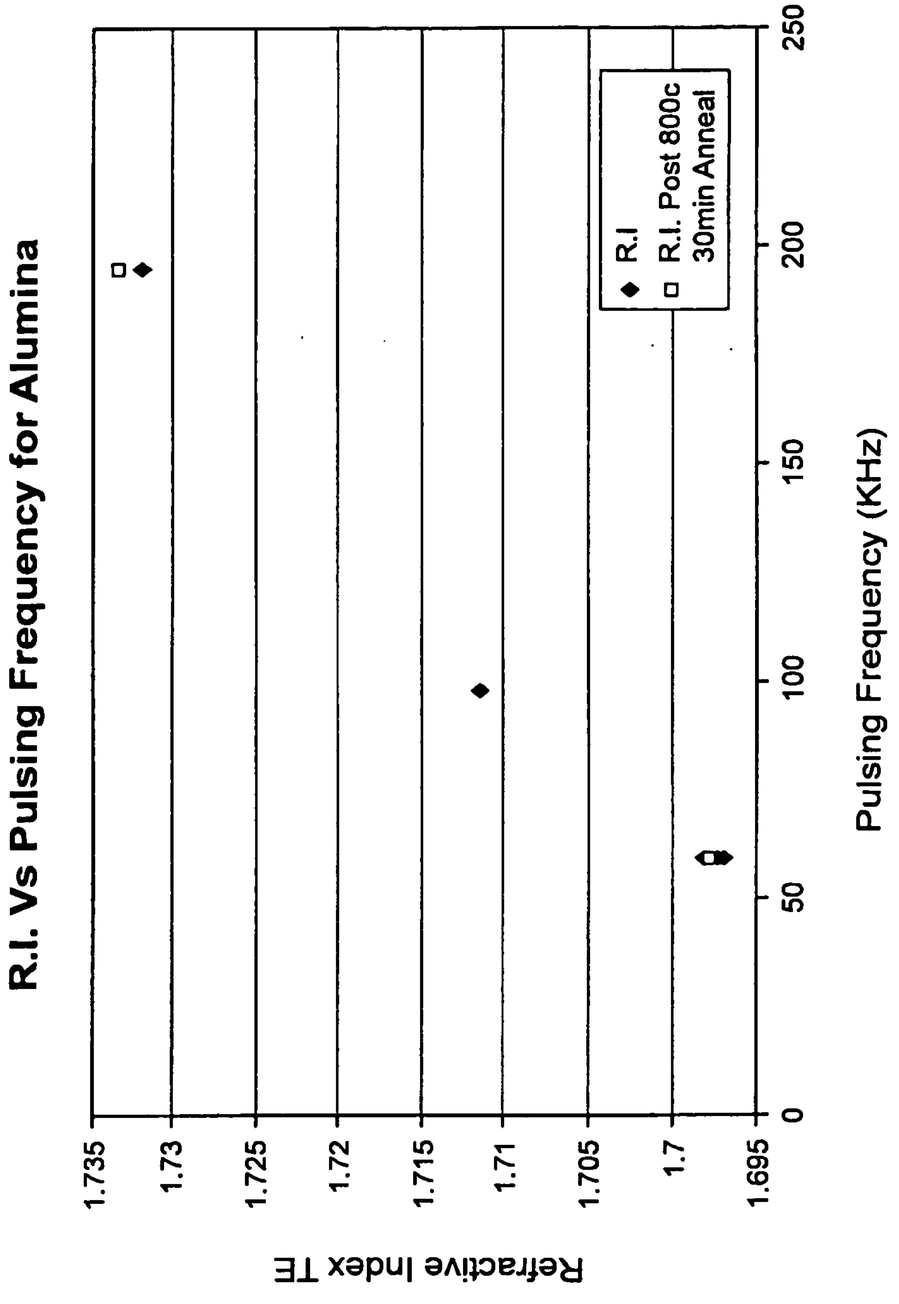
R.I. Vs Pulsing Frequency for Alumina
Refractive Index TE
1.735
1.73
1.725
1.72
1.715
1.71
1.705
1.7
1.695
Pulsing Frequency (KHz)
0
50
100
150
200
250
◆ R.I
□ R.I. Post 800c 30min Anneal

FIG. 12

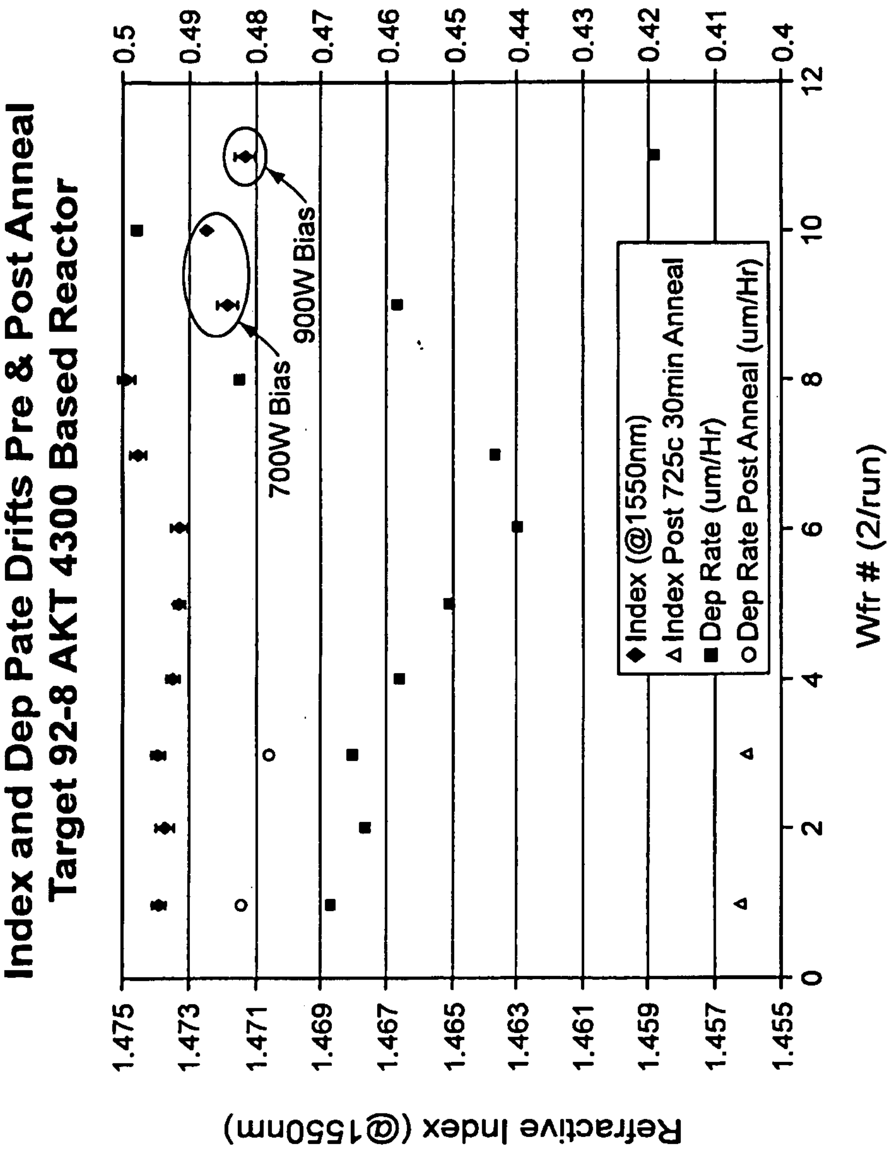
Index and Dep Pate Drifts Pre & Post Anneal
Target 92-8 AKT 4300 Based Reactor
Refractive Index (@1550nm)
1.475
1.473
1.471
1.469
1.467
1.465
1.463
1.461
1.459
1.457
1.455
0.5
0.49
0.48
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.4
0
2
4
6
8
10
12
Wfr # (2/run)
700W Bias
900W Bias
◆ Index (@1550nm)
△ Index Post 725c 30min Anneal
■ Dep Rate (um/Hr)
○ Dep Rate Post Anneal (um/Hr)

FIG. 13

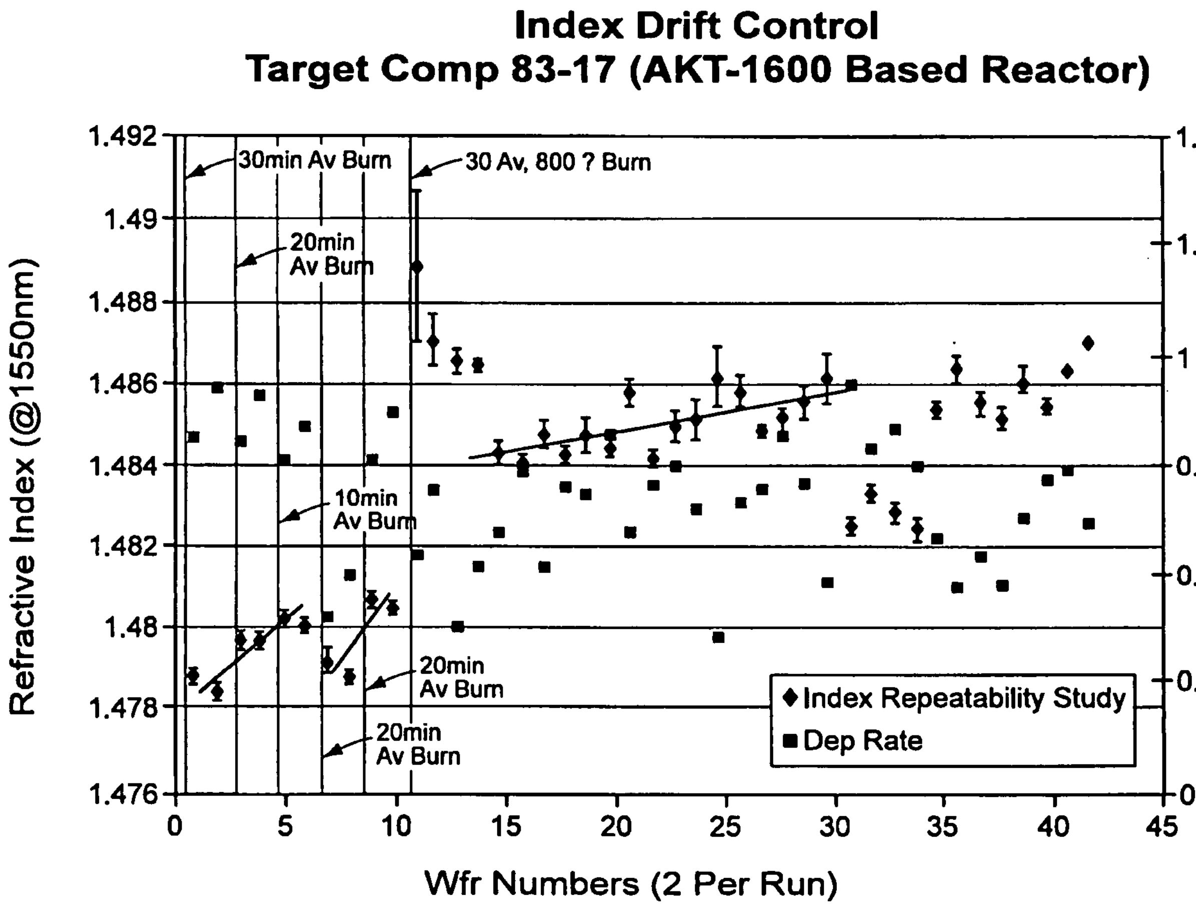
Index Drift Control
Target Comp 83-17 (AKT-1600 Based Reactor)
Refractive Index (@1550nm)
1.492
1.49
1.488
1.486
1.484
1.482
1.48
1.478
1.476
1.1
1.05
1
0.95
0.9
0.85
0.8
30min Av Burn
20min Av Burn
10min Av Burn
20min Av Burn
20min Av Burn
30 Av, 800 ? Burn
◆ Index Repeatability Study
■ Dep Rate
0
5
10
15
20
25
30
35
40
45
Wfr Numbers (2 Per Run)

FIG. 14

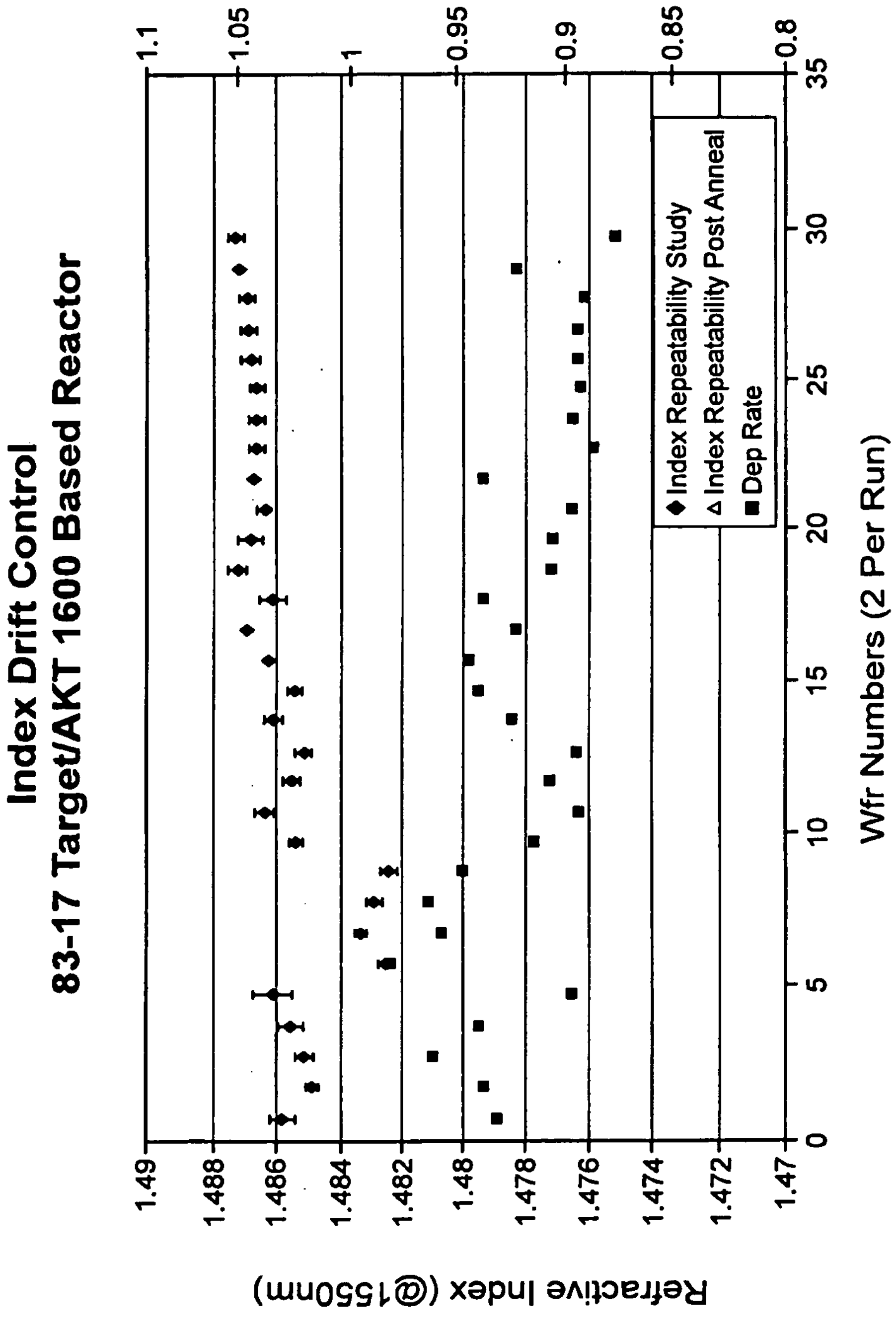
Index Drift Control
83-17 Target/AKT 1600 Based Reactor
Refractive Index (@1550nm)
1.49
1.488
1.486
1.484
1.482
1.48
1.478
1.476
1.474
1.472
1.47
1.1
1.05
1
0.95
0.9
0.85
0.8
0
5
10
15
20
25
30
35
Wfr Numbers (2 Per Run)
◆ Index Repeatability Study
Δ Index Repeatability Post Anneal
■ Dep Rate

FIG. 15

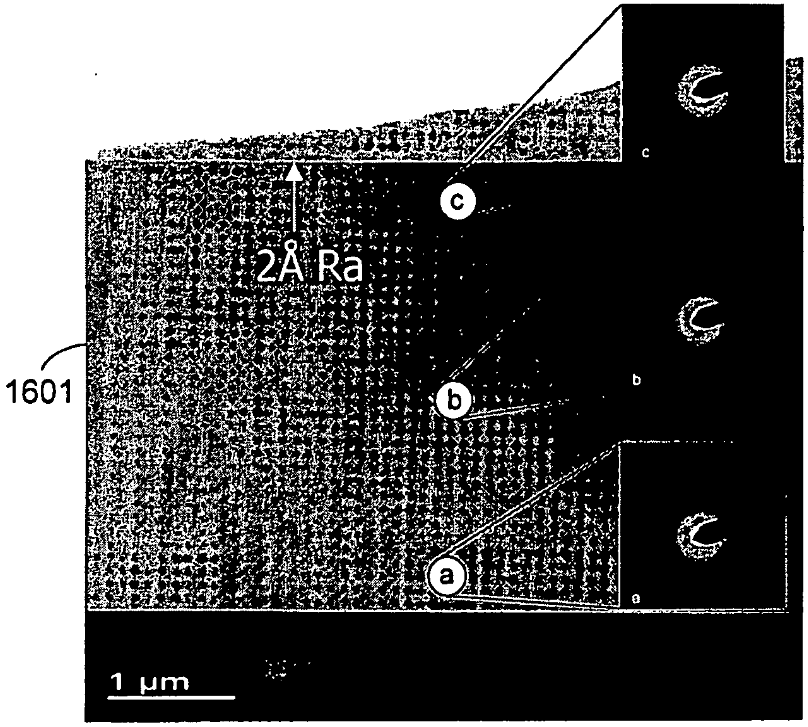

FIG. 16D

FIG. 16C

FIG. 16B

FIG. 16A

SYMMORPHIX PVD ALUMINOSILICATE

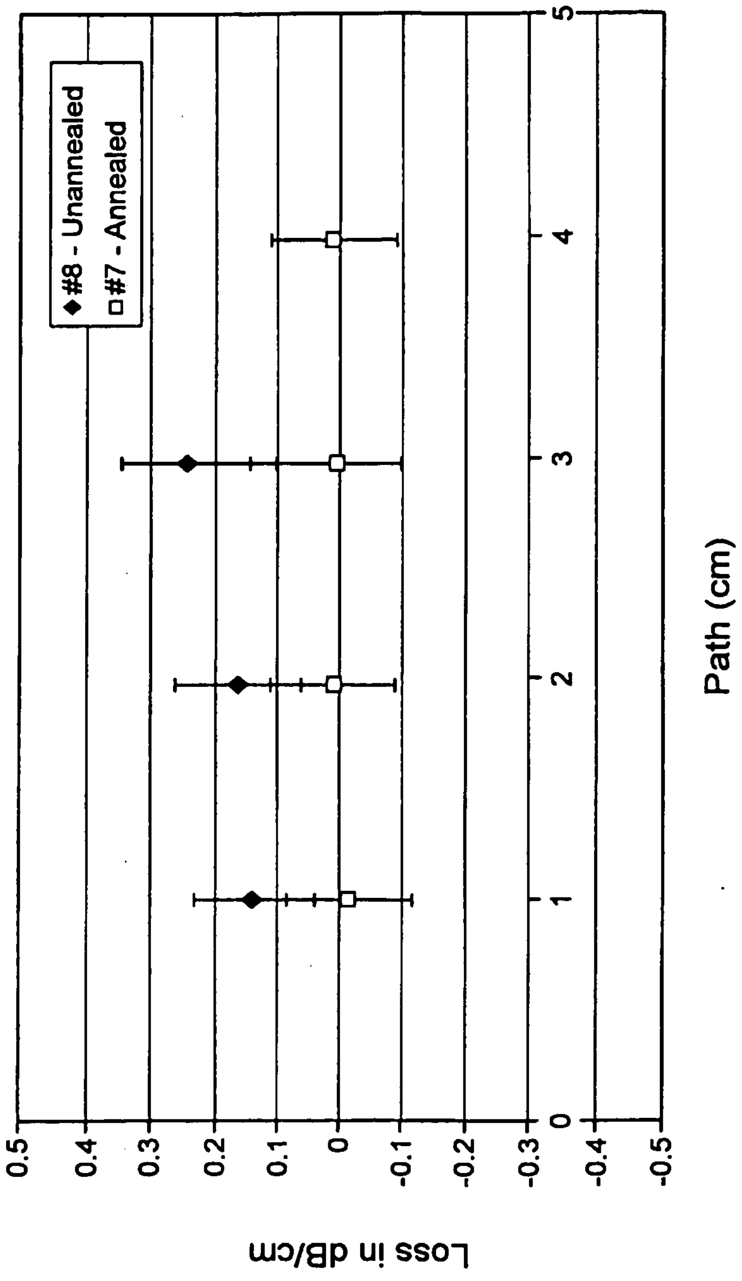
◆ #8 - Unannealed
□ #7 - Annealed
Loss in dB/cm
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
Path (cm)
0
1
2
3
4
5

FIG. 17

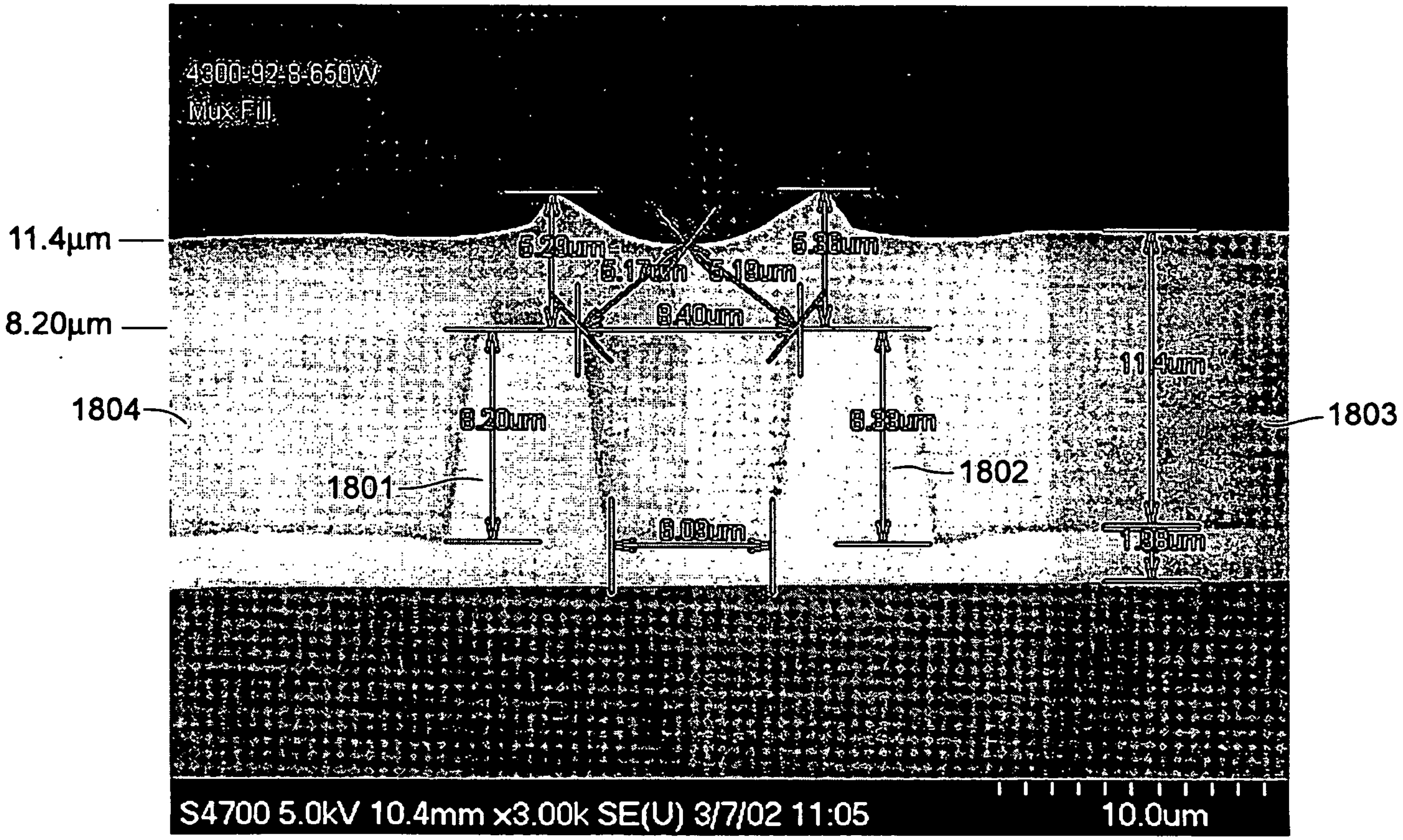
4300-92-8-650W
Mux Fill
11.4µm
8.20µm
1804
1801
1802
1803
6.29um
6.17um
6.19um
6.38um
8.40um
8.20um
8.33um
6.09um
11.4um
1.38um
S4700 5.0kV 10.4mm x3.00k SE(U) 3/7/02 11:05
10.0um

FIG. 18

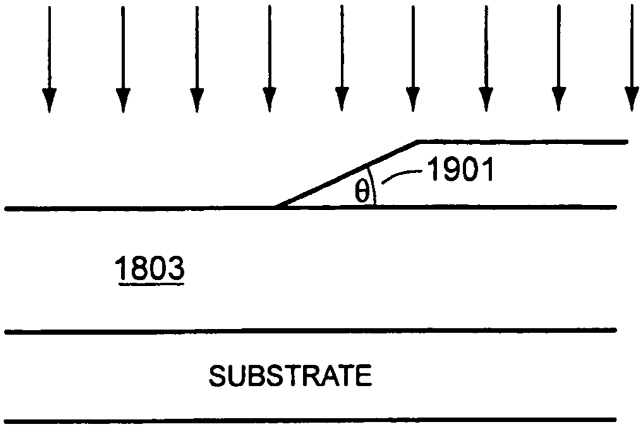
θ
1901
1803
SUBSTRATE

FIG. 19

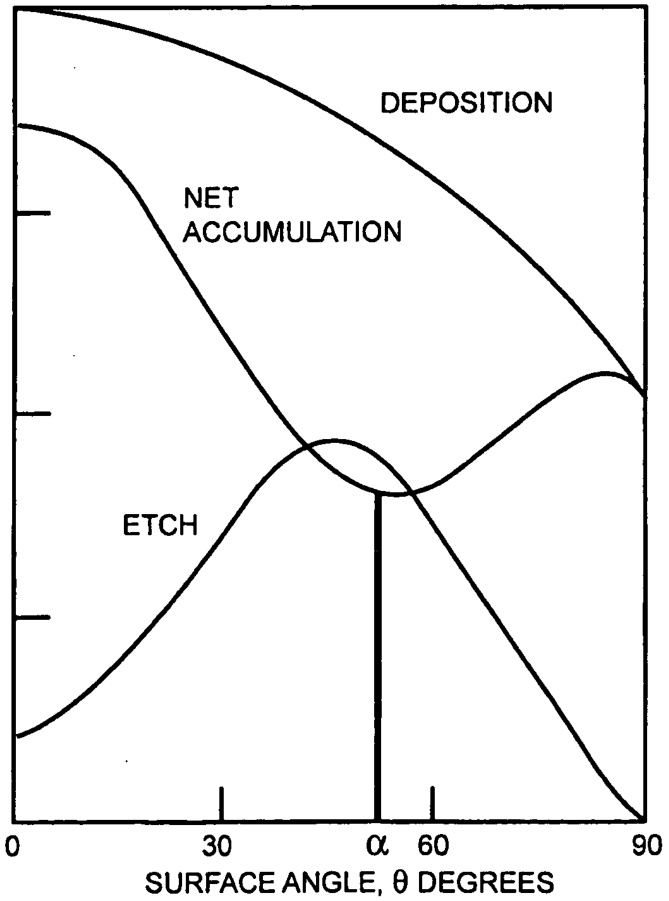
DEPOSITION
NET
ACCUMULATION
ETCH
0
30
α
60
90
SURFACE ANGLE, θ DEGREES

FIG. 20

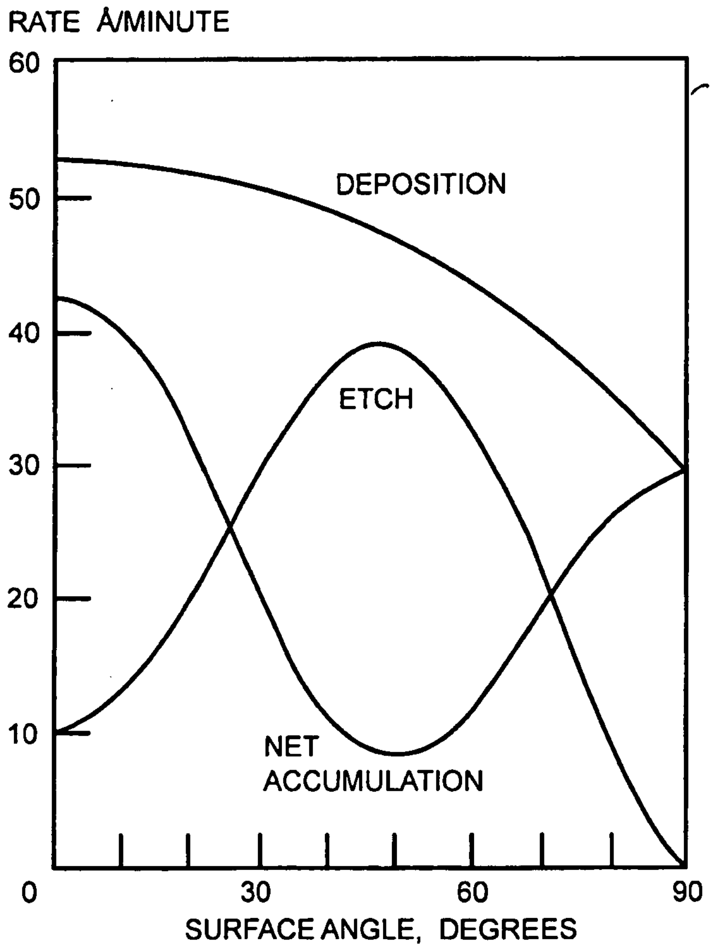
RATE Å/MINUTE
60
50
40
30
20
10
0
30
60
90
SURFACE ANGLE, DEGREES
DEPOSITION
ETCH
NET
ACCUMULATION

FIG. 21

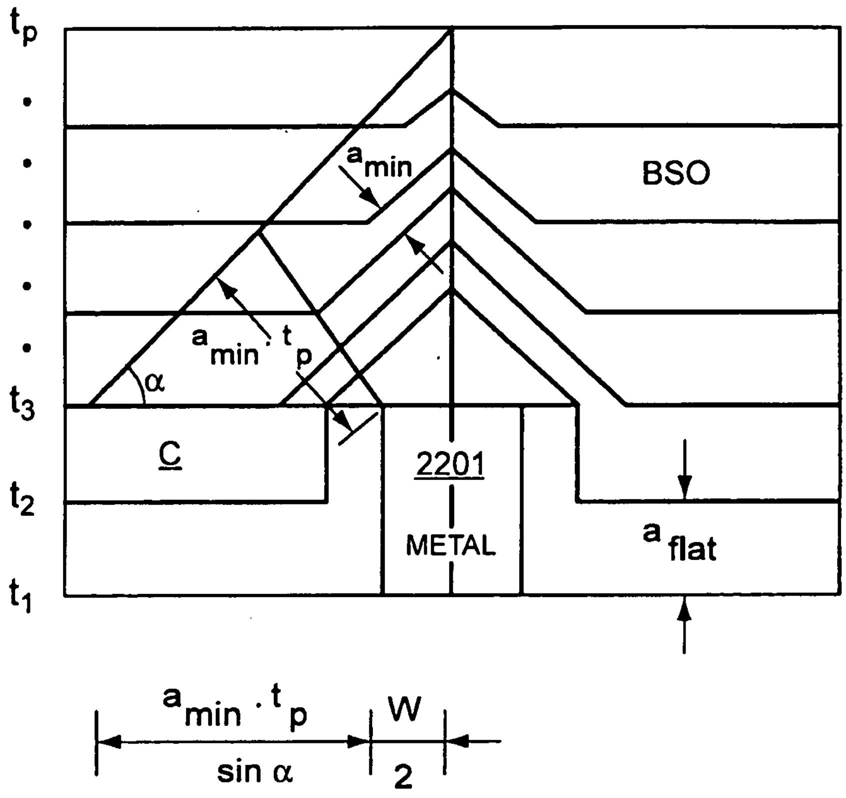
$t_p$
$t_3$
$t_2$
$t_1$
$a_{min}$
BSO
$a_{min} \cdot t_p$
α
C
2201
METAL
$a_{flat}$
$\frac{a_{min} \cdot t_p}{\sin \alpha}$
$\frac{W}{2}$

FIG. 22


4300-92-6-Home
S4700 5.0kV 9.8mm x3.00k SE(U) 2/25/02 15:02
10.0um
1801
2301
1802
1803
1804

FIG. 23

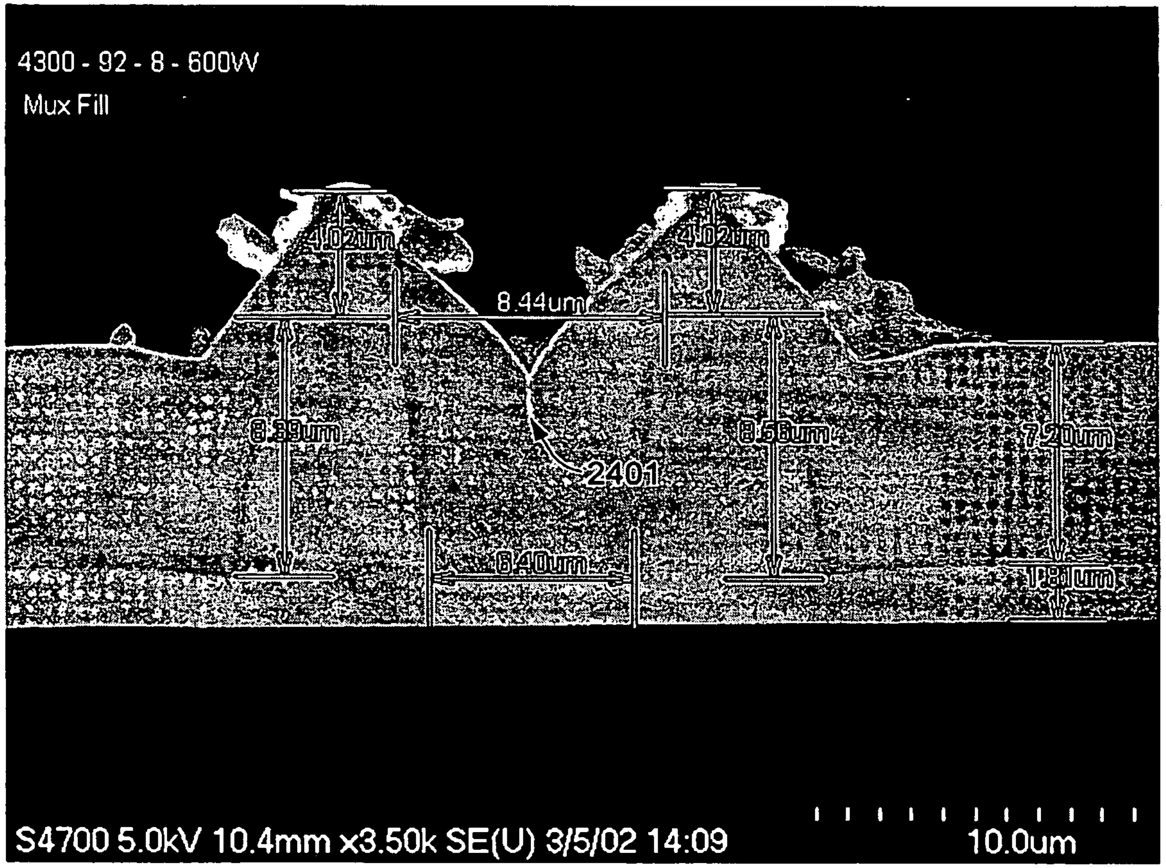
4300 - 92 - 8 - 600W
Mux Fill
4.02um
4.02um
8.44um
8.39um
8.58um
7.20um
2401
6.40um
1.81um
S4700 5.0kV 10.4mm x3.50k SE(U) 3/5/02 14:09
10.0um

FIG. 24

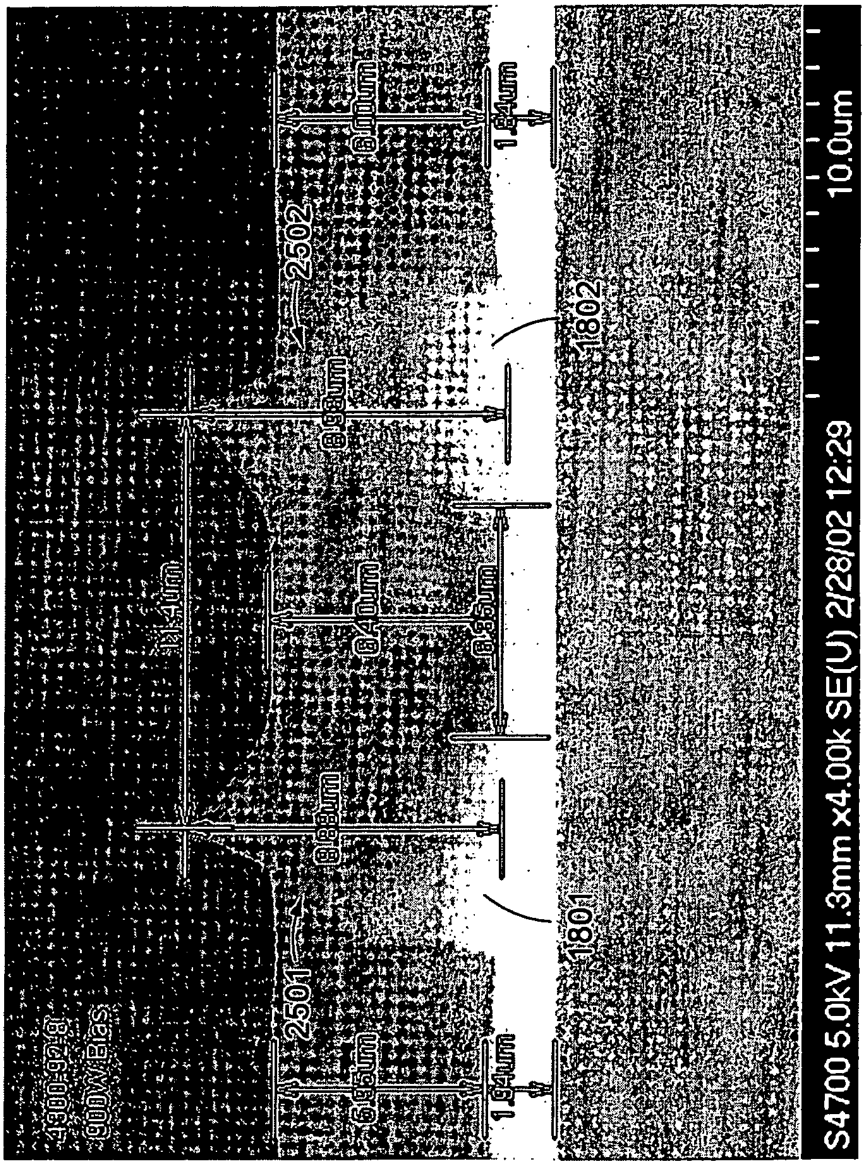
4300-92-8
900W Bias
2501
2502
1801
1802
1.94um
6.15um
8.88um
11.40um
8.40um
8.35um
8.98um
6.00um
1.94um
S4700 5.0kV 11.3mm x4.00k SE(U) 2/28/02 12:29
10.0um

FIG. 25

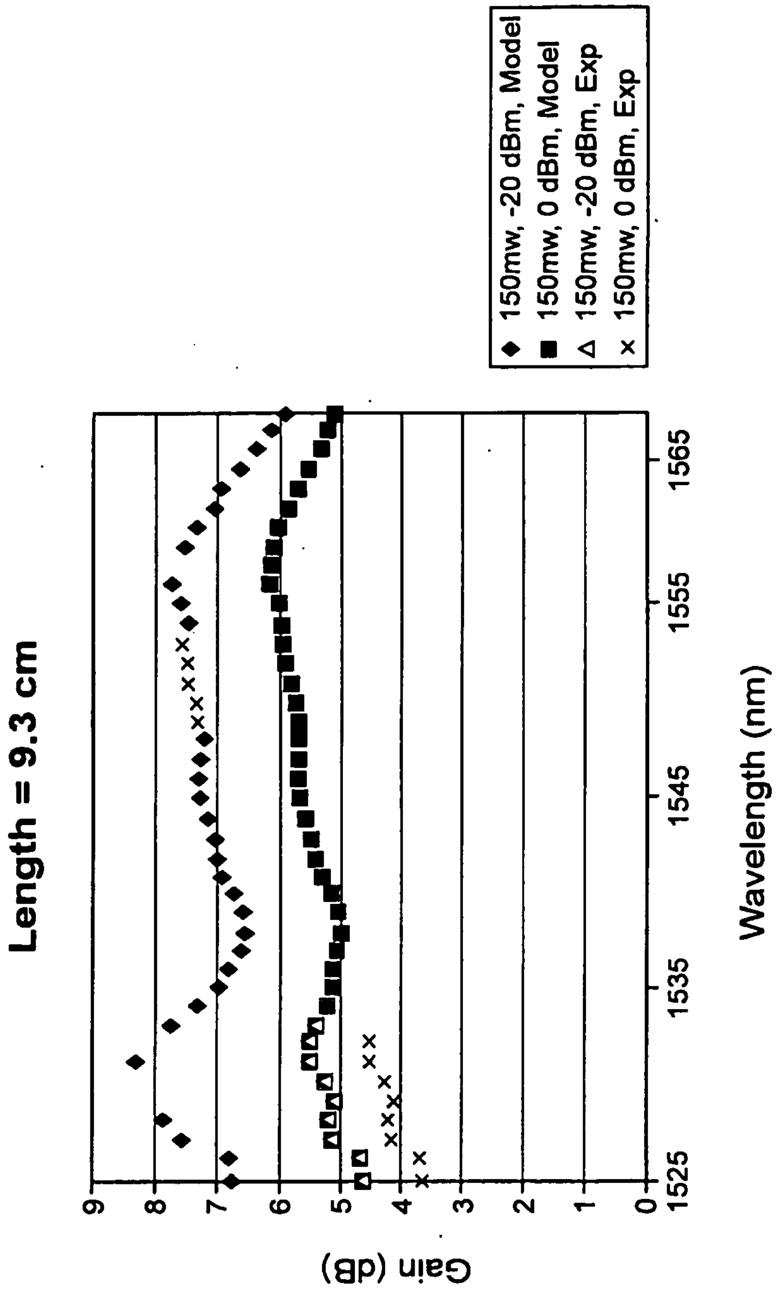
Length = 9.3 cm
Gain (dB)
9
8
7
6
5
4
3
2
1
0
1525
1535
1545
1555
1565
Wavelength (nm)
◆ 150mw, -20 dBm, Model
■ 150mw, 0 dBm, Model
△ 150mw, -20 dBm, Exp
× 150mw, 0 dBm, Exp

FIG. 26

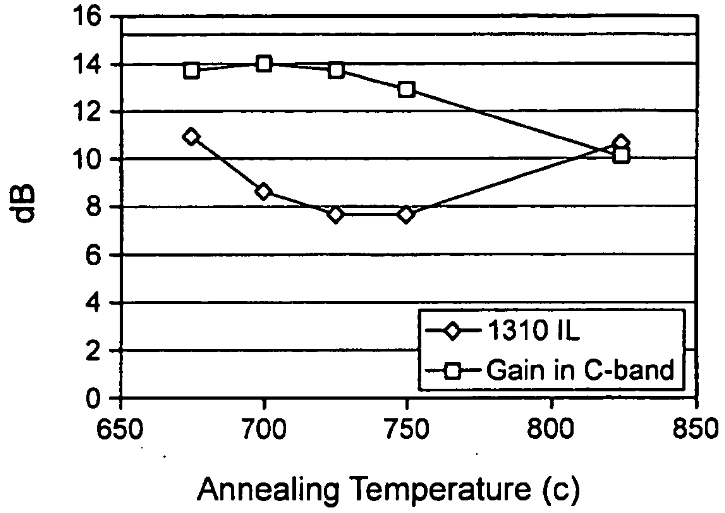
16
14
12
10
8
6
4
2
0
dB
650
700
750
800
850
Annealing Temperature (c)
1310 IL
Gain in C-band

FIG. 27

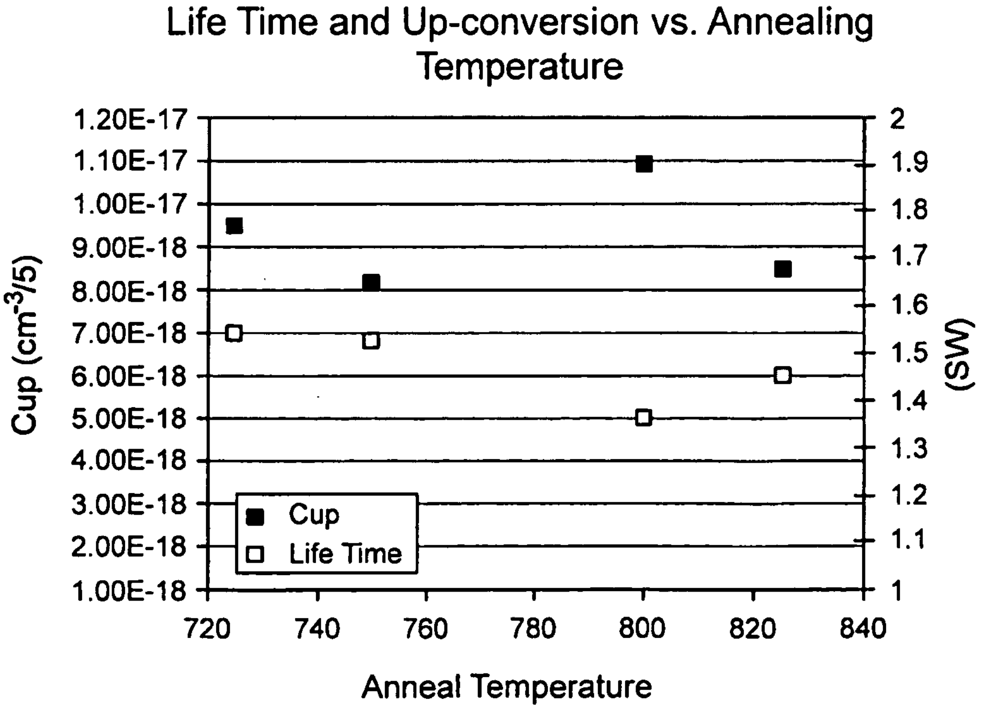
Life Time and Up-conversion vs. Annealing Temperature
1.20E-17
1.10E-17
1.00E-17
9.00E-18
8.00E-18
7.00E-18
6.00E-18
5.00E-18
4.00E-18
3.00E-18
2.00E-18
1.00E-18
Cup (cm^3/5)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
(SW)
720
740
760
780
800
820
840
Anneal Temperature
Cup
Life Time

FIG. 28

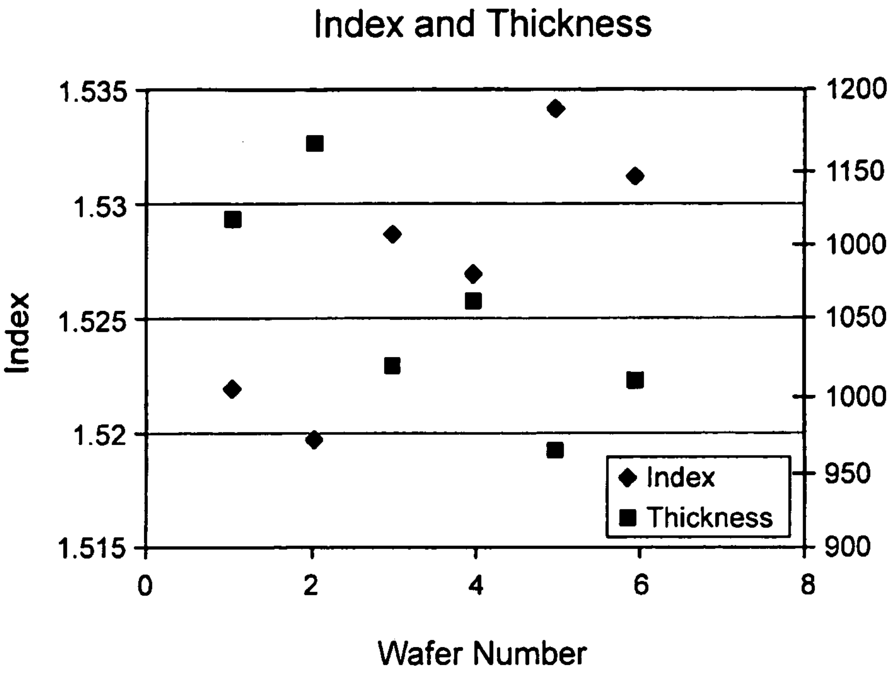
Index and Thickness
1.535
1.53
1.525
1.52
1.515
Index
1200
1150
1000
1050
1000
950
900
0
2
4
6
8
Wafer Number
◆ Index
■ Thickness

FIG. 29

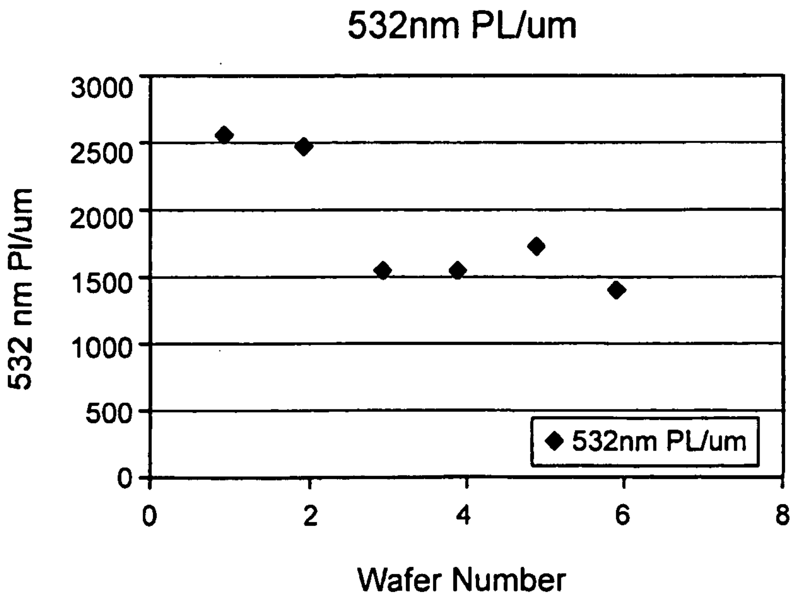
532nm PL/um
3000
2500
2000
1500
1000
500
0
532 nm Pl/um
0
2
4
6
8
Wafer Number
◆ 532nm PL/um

FIG. 30

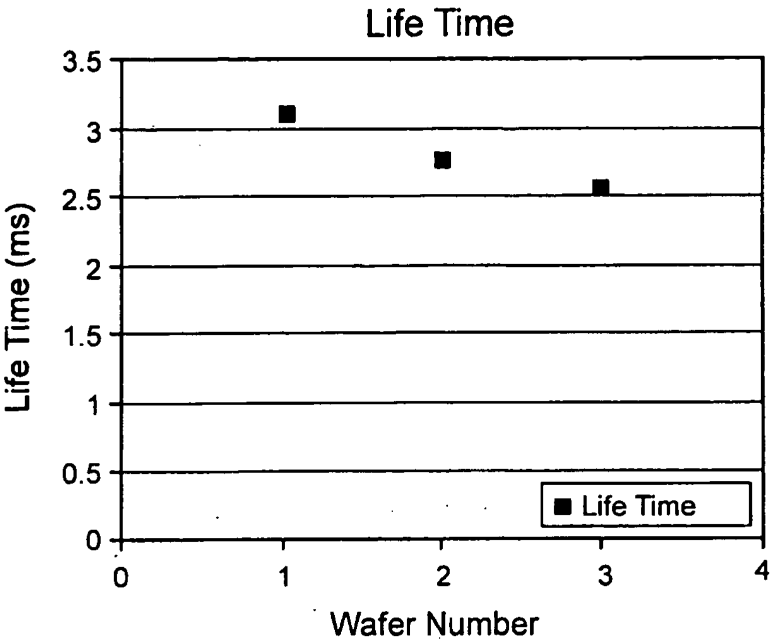
Life Time
Life Time (ms)
3.5
3
2.5
2
1.5
1
0.5
0
0
1
2
3
4
Wafer Number
■ Life Time

FIG. 31

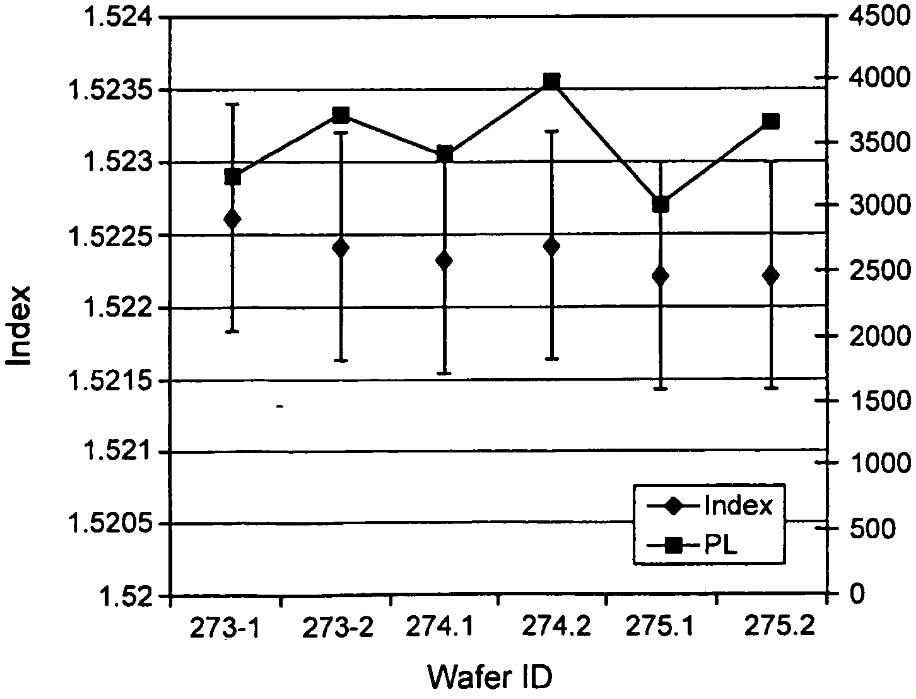
1.524
1.5235
1.523
1.5225
1.522
1.5215
1.521
1.5205
1.52
Index
4500
4000
3500
3000
2500
2000
1500
1000
500
0
273-1
273-2
274.1
274.2
275.1
275.2
Wafer ID
Index
PL

FIG. 32

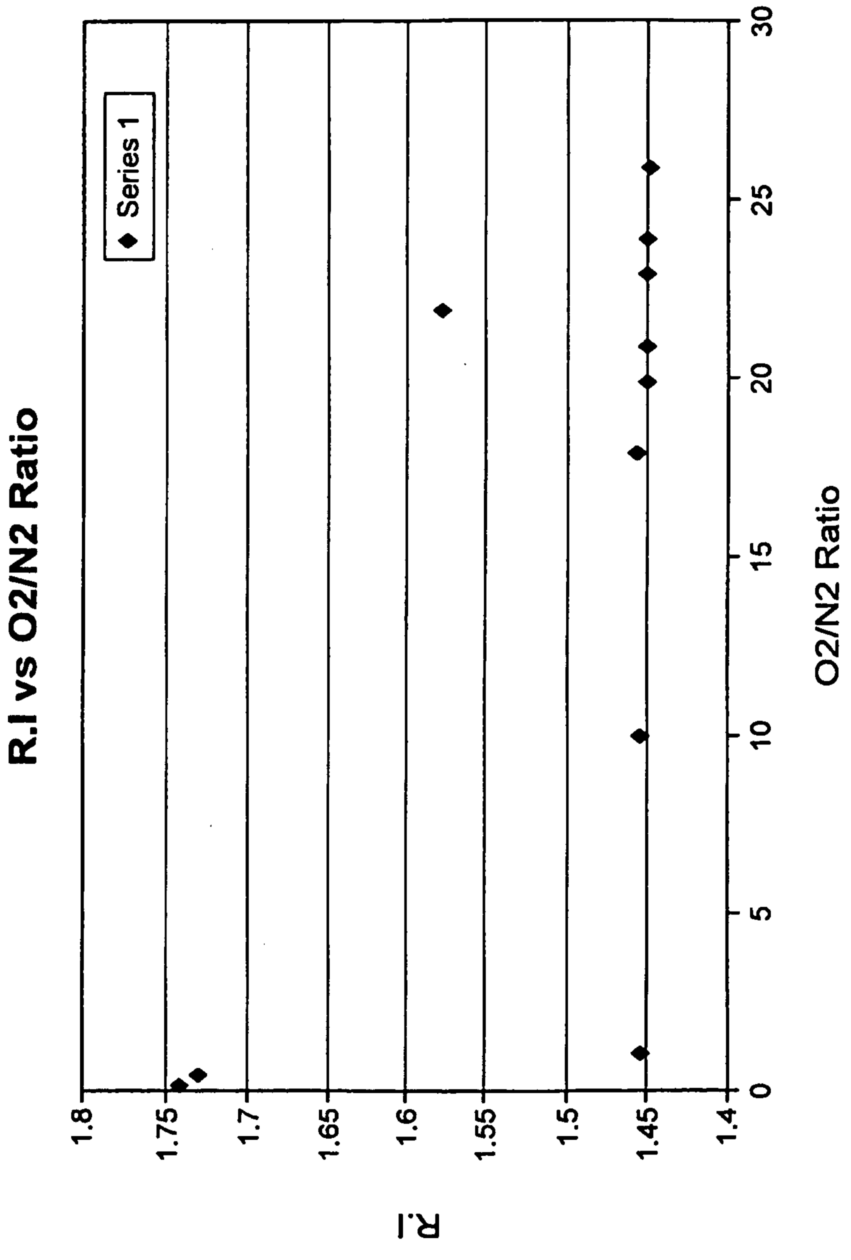
R.I vs O2/N2 Ratio
Series 1
R.I
1.8
1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4
0
5
10
15
20
25
30
O2/N2 Ratio

FIG. 33

| | | | |
|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | Complete if Known | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | Application Number | 10/101,863 |
| | | Filing Date | March 16, 2002 |
| | | First Named Inventor | Hongmei ZHANG |
| | | Art Unit | 2823 |
| *(Use as many sheets as necessary)* | | Examiner Name | ESTRADA, Michelle |
| Sheet 1 | of 1 | Attorney Docket Number | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | 5,478,456 | 12-26-1995 | Humpal et al. | |
| | | 6,846,765 B2 | 1-25-2005 | Imamura et al. | |
| | | | | | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

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|---|---|---|---|---|---|---|
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|---|---|---|---|
| | | DOREY, R.A., "Low temperature micromoulding of functional ceramic devices," Grant summary for GR/S84156/01 for the UK Engineering and Physical Sciences Research Council, 2 pages (2004). | |
| | | HOWSON, R.P., "The reactive sputtering of oxides and nitrides," *Pure & Appl. Chem.* *66*(6):1311-1318 (1994). | |
| | | Office Action issued September 21, 2005 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01). | |
| | | Office Action issued on August 8, 2005 in U.S. Serial No. 10/101,341 (Attorney Docket No. 09140-0017-00). | |
| | | Office Action issued on October 3, 2005 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00). | |
| | | Office Action issued on October 19, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |

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| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 2/8/06 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS ) Confirmation No.: 6938
)

**MAIL STOP RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed February 14, 2006, and filed concurrently with a Request for Continued Examination, Applicants propose that this application be amended as follows:

**Amendments to the Claims** are reflected in the listing of claims in this paper beginning on page 2.

**Remarks/Arguments** follow the amendment sections of this paper beginning on page 5.

## AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Currently Amended): The method of Claim ~~1~~21, further including holding the temperature of the substrate substantially constant.

3. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Currently Amended): The method of Claim 4, wherein the filter is a band rejection filter at the frequency of the bias power.

6. (Currently Amended): The method of claim 4, wherein the RF bias power is zero.

7. (Currently Amended): The method of Claim ~~1~~21, wherein the film is an upper cladding layer of a waveguide structure and the RF bias power is optimized to provide planarization.

8. (Currently Amended): The method of Claim ~~1~~21, wherein ~~the~~a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Currently Amended): The method of Claim ~~9~~8, wherein the ~~Oxygen flow~~mixture is adjusted to adjust the index of refraction of the film.

10. (Currently Amended): The method of Claim 8, wherein the~~ process gas~~mixture further includes nitrogen.

11. (Currently Amended): The method of Claim ~~1~~21, wherein ~~providing~~applying pulsed DC power to ~~a~~the target includes ~~providing~~adjusting pulsed DC power to a target which has an area

larger than that of the substrate.

12. (Currently Amended): The method of Claim ~~1~~21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Previously Presented): A method of depositing a film on a substrate, comprising:
providing pulsed DC power through a filter to a target;
providing RF bias power to a substrate positioned opposite the target; and
providing process gas between the target and the substrate, and
depositing a film on the backside of the target,
wherein the filter protects a pulsed DC power supply from the bias power, and
wherein a plasma is created between the target and the substrate.

15.-20. (Cancelled).

21. (Currently Amended): A method of depositing a film on a substrate, comprising:
conditioning a target;
preparing the substrate;
adjusting an RF bias power to the substrate;
setting a process gas flow; and
applying pulsed DC power to the target through a filter to create a plasma and deposit the film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface.

22. (Previously Presented ): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power

includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

## REMARKS

Claims 1-14 and 20-24 are pending in the above identified application. The Examiner has rejected claims 1-13 and 20, and allowed claims 14 and 21-24. With this paper, Applicants have amended claims 2-12 to depend upon allowed claim 21, and amended claim 21 for a typographical error, and cancelled claims 1 and 20. Applicants reserve the right to pursue claims 1 and 20 in a separate application.

The Examiner rejected claims 1, 8, 10-13, and 20 under 35 U.S.C. § 102(b) as being anticipated by Smolanoff et al. (6,117,279). Further, the Examiner rejected claims 2-6 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. and further in view of Fukui et al. (5,755,938). Without agreeing or acquiescing with the Examiner's comments regarding the claims and the prior art, Applicants have canceled claims 1 and 20 and amended claims 8, 2-6, and 10-13 to depend from allowed claim 21. Therefore, claims 2- 6, 8, and 10-13 are allowable for at least the same reasons as is claim 21.

The Examiner has allowed claims 14 and 21-24.

## Conclusion

Applicant respectfully requests that this Amendment be entered by the Examiner, placing claims 2-14 and 21-24 in condition for allowance. Applicants submit that the proposed amendments of claims 2-12 and 21 do not raise new issues or necessitate the undertaking of any additional search of the art by the Examiner, since all of the elements and their relationships claimed were either earlier claimed or inherent in the claims as examined. Therefore, this Amendment should allow for immediate action by the Examiner.

In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 24, 2006

By:____________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 746094839 US**

OIPE IAP50
FEB 24 2006
PATENT & TRADEMARK OFFICE

2-27-06

Rce/2823$

# REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL

Address to:
**Mail Stop RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

| | |
|---|---|
| Application Number: 10/101,863 | Confirmation Number: 6938 |
| Filing Date: March 16, 2002 | |
| First Named Inventor: ZHANG, Hongmei | |
| Group Art Unit: 2823 | |
| Examiner: ESTRADA, Michelle | |
| Attorney Docket Number: 9140.0016-00 | |
| **Attorney Customer Number: 22,852** | |

**This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of the above-identified application.**

Request for Continued Examination (RCE) practice under 37 C.F.R. § 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application.

1. **Submission required under 37 C.F.R. § 1.114: Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment.**
   - a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.
     - i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on ____________.
     - ii. ☐ Other ________________________________________
   - b. ☐ **DO NOT ENTER** the amendment(s) previously filed on __________. An alternate submission is attached.
   - c. ☒ Enclosed submission: .
     - i. ☒ Amendment/Reply
     - ii. ☐ Affidavit(s)/Declaration(s)
     - iii. ☒ Information Disclosure Statement
     - iv. ☐ Other ________________

2. Miscellaneous
   - a. ☐ Suspension of action on the above-mentioned application is requested under 37 C.F.R. § 1.103(c) for a period of months. (Period of suspension shall not exceed 3 months; fee under 37 C.F.R. § 1.17(i) required.)
   - b. ☐ Other ________________________________________

3. Fees
   - a. ☒ The filing fee is calculated as follows:
     - i. ☒ $790.00 RCE fee required under 37 C.F.R. § 1.17(e)
     - ii. ☐ Petition for extension of time for ( Months) $
     - iii. ☐ Other ________________________________________
   - b. ☒ The Commissioner is hereby authorized to charge the fee of $790.00 to Deposit Account No. 06-0916.
   - c. ☒ The Commissioner is authorized to charge any deficiencies in the filing fees, or credit any overpayments to Deposit Account No. 06-0916.

**Signature of Applicant, Attorney, or Agent Required**

| | |
|---|---|
| Name: Gary J. Edwards | Reg. No.: 41,008 |
| Signature: Gary J Edwards | Date: February 24, 2006 |

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FEB 24 2006
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PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
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Filed: March 16, 2002 )
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For: BIASED PULSE DC REACTIVE ) Confirmation No.: 6938
SPUTTERING OF OXIDE FILMS )

**MAIL STOP RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## FIFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 24, 2006

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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| Sheet | 1 | of | 3 |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-3,309,302 | 03-14-1967 | Heil | |
| | | US-5,338,625 | 08-16-1994 | Bates et al. | |
| | | US-5,561,004 | 10-01-1996 | Bates et al. | |
| | | US-5,930,046 | 07-27-1999 | Solberg et al. | |
| | | US-6,242,129 B1 | 06-05-2001 | Johnson | |
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| | | US-6,683,244 B2 | 01-27-2004 | Fujimori et al. | |
| | | US 2002/0001746 A1 | 01-03-2002 | Jenson | |
| | | US 2002/0076133 A1 | 06-20-2002 | Li et al. | |
| | | US 2002/0140103 A1 | 10-03-2002 | Kloster et al. | |
| | | US 2003/0178637 A1 | 09-25-2003 | Chen et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | WO 2004/106581 A2 | 12-09-2004 | Symmorphix, Inc. | | |
| | | WO 2004/106582 A2 | 12-09-2004 | Symmorphix, Inc. | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | KIM, H-K. and YOON, Y., "Characteristics of rapid-thermal-annealed $LiCoO_2$ cathode film for an all-solid-state thin film microbattery," *J. Vac. Sci. Technol. A 22*(4):1182-1187 (2004). | |
| | | Response to Office Action filed on October 17, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00). | |

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|---|---|---|---|
| Examiner Signature | | Date Considered | |

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| Sheet | 2 | of | 3 |

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| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

| | | **NON PATENT LITERATURE DOCUMENTS** | |
|---|---|---|---|
| | | Final Office Action issued on December 14, 2005 in U.S. Application No. 10/291,179 (Attorney Docket No. 09140-0001-00). | |
| | | PCT Invitation to Pay Additional Fees for PCT/US01/22750, dated March 13, 2002 (Attorney Docket No. 09140.0002-00304). | |
| | | PCT International Search Report for PCT/US01/22750, dated July 19, 2002 (Attorney Docket No. 09140.0002-00304). | |
| | | PCT Written Opinion for PCT/US01/22750, dated July 23, 2002 (Attorney Docket No. 09140.0002-00304). | |
| | | PCT International Preliminary Examination Report for PCT/US01/22750, dated October 8, 2002 (Attorney Docket No. 09140.0002-00304). | |
| | | Office Action issued on November 28, 2005 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00). | |
| | | Response to Office Action filed on December 21, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01). | |
| | | Response to Office Action filed on July 25, 2005 in Application No. 10/954,182 (Attorney Docket No. 09140.0016-01). | |
| | | Office Action issued on October 25, 2005, in U.S. Appl. No. 10/954,182 (Attorney Docket No. 09140-0016-01000). | |
| | | Response to Office Action filed on November 8, 2005, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00). | |
| | | Office Action issued on February 13, 2006, in U.S. Application No. 10/101,341 (Attorney Docket No. 09140-0017-00). | |
| | | Response to Office Action filed on January 3, 2006 in U.S. Application No. 10/650,461 (Attorney Docket No. 09140-0025-00). | |
| | | PCT International Preliminary Examination Report mailed April 15, 2004 in PCT/US03/24809 (Attorney Docket No. 09140-0025-00304). | |
| | | Office Action issued on December 2, 2005 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00). | |
| | | Specification and Preliminary Amendment as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0030-01). | |
| | | Office Action issued on March 24, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |
| | | Response to Office Action dated July 25, 2005 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140-0033-00). | |
| | | Response to Office Action filed January 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |

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| Examiner Signature | | Date Considered | |

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| Sheet | 3 | of | 3 |

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| *First Named Inventor* | ZHANG, Hongmei |
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| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| | | | |
|---|---|---|---|
| | | PCT International Search Report and Written Opinion for Application No. PCT/US2004/014524 dated March 2, 2005 (Attorney Docket No. 09140.0033-00304). | |
| | | PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014524, dated December 8, 2005 (Attorney Docket No. 09140.0033-00304). | |
| | | PCT International Search Report for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304). | |
| | | PCT Written Opinion for Application No. PCT/US2004/014523 dated January 17, 2005 (Attorney Docket No. 09140.0034-00304). | |
| | | PCT International Preliminary Report on Patentability for Application No. PCT/US2004/014523, dated December 8, 2005 (Attorney Docket No. 09140.0034-00304). | |
| | | Specification as filed for U.S. Appl. No. 11/297,057 (Attorney Docket No. 09140.0042-00). | |

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(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **DEMARAY, Richard, Ernest** [US/US]; 190 Fawn Lane, Portola Valley, CA 94028 (US). **NARASIMHAN, Mukundan** [IN/US]; 293 Bluefield Drive, San Jose, CA 91536 (US).

(74) Agent: **GARRETT, Arthur, S.**; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street N.W., Washinton, D.C. 20005-3315 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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WO 2004/106581 A2

# (54) Title: TRANSPARENT CONDUCTIVE OXIDES

**(57) Abstract:** A method of deposition of a transparent conductive film from a metallic target is presented. A method of forming a transparent conductive oxide film according to embodiments of the present invention include depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias, and controlling at least one process parameter to affect at least one characteristic of the conductive oxide film. The resulting transparent oxide film, which in some embodiments can be an indium-tin oxide film, can exhibit a wide range of material properties depending on variations in process parameters. For example, varying the process parameters can result in a film with a wide range of resistive properties and surface smoothness of the film.

# Transparent Conductive Oxides

## Related Applications

**[0001]** The present application claims priority to U.S. Provisional Application 60/473,379, "Transparent Conductive Oxides from a Metallic Target," by R. Ernest Demaray and Mukundan Narasimhan, filed on May 23, 2003, herein incorporated by reference in its entirety.

## Background

1. Field of the Invention

**[0002]** The present invention is related to deposition of oxides on a substrate and, in particular, deposition of transparent conductive oxides.

2. Discussion of Related Art

**[0003]** Transparent conductive oxides have a wide variety of uses, including applications to solar cells, organic light emitting diodes (OLEDs), electric field devices, current devices (i.e. touch screens), energy efficient windows, conductive anti-reflective devices, electromagnetic interference shields, heaters, transparent electrodes, coatings for cathode ray tube (CRT) displays, to name only a few. Another important application is for touch sensitive MEMS devices, such as those used, for example, in fingerprint sensors and such. In many cases, the electrical properties of the conducting film is of great importance.

**[0004]** Specifically, for OLED applications, films deposited with current technologies are generally rough, resulting in stress risers and field concentration issues, that can cause leakage. Further, asperities in the resulting film can induce lifetime dependent defects in nearest neighbor films that can shorten device lifetimes. Additionally, the brightness of the emergent light from the OLED can be reduced.

**[0005]** Transparent conductive oxides have been deposited from ceramic targets by RF magnetron sputtering. However, the surface of properties of the resulting films often include nodules or asperites which can cause arcing, defects, surface roughness, and other deleterious effects in the resulting film. Additionally, ceramic targets tend to be more expensive to produce than metallic targets.

**[0006]** Previous attempts at deposition of transparent conductive oxides, for example indium tin oxide (ITO), with metallic targets have presented numerous problems, including small process windows, problems in process controllability, a disappearing anode effect, and particle deposition on the film. Such attempts have been abandoned. Deposition with ceramic targets has also been difficult, including problems with particles, nodule formation, and arching during deposition. In both cases, film smoothness has presented major difficulties. Additionally, control of film parameters such as, for example, resistivity and transparency has been difficult.

**[0007]** Therefore, there is need for cost effective deposition of smoother layers of transparent conductive oxides with greater control over layer properties such as resistivity and transparency.

## Summary

**[0008]** In accordance with the present invention, a method of depositing of a transparent conductive film from a metallic target is presented. A method of forming a transparent conductive oxide film according to embodiments of the present invention includes depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias, and controlling at least one process parameter to provide at least one characteristic of the conductive oxide film at a particular value.

**[0009]** A method of depositing a transparent conductive oxide film on a substrate according to some embodiments of the invention, then, includes placing the substrate in a reaction chamber, adjusting power to a pulsed DC power supply coupled to a target in the reaction chamber, adjusting an RF bias power coupled to the substrate, adjusting gas flow into the reaction chamber, and providing a magnetic field at the target in order to direct deposition of the transparent conductive oxide film on the substrate in a pulsed-dc biased reactive-ion deposition process, wherein the transparent conductive oxide film has a particular characteristic.

**[0010]** The resulting transparent oxide film, which can be deposited according to some embodiments of the present invention, can be an indium-tin oxide (ITO) film. An ITO film can have a wide range of material properties depending on variations in process parameters. For example, varying the process parameters according to some embodiments of the present invention can result in a wide range of resistive properties and surface smoothness of the film.

**[0011]** These and other embodiments of the invention are further discussed below with reference to the following figures.

## Short Description of the Figures

[0012] Figures 1A and 1B illustrate a pulsed-DC biased reactive ion deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[0013] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B

[0014] Figure 3A shows an Atomic Force Microscopy (AFM) image of an indium-tin-oxide (ITO) process according to some embodiments of the present invention.

[0015] Figure 3B shows an Atomic Force Microscopy (AFM) image of another ITO process deposited using a process according to some embodiments of the present invention.

[0016] Figure 4 shows the variation of bulk resistivity of an ITO layer according to some embodiments of the present invention as a function of the oxygen flow for two different target powers before and after a 250 °C anneal in vacuum.

[0017] Figure 5 shows the variation of the sheet resistance of an ITO layer according to some embodiments of the present invention as a function of the oxygen flow used for two different target powers before and after a 250 °C anneal in vacuum.

[0018] Figure 6 shows the target current and voltage (min and max) as a function of oxygen flow.

[0019] Figure 7 shows the thickness change in layers of ITO according to embodiments of the present invention as a function of oxygen flow.

[0020] Figure 8 illustrates the relationship between oxygen flow and oxygen partial pressure for a metallic target.

[0021] Figures 9A-9D illustrate the smoothness of transparent conductive oxides deposited with ceramic targets according to the present invention.

[0022] In the figures, elements having the same designation have the same or similar function.

## Detailed Description

[0023] Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films are deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101863.

[0024] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These Komatsu reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[0025] Apparatus 10 includes target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[0026] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[0027] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[0028] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[0029] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

[0030] However, both RF and pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications. By applying a RF bias on wafer 16 during deposition, the deposited film can be densified by energetic ion bombardment and the columnar structure can be substantially eliminated.

[0031] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between -50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 600 mm.

[0032] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

[0033] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[0034] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission or absorptivity.

[0035] Target 12 can be formed of any materials. Typically metallic materials, for example, include combinations of In and Sn. Therefore, in some embodiments, target 12 includes a metallic target material formed from intermetallic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetallics. *See* U.S. Application Serial No. 10/101,341. Typical ceramic target materials include alumina, silica, alumina silicates, and other such materials.

[0036] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 to 20 individual tiles. Tiles can be finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[0037] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0038] Reactive gases that provide a constant supply of ionic oxygen to keep the target surface oxidized can be provided to expand the process window. Some examples of the gases that can be utilized for controlling surface oxidation are $CO_2$, water vapor, hydrogen, $N_2O$, fluorine, helium, and cesium. Additionally, a feedback control system can be incorporated to control the oxygen partial pressure in the reactive chamber. Therefore, a wide range of oxygen flow rates can be controlled to keep a steady oxygen partial pressure in the resulting plasma. Other types of control systems such as target voltage control and optical plasma emission control systems can also be utilized to control the surface oxidation of the target. As shown in Figure 1A, power to target 12 can be controlled in a feedback loop at supply 14. Further, oxygen partial pressure controller 20 can control either oxygen or argon partial pressures in plasma 53.

[0039] In some embodiments, transparent conductive oxides can be deposited on various substrates utilizing an inidium-tin (In/Sn) metallic target. A series of depositions on glass in accordance with the present invention is illustrated in Table I. The parameters in the process column of Table I are in the format (pulsed DC power/RF bias power/pulsing frequency/reverse time/deposition time/Ar flow (sccms)/$O_2$ flow (sccms)). An indium-tin (In/Sn: 90%/10% by weight) target using a reactive-pulsed DC (RPDC) process such as that described in U.S. Application Serial No. 10/101,863 was utilized. A power supply with 2MHz RF bias applied to substrate 16 was utilized in the process. Along with the process parameters for each of the separate depositions, each defined by a "Slot" number in the first column, the target voltage, and target current ranges for each of the depositions is also listed.

[0040] Table 2 shows the results obtained by using the process parameters in Table 1. The results include the sheet resistance, thickness, bulk resistivity, and refractive indices of the resulting films. Again, the first column indicates the slot number of the deposition. The process for each slot number is reiterated in column 2 of Table 2. The sheet resistance of selected ones of the films resulting from the deposition is listed in the third column and the uniformity of the sheet resistance is indicated in the fourth column. The thickness of the film and its uniformity of each of the films deposited by the indicated process is indicated in the fifth and sixth columns. The bulk resistance of selected ones of the films, ρ, is also indicated. Additionally, the refractive index taken at 632 nm is indicated along with the film uniformity of that index. The comments section of Table 2 indicates whether the resulting film is transparent, translucent, or metallic in character.

**[0041]** Figure 3A shows the Atomic Force Microscopy (AFM) image of an ITO film produced by the process identified in slot #5 in tables 1 and 2. That process, with particularly low oxygen flow rates (24 sccm), produced a rough film with an Ra of about 70 Å and an Rms of about 90 Å. The film also appears to be metallic with this particular oxygen flow and the film roughness is high. Such a film could be applicable to large surface area requirements, for example solar cell applications. Wile not being limited by any particular theory, it is suspected that the roughness of this film reflects the sub-stoichiometric nature of the film caused by insufficient oxygen flow in the plasma. As can be seen in Figure 3B, where the oxygen flow during deposition has been significantly increased to about 36 sccm, the film is smooth.

**[0042]** Figure 3B shows an Atomic Force Microscopy (AFM) image of an ITO film deposited using the process described in slot #19 of Tables 1 and 2. In that process, the oxygen flow rate is increased to 36 sccm. The film appears to be transparent and conductive and the surface roughness is ~6Å Ra and Rms of about 13 Å, which is acceptable for OLED requirements. As can be seen from Figures 3A and 3B, variation in oxygen partial pressure (as indicated by increased flow rate) has a large influence on the characteristics of the resulting deposited film.

**[0043]** The resistivity of the film layer and the smoothness of the film layer can be related. In general, the higher the resistivity of the film layer, the smoother the film layer. Figure 4 shows the variation of bulk resistivity of the ITO as a function of the oxygen flow rate used for two different target powers before and after a 250 °C anneal in vacuum. The bulk resistivity of the film exhibits a sudden transition downward as the oxygen flow rate is lowered. This transition occurs when the target surface becomes metallic from being poisoned with oxygen. The data utilized to form the graph shown in Figure 4 has been taken from Tables 1 and 2.

[0044] Figure 5 shows the variation of the sheet resistance of an ITO film as function of the $O_2$ flow used for two different target powers before and after a 250C anneal in vacuum. As shown in Figure 5, the sheet resistance follows similar trends as the bulk resistivity of the film.

[0045] Figure 6 shows the target current and voltage (min and max) as a function of the oxygen flow rate. The target voltage increases as the oxygen flow rate is lowered. It could be seen here that at a 40 sccm oxygen flow rate through repeated depositions, the target voltage is not constant. This illustrates the utility of a target voltage feedback control system that adjusts the power supplied to target 12 to hold the target voltage constant. Therefore, as shown in Figure 1A, PDC power 14 can include feedack loop to control the voltage on target 12.

[0046] Figure 7 shows the thickness change of a resulting film as a function of oxygen flow rate in sccm. The thickness of the film increases as the oxygen flow decreases but this could make opaque metallic films and so choosing the correct oxygen flow and utilizing an oxygen flow feedback control system to control material characteristics such as, for example, transparency or conductivity can be desirable.

[0047] In some embodiments, instead of oxygen flow rate, oxygen partial pressure can be controlled with a feedback system 20 (see Figure 1A). Controlling the oxygen partial pressure can provide better control over the oxygen content of the plasma, and therefore the oxygen content of the resulting films, and allows better control over the film characteristics. Figure 8 illustrates the relationship between the flow rate and partial pressure. As can be seen from Figure 8, in order to reach the saturated region (e.g., when target 12 is completely poisoned with oxygen), no increase in flow rate is required. In some embodiments, reactor 10 can include a partial pressure feedback loop controller 20 that controls the oxygen flow in order to maintain a desired partial pressure of oxygen in the plasma. Such a controller can be the IRESS system, that can be purchased from Advanced Energy, Inc., Ft. Collins, Colorado. It has been found that film parameters such as resistivity, smoothness, and transparency can be highly dependent on oxygen partial pressures, and therefore these characteristics of the resulting deposited layer can be controlled by adjusting the oxygen partial pressures.

[0048] Some embodiments of the present invention can be deposited with ceramic targets. An example target is an ITO (In/Sn 90/10) ceramic target can be utilized. Table 3 illustrates some example processes for deposition of ITO utilizing a ceramic target according to the present invention. Bulk resistivity, sheet resistance, resistance, thicknesses, deposition rates, and index of refraction of the resulting films are shown along with the process parameters utilized in the deposition. Figure 9A shows an AFM depiction of a transparent conductive oxide film corresponding to run #10 in Table 3. Figure 9B shows an AFM depiction of a transparent conductive oxide film corresponding to run #14 in Table 3. Figure 9C shows an AFM depiction of a transparent conductive oxide film corresponding to run #16 in Table 3. Figure 9D shows an AFM depiction of a transparent conductive oxide film layer corresponding to run #6 in Table 3.

[0049] Figures 9A through 9D illustrate the roughnesses of selective depositions of ITO deposited utilizing the ceramic target. In Figure 9A, the roughest surface shown, the film was deposited using 3kW RF power, 100W bias, 3 sccm $O_2$ and 60 sccm Ar at a temperature of 280 °C. The layer grew to a thickness of 1200 Å in 100 seconds of deposition time and exhibited a sheet resistance of 51 ohms/sq. The roughness illustrated in Figure 9A is characterized by an Ra=2.3 nm and $R_{MS}$ of 21 nm.

[0050] The ITO film shown in Figure 9B was deposited using 3 kW RF power, 300 W bias, 3 sccm $O_2$ and 60 sccm Ar at a temperature of 280 °C. The layer illustrated in Figure 9B grew to a thickness of 1199 Å in 100 sec. The layer in Figure 9B exhibited a sheet resistance of 39 ohms/sq. The roughness illustrated in Figure 9B is characterized by an Ra=1.1 nm and Rmax of 13 nm.

[0051] The ITO film shown in Figure 9C was deposited using 3 kW RF power, 300 W bias, 3 sccm $O_2$, 30 sccm Ar at a temperature of 280 °C. The layer grew to a thickness of 1227 Å in 100 seconds of deposition time and exhibited a sheet resistance of 57 ohms/sq. The roughness illustrated in Figure 9C can be characterized by an Ra=0.88 nm and a Rmax of 19.8 nm.

[0052] Figure 9D was deposited using 1.5 kW RF power, 300 W bias, 0 sccm $O_2$, 30 sccm Ar at a temperature of 280 C. The layer grew to a thickness of 580 Å in 100 seconds of deposition time and exhibited a sheet resistance of 106 ohms/sq. The roughness illustrated in Figure 9C can be characterized by an Ra=0.45 nm and an Rmax of 4.6 nm.

[0053] Utilizing the example depositions described herein, the roughness and resistivity of a transparent oxide film can be tuned to particular applications. In general, particularly high resistivities can be obtained, which are useful for touch sensitive devices. As shown in Table 3, the sheet resistance ranged from about 39 Ω/sq for trial # 14 to a high of 12,284 Ω/sq for trial #1. Careful variation of the process parameters, therefore, allow control of sheet resistance over an extremely broad range. Low resistivities can be obtained by adjusting the process parameters for uses in devices such as OLEDS and MEMS display devices. As is illustrated in Table 3, the bulk resistivity can be controlled to be between about 2E-4 micro-ohms-cm to about 0.1 micro-ohms-cm. Additionally, other parameters such as refractive index and transparency of the film can be controlled.

[0054] Further, deposition of transparent conductive oxide layers, for example ITO, can be doped with rare-earth ions, for example erbium or cerium, can be utilized to form color-conversion layers and light-emission sources. In some embodiments, a rare-earth doped target can be made in a single piece to insure uniformity of doping. Co-doping can be accomplished in the target.

[0055] Similar processes for other metallic conductive oxides can also be developed. For example, deposition of zinc oxide films. Further, as can be seen in the examples shown in Table 3, low temperature depositions can be performed. For example, transparent conductive oxides according to the present invention can be deposited at temperatures as low as about 100 °C. Such low temperature depositions can be important for depositions on temperature sensitive materials such as plastics.

[0056] Other thin film layers according to the present invention include deposition of other metal oxides to form conducting and semi-conducting films. Thin films formed according to the present invention can be utilized in many devices, including, but not limited to, displays, photovoltaics, photosensors, touchscreens, and EMI shielding.

[0057] Embodiments of the invention disclosed here are examples only and are not intended to be limiting. Further, one skilled in the art will recognize variations in the embodiments of the invention described herein which are intended to be included within the scope and spirit of the present disclosure. As such, the invention is limited only by the following claims.

Table I

| Slot # | Process | Target Voltage (V) | | Target Current (Amps) | |
|---|---|---|---|---|---|
| | | Min | Max | Mix | Max |
| 14 | 1.5kw/100w/200khz/2.2μs/300s/20Ar/80$O_2$ | 244 | 252 | 5.94 | 6.14 |
| 15 | 1.5kw/100w/200khz/2.2μs/300s/20Ar/40$O_2$ | 254 | 263 | 5.7 | 5.9 |
| 17 | 1.5kw/100w/200khz/2.2μs/300s/20Ar/40$O_2$ | 252 | 260 | 5.76 | 5.96 |
| 19 | 1.5kw/100w/200khz/2.2μs/300s/20Ar/36$O_2$ | 254 | 263 | 5.72 | 5.92 |
| 21 | 1.5kw/100w/200khz/2.2μs/300s/20Ar/30$O_2$ | 255 | 268 | 5.76 | 5.9 |
| 1 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 80$O_2$ | 224 | 233 | 4.32 | 4.5 |
| 2 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 36$O_2$ | 231 | 243 | 4.12 | 4.3 |
| 3 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 32$O_2$ | 232 | 242 | 4.12 | 4.28 |
| 4 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 28$O_2$ | 237 | 243 | 4.1 | 4.22 |
| 5 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 24$O_2$ | 233 | 243 | 4.1 | 4.34 |
| 6 | 1kw/100w/200khz/2.2μs/300s/20Ar/ 28$O_2$ | 231 | 245 | 4.12 | 4.3 |

Table II

| Slot # | Process | Rs (Ohms/ Sq) | Rs unif % | Th (nm) | Th std 1sig | Bulk Rho (µOhm-cm) | R.I (@632nm) | R.I Unif (%) | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 14 | 1.5kw/100w/200khz/2.2µs/ 300s/20Ar/80O2 | | | 38.59 | 0.16 | | 1.980758 | 0.000005 | transparent |
| 15 | 1.5kw/100w/200khz/2.2µs/ 300s/20Ar/40O2 | 94112 | 2 | 57.28 | 0.51 | 539073.5 | 1.951452 | 0.029342 | translucent |
| 17 | 1.5kw/100w/200khz/2.2µs/ 300s/20Ar/40O2 | 33927 | 60.282 | 58.48 | 1.37 | 198405.1 | 1.936166 | 0.040957 | translucent |
| 19 | 1.5kw/100w/200khz/2.2µs/ 300s/20Ar/36O2 | 7335.32 | 72.49 | 67.75 | 1.03 | 49696.8 | 1.980746 | 0.000018 | translucent |
| 21 | 1.5kw/100w/200khz/2.2µs/ 300s/20Ar/30O2 | 22.3507 | 2.995 | 80 | | 178.8 | | | metallic |
| 1 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/80O2 | | | 26.69 | 0.32 | | 1.980326 | 0.00096 | transparent |
| 2 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/36O2 | | | 36.4 | 0.13 | | 1.980756 | 0.000003 | transparent |
| 3 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/32O2 | | | 39.3 | 0.15 | | 1.980761 | 0 | transparent |
| 4 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/28O2 | | | 44.02 | 0.24 | | 1.98076 | 0.000001 | transparent |
| 5 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/24O2 | 58.1031 | 7.467 | 50 | | 290.5 | | | metallic |
| 6 | 1kw/100w/200khz/2.2µs/ 300s/20Ar/28O2 | 58.0992 | 10.566 | 45 | | 261.4 | | | metallic |

**Table III**

| Trial | Run (sec) | Target Power (kW) | Bias/ W | O2 | Ar | T (oC) | Rs (Ohms/Sq) | Rs (non-unif) | Bulk Rho (uOhmcm) | Thickness (Å) | n | DepRate (A/sec) | Target /V | Target/I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | 100 | 3 | 300 | 3 | 60 | 280 | 38.69 | 4.07% | 4.64E-04 | 1200 | 1.864 | 12 | | |
| 16 | 100 | 3 | 300 | 3 | 30 | 280 | 56.90 | 7.94% | 6.98E-04 | 1227 | 1.888 | 12.27 | 288-308 | 9.86-10.42 |
| 10 | 100 | 3 | 100 | 3 | 60 | 280 | 50.98 | 11.89% | 6.25E-04 | 1225 | 1.933 | 12.25 | 265-275 | 10.92-11.36 |
| 4 | 100 | 1.5 | 100 | 3 | 30 | 280 | 383.62 | 21.72% | 2.09E-03 | 543.9 | 2.016 | 5.439 | 238-251 | 5.98-6.32 |
| 8 | 100 | 1.5 | 300 | 3 | 30 | 280 | 504.02 | 7.23% | 2.44E-03 | 483.5 | 2.082 | 4.835 | 239-250 | 5.98-6.33 |
| 2 | 100 | 1.5 | 100 | 3 | 30 | 280 | 402.52 | 26.80% | 2.10E-03 | 520.7 | 2.056 | 5.207 | 225-239 | 6.46-6.68 |
| 6 | 100 | 1.5 | 300 | 0 | 30 | 280 | 106.21 | 6.12% | 6.17E-04 | 580.5 | 1.945 | 5.805 | 237-250 | 5.98-6.38 |
| 12 | 100 | 3 | 100 | 4 | 30 | 280 | 374.34 | 19.43% | 4.18E-03 | 1116 | 1.917 | 11.16 | 285-300 | 9.98-10.52 |
| 15 | 100 | 3 | 300 | 4 | 30 | 100 | 6264.69 | 58.18% | 6.81E-02 | 1087 | 1.897 | 10.87 | 282-304 | 10.00-10.62 |
| 7 | 100 | 1.5 | 200 | 4 | 30 | 100 | 7509.45 | 44.14% | 2.95E-02 | 392.3 | 2.149 | 3.923 | 237-250 | 6.02-632 |
| 1 | 100 | 1.5 | 100 | 4 | 30 | 100 | 12284.82 | 112.55% | 4.78E-02 | 389.1 | 2.236 | 3.891 | 238-250 | 6.04-632 |

**Table III (Cont.)**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 100 | 3 | 100 | 3 | 60 | 100 | 631.77 | 49.40% | 7.30E-03 | 1155 | 1.958 | 11.55 | 266-273 | 10.96-11.38 |
| 9 | 100 | 3 | 100 | 0 | 30 | 100 | 43.78 | 7.47% | 5.55E-04 | 1268 | 1.945 | 12.68 | 288-307 | 9.78-10.42 |
| 5 | 100 | 1.5 | 200 | 3 | 60 | 100 | 1293.53 | 14.82% | 5.88E-03 | 454.8 | 2.149 | 4.548 | 225-235 | 6.46-6.68 |
| 3 | 100 | 1.5 | 100 | 4 | 60 | 100 | 4154.43 | 28.25% | 1.78E-02 | 428.8 | 2.211 | 4.288 | 226-235 | 6.44-6.64 |
| 13 | 100 | 3 | 200 | 0 | 60 | 100 | 49.05 | 7.24% | 6.16E-04 | 1256 | 1.913 | 12.56 | 264-275 | 10.96-11.38 |
| 18 | 100 | 2.25 | 100 | 3 | 30 | 100 | 1476.79 | 21.54% | 1.10E-02 | 744.5 | 2.044 | 7.445 | 263-277 | 8.08-8.56 |
| 17 | 100 | 1.5 | 150 | 0 | 60 | 100 | 157.23 | 8.83% | 9.91E-04 | 630.5 | 1.931 | 6.305 | 225-231 | 6.48-6.74 |
| 19 | 100 | 2.25 | 150 | 3 | 60 | 100 | 526.72 | 13.01% | 4.29E-03 | 814.2 | 2.021 | 8.142 | 247-255 | 8.78-9.14 |

## Claims

We claim:

1. A method of forming a transparent conductive oxide film, comprising:

depositing the transparent conductive oxide film in a pulsed DC reactive ion process with substrate bias; and

controlling at least one process parameter to provide at least one characteristic of the conductive oxide film at a particular value.

2. The method of claim 1, wherein controlling at least one process parameter includes controlling the oxygen partial pressure.

3. The method of claim 1, wherein the transparent conductive oxide film includes indiuim-tin oxide.

4. The method of claim 1, wherein the at least one characteristic includes sheet resistance.

5. The method of claim 1, wherein the at least one characteristic includes film roughness.

6. The method of claim 5, wherein the transparent conductive oxide film includes an indium-tin oxide film and the film roughness is characterized by $R_a$ less than about 10 nm with Rms of less than about 20 nm.

7. The method of claim 4, wherein the bulk resistance can be varied between about $2x10^{-4}$ micro-ohms-cm to about 0.1 micro-ohms-cm.

8. The method of claim 1, wherein the at least one process parameter includes a power supplied to a target.

9. The method of claim 1, wherein the at least one process parameter includes an oxygen partial pressure.

10. The method of claim 1, wherein the at least one process parameter includes bias power.

11. The method of claim 1, wherein the at least one process parameter includes deposition temperature.

12. The method of claim 1, wherein the at least one process parameter includes an argon partial pressure.

13. The method of claim 1, further including supplying a metallic target.

14. The method of claim 1, further including supplying a ceramic target.

15. The method of claim 1, wherein the transparent conductive oxide film is doped with at least one rare-earth ions.

16. The method of claim 15, wherein the at least one rare-earth ions includes erbium.

17. The method of claim 15, wherein the at least one rare-earth ions includes cerium.

18. A method of depositing a transparent conductive oxide film on a substrate, comprising:

placing the substrate in a reaction chamber;

adjusting power to a pulsed DC power supply coupled to a target in the reaction chamber;

adjusting an RF bias power coupled to the substrate;

adjusting gas flow into the reaction chamber; and

providing a magnetic field at the target in order to direct deposition of the transparent conductive oxide film on the substrate in a pulsed-dc biased reactive-ion deposition process, wherein the transparent conductive oxide film exhibits at least one particular property.

19. The method of claim 18, wherein at least one particular property of the transparent conductive oxide film is determined by parameters of the pulsed-dc biased reactive ion deposition process.

20. The method of claim 19, wherein the at least one particular property includes resistivity of the transparent conductive oxide film.

21. The method of claim 19, wherein the transparent conductive oxide film includes an indium-tin oxide film.

22. The method of claim 19, wherein the parameters include oxygen partial pressure.

23. The method of claim 19, wherein the parameters include bias power.

24. The method of claim 18, wherein the target can include at least one rare-earth ions.

25. The method of claim 24, wherein the at least one rare-earth ions includes erbium.

26. The method of claim 24, wherein the at least one rare-earth ion includes cerbium.

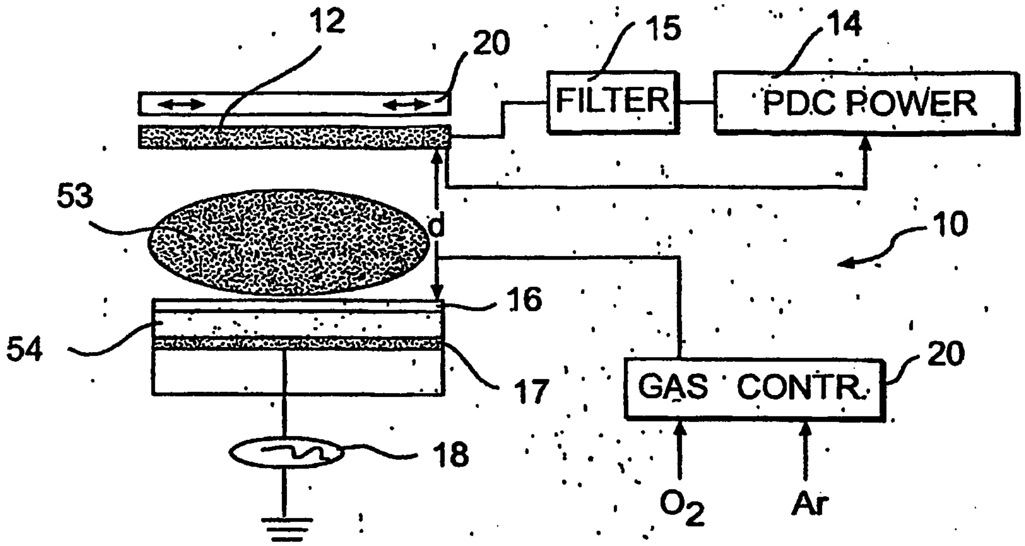

12
20
15
FILTER
14
PDC POWER
53
d
10
16
54
17
GAS CONTR.
20
18
$O_2$
Ar

FIG. 1A

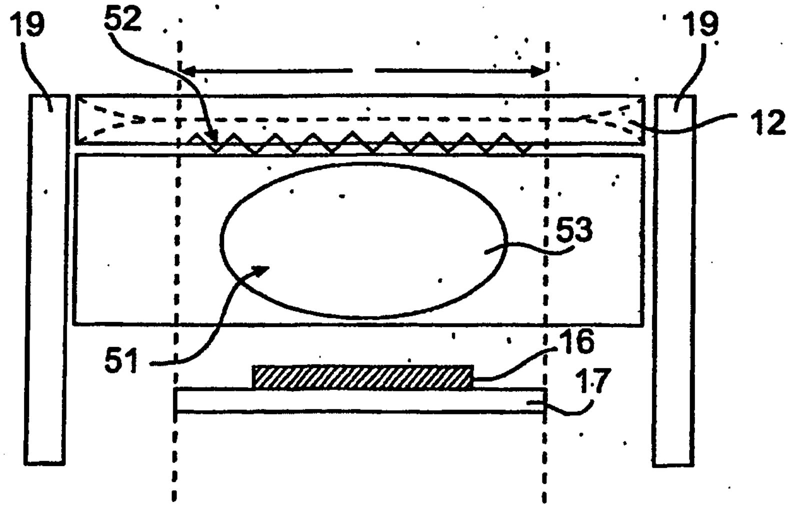

19
52
19
12
53
51
16
17

FIG. 1B

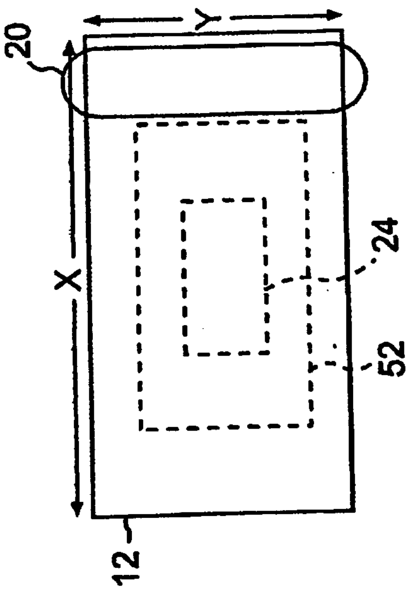
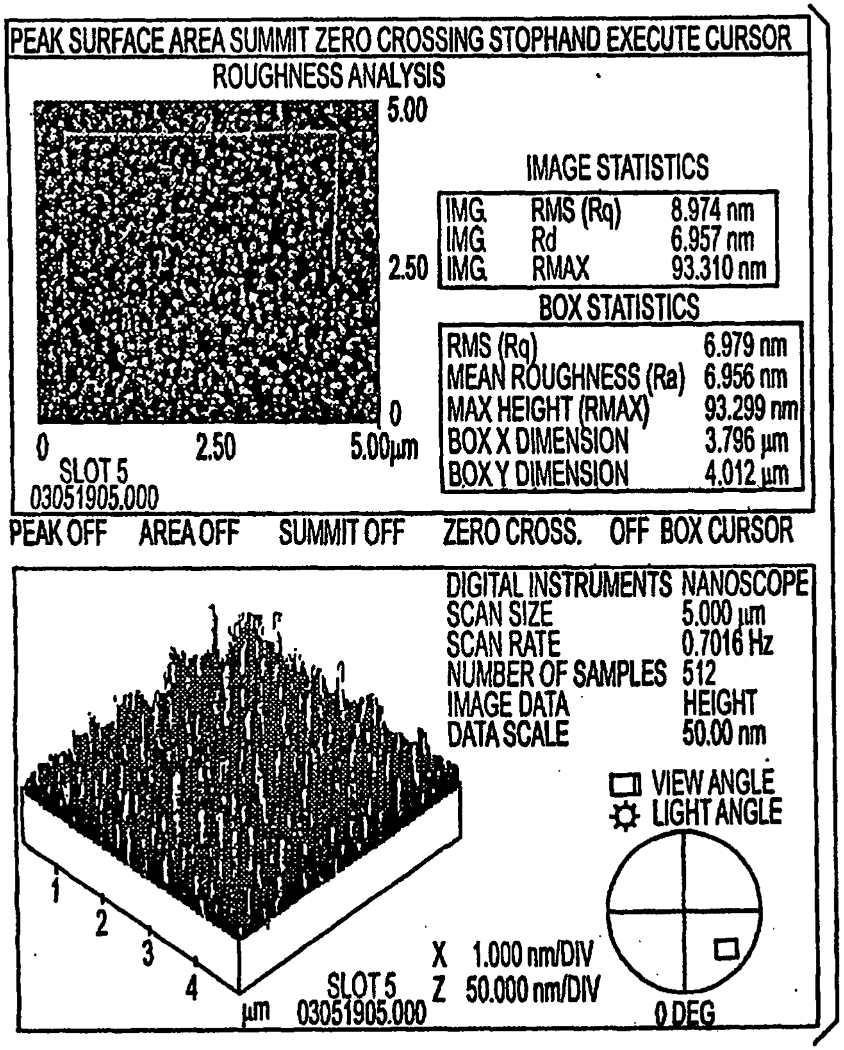


FIG. 2



SLOT 5
03051905.000

IMAGE STATISTICS

| | | |
|---|---|---|
| IMG | RMS (Rq) | 8.974 nm |
| IMG | Rd | 6.957 nm |
| IMG | RMAX | 93.310 nm |

BOX STATISTICS

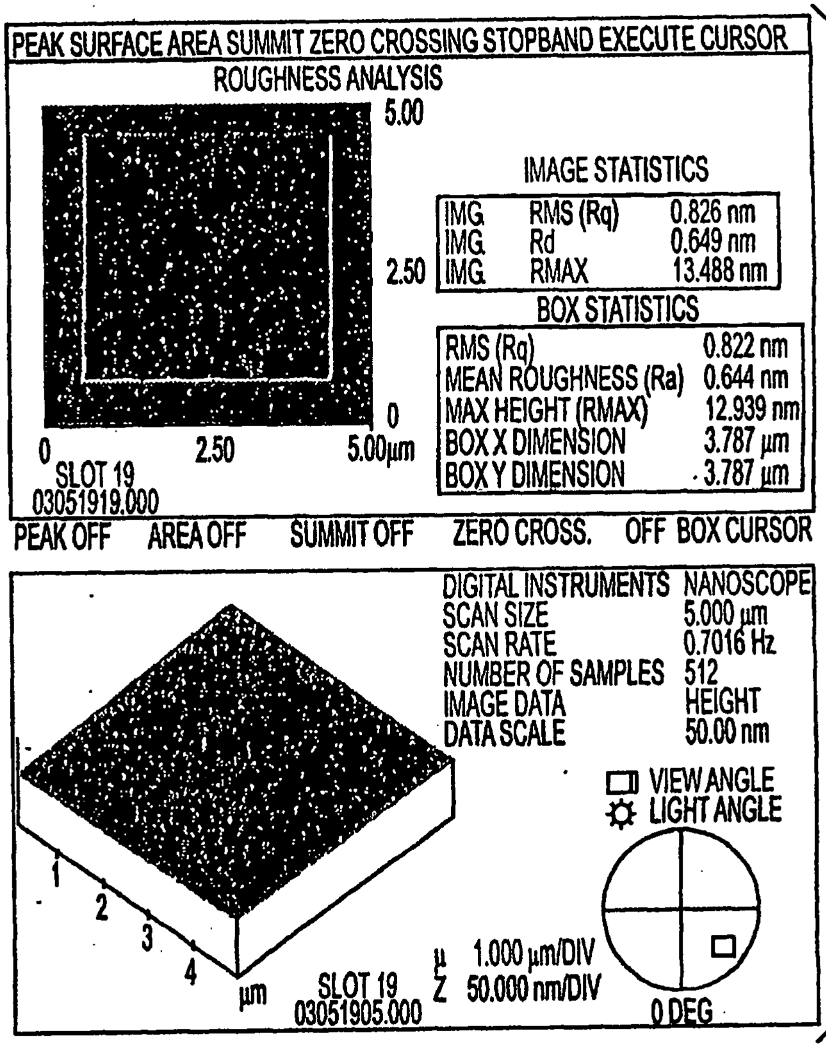
| | |
|---|---|
| RMS (Rq) | 6.979 nm |
| MEAN ROUGHNESS (Ra) | 6.956 nm |
| MAX HEIGHT (RMAX) | 93.299 nm |
| BOX X DIMENSION | 3.796 µm |
| BOX Y DIMENSION | 4.012 µm |

| | |
|---|---|
| DIGITAL INSTRUMENTS | NANOSCOPE |
| SCAN SIZE | 5.000 µm |
| SCAN RATE | 0.7016 Hz |
| NUMBER OF SAMPLES | 512 |
| IMAGE DATA | HEIGHT |
| DATA SCALE | 50.00 nm |

SLOT 5
03051905.000

X 1.000 nm/DIV
Z 50.000 nm/DIV

FIG. 3A



SLOT 19
03051919.000

IMAGE STATISTICS

| | | |
|---|---|---|
| IMG | RMS (Rq) | 0.826 nm |
| IMG | Rd | 0.649 nm |
| IMG | RMAX | 13.488 nm |

BOX STATISTICS

| | |
|---|---|
| RMS (Rq) | 0.822 nm |
| MEAN ROUGHNESS (Ra) | 0.644 nm |
| MAX HEIGHT (RMAX) | 12.939 nm |
| BOX X DIMENSION | 3.787 µm |
| BOX Y DIMENSION | 3.787 µm |

| | |
|---|---|
| DIGITAL INSTRUMENTS | NANOSCOPE |
| SCAN SIZE | 5.000 µm |
| SCAN RATE | 0.7016 Hz |
| NUMBER OF SAMPLES | 512 |
| IMAGE DATA | HEIGHT |
| DATA SCALE | 50.00 nm |

SLOT 19
03051905.000

µ 1.000 µm/DIV
Z 50.000 nm/DIV

FIG. 3B

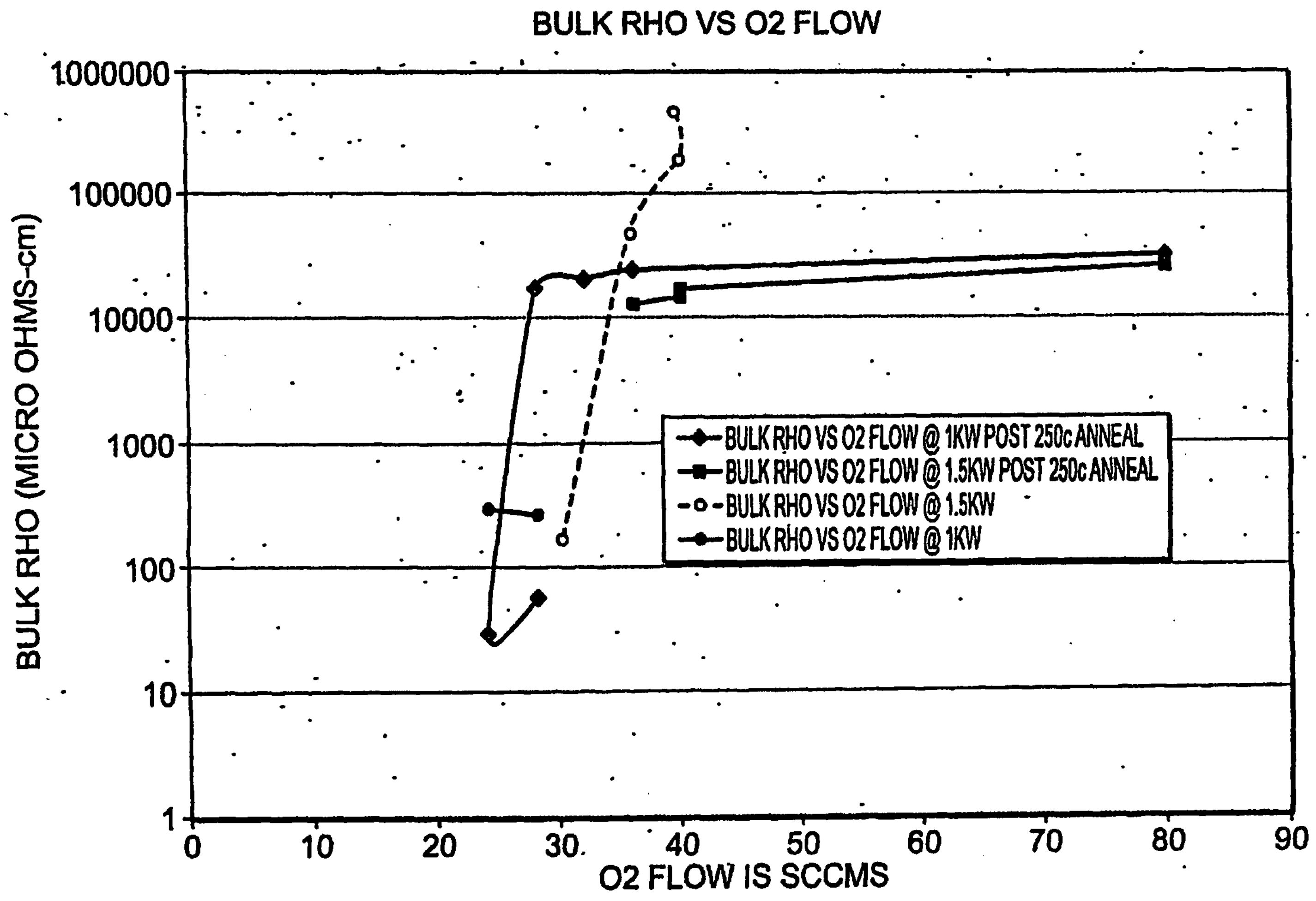

BULK RHO VS O2 FLOW
BULK RHO (MICRO OHMS-cm)
1000000
100000
10000
1000
100
10
1
0
10
20
30
40
50
60
70
80
90
O2 FLOW IS SCCMS
BULK RHO VS O2 FLOW @ 1KW POST 250c ANNEAL
BULK RHO VS O2 FLOW @ 1.5KW POST 250c ANNEAL
BULK RHO VS O2 FLOW @ 1.5KW
BULK RHO VS O2 FLOW @ 1KW

FIG. 4

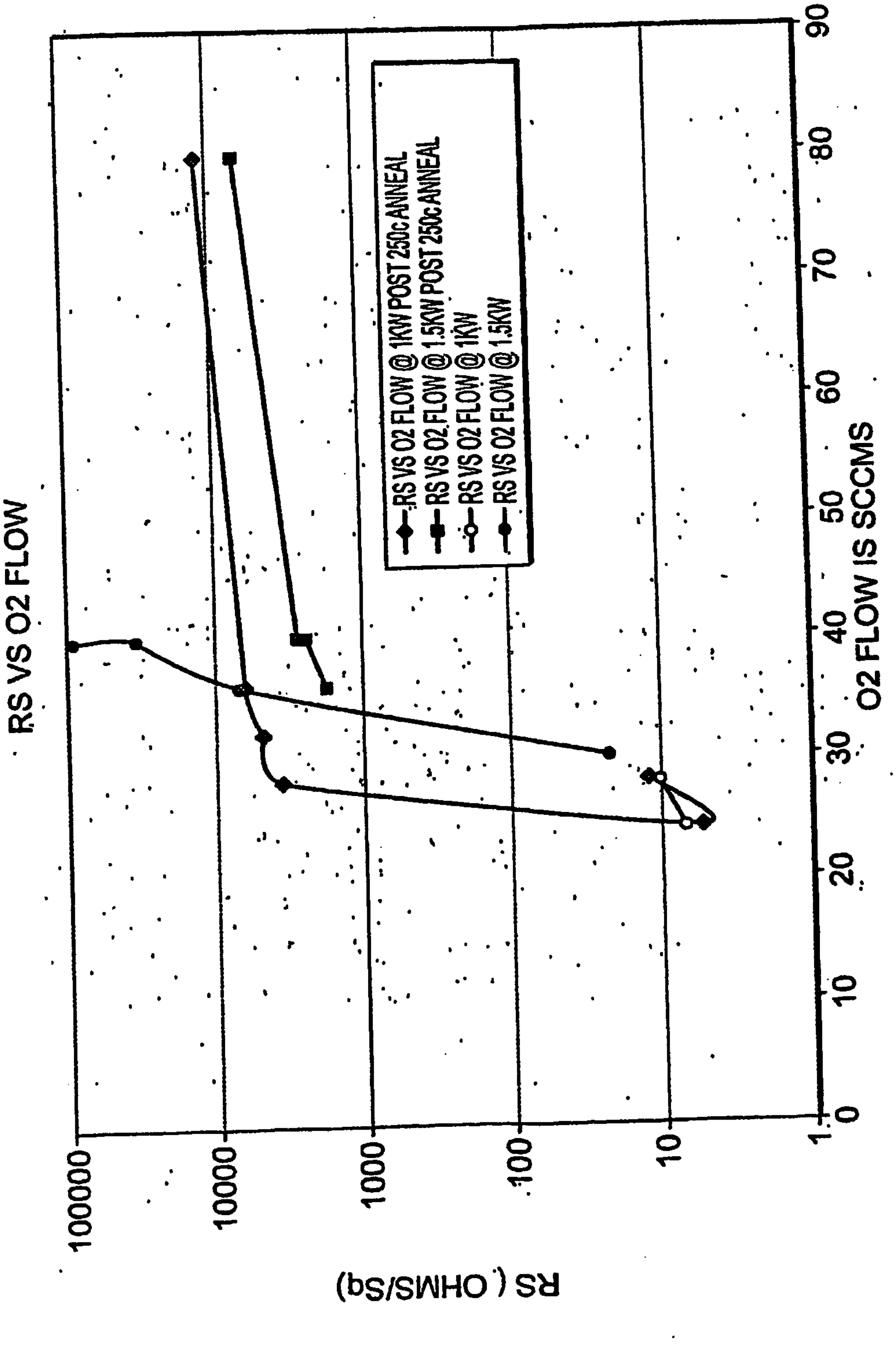

RS VS O2 FLOW
RS (OHMS/Sq)
100000
10000
1000
100
10
1.0
0
10
20
30
40
50
60
70
80
90
O2 FLOW IS SCCMS
RS VS O2 FLOW @ 1KW POST 250c ANNEAL
RS VS O2 FLOW @ 1.5KW POST 250c ANNEAL
RS VS O2 FLOW @ 1KW
RS VS O2 FLOW @ 1.5KW

FIG. 5

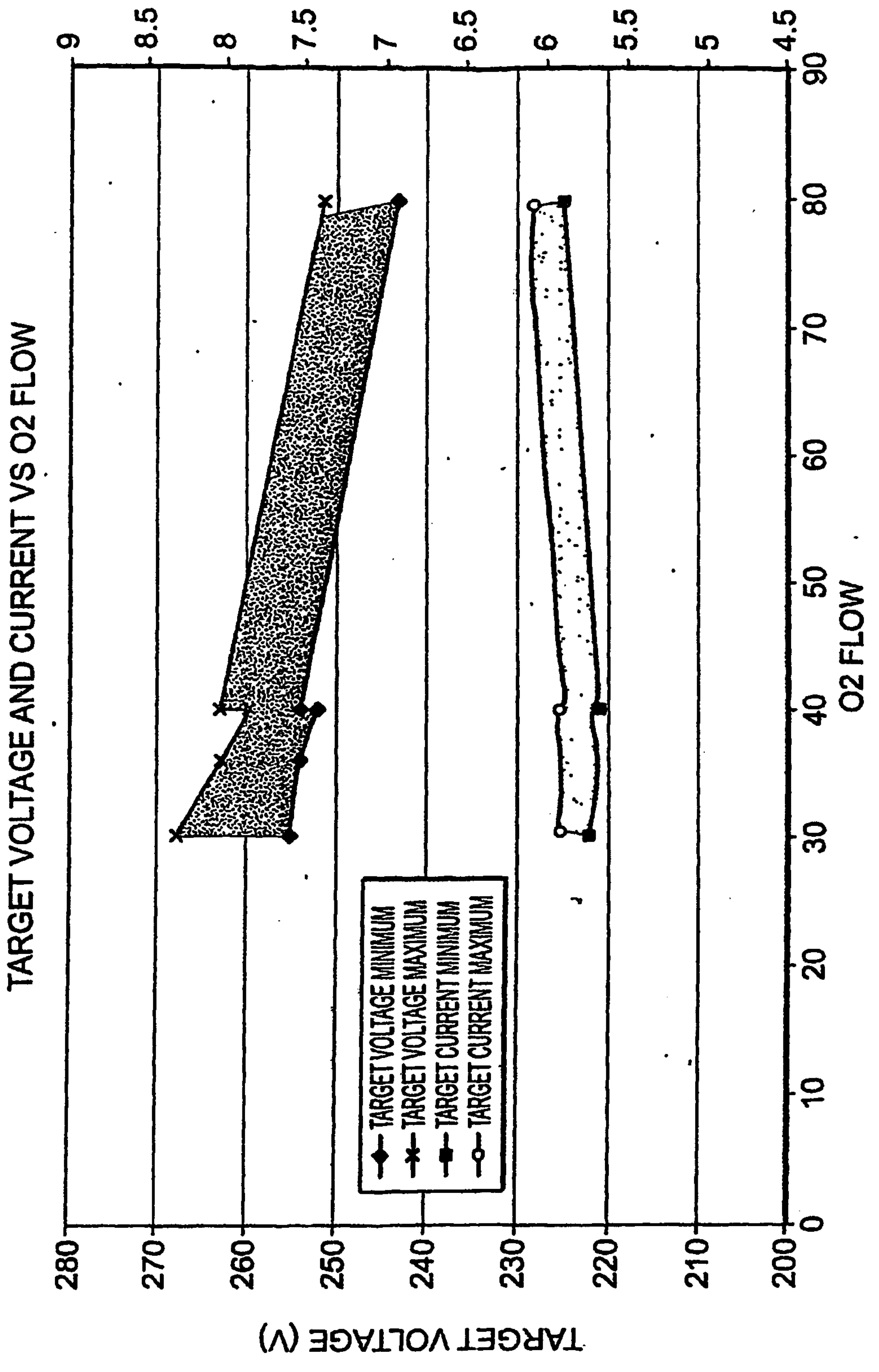

TARGET VOLTAGE AND CURRENT VS O2 FLOW
TARGET VOLTAGE (V)
280
270
260
250
240
230
220
210
200
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
0
10
20
30
40
50
60
70
80
90
O2 FLOW
TARGET VOLTAGE MINIMUM
TARGET VOLTAGE MAXIMUM
TARGET CURRENT MINIMUM
TARGET CURRENT MAXIMUM

FIG. 6

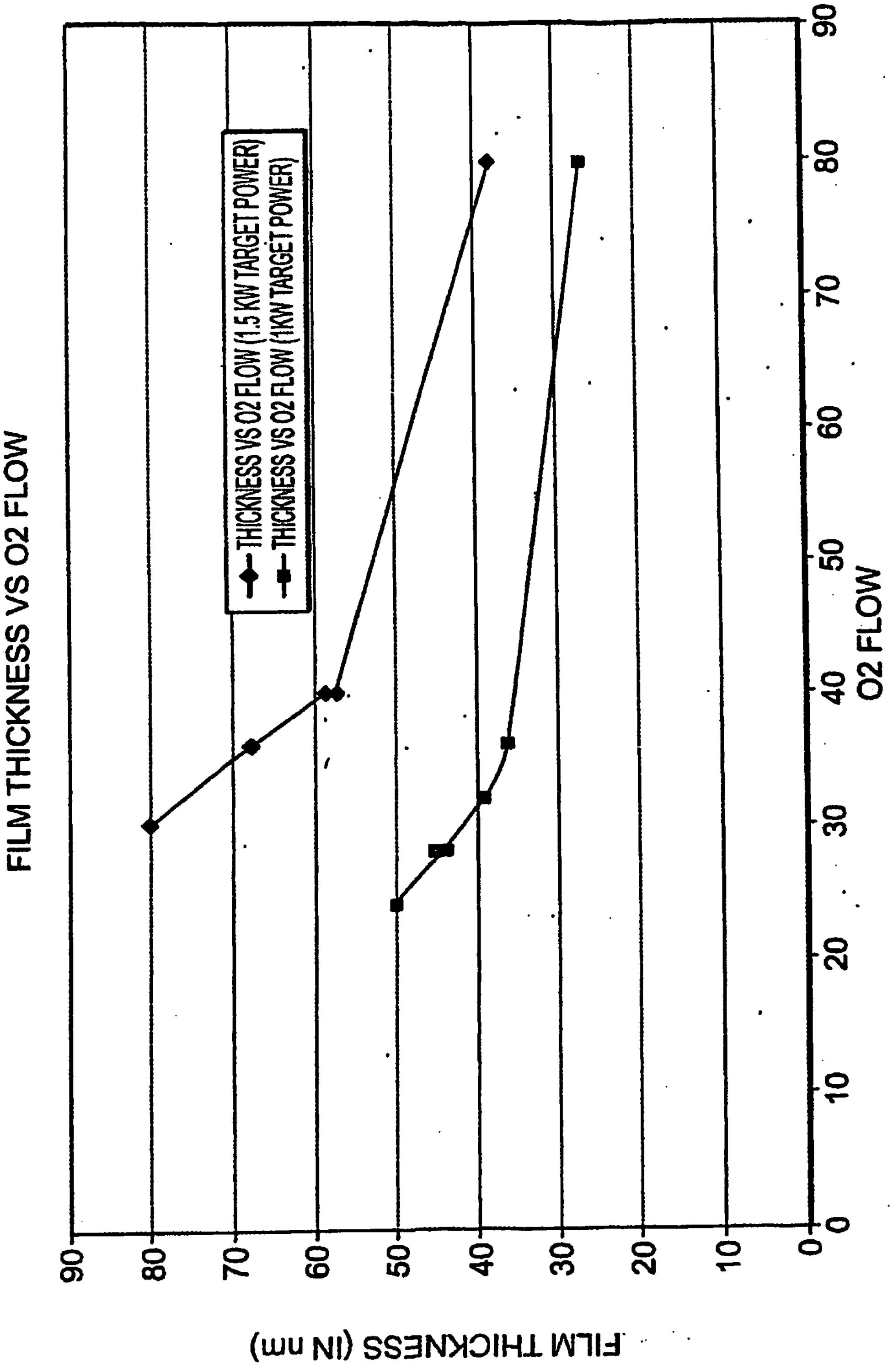

FILM THICKNESS VS O2 FLOW
THICKNESS VS O2 FLOW (1.5 KW TARGET POWER)
THICKNESS VS O2 FLOW (1KW TARGET POWER)
FILM THICKNESS (IN nm)
90
80
70
60
50
40
30
20
10
0
O2 FLOW
0
10
20
30
40
50
60
70
80
90

FIG. 7

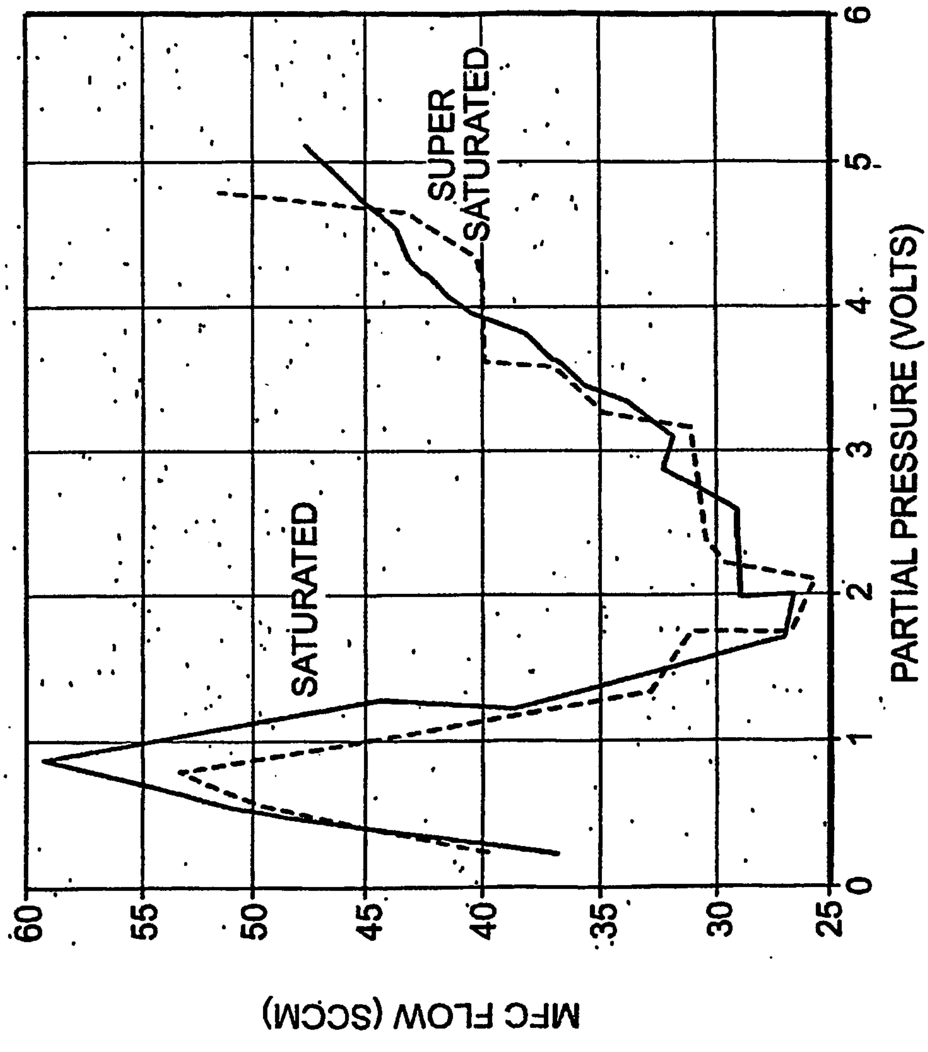

SUPER SATURATED
SATURATED
60
55
50
45
40
35
30
25
MFC FLOW (SCCM)
0
1
2
3
4
5
6
PARTIAL PRESSURE (VOLTS)

FIG. 8

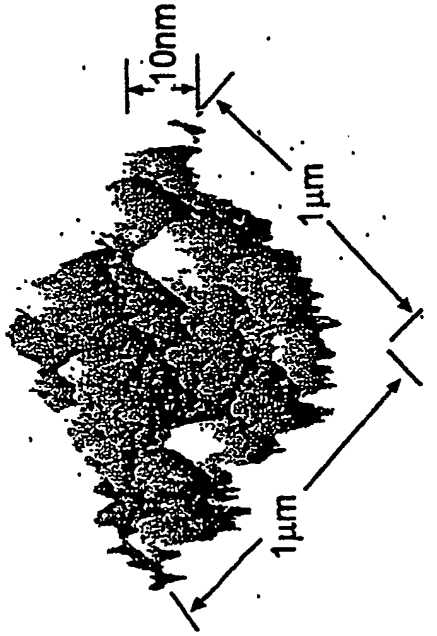


FIG. 9A

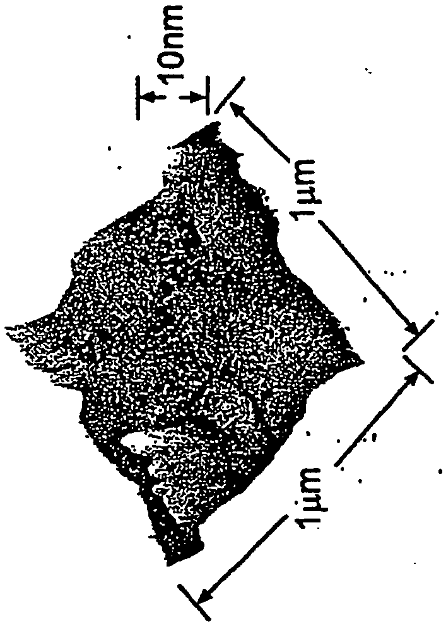


FIG. 9B

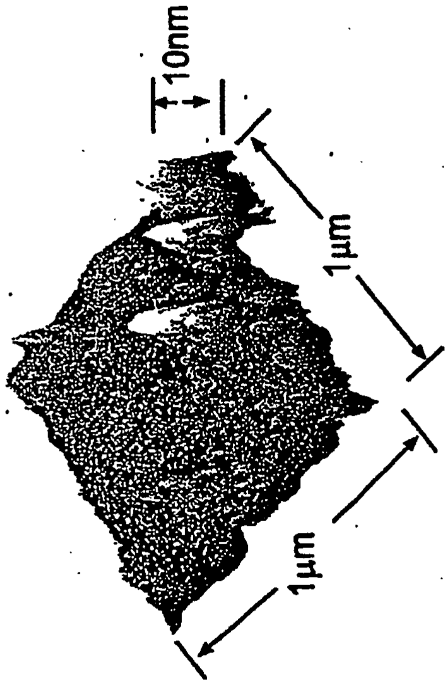


FIG. 9C

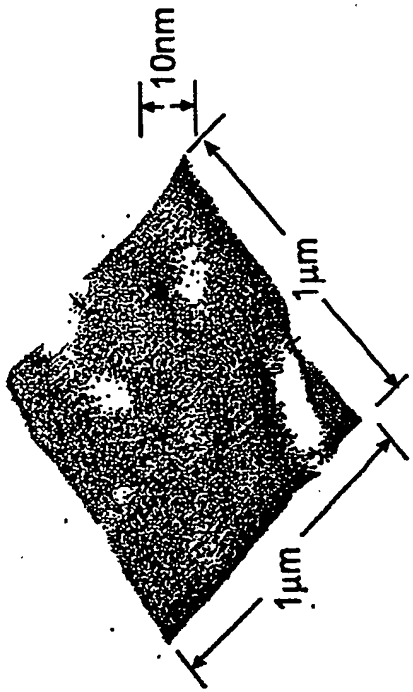


FIG. 9D

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— *without international search report and to be republished upon receipt of that report*

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WO 2004/106582 A2

(54) **Title:** ENERGY CONVERSION AND STORAGE FILMS AND DEVICES BY PHYSICAL VAPOR DEPOSITION OF TITANIUM AND TITANIUM OXIDES AND SUB-OXIDES

(57) **Abstract:** High density oxide films are deposited by a pulsed-DC, biased reactive sputtering process from a titanium containing target to form high quality titanium containing oxide films. A method of forming a titanium based layer or film according to the present invention includes depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate. In some embodiments, the layer is $TiO_2$. In some embodiments, the layer is a sub-oxide of Titanium. In some embodiments, the layer is $Ti_xO_y$ wherein x is between about 1 and about 4 and y is between about 1 and about 7. In some embodiments, the layer can be doped with one or more rare-earth ions. Such layers are useful in energy and charge storage, and energy conversion technologies.

# Energy Conversion and Storage Films and Devices by Physical Vapor Deposition of Titanium and Titanium Oxides and sub-Oxides

## Related Applications

The present invention claims priority to U.S. Provisional Application Serial No. 60/473,375, "Energy Conversion and Storage Devices by Physical Vapor Deposition of Titanium Oxides and Sub-Oxides," by Richard E. Demaray and Hong Mei Zhang, filed on May 23, 2003, herein incorporated by reference in its entirety.

## Background

### 1. Field of the Invention

**[0001]** The present invention is related to fabrication of thin films for planar energy and charge storage and energy conversion and, in particular, thin films deposited of titanium and titanium oxides, sub oxides, and rare earth doped titanium oxides and sub oxides for planar energy and charge storage and energy conversion.

### 2. Discussion of Related Art

**[0002]** Currently, titanium oxide layers are not utilized commercially in energy storage, charge storage, or energy conversion systems because such layers are difficult to deposit, difficult to etch, are known to have large concentrations of defects, and have poor insulation properties due to a propensity for oxygen deficiency and the diffusion of oxygen defects in the layers. Additionally, amorphous titania is difficult to deposit due to its low recrystalization temperature (about 250 °C), above which the deposited layer is often a mixture of crystalline anatase and rutile structures.

**[0003]** However, such amorphous titania layers, if they can be deposited in sufficient quality, have potential due to their high optical index, n~2.7, and their high dielectric constant, k less than or equal to about 100. Further, they have substantial chemical stability. There are no known volatile halides and titania is uniquely resistant to mineral acids. Amorphous titania is thought to have the further advantage that there are no grain boundary mechanisms for electrical breakdown, chemical corrosion, or optical scattering. It is also well known that the sub oxides of titanium have unique and useful properties. *See, e.g.*, Hayfield, P.C.S., "Development of a

New Material- Monolithic $Ti_4O_7$ Ebonix Ceramic", Royal Society Chemistry, ISBN 0-85405-984-3, 2002. Titanium monoxide, for example, is a conductor with a uniquely stable resistivity with varying temperature. Additionally, $Ti_2O_3$, which can be pinkish in color, is known to have semiconductor type properties. However, these materials have not found utilization because of their difficult manufacture in films and their susceptibility to oxidation. Further, $Ti_4O_7$ demonstrates both useful electrical conductivity and unusual resistance to oxidation. $Ti_4O_7$, however, is also difficult to fabricate, especially in thin film form.

**[0004]** Additional to the difficulty of fabricating titanium oxide or sub oxide materials in useful thin film form, it also has proven difficult to dope these materials with, for example, rare earth ions, in useful or uniform concentration.

**[0005]** Therefore, utilization of titanium oxide and suboxide films, with or without rare earth doping, has been significantly limited by previously available thin film processes. If such films could be deposited, their usefulness in capacitor, battery, and energy conversion and storage technologies would provide for many value-added applications.

**[0006]** Current practice for construction of capacitor and resistor arrays and for thin film energy storage devices is to utilize a conductive substrate or to deposit the metal conductor or electrode , the resistor layer, and the dielectric capacitor films from various material systems. Such material systems for vacuum thin films, for example, include copper, aluminum, nickel, platinum, chrome, or gold depositions, as well as conductive oxides such as ITO, doped zinc oxide, or other conducting materials.

**[0007]** Materials such as chrome-silicon monoxide or tantalum nitride are known to provide resistive layers with 100 parts per million or less resistivity change per degree Centigrade for operation within typical operating parameters. A wide range of dielectric materials such as silica, silicon nitride, alumina, or tantalum pentoxide can be utilized for the capacitor layer. These materials typically have dielectric constants k of less than about twenty four (24). In contrast, $TiO_2$ either in the pure rutile phase or in the pure amorphous state can demonstrate a dielectric constant as high as 100. *See, e.g.*, R. B. van Dover, "Amorphous Lanthanide-Doped $TiO_2$ Dielectric Films," Appl. Phys Lett., Vol. 74, no. 20, p. 3041-43 (May 17, 1999).

**[0008]** It is well known that the dielectric strength of a material decreases with increasing value of dielectric constant k for all dielectric films. A 'figure of merit' ( FM) is therefore obtained by the product of the dielectric constant k and the dielectric strength measured in Volts per cm of dielectric thickness. Capacitive density of 10,000 to 12,000 pico Farads /mm$^2$ is very difficult to achieve with present conductors and dielectrics. Current practice for reactive deposition of titanium oxide has achieved a figure-of-merit, FM, of about 50 (k MV/cm). *See* J.-Y. Kim et al., "Frequency-Dependent Pulsed Direct Current Magnetron Sputtering of Titanium Oxide Films," J. Vac. Sci. Technol. A 19(2), Mar/Apr 2001.

**[0009]** Therefore, there is an ongoing need for titanium oxide and titanium sub-oxide layers, and rare-earth doped titanium oxide and titanium sub-oxide layers, for various applications.

## Summary

**[0010]** In accordance with the present invention, high density oxide films are deposited by a pulsed-DC, biased, reactive sputtering process from a titanium containing target. A method of forming a titanium based layer or film according to the present invention includes depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate. In some embodiments, the layer is $TiO_2$. In some embodiments, the layer is a sub-oxide of Titanium. In some embodiments, the layer is $Ti_xO_y$ wherein x is between about 1 and about 4 and y is between about 1 and about 7.

**[0011]** In some embodiments of the invention, the figure of merit of the layer is greater than 50. In some embodiments of the invention, the layer can be deposited between conducting layers to form a capacitor. In some embodiments of the invention, the layer includes at least one rare-earth ion. In some embodiments of the invention, the at least one rare-earth ion includes erbium. In some embodiments of the invention, the erbium doped layer can be deposited between conducting layers to form a light-emitting device. In some embodiments of the invention, the erbium doped layer can be an optically active layer deposited on a light-emitting device. In some embodiments of the invention, the layer can be a protective layer. In some embodiments, the protective layer can be a catalytic layer.

**[0012]** In some embodiments of the invention, the layer and a $TiO_2$ layer can be deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the $TiO_2$ layer. In some embodiments, the $TiO_2$ layer can be a layer deposited according to some embodiments of the present invention.

**[0013]** These and other embodiments of the present invention are further discussed below with reference to the following figures.

## Short Description of the Figures

**[0014]** Figures 1A and 1B illustrate a pulsed-DC biased reactive ion deposition apparatus that can be utilized in the deposition according to the present invention.

**[0015]** Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B.

**[0016]** Figures 3A and 3B illustrate various configurations of layers according to embodiments of the present invention.

**[0017]** Figures 4A and 4B illustrate further various configurations of layers according to embodiments of the present invention.

**[0018]** Figure 5 shows another layer structure involving one or more layers according to the present invention.

**[0019]** Figure 6 shows a transistor gate with a TiOy layer according to the present invention.

**[0020]** Figure 7 illustrates the roll-off of the dielectric constant with decreasing film thickness.

**[0021]** Figure 8 illustrates data points from a bottom electrode that helps reduce or eliminate the roll-off illustrated in Figure 7.

**[0022]** Figures 9A and 9B illustrate an SEM cross-section of a $Ti_4O_7$ target obtained from Ebonex™ and an SEM cross section of the $Ti_4O_{6.8}$ film deposited from the Ebonex™ target according to the present invention.

**[0023]** Figure 10 shows the industry standard of thin-film capacitor performance in comparison with layers according to some embodiments of the present invention.

**[0024]** Figure 11 shows the performance of various thin films deposited according to the present invention in a capacitor structure.

**[0025]** Figure 12 shows a cross-section TEM and diffraction pattern amorphous and crystalline layers of $TiO_2$ on n++ wafers.

**[0026]** Figure 13 shows a comparison of the leakage current for $TiO_2$ films according to embodiments of the present invention with and without erbium ion doping.

**[0027]** Figures 14A and 14B show a photoluminescence signal measured from a 5000 Å layer of 10% erbium containing $TiO_2$ deposited from a 10% erbium doped TiO conductive target and a photoluminescence signal measured from the same layer after a 30 minute 250 °C anneal.

**[0028]** In the figures, elements having the same designation have the same or similar functions.

## Detailed Description

**[0029]** Miniaturization is driving the form factor of portable electronic components. Thin film dielectrics with high dielectric constants and breakdown strengths allow production of high density capacitor arrays for mobile communications devices and on-chip high-dielectric capacitors for advanced CMOS processes. Thick film dielectrics for high energy storage capacitors allow production of portable power devices.

**[0030]** Some embodiments of films deposited according to the present invention have a combination of high dielectric and high breakdown voltages. Newly developed electrode materials allow the production of very thin films with high capacitance density. The combination of high dielectric and high breakdown voltages produce thick films with new levels of available energy storage according to $E=1/2CV^2$.

**[0031]** Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent

Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Additionally, deposition of materials is further described in U.S. Patent 6,506,289, which is also herein incorporated by reference in its entirety.

**[0032]** Figure 1A shows a schematic of a reactor apparatus 10 for sputtering of material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC (PDC) power is supplied to the target and RF power is supplied to the substrate during deposition of a material film. The PDC power supply 14 can be protected from RF bias power 18 by use of a filter 15 coupled between PDC power supply 14 and target 12.

**[0033]** Apparatus 10 includes a target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. Magnet 20 is scanned across the top of target 12.

**[0034]** For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that depends on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulsed DC magnetron sputtering in apparatus 10.

**[0035]** Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this example supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 KHz. In some embodiments, the reverse voltage is 10% of the negative target voltage. Utilization of other power supplies will lead to different power characteristics, frequency characteristics, and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted to between 0 and 5 μs.

**[0036]** Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

**[0037]** Therefore, filter 15 can be a 2 MHz band sinusoidal rejection filter. In some embodiments, the bandwidth of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 18.

**[0038]** However, both RF sputtered and pulsed DC sputtered films are not fully dense and may typically have columnar structures. These columnar structures are detrimental to thin film applications. By applying a RF bias on wafer 16 during deposition, the deposited film can be densified by energetic ion bombardment and the columnar structure can be substantially eliminated or completely eliminated.

**[0039]** In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be held at between –50C and 500C by introduction of back-side gas in a physical or electrostatic clamping of the substrate, thermo-electric cooling, electrical heating, or other methods of active temperature control. In Figure 1A, a temperature controller 22 is shown to control the temperature of substrate 16. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 millitorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimension about 150 mm by 600 mm.

**[0040]** Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, where physical and chemical uniformity provide refractive index uniformity, for example. Figure 2 indicates that region 52 of target 12 that provides thickness uniformity is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity. In optimized processes, however, regions 52 and 24 may be coextensive.

**[0041]** In some embodiments, magnet 20 extends beyond area 52 in one direction, the Y direction in Figure 2, so that scanning is necessary in only one direction, the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

**[0042]** The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the surface of target 12, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission, or absorptivity.

**[0043]** Target 12 can be formed of any materials, but is typically metallic materials such as, for example, combinations of In and Sn. Therefore, in some embodiments, target 12 includes a metallic target material formed from intermetallic compounds of optical elements such as Si, Al, Er and Yb. Additionally, target 12 can be formed, for example, from materials such as La, Yt, Ag, Au, and Eu. To form optically active films on substrate 16, target 12 can include rare-earth ions. In some embodiments of target 12 with rare earth ions, the rare earth ions can be pre-alloyed with the metallic host components to form intermetallics. *See* U.S. Application Serial No. 10/101,341.

**[0044]** In several embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 to 20 individual tiles. Tiles are finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of the tiles. The distance between the tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or provide for thermal expansion tolerance during processing, chamber conditioning, or operation.

**[0045]** As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12, can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, region 52 in which deposition provides uniformity of deposited film can be larger than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[0046] Figure 3A illustrates deposition of a layer 102 according to the present invention deposited on a substrate 101. In some embodiments, layer 102 can be a conducting protective layer of $TiO_y$. Figure 3B shows a first layer 102 according to the present invention deposited over a second layer 103, which can also be a layer according to some embodiments of the present invention. In some embodiments, first layer 102 can be a conducting protective layer and second layer 103 can be a titanium or other conducting layer. Layer 103 is deposited on substrate 101.

[0047] The fabrication of high density capacitor and resistor arrays as well as high energy storage solid state devices can be accomplished with embodiments of processes according to the present invention on a wide variety of substrates such as silicon wafers or glass or plastic sheets at low temperature and over wide area. With reference to Figure 3B, layer 102 can be an amorphous film of $TiO_2$, which is deposited by a process such as that described in U.S. Application Serial No. 10/101,341. Utilization or formation of a conducting layer 103 such as TiO or $Ti_4O_7$ between a conducting layer of titanium, which is substrate 101, and the dielectric $TiO_2$ layer 102 is shown in the present invention to substantially reduce or eliminate the 'roll off' of the dielectric constant k with decreasing film thickness below about 1000 Angstroms. Consequently, capacitors fabricated from titanium on low temperature substrates result in high value planar capacitors and capacitor arrays with very high capacitive density and low electrical leakage. Such electrical arrays are useful for shielding and filtering and buffering high frequency and may be used in stationary as well as in portable electronic devices.

[0048] In particular, the low temperature deposition of amorphous titania capacitors provides for the fabrication of integrated passive electronic circuits on plastic and glass. It also provides for the integration of such devices on other electronic devices and arrays at low temperature.

[0049] Similarly, a conducting layer of TiO or $Ti_4O_7$ as layer 103 in Figure 3B, deposited between a conducting layer of titanium as layer 101 and a layer of titania as layer 102 of Figure 3B can be deposited so as to provide an increase in the surface smoothness by planarization of the titanium in layer 101 or other metallurgical conductive substrate layer 101 of Figure 3B. Consequently, roughness or asperity based defects can be minimized or eliminated. As an example, charge injection from a metallurgical electrode can be decreased at the interface with a dielectric. The titanium based dielectric layer can be formed on a smooth conducting oxide layer, which according to some theories can prevent charge depletion of the high k dielectric layer, decrease point charge accumulation and support dipole formation at the conductor-dielectric interface, sometimes referred to as dipole coupling. These features are important to prevent the roll-off of the dielectric strength of the dielectric layer as the layer thickness is decreased below about 1000 Å. It is consequently useful in the formation of thin layers having high capacitive value.

**[0050]** A thick film of dielectric material may be deposited having a high dielectric strength for the storage of electrical energy. Such energy is well known to increases with the square of the applied Voltage. For example, in Figure 3B layer 102 can be a thick layer of dielectric according to the present invention. Layer 104 in Figure 3B, then, can be a conducting layer deposited on layer 102 while layer 103 is a conducting layer deposited between a substrate 101 and layer 102 to form a capacitor. As the dielectric strength of the amorphous dielectric layer of layer 102 increases in proportion to it's thickness, the energy storage also increases effectively as the square of the thickness. It is shown that both record capacitance density and electrical energy storage density result for films according to the present invention. For thick film applications, smoothing of the metallurgical electrode by a conductive sub-oxide can decrease leakage at the interface in high voltage applications.

**[0051]** Protective conductive sub-oxide films of titanium can also be deposited on conductive and insulating substrates to protect them from harmful chemical attack while acting as conducting layers. For example, as illustrated in Figure 3A layer 102 can be a protective conductive sub-oxide film deposited on substrate 101. These layers can be used to protect an electrode, which can be substrate 101, from oxidation in the gas phase and in the liquid phase as well as the solid phase. Examples of such applications include electrolytic energy storage or as an active electrode surface for catalytic reactions and energy conversion such as in the oxygen-hydrogen fuel cell. Transparent oxides and semi-transparent sub-oxides can be deposited sequentially so that the conducting sub-oxides are protected by the transparent non-conducting oxides for purposes of photovoltaic or electrochromic energy conversion devices. It is well known that organic based photovoltaic cells are enhanced by the presence of titania in the organic absorbing layer. Layers according to the present invention can be utilized both for the conductivity of electricity, the enhancement of the organic absorber, as well as the overall protection of the device.

**[0052]** $TiO_2$ layers, for example, can photocatylitically produce ozone in the presence of sunlight. However, in the course of such activity, the $TiO_2$ layer can build up a fixed charge. Absent a metallurgical conductor, as shown in Figure 3B layer 102 can be a catalytic oxide while layer 103 can be a conducting suboxide while substrate 101 is a dielectric substrate such as glass or plastic and layer 104 is absent. In such a two-layer device, where the oxide is provided on the surface of the sub-oxide, the sub-oxide can form an electrode so that electric charge can be conducted to the oxide layer for enhanced photochemical photalysis such as in an AC device, or for the purpose of charge dissipation.

**[0053]** Protective conductive sub-oxide films of titanium can also be deposited on conductive and insulating substrates to protect them from harmful chemical attack while acting as conducting layers for electrolytic energy storage or as an active electrode for catalytic energy conversion. Transparent and semi-transparent oxides can be deposited sequentially so that the conducting suboxides are protected by the transparent non-conducting oxide for purposes of protecting layered devices. Alternatively, it is well known that certain crystalline suboxides of titania, collectively referred to as Magnelli phases, posses unusual levels of durability to mineral acid solutions and other corrosive gassious or liquid environments. Hayfield, P.C.S., "Development of a New Material- Monolithic $Ti_4O_7$ Ebonix Ceramic", Royal Society Chemistry, ISBN 0-85405-984-3, 2002 describes these in detail and discusses many applications of the monolithic suboxides. Hayfield also explains that the basis of conductivity of sub-oxides is due to the presence of the $Ti^{+2}$ cation in layers having the stoichometry TiO. Of the several compositions, $Ti_4O_7$ in particular is known to posses both useful conductivity and also chemical resistance to both anodization, which would decrease it's conductivity, as well as reduction, which would decrease it's chemical durability. Therefore, as shown in Figure 3A, substrate 101 can be a metallurgical substrate such as aluminum or titanium and layer 102 can be $Ti_4O_7$. An example is the catalytic of $H_2$ and $O_2$ to make water and electricity.

**[0054]** In this disclosure, an amorphous coating layer according to embodiments of the present invention, derived from a crystalline target of $Ti_4O_7$, can obtain a similar composition as described above, measured as $Ti_4O_{6.8}$. Similar useful levels of chemical conductivity can be obtained. The sputtered film was dense, adherent, and also displayed robust durability to immersion in concentrated mineral acid and oxidizing solution. A similar material was deposited directly from a titanium target using the subject reactive sputtering process.

**[0055]** The increased density of the amorphous sputtered film according to embodiments of the present invention such as film 102 shown in Figure 3A can provide high levels of impermeability. Planarization can also be achieved by layer 102 over structures on substrate 101. Layer 102 can therefore achieve ‘atomic’ smooth surfaces on otherwise rough substrates. The sputtering process according to the present invention also allows the formation of a continuous range of stoicheometry between what are, in their crystalline environment, ‘line compounds’ with whole number integer ratios of titanium cations to oxygen atoms. In the present amorphous films, as long as one $Ti^{+2}$ has a nearest neighbor cation in the amorphous glass matrix with the $Ti^{+2}$ valence, conductive paths will be available in the sputtered film.

**[0056]** The sputtered sub-oxides also have the advantage that they can be layered, without removal from the vacuum system, with metallic titanium, other sub-oxides, as well as $TiO_2$ for connection to electrical conduction and insulation. This feature provides the utility of multiplayer depositions by integrated processes in one vacuum chamber. Where thick films of a particular sub-oxide are desired, a target 12 (Figure 1) fabricated of the desired sub-oxide can be utilized. TiO is particularly a good conductor and possesses very stable resistivity with temperature variation. $Ti_2O_3$ is a semiconductor. The higher oxygen-containing Magnelli compositions obtain higher resistivity as well as increased chemical stability and robustness and can be utilized as a resistive layer or as a protective, conductive layer.

**[0057]** Erbium doped $TiO_2$ is known to display useful levels of photoluminescence. And rare earth doped titanium oxide is known to display decreased levels of electrical leakage current under conditions of high electrical field. Layer 102 of Figure 3B, deposited according to some embodiments of the present invention, then can be erbium doped $TiO_2$ and therefore displays very high level of breakdown and very low leakage under electrical stress. Additionally, a capacitor can be formed by deposition of conductors as layers 103 and 104 on a substrate 101. Consequently, capacitive and energy storage devices formed from rare earth doped layers formed according to the present invention are extremely useful for very high field applications such as capacitors, high voltage dielectric batteries, and electro luminescent devices and also for low-leakage devices.

**[0058]** A TiO or erebium-doped TiO target, target 12 of Figure 1A, can be formed by mixing of TiO powder or TiO powder and Erbium or Erbium-Oxide powder. TiO powder can be formed from the partial oxygenation in a controlled furnace. The mixed powder is then hipped under a controlled environment (for example hydrogen or $CO_2$) to a high density to form tiles. As discussed above, such tiles can be mounted to form target 12. Additionally, other rare-earth doped titanium containing targets can be formed in the same fashion.

**[0059]** As an example, a layer of erbium doped titania or titania containing alloy deposited by means of the present invention, could be coupled as a continuous oxide layer to a photo diode constructed proximate to dielectric layer 102 of Figure 3A. Such an arrangement could provide an optical means for the measurement of the applied electrical field or the leakage current.

**[0060]** Alternatively, such a rare earth doped dielectric layer 102 might be coupled to conducting transparent oxides so that a light wave device might be provided for the conversion of electrical energy to light energy. In another embodiment, a titanium oxide containing a rare earth ion can be deposited directly on a light emitting diode device so that the rare earth ion can absorb some or all of the light emitted by the diode and re-fluoresce that light at another wavelength. In this embodiment, layer 102 can be a rare earth containing titanium oxide or sub oxide and substrate 101 includes a light emitting diode. An example of this may be the conversion of blue light from a LED to yellow-green light by layer 102. In that case, layer 102 may be cerium doped titanium oxide or sub-oxide. Partial absorption of the blue light by layer 102 with conversion to yellow-green light by layer 102 would result in a white light source. Other colors of light can be obtained by doping the titanium oxide or sub-oxide with other rare earth ions.

**[0061]** Figures 4A and 4B illustrate further stackings of layers according to embodiments of the present invention. For example, layer 201 can be a $TiO_2$ dielectric protective deposited over a conducting layer 103 on substrate 101. Figure 4B can show dielectric protective layer 201 deposited over conducting protective layer 102 of $TiO_y$, which is deposited on a metal conducting layer 103 on substrate 101. The $TiO_y$ conducting protective layer can act as a smoothing layer, resulting in a better barrier layer in dielectric 201. The end result is a better roll-off characteristic than has previously been obtained.

**[0062]** In general, layer 102 can be formed of any $Ti_xO_y$ layer or rare earth doped $Ti_xO_y$ layer according to the present invention. As illustrated here, layers of various compositions of $Ti_xO_y$, with or without rare-earth doping, have various properties. In some embodiments of the invention, x can be between about 1 and about 4 and y can be between about 1 and about 7.

**[0063]** Figure 5 shows an example of a capacitor stack according to the present invention. A metal conducting layer 103 is deposited on substrate 101. A conducting protective layer 102 is deposited over conducting layer 103 and a $TiO_2$ dielectric protective layer is deposited over the protective conducting layer 102. Another protective conducting layer 102 can be deposited over the $TiO_2$ dielectric layer and a metal layer can be deposited over the protective conducting layer 102. The resulting capacitor stack has upper and lower smoothing due to the two $TiO_y$ layers and results in improved roll-off characteristics in the dielectric constant. Such capacitor stacks can be very useful in energy storage devices.

**[0064]** Figure 6 shows a transistor structure according to the present invention. A source 401, drain 402 and gate structure 404 are deposited on a semiconducting substrate 403. An intermediate dielectric 400 can then be deposited over the source, drain and gate structure. A protective conducting layer 102, which can be formed of $TiO_y$, can then be deposited over an opening in the intermediate dielectric layer 400 followed by a conducting layer 103. The protective conducting layer 102 prevents roll-off of the gate dielectric 404.

Example 1. Deposition of $Ti_4O_7$ film

**[0065]** In this example, $Ti_4O_7$ films were deposited using a Pulse DC scanning magnetron PVD process as was previously described in U.S. Application Serial No. 10/101,341. The target was a about 1mm thick, about 16.5x12.5 mm$^2$ tiles of titanium oxide target obtained from a sheet of Ebonex™ which compounded of bulk $Ti_4O_7$ was bonded onto a backing plate. Ebonex™ can be obtained from Atraverda Ltd., Oakham Business Park, Mansfield, UK. A pulsed DC generator from Advanced Energy (Pinnacle Plus) was used as the target power supply. The pulsing frequency can be varied from 0-350 KHz. Reversed duty cycle can be varied from 1.3µs to 5µs depending on the pulsing frequency. Target power was fixed at 2 KW and pulsing frequency was 200KHz during deposition, Ar flow rate is 100sccm. The deposition rate at this condition is 14Å/sec over a 40 by 50 cm substrate 101. A 100 W at 2 MHz bias was supplied to the substrate. The bias power supply can be an RF supply produced by ENI.

**[0066]** Utilizing the above parameters, a layer 102 of Figure 3A was deposited on a substrate 101 of 150mm p-type Si wafer. The sheet resistance was measured using 4 point probe to be 140 ohms/sq, with film thickness of 1.68µm. The resistivity of the resulting film is measured to be 0.023 ohms-cm. The composition of film was determined using EDX to be $Ti_4O_{6.8}$.

Example 2. Deposition of TiO2 on Ti-Ti4O7 film Stack

**[0067]** In this example, $TiO_2$ films were deposited using a 2MHz RF biased, Pulse DC scanning magnetron PVD process as was previously described in U.S. Application Serial No. 10/101,341. The substrate size can be up to 600x720mm$^2$. The target was a ~7mm thick, ~630x750 mm$^2$ Ti plate of 99.9% purity. A pulsed DC generator, or PDC power supply from Advanced Energy (Pinnacle Plus) was used as the target power supply. The pulsing frequency can be varied from 0-350 KHz. Reversed duty cycle can be varied from 1.3µs to 5µs depending on the pulsing frequency. An ENI RF generator and ENI Impedance matching unit were used for the substrate bias. A 100 W with a 2 MHz RF generator, which can be an EFI supply, was utilized. The chamber base pressure was kept below $2x10^{-7}$ Torr. The substrate temperature was below 200°C during deposition.

[0068] A systematic DOE (design of experiments) were carried out on both n++ type bare Si wafers and Al metallized wafers. All n++ wafers were HF cleaned just before loading into the chamber for deposition. A series of 150nm thick, Al films were deposited onto the bare Si wafers using the same PVD system at low temperature (<100°C).

[0069] The total PDC target power, pulsing frequency, oxygen partial pressure, and substrate bias power were variables in the DOE. Total gas flow of Ar and $O_2$ were kept constant at 100 sccm. The PDC target power was between 4 and 7 kW with a pulsing frequency of between 100 and 250 kHz. The oxygen flow rate ranged from 30 to 60%. The bias power ranged from 0 to 300 W at 2 Mhz. Both dielectric strength and breakdown voltage were measured using a mercury probe. Film thickness in this DOE range from 100nm to 270nm.

[0070] Therefore, with reference to Figure 3B, layer 101 is the Si wafer substrate, layer 103 is the 150 nm thick Al layer, layer 102 is the $Ti_4O_7$ layer, and layer 104 is $TiO_2$. Figure 7 shows the thickness dependence of the dielectric constant of layer 102, showing the roll off effect. The capacitance of the layer stack 101, 103, 102, and 104 was measured with a mercury electrode impressed upon layer 104 and coupled to layer 103. The precise thickness of dielectric layer 104 was measured optically. The dielectric constant of layer 104 was then calculated from the measured capacitance. As shown in Figure 7, the $TiO_2$ film thickness decreases, so does the dielectric constant of the $TiO_2$ film.

[0071] However, this roll-off effect can be greatly reduced or eliminated in certain embodiments of the present invention. Figure 8 shows two additional data points shown as circles which represent the dielectric constant of thin $TiO_2$ layers for layer 104 with Ti-$Ti_4O_7$ deposited as layer 102 of Figure 3B.

Example 3. Deposition of $TiO_2$ on $Ti\text{-}TiO_x$ ($x<2$) film Stack

**[0072]** A layer of $TiO_2$ was deposited on a titanium coated substrate. About 2000 Å of Ti metal was deposited at 7KW of PDC target power, with Ar flow of 100 sccm and bias power of 200W. After Ti deposition, $TiO_2$ was deposited in the same chamber without oxide burn in. This process resulted in a $Ti\text{-}TiO_y\text{-}TiO_2$ ($y<2$) film stack. The k value of a 200Å film was as high as 60.

**[0073]** Figures 9A and 9B illustrate an SEM cross-section of a $Ti_4O_7$ Ebonex™ target (Figure 9A) and an SEM cross section of the $Ti_4O_{6.8}$ layer (Figure 9B) deposited from the Ebonex™ target according to the present invention. The deposited film shows smooth deposition of the layer. The Ebonex™ target shown in Figure 9A shows an open porousity material with high roughness. The deposited layer shown in Figure 9B, however, shows a highly dense layer with a smooth surface condition.

**[0074]** Table I shows the effects of the dielectric properties of $TiO_2$ deposited according the present invention in comparison with previously obtained values. The values for the previously obtained reactive sputtering was taken from the paper "Frequency-Dependent Pulsed Direct Current magnetron Sputtering of Titanium Oxide Films," by J. Y. Kim et al., J. Vac. Sci. Techn., A 19(2), Mar/Apr. 2001. The values for PDC PVD with bias was experimentally obtained from layers deposited as described in Example 2 above.

Table I

| Process | $V_{bd}$ (Mv/cm) | K | FM |
|---|---|---|---|
| Reactive Sputtering | 0.46 ~ 1.35 | 34 ~ 65.9 | 19 ~ 50 |
| PDC physical Vapor Deposition with Bias | 3.48 | 83 | 288 |

**[0075]** As can be seen from Table I, the breakdown voltage $V_{bd}$ is significantly improved in layers according to the present invention. Further, the dielectric constant of the resulting layer is also higher. The figure of merit (FM) then for the deposited layer was 288, very much higher than that report by Kim et al. The reference Kim et al. was the reference reporting the best quality $TiO_2$ films available at the time of filing of the prior application to which this disclosure claims priority.

**[0076]** Figure 10 shows data of capacitance made with layers according to the present invention in processes as described in Example 2 above are shown in comparison with available industry values. As is observed in Figure 10, layers of $TiO_2$ deposited according to the present invention have higher dielectric breakdown voltages than other dielectric films utilized in industry, which is represented by the solid line. However, due to the roll-off in dielectric constant K in films below about 1000 Å in thickness (as is indicated in the top two points in Figure 10), a capacitance density above about 5000 or 6000 pF/mm2 could not be achieved using thinner films. This is also shown in Figure 7.

**[0077]** However, combined with the use of a conductive sub-oxide and the higher dielectric constant of thinner films as shown in Figure 11, a capacitance density of 12000 pF/mm2 can be achieved with a 500 Å thickness film and a capacitance density of greater than 24000 pF/mm2 can be achieved with a 220 Å film, as is shown in Figure 11. These film stacks were deposited as described in Example 3 above.

**[0078]** Figure 12 shows a deposited layer 102 on a substrate 101 formed of n++ silicon wafer. Layer 102 is formed of $TiO_2$ deposited according to the present invention. As shown in the SEM cross-section, the $TiO_2$ layer shows several layers. A layer 1201 is formed of $SiO_2$ formed on substrate 101 and is formed about 20 Å thick. An amorphous layer 1202 of thickness about 250 Å is then formed above layer 1201. Finally, a crystalling $TiO_2$ layer 1203 is formed about 4000 Å thick. In some embodiments of the present invention, a continuous deposition on a substrate results in a first amorphous layer deposited at initially cooler temperature followed by a further crystalline layer deposited during the increased temperature of the process. A diffraction pattern inset in Figure 12 illustrates the crystalline nature of layer 1203.

**[0079]** Table II tabulates data taken from a number of bi-layer film such as that shown in Figure 12 and completely amorphous films formed by repeated initial deposition layers at cool deposition conditions. Films near 1000 Å of thickness are compared and display similar values for the dielectric constant. However, the amorphous film exhibits much higher dielectric breakdown strengths. Due to the similar thickness and values of the dielectric constant, the two films exhibit similar values for capacitance. However, the amorphous film illustrates superior breakdown voltage and therefore has a higher figure of merit (FM). These trends are more pronounced in the thicker films with thicknesses close to 2000 Å. In this case, the values of the dielectric constant and capacitance are nearly identical but again there is a significantly higher breakdown voltage in the amorphous film, which results in a significant improvement in the figure of merit for the amorphous films.

Table II

| Film Thickness (nm) | k | $V_{bd}$ (MV/cm) | FM | C (pF/mm2) | Breakdown Voltage (V) | Film Morphology |
|---|---|---|---|---|---|---|
| 969 | 63 | 3.6 | 227 | 540 | 348 | Bi-layer |
| 1036 | 62 | 6.4 | 396 | 538 | 660 | Amorphous |
| 2020 | 98 | 3.5 | 335 | 429 | 705 | Bi-Layer |
| 2322 | 98 | 5.5 | 539 | 429 | 1110 | Amorphous |

**[0080]** Therefore, it is clear that amorphous $TiO_2$ films have much better performance. As discussed above, those layers are the result of low temperature depositions. Therefore, as was demonstrated with the data shown in Table II, one method of producing thick amorphous $TiO_2$ layers is to simply utilize a sequence of low temperature depositions, halting the deposition prior to thermal heating of the depositing film. However, this method can take a significant amount of production time for thick films. Another embodiment of obtaining thick $TiO_2$ amorphous films is to apply active cooling to the substrate in an amount sufficient to provide continuously amorphous $TiO_2$ films.

**[0081]** Figure 13 shows a comparison of the leakage current for $TiO_2$ films according to embodiments of the present invention with and without erbium ion doping. The lower data points in Figure 13 are from capacitors formed from films deposited from a 10 at. % Er doped TiO target. The target was electrically conductive. One example of the 10% doped film of 1000 Å thickness was formed with 60 sccm Ar, 6 sccm $O_2$, with a target power of 3 kW, bias power of 100 W, with a deposition time of 200 sec on a metal coated glass wafer. With the metal coating forming a copper titanium lower electrode and a titanium copper gold upper electrode patterned as 1X1 mm, discreet capacitors was then formed. The layers corresponding to the upper data points were deposited from a pure titanium target with no erbium doping on a TaN substrate with a evaporated platinum upper electrode. This structure of the bottom data is illustrated in Figure 4B where, for example, layer 101 is a glass substrate, layer 103 is a copper titanium layer, layer 102 is the erbium doped $TiO_2$ layer, and layer 201 is a titanium copper gold layer.

**[0082]** As can be seen in Figure 13, the leakage current density is reduced by many orders of magnitude by addition of erbium.

**[0083]** Figures 14A and 14B show a photoluminescence signal with excitation at 580 nm and measurement at 1.53 μm, measured from a 5000 Å layer of 10% erbium containing $TiO_2$ deposited from a 10% erbium doped TiO conductive target and a photoluminescence signal measured from the same layer after a 30 minute 250 °C anneal, respectively. Table III shows similar data for several layers deposited from the erbium-doped TiO conductive target.

Table III

| Thickness | Before Anneal | Anneal (°C) | After Anneal |
|---|---|---|---|
| 5000 Å | 6704 | 150 | 5809 |
| 5000 Å | 6493 | 200 | 4042 |
| 5000 Å | 6669 | 250 | 2736 |
| 5000 Å | 6493 | 300 | 3983 |
| 1 μm | 6884 | 150 | 6743 |
| 1 μm | 5197 | 200 | 3685 |
| 1 μm | 6253 | 250 | 3612 |
| 1 μm | 5324 | 300 | 3381 |

**[0084]** According to some explanations of the reduction of leakage current in layers as illustrated by Figure 13, fast electrons that have sufficient energy to excite the erbium ion would cause the rare earth ion to undergo excitation upon electron impact or passage within a distance sufficient for energy exchange. Consequently, the leakage current electrons capable of causing ionization within the dielectric oxide would be reduced by electron collisions with erbium ions. Excited state ions have at least two relaxation mechanisms for disposal of the energy: radiative and non-radiative. In radiative relaxation, the excited ion emits light. In non-radiative relaxation, the excited ion undergoes a cooperative process with vibrational modes of it's host dielectric oxide and produces a vibration which is the elemental form of heat. In the data illustrated in Figure 13, it was not possible to observe light in the leakage test, but photoluminescence was observed from optical excitation of the similar 10% Er doped $TiO_2$ deposited from the 10% Er doped TiO conductive target, as shown in Table III.

**[0085]** As can be seen from the data in Table III, an erbium doped layer of titanium oxide was shown to fluoresce strongly under optical excitation by light of a wavelength 580 nm, using a Phillips PhotoLuminescence Microscope, model no. PLM-100. The target was electrically conductive and sputtered at a higher rate and a lower oxygen partial pressure than characteristic of a metallic titanium target. One example of the 10% doped film of 2,032 angstroms was 60 sccm Ar, 6 sccm $O_2$, with a target power of 3 kW, bias power of 100 W, with a deposition time of 300 sec.

**[0086]** The level of photoluminescence observed from the layer was similar to that obtained in as-deposited and annealed films providing commercial levels of optical absorption and fluorescence for applications to planar waveguide amplifiers having at least 15 dB gain for signals as weak as -40dB at the 1.5 micron wavelength utilized for photonic C band communications.

**[0087]** Such a device can be illustrated with Figure 3B, where layer 103 can be a conductive layer deposited on substrate 101, layer 102 can be a rare-earth doped $TiO_2$ layer deposited according to embodiments of the present invention, and layer 104 can be a further conductive layer or a conductive transparent layer to form an metal-insulating-metal (MIM) capacitor structure. Such a structure could function as a light emitting layer under either DC or AC electrical excitation. In another embodiment, layer 103 can be a lift-off layer such as $CaF_2$ or other organic material, layer 102 is the rare-earth doped $TiO_2$ layer, and layer 104 is absent, then upon lift-off or upon transfer of layer 102, a free standing or applied layer having electroluminescent or photoluminescent applications can be provided over a selected device.

**[0088]** Thin films according to the present invention can be utilized in advanced display devices, electrical energy storage and conversion, and to form optical and electronic films with scratch resistance and barrier properties. Advanced display product applications include OLED encapsulation, barriers for flexible polymer substrates, outcoupling mirrors and anti-reflection coatings, transparent conducting oxides, and semiconducting materials for active matrix displays. Electrical energy storage and conversion applications include high density capacitor arrays for mobile communication devices, on-chip high "K" capacitors for advanced CMOS, and high voltage energy storage for portable power devices. Other applications include touch-sensitive devices and durable bar code scanners and see-through sensors as well as implantable biometric devices.

**[0089]** The embodiments described in this disclosure are examples only and are not intended to be limiting. Further, the present invention is not intended to be limited by any particular theory or explanation presented to explain experimental results. As such, examples of titanium oxide and titanium sub-oxide films illustrated herein and their applications are not intended to be limiting. One skilled in the art may contemplate further applications or films that are intended to be within the spirit and scope of the present invention. As such, the invention is limited only by the following claims.

## Claims

We claim:

1. A method of forming a titanium based layer, comprising:

depositing a layer of titanium containing oxide by pulsed-DC, biased reactive sputtering process on a substrate.

2. The method of claim 1, wherein the layer is $TiO_2$.

3. The method of claim 2, wherein the figure of merit of the layer is greater than 50.

4. The method of claim 2, wherein the layer is deposited between conducting layers to form a capacitor.

5. The method of claim 2, wherein the layer includes at least one rare-earth ion.

6. The method of claim 5, wherein the layer is deposited between conducting layers to form a capacitor.

7. The method of claim 5, wherein the at least one rare-earth ion includes erbium.

8. The method of claim 5, wherein the layer is deposited between conducting layers to form a light-emitting device.

9. The method of claim 5, wherein the layer is an optically active layer deposited on a light-emitting device.

10. The method of claim 5, wherein the layer is an optically active layer applied to a light-emitting device.

11. The method of claim 1, wherein the layer is a sub-oxide of Titanium.

12. The method of claim 11, wherein the figure of merit of the layer is greater than 50.

13. The method of claim 11, wherein the layer is deposited between conducting layers to form a capacitor.

14. The method of claim 11, wherein the layer includes at least one rare-earth ion.

15. The method of claim 14, wherein the layer is deposited between conducting layers to form a capacitor.

16. The method of claim 14, wherein the at least one rare-earth ion includes erbium.

17. The method of claim 14, wherein the layer is deposited between conducting layers to form a light-emitting device.

18. The method of claim 14, wherein the layer is an optically active layer deposited on a light-emitting device.

19. The method of claim 14, wherein the layer is an optically active layer applied to a light-emitting device.

20. The method of claim 2, wherein the layer is a protective layer.

21. The method of claim 20, wherein the protective layer is a catalytic layer.

22. The method of claim 20, wherein the protective layer includes at least one rare-earth ion.

23. The method of claim 1, wherein the layer is $Ti_xO_y$ wherein x is between about 1 and about 4 and y is between about 1 and about 7.

24. The method of claim 23, wherein the figure of merit of the layer is greater than 50.

25. The method of claim 23, further including depositing an $TiO_2$ layer on the layer wherein the layer and the $TiO_2$ layers are deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the $TiO_2$ layer.

26. The method of claim 23, wherein the $TiO_2$ layer is an amorphous layer deposited by a pulsed DC, biased, reactive ion process.

27. The method of claim 23, wherein the layer includes at least one rare-earth ion.

28. The method of claim 27, wherein the at least one rare-earth ion includes erbium.

29. The method of claim 27, wherein the layer is deposited between conducting layers to form a light-emitting device.

30. The method of claim 27, wherein the layer is an optically active layer deposited on a light-emitting device.

31. The method of claim 27, wherein the layer is an optically active layer applied to a light-emitting device.

32. The method of claim 23, wherein the layer is a conducting oxide.

33. The method of claim 32, wherein the substrate is a conducting electrode and the layer is a protective layer.

34. The method of claim 33, wherein the protective layer is a catalytic layer.

35. The method of claim 33, wherein the protective layer includes at least one rare-earth ion.

36. The method of claim 32, wherein the substrate is a dielectric and the layer is a protective layer.

37. The method of claim 36, wherein the protective layer is a catalytic layer.

38. The method of claim 1, further including

controlling the temperature of the substrate during deposition.

39. The method of claim 38, wherein controlling the temperature includes active temperature control.

40. The method of claim 1, wherein the layer is an amorphous layer.

41. The method of claim 1, wherein the substrate includes a transistor structure.

42. A titanium based layer, comprising:

a layer compounded from titanium and oxygen deposited by pulsed-DC, biased reactive sputtering process on a substrate.

43. The layer of claim 42, wherein the layer is $TiO_2$.

44. The layer of claim 43, wherein the figure of merit of the layer is greater than 50.

45. The layer of claim 43, wherein the layer is deposited between conducting layers to form a capacitor.

46. The layer of claim 43, wherein the layer includes at least one rare-earth ion.

47. The layer of claim 46, wherein the layer is deposited between conducting layers to form a capacitor.

48. The layer of claim 46, wherein the at least one rare-earth ion includes erbium.

49. The layer of claim 46, wherein the layer is deposited between conducting layers to form a light-emitting device.

50. The layer of claim 46, wherein the layer is an optically active layer deposited on a light-emitting device.

51. The layer of claim 46, wherein the layer is an optically active layer applied to a light-emitting device.

52. The layer of claim 42, wherein the layer is sub-oxide of Titanium.

53. The layer of claim 52, wherein the figure of merit is greater than 50.

54. The layer of claim 52, wherein the layer is deposited between conducting layers to form a capacitor.

55. The layer of claim 52, wherein the layer includes at least one rare-earth ion.

56. The layer of claim 55, wherein the layer is deposited between conducting layers to form a capacitor.

57. The layer of claim 55, wherein the at least one rare-earth ion includes erbium.

58. The layer of claim 55, wherein the layer is deposited between conducting layers to form a light-emitting device.

59. The layer of claim 55, wherein the layer is an optically active layer deposited on a light-emitting device.

60. The layer of claim 55, wherein the layer is an optically active layer applied to a light-emitting device.

61. The layer of claim 43, wherein the layer is a protective layer.

62. The layer of claim 61, wherein the protective layer is a catalytic layer.

63. The layer of claim 61, wherein the protective layer includes at least one rare-earth ion.

64. The layer of claim 42, wherein the layer is $Ti_xO_y$ wherein x is between about 1 and about 4 and y is between about 1 and about 7.

65. The layer of claim 64, wherein the figure of merit is greater than 50.

66. The layer of claim 64, further including depositing an $TiO_2$ layer on the layer wherein the layer and the $TiO_2$ layers are deposited between conducting layers to form a capacitor with decreased roll-off characteristics with decreasing thickness of the $TiO_2$ layer.

67. The layer of claim 64, wherein the $TiO_2$ layer is an amorphous layer deposited by a pulsed DC, biased, reactive ion process.

68. The layer of claim 64, wherein the layer includes at least one rare-earth ion.

69. The layer of claim 68, wherein the at least one rare-earth ion includes erbium.

70. The layer of claim 68, wherein the layer is deposited between conducting layers to form a light-emitting device.

71. The layer of claim 68, wherein the layer is an optically active layer deposited on a light-emitting device.

72. The layer of claim 68, wherein the layer is an optically active layer applied to a light-emitting device.

73. The layer of claim 64, wherein the layer is a conducting oxide.

74. The layer of claim 73, wherein the substrate is a conducting electrode and the layer is a protective layer.

75. The layer of claim 74, wherein the protective layer is a catalytic layer.

76. The layer of claim 74, wherein the protective layer includes at least one rare-earth ion.

77. The layer of claim 73, wherein the substrate is a dielectric and the layer is a protective layer.

78. The layer of claim 77, wherein the protective layer is a catalytic layer.

79. The layer of claim 42, further including

controlling the temperature of the substrate during deposition.

80. The layer of claim 79, wherein controlling the temperature includes active temperature control.

81. The layer of claim 42, wherein the substrate includes a transistor structure.

82. The layer of claim 42, wherein the layer is an amorphous layer.

83. A target, comprising:

hipped TiO having composition TiO.

84. The target of claim 83, further including at least one rare-earth dopant.

85. A method of forming a target, comprising:

forming a TiO powder;

mixing the TiO powder to form a mix;

hipping the mix under a controlled atmosphere to form tiles; and

forming a target from the tiles.

86. The method of claim 85, further including mixing at least one rare-earth oxide powder with the mix.

87. The method of claim 86, wherein the at least one rare-earth oxide includes erbium oxide.

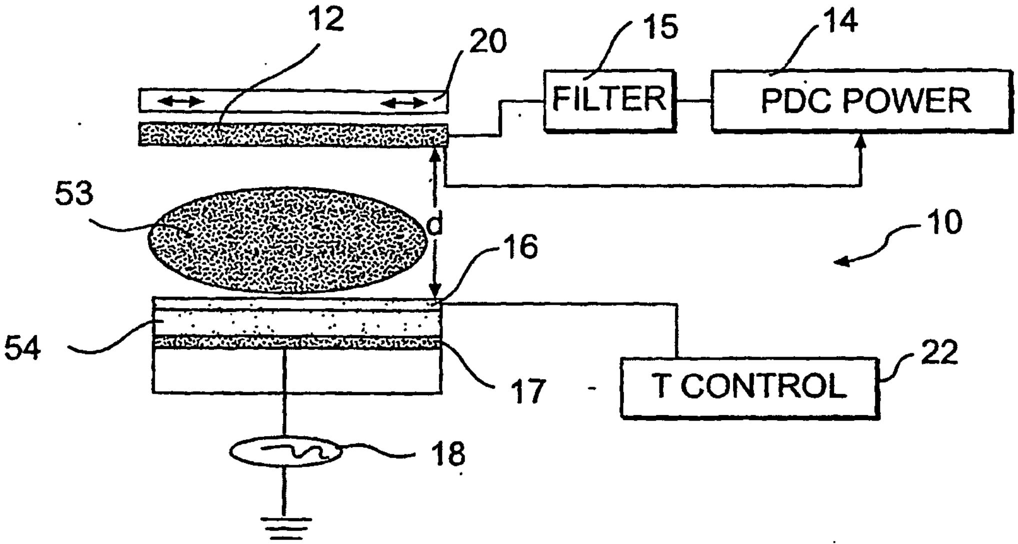

12
20
15
FILTER
14
PDC POWER
53
d
10
16
54
17
T CONTROL
22
18

FIG. 1A

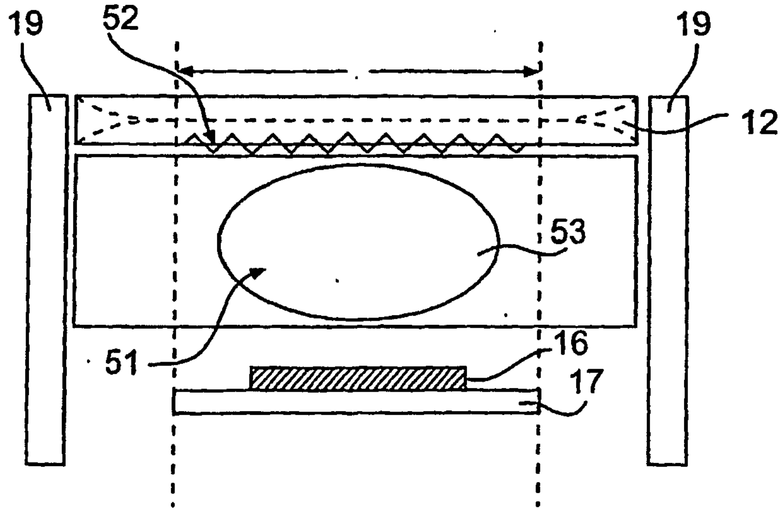

19
52
19
12
53
51
16
17

FIG. 1B

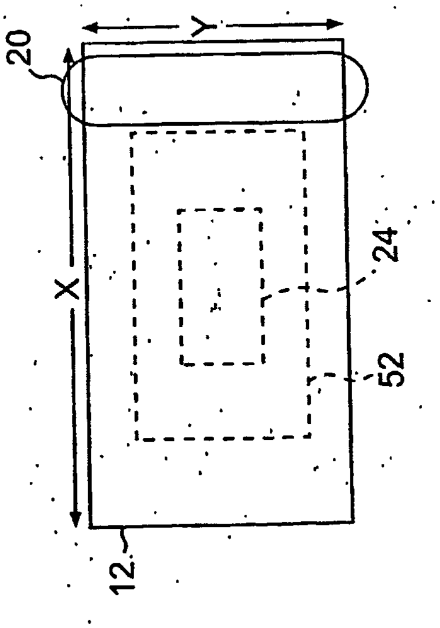


FIG. 2

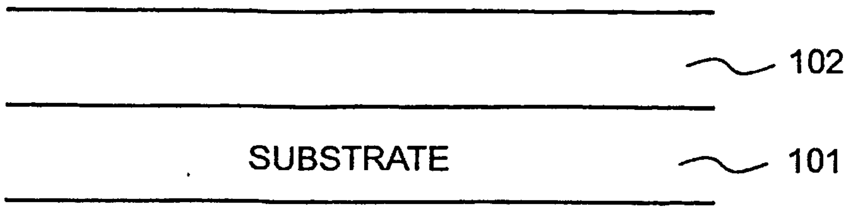


FIG. 3A

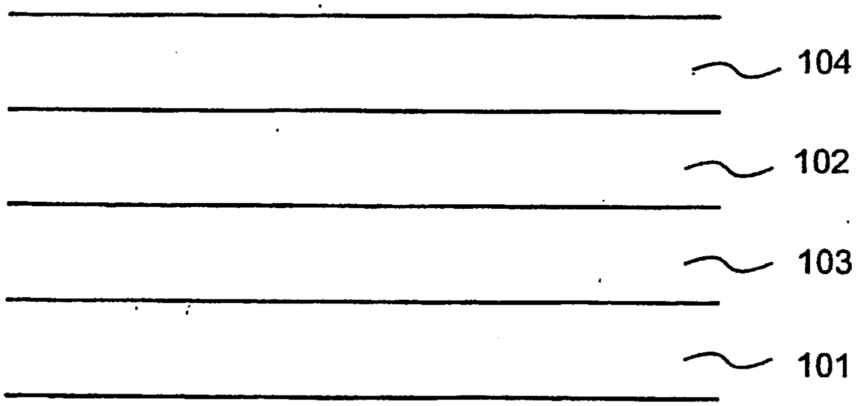


FIG. 3B

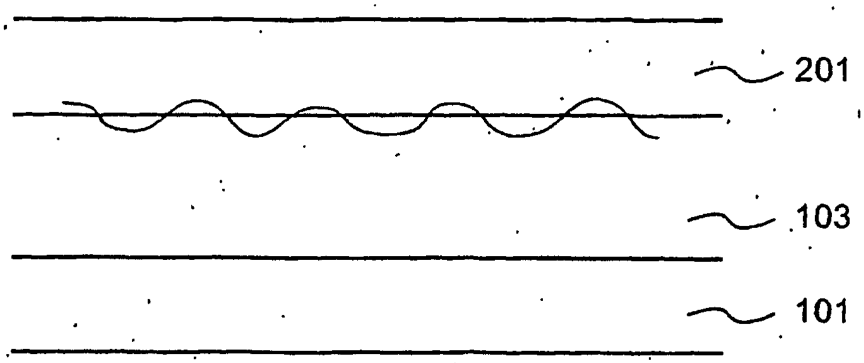


FIG. 4A

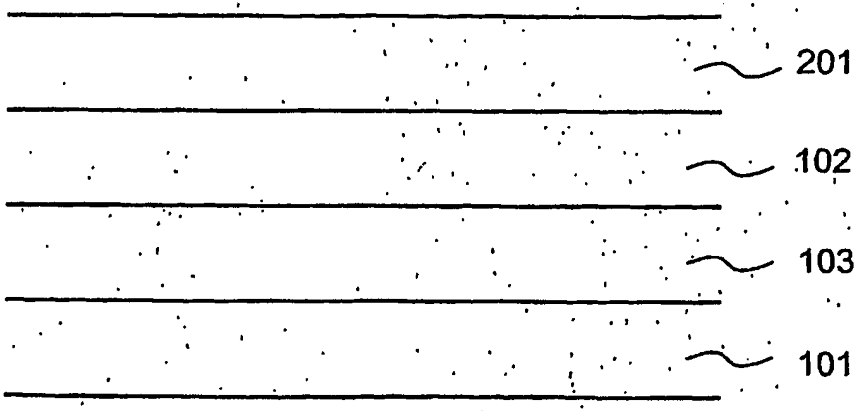


FIG. 4B

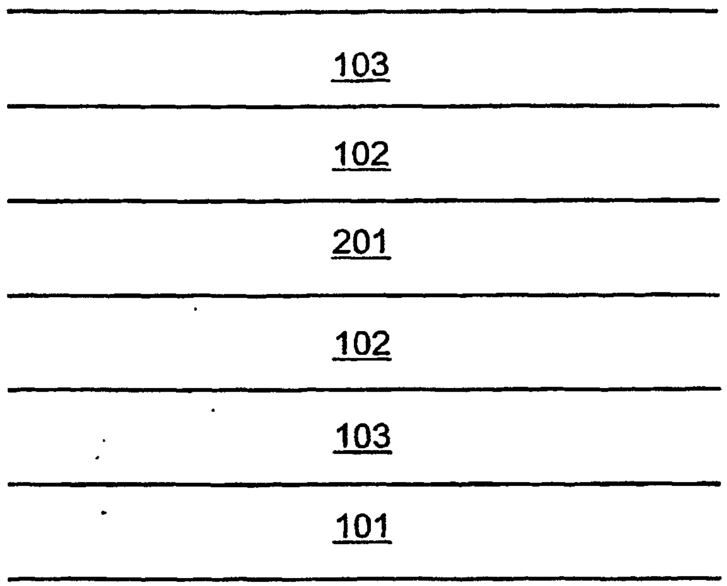


FIG. 5

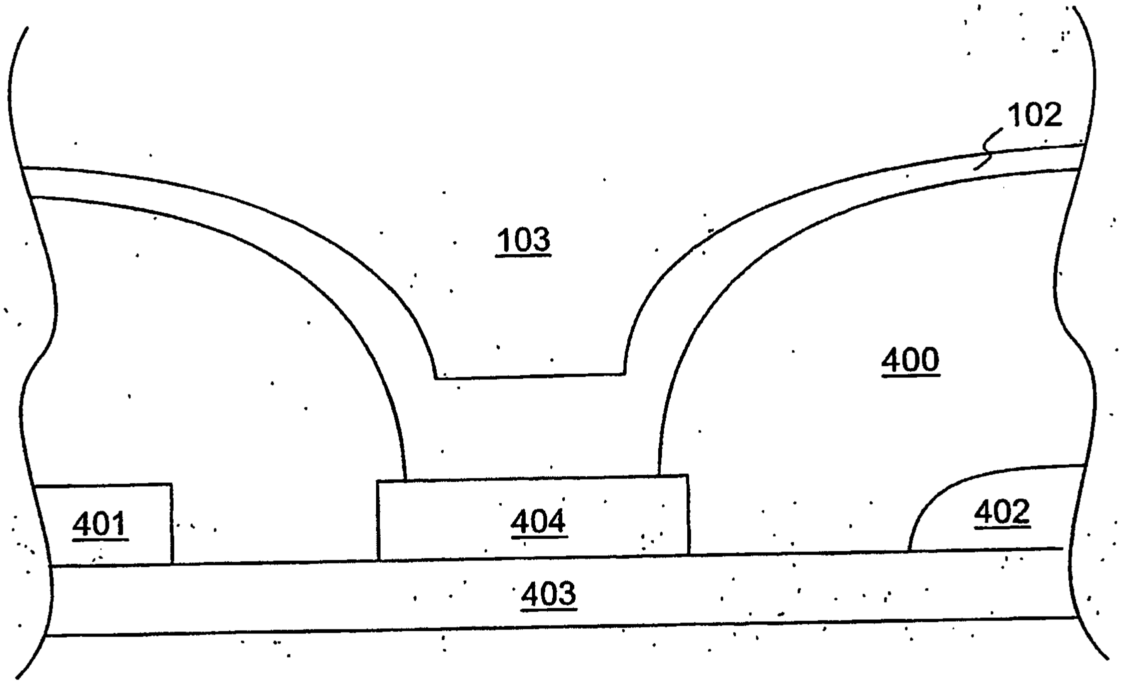


FIG. 6

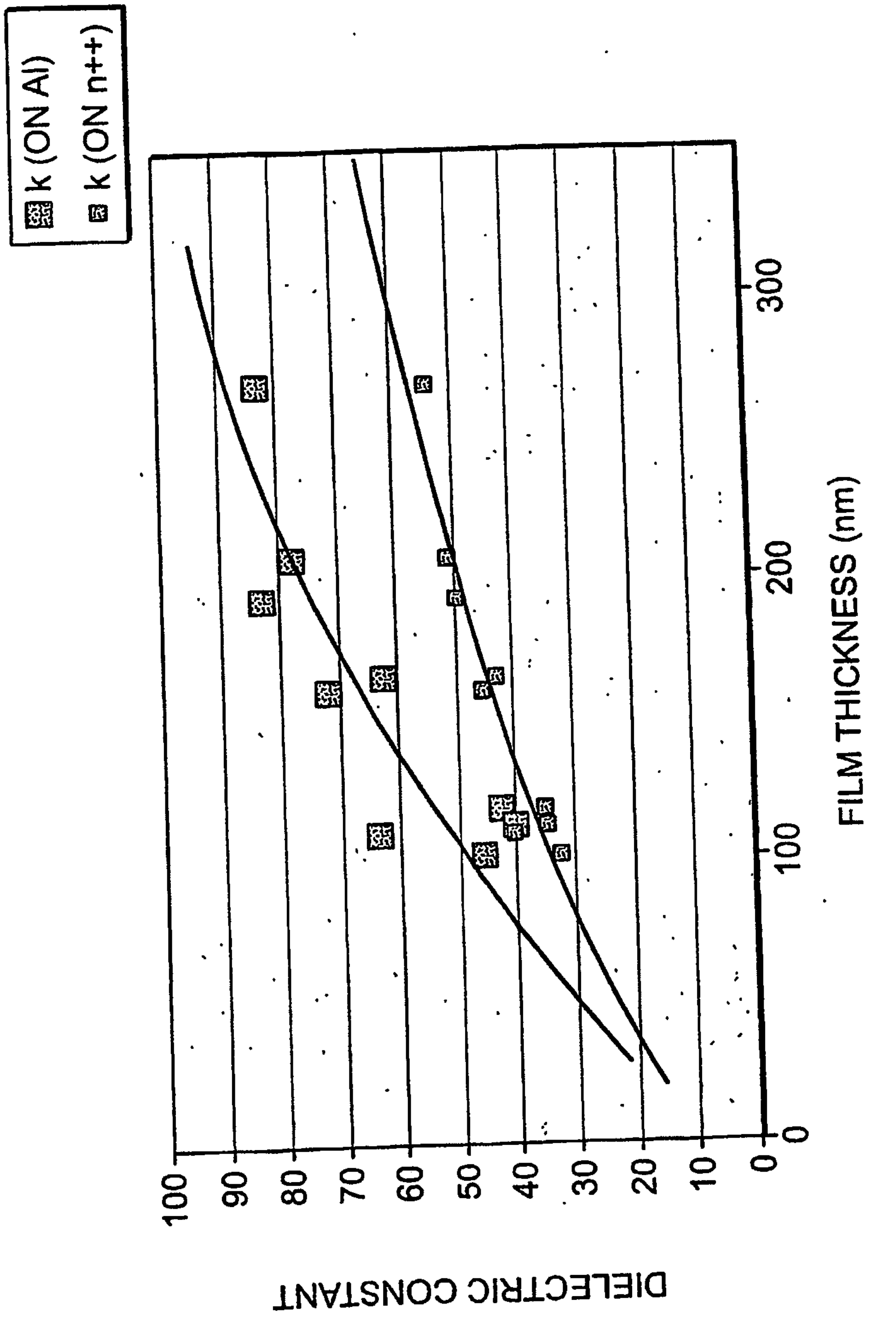

▨ k (ON Al)
▨ k (ON n++)
DIELECTRIC CONSTANT
100
90
80
70
60
50
40
30
20
10
0
FILM THICKNESS (nm)
0
100
200
300

FIG. 7

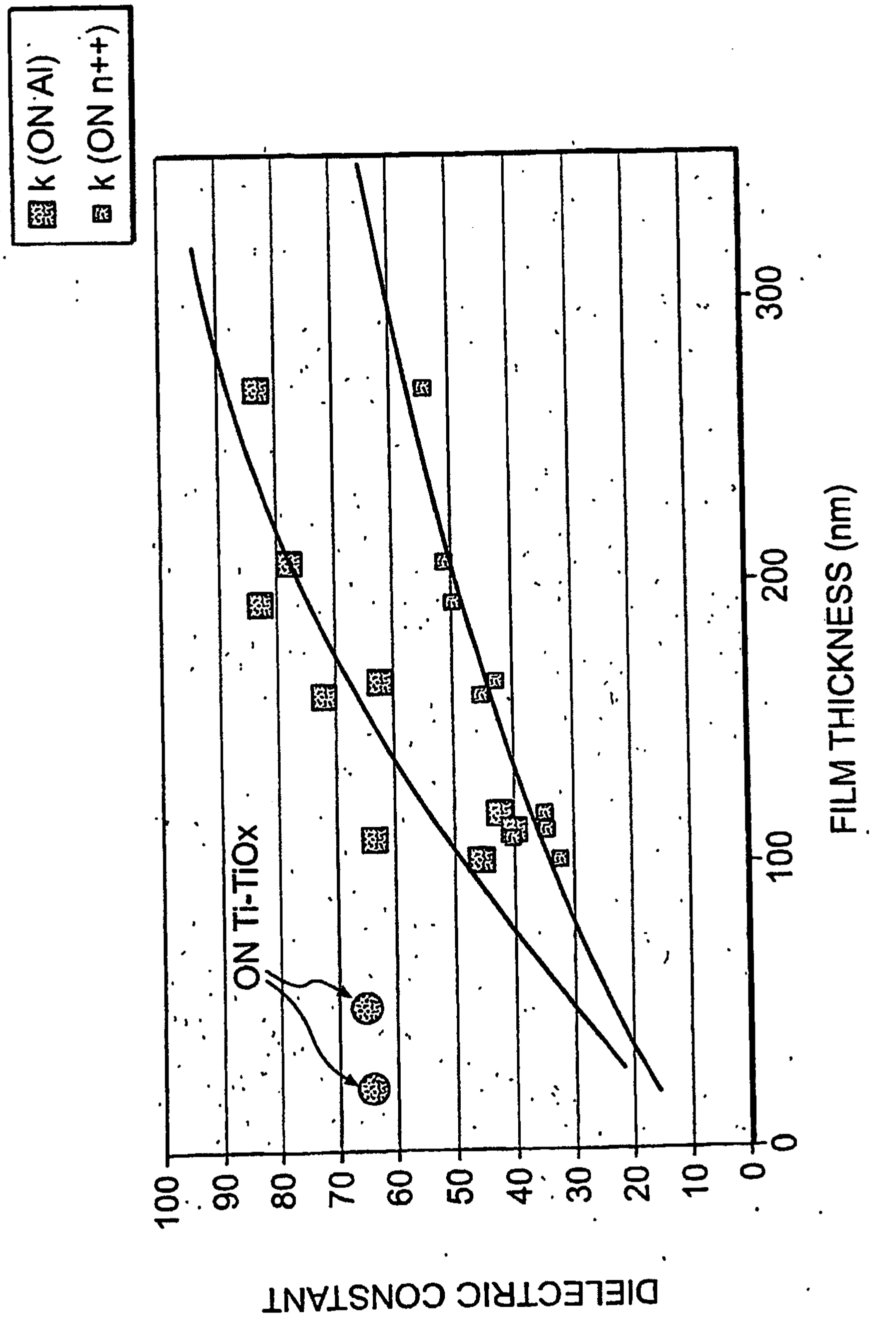

▨ k (ON Al)
▨ k (ON n++)
ON Ti-TiOx
DIELECTRIC CONSTANT
0
10
20
30
40
50
60
70
80
90
100
FILM THICKNESS (nm)
0
100
200
300

FIG. 8

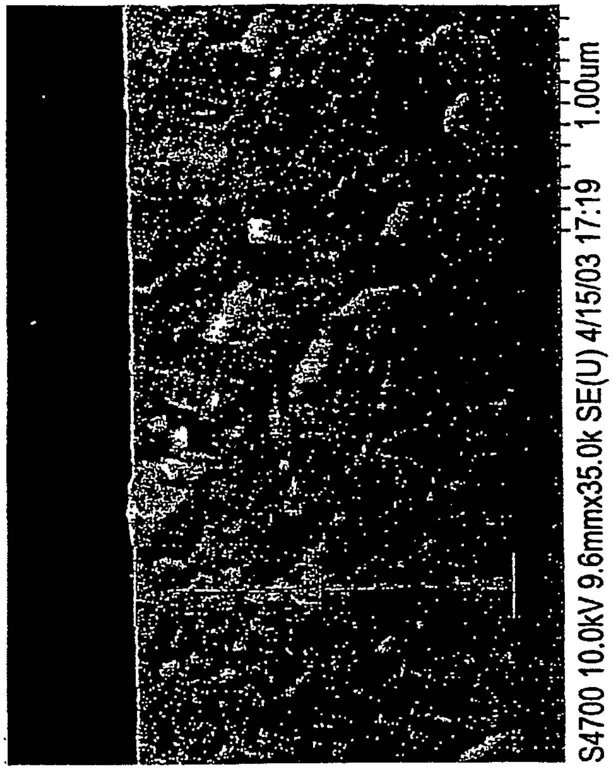

S4700 10.0kV 9.6mmx35.0k SE(U) 4/15/03 17:19
1.00um

FIG. 9B

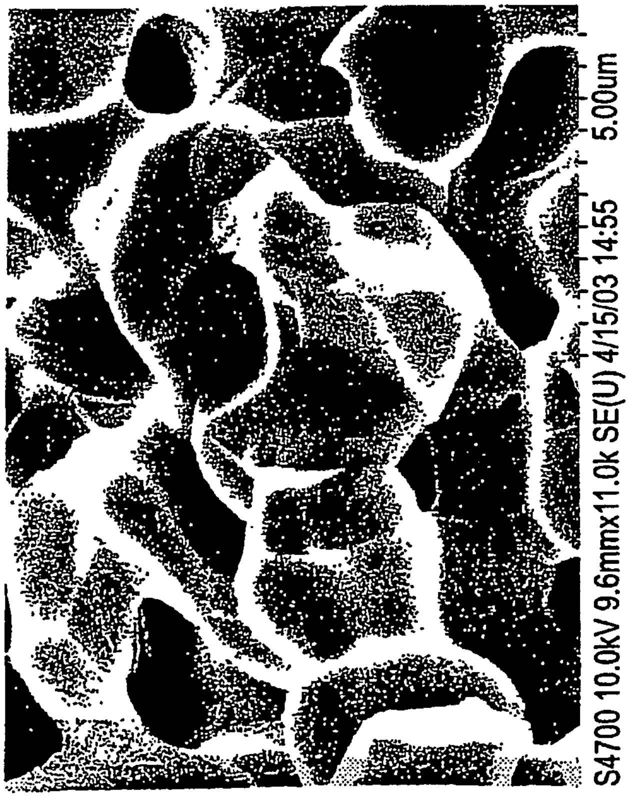

S4700 10.0kV 9.6mmx11.0k SE(U) 4/15/03 14:55
5.00um

FIG. 9A

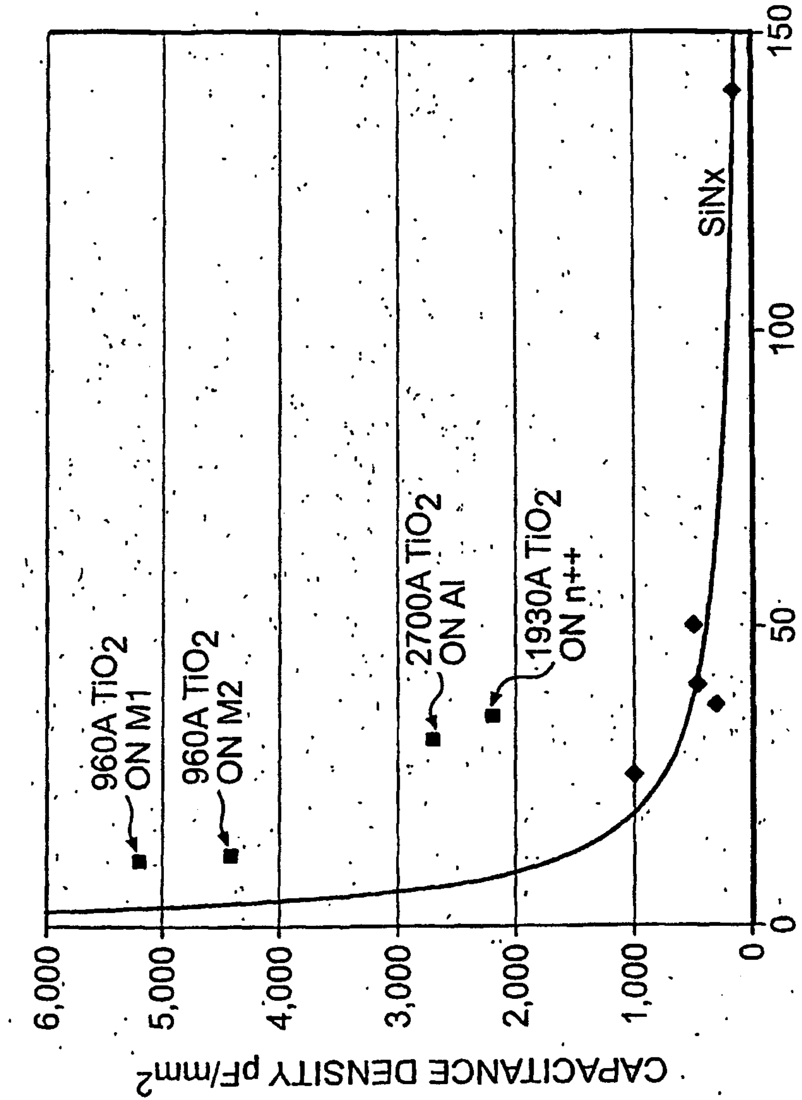

CAPACITANCE DENSITY pF/mm$^2$
6,000
5,000
4,000
3,000
2,000
1,000
0
0
50
100
150
OPERATING VOLTAGE (V)
960A TiO$_2$ ON M1
960A TiO$_2$ ON M2
2700A TiO$_2$ ON Al
1930A TiO$_2$ ON n++
SiNx

FIG. 10

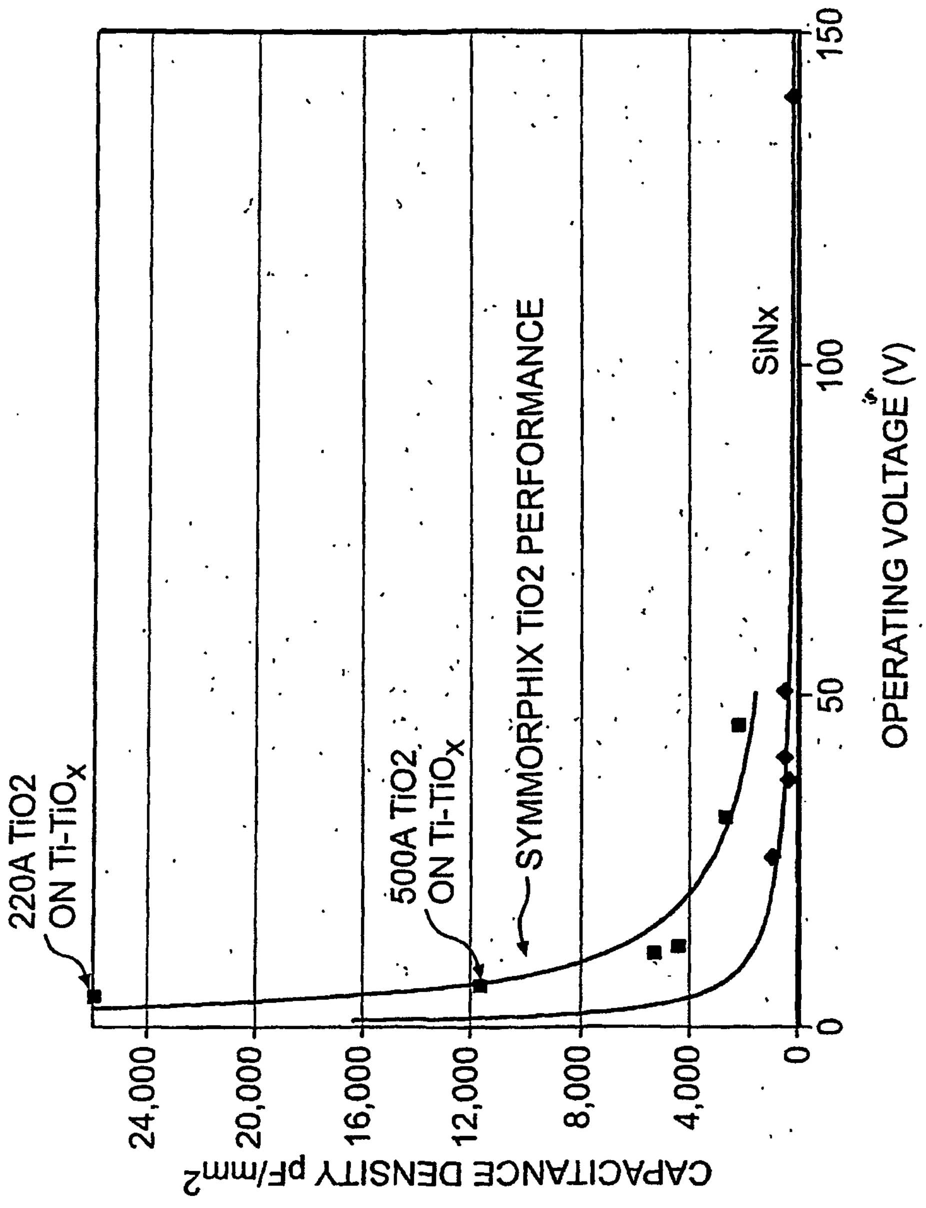

CAPACITANCE DENSITY pF/mm$^2$
24,000
20,000
16,000
12,000
8,000
4,000
0
0
50
100
150
OPERATING VOLTAGE (V)
220A TiO2 ON Ti-TiO$_X$
500A TiO2 ON Ti-TiO$_X$
SYMMORPHIX TiO2 PERFORMANCE
SiNx

FIG. 11

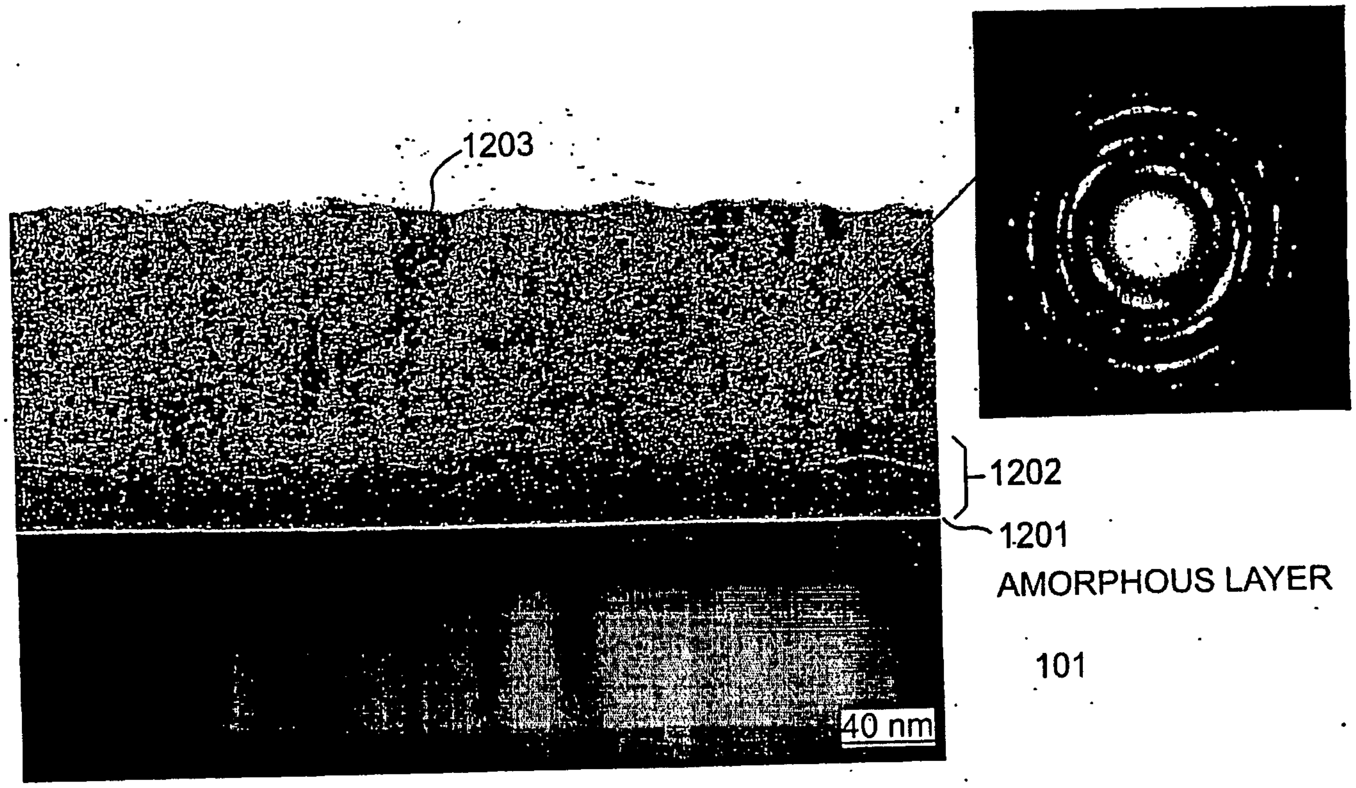


FIG. 12

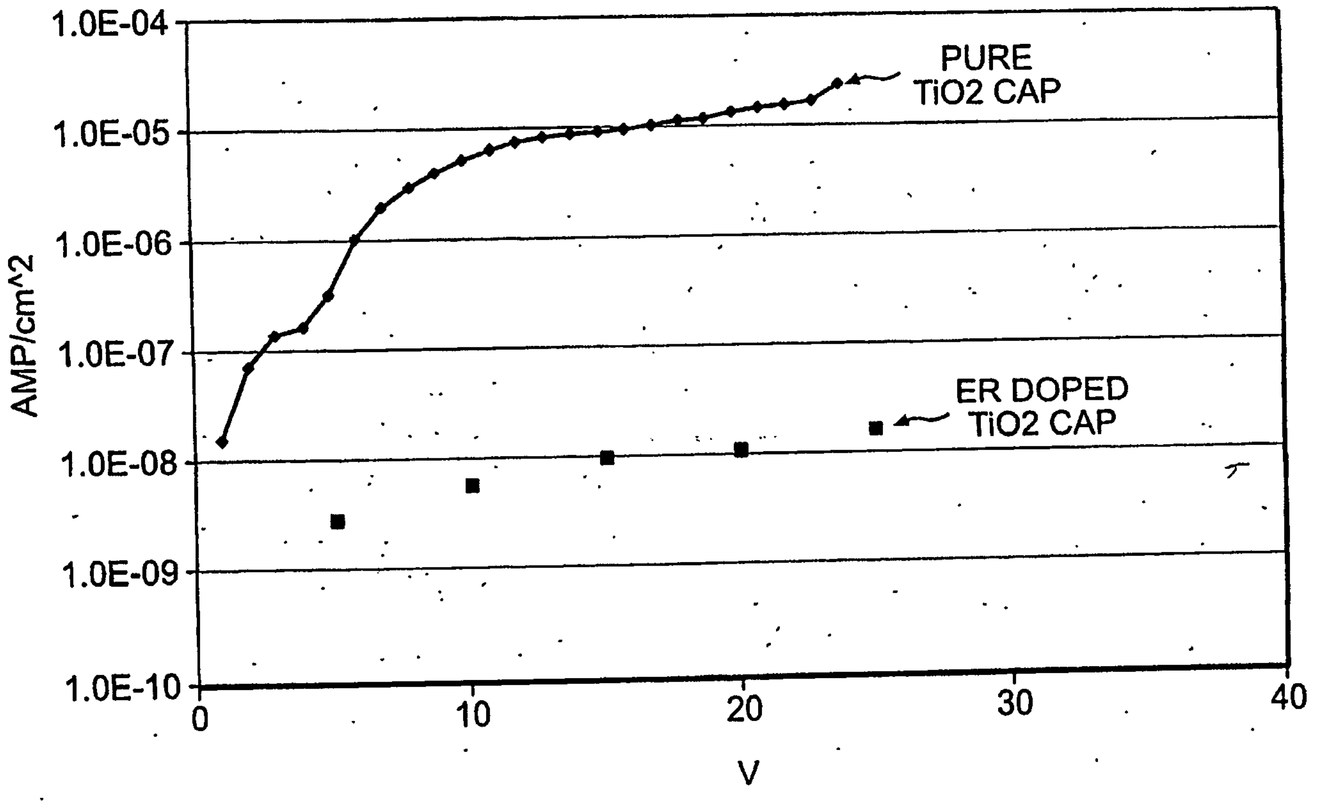
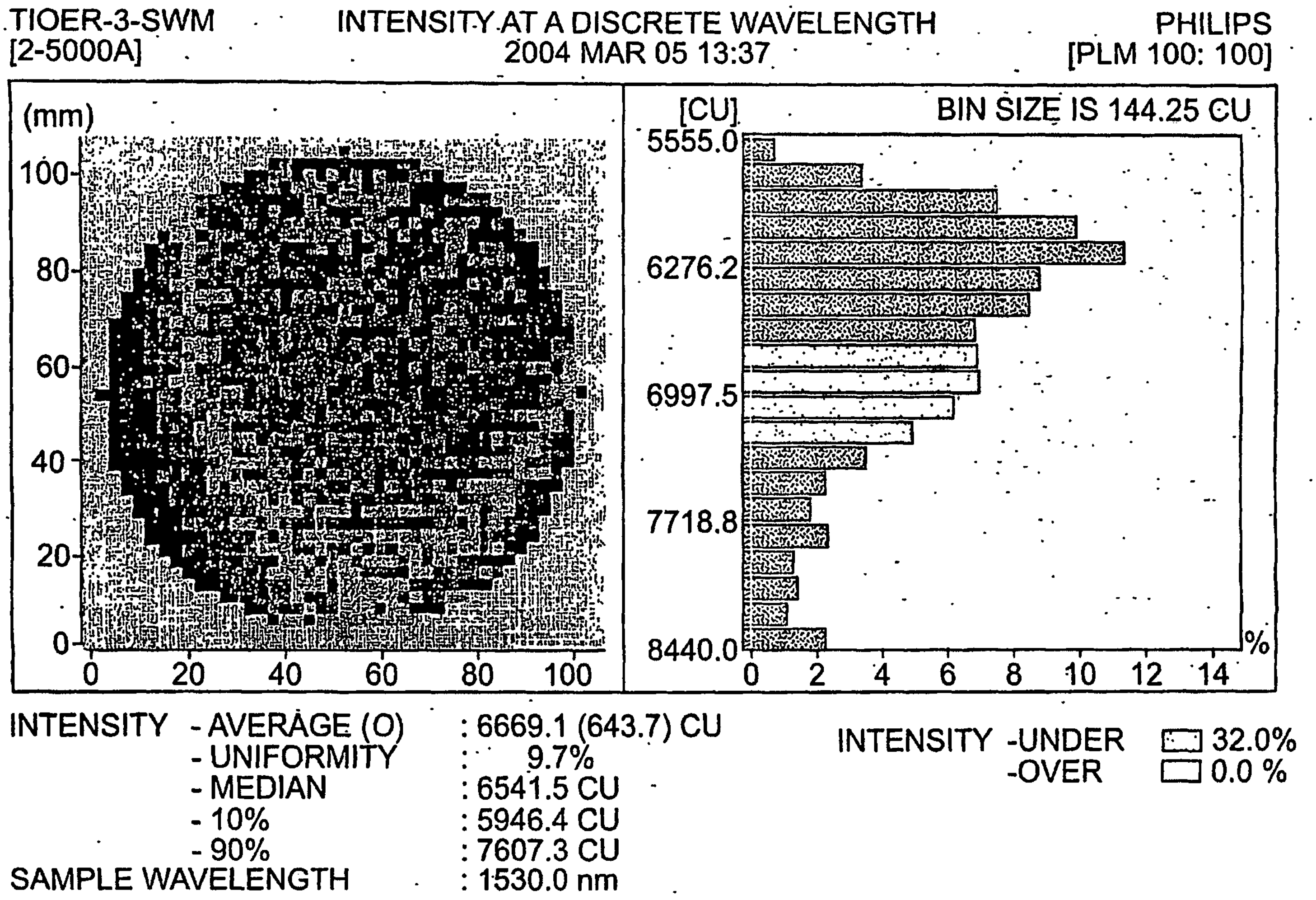

1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
AMP/cm^2
0
10
20
30
40
V
PURE
TiO2 CAP
ER DOPED
TiO2 CAP

FIG. 13



TIOER-3-SWM
[2-5000A]

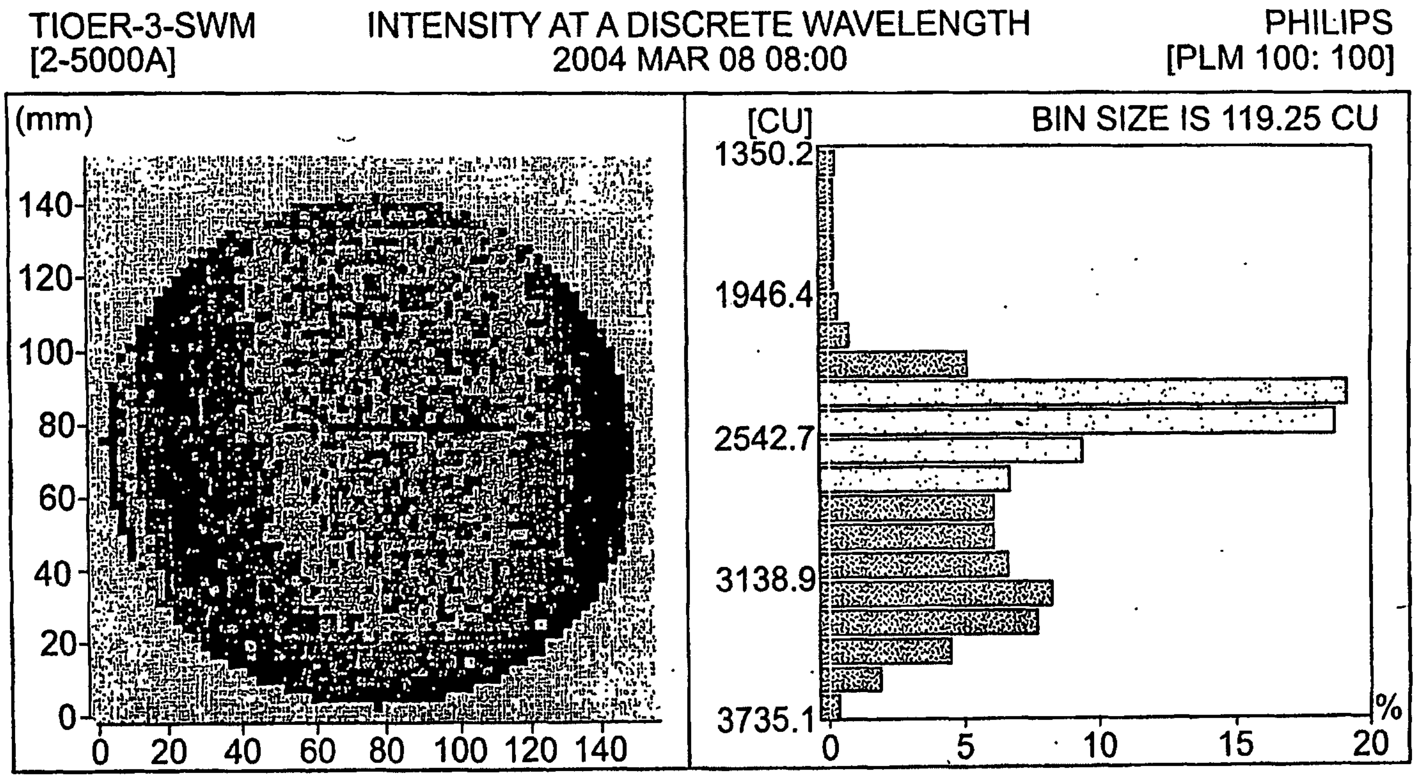
INTENSITY AT A DISCRETE WAVELENGTH
2004 MAR 05 13:37

PHILIPS
[PLM 100: 100]

INTENSITY - AVERAGE (O) : 6669.1 (643.7) CU
- UNIFORMITY : 9.7%
- MEDIAN : 6541.5 CU
- 10% : 5946.4 CU
- 90% : 7607.3 CU
SAMPLE WAVELENGTH : 1530.0 nm

INTENSITY -UNDER ▨ 32.0%
-OVER ☐ 0.0 %

FIG. 14A



INTENSITY - AVERAGE (O) : 2736.0 (382.3) CU
- UNIFORMITY : 14.0 %
- MEDIAN : 2615.1 CU
- 10% : 2330.0 CU
- 90% : 3307.5CU
SAMPLE WAVELENGTH : 1530.0 nm

INTENSITY -UNDER ▨ 34.9%
-OVER ☐ 0.0 %

FIG. 14B

3-01-06 IFW 2823

OIPE IAP80
FEB 27 2006
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SIXTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the U.S. patents and patent publications cited are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 27, 2006

By:____________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 860819704 US**

OIPE
IAP80
FEB 27 2006
PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| | | | |
|---|---|---|---|
| Sheet | 1 | of | 1 |

| ***Complete if Known*** | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US 5,909,346 | 06-01-1999 | Malhotra et al. | |
| | | US 6,000,603 | 12-14-1999 | Koskenmaki et al. | |
| | | US 6,133,670 | 10-17-2000 | Rodgers et al. | |
| | | US 6,356,694 B1 | 03-12-2002 | Weber | |
| | | US 6,768,855 B1 | 07-27-2004 | Bakke et al. | |
| | | US 6,683,749 B2 | 01-27-2004 | Daby et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | | |
| | | | |
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| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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**EV 860819704 US**

03-02-06

2823
IFW

OIPE
IAP25
FEB 2 8 2006
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SEVENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

A copy of the document cited is enclosed.

Applicants respectfully request that the Examiner consider the listed document and indicate that it was considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed document, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 28, 2006

By: ______________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 860819602 US**

OIPE IAP25 FEB 2 8 2006 PATENT & TRADEMARK OFFICE

| | | | | | |
|---|---|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO<br>**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**<br>*(Use as many sheets as necessary)* | | | | ***Complete if Known*** | |
| | | | | *Application Number* | 10/101,863 |
| | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of | 1 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01). | |
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|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EV 860819602 US**

RCE filed 2-24-06

PTO/SB/06 (12-04)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875 Effective December 8, 2004

Application or Docket Number 10/101,863

## APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | RATE ($) | FEE ($) | | RATE ($) | FEE ($) |
| BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | 150.00 | | N/A | 300.00 |
| SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | $250 | | N/A | $500 |
| EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | $100 | | N/A | $200 |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X$ 25 = | | OR | X$50 = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X100 = | | | X200 = | |
| APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | +180= | | | +360= | |
| | | | TOTAL | | | TOTAL | |

* If the difference in column 1 is less than zero, enter "0" in column 2.

## APPLICATION AS AMENDED – PART II

| AMENDMENT A | 2-24-06 | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | SMALL ENTITY RATE ($) | ADDITIONAL FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total (37 CFR 1.16(i)) | * 17 | Minus | ** 39 | = | X$ 25 = | | OR | X$50 = | |
| | Independent (37 CFR 1.16(h)) | * 2 | Minus | *** 5 | = | X100 = | | OR | X200 = | |
| | Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | +180= | | OR | +360= | |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

| AMENDMENT B | | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | OR | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total (37 CFR 1.16(i)) | * | Minus | ** | = | X$ 25 = | | OR | X$50 = | |
| | Independent (37 CFR 1.16(h)) | * | Minus | *** | = | X100 = | | OR | X200 = | |
| | Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | +180= | | OR | +360= | |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

is collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the PTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, luding gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent d Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS DRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2*

## CLAIMS ONLY

2-24-06

| Application Number | Filing Date |
|---|---|
| 10/101,863 | |
| Applicant(s) | |

| CLAIMS | AS FILED | | AFTER FIRST AMENDMENT | | AFTER SECOND AMENDMENT | |
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| Total Depend. | | | 15 | | | |
| Total Claims | | | 17 | | | |

* May be used for additional claims or amendments

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03-06-06

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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## EIGHTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

A copy of the document cited is enclosed.

Applicants respectfully request that the Examiner consider the listed document and indicate that it was considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any

claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed document, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 3, 2006

By:
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 860819633 US**

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

OIPE
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TRADEMARK

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 1 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US 6,290,821 B1 | 09-18-2001 | McLeod | |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action filed February 20, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01). | |
| | | Response to Office Action filed July 17, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140-0002-01). | |
| | | Response to Office Action filed February 28, 2006 in U.S. Application No. 09/903,081 (Attorney Docket No. 09140-0014-00). | |
| | | Response to Office Action filed March 2, 2006 in U.S. Application No. 10/789,953 (Attorney Docket No. 09140.0030-00). | |

| Examiner Signature | | Date Considered | |
|---|---|---|---|

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EV 860819633 US**

# EAST Search History

| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
|---|---|---|---|---|---|---|
| L1 | 14 | sputter$3 with metallic with (poison or poisonous) | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:23 |
| L2 | 1083543 | @ad>"20020316" or @rlad>"20020316" | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:22 |
| L3 | 8 | 1 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:22 |
| L4 | 5 | sputter$3 with metallic with (poison or poisonous) with target | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:24 |
| L5 | 1 | 4 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:23 |
| L6 | 14 | (sputter$3 with metallic with (poison or poisonous)) same target | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:24 |
| L7 | 8 | 6 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:25 |
| L8 | 8 | 3 and 7 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:28 |
| L9 | 458 | backside with target | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:28 |
| L10 | 19 | "pulsed DC" and "RF bias" and plasma and filter | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:30 |
| L11 | 4 | 10 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:30 |
| L12 | 1 | 11 and 9 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:30 |
| L13 | 79 | "pulsed DC" and "RF bias" | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:31 |
| L14 | 5 | 9 and 13 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:30 |
| L15 | 1 | 14 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:30 |
| L16 | 4869 | "pulsed DC" or "RF bias" | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:31 |
| L17 | 50 | 9 and 16 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:31 |
| L18 | 27 | 17 not 2 | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:35 |
| L19 | 1 | ("6290821").PN. | US-PGPUB; USPAT | OR | OFF | 2006/03/16 16:36 |
| L20 | 6 | (("5909346") or ("6000603") or ("6133670") or ("6356694") or ("6768855") or ("6683749")).PN. | US-PGPUB; USPAT | OR | OFF | 2006/03/16 17:07 |

# EAST Search History

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|---|---|---|---|---|---|---|
| L21 | 13 | ("20020001746"\|"20020076133"\|"20020140103"\|"20030178637"\|"3309302"\|"5338625"\|"5561004"\|"5930046"\|"6242129"\|"6280875"\|"6376027"\|"6632563"\|"6683244").PN. | US-PGPUB; USPAT | OR | OFF | 2006/03/16 17:07 |

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | M-12245 US | 6938 |

22852 7590 03/22/2006

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |

| ART UNIT | PAPER NUMBER |
|---|---|
| 2823 | |

DATE MAILED: 03/22/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 10/03)

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|---|---|---|---|
| ***Office Action Summary*** | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. | |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 | |

***-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --***

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

1)☒ Responsive to communication(s) filed on *24 February 2006*.
2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.
3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

4)☒ Claim(s) *2-14 and 21-24* is/are pending in the application.
4a) Of the above claim(s) _____ is/are withdrawn from consideration.
5)☒ Claim(s) *14* is/are allowed.
6)☒ Claim(s) *2-14 and 21-24* is/are rejected.
7)☐ Claim(s) _____ is/are objected to.
8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

**Application Papers**

9)☐ The specification is objected to by the Examiner.
10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
a)☐ All b)☐ Some * c)☐ None of:
1.☐ Certified copies of the priority documents have been received.
2.☐ Certified copies of the priority documents have been received in Application No. _____.
3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date 2/24/06,2/27/06, 2/28/06, 3/3/06
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

## DETAILED ACTION

### *Continued Examination Under 37 CFR 1.114*

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 2/24/06 has been entered.

### *Claim Rejections - 35 USC § 103*

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13 and 21 rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claim 21, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33).

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claim 12, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claim 13, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

Claims 2-6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Fukui et al. (5,755,938).

With respect to claims 2-4, 6 and 22-24, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

With respect to claim 5, Smolanoff et al. do not specifically disclose wherein the filter is a band reject filter at the frequency of the bias power.

Fukui et al. disclose a sputtering process wherein the DC power supply (28) is connected through a band-pass filter (27) at the frequency of the bias power.

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fukui et al. to enable the filter type of Smolanoff et al. to be the same according to the teachings of Fukui et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable types of filters for the disclosed filter step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

### *Allowable Subject Matter*

Claim 14 is allowed.

### *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
March 16, 2006

OIPE IAP50 FEB 24 2006 PATENT & TRADEMARK OFFICE

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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| Sheet | 1 | of | 3 |
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| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 3/16/06 |

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| Sheet | 2 | of | 3 |
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| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Signature | Michelle Estrada | Date Considered | 3/16/06 |

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| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

Sheet 1 of 1

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| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Signature | Michelle Estrada | Date Considered | 3/16/06 |

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| *Application Number* | 10/101,863 |
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| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Signature | Michelle Estrada | Date Considered | 3/16/06 |

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| ***Notice of References Cited*** | Application/Control No.<br>10/101,863 | Applicant(s)/Patent Under Reexamination<br>ZHANG ET AL. |
| | Examiner<br>Michelle Estrada | Art Unit<br>2823 — Page 1 of 1 |

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| | E | US- | | | |
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| | G | US- | | | |
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U.S. Patent and Trademark Office
PTO-892 (Rev. 01-2001) **Notice of References Cited** Part of Paper No. 20060316

| **Search Notes** | Application No.<br>10/101,863 | Applicant(s)<br>ZHANG ET AL. | |
|---|---|---|---|
| | Examiner<br>Michelle Estrada | Art Unit<br>2823 | |

**SEARCHED**

| Class | Subclass | Date | Examiner |
|---|---|---|---|
| 438 | 769 | 2/12/04 | ME |
| 438 | 770 | | |
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| 438 | 787 | | |
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| 427 | 533 | | |
| 204 | 192.12 | | |
| 204 | 192.15 | 2/12/2004 | ME |
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**INTERFERENCE SEARCHED**

| Class | Subclass | Date | Examiner |
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**SEARCH NOTES (INCLUDING SEARCH STRATEGY)**

| | DATE | EXMR |
|---|---|---|
| See East search attached | 2/12/2004 | ME |
| See East search attached | 7/29/05 | ME |
| See East search attached | 3/16/06 | ME |
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PATENT
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Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
)
For: BIASED PULSE DC REACTIVE ) Confirmation No.: 6938
SPUTTERING OF OXIDE FILMS )

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
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Sir:

## AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed March 22, 2006, Applicants propose that this application be amended as follows:

**Amendments to the Claims** are reflected in the listing of claims in this paper beginning on page 2.

**Remarks/Arguments** follow the amendment sections of this paper beginning on page 6.

**Attachment** to this amendment include Declaration of R. E. Demaray under 37 C.F.R. §1.132.

## AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the film is an upper cladding layer of a waveguide structure and the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14. (Previously Presented): A method of depositing a film on a substrate, comprising:

providing pulsed DC power through a filter to a target;
providing RF bias power to a substrate positioned opposite the target; and
providing process gas between the target and the substrate, and
depositing a film on the backside of the target,
wherein the filter protects a pulsed DC power supply from the bias power, and
wherein a plasma is created between the target and the substrate.

15.-20. (Cancelled).

21. (Currently amended): A method of depositing a film on a substrate, comprising:

conditioning a target;
preparing the substrate;
adjusting an RF bias power to the substrate;
setting a process gas flow; and
applying pulsed DC power to the target through a filter to create a plasma and deposit the film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface, and

wherein the filter is a band rejection filter at a frequency of the bias power.

22. (Previously Presented ): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power

includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (New): The method of claim 21, wherein the band rejection filter is a narrow band-pass filter.

41. (New): The method of claim 21, wherein a bandwidth of the band rejection filter is about 100 kHz.

42. (New): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (New): A method of depositing a film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power.

44. (New): The method of claim 43, wherein a bandwidth of the band rejection filter is about 100 kHz.

45. (New): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (New): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (New): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (New): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (New): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (New): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

## REMARKS

Claims 2-14 and 21-24 are pending in this application. The Examiner has allowed claim 14 and rejected claims 2-14 and 21-24. Applicants have amended claim 21, canceled claim 5, and added new claims 40-50. Applicants traverse the Examiner's rejection and request reconsideration of the pending claims.

### Information Disclosure Statement

One of the references cited in the Seventh Supplemental Information Disclosure Statement submitted on February 27, 2006, was not initialed by the Examiner. Therefore, Applicants have listed such reference for the Examiner to initial in the enclosed Ninth Supplemental Information Disclosure Statement.

Additionally, the Examiner states the Dayco reference "Response to Office Action filed February 17, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 09140.0015-01)" was not attached with the Eighth Supplemental Information Disclosure Statement filed on February 28, 2006. Therefore, Applicants have provided a copy and re-listed such Dayco reference on the attached Ninth Supplemental Information Disclosure Statement for the Examiner's initials.

### Claim Rejections under 35 U.S.C. § 103

The Examiner has rejected claims 2-13 and 21-24 under 35 U.S.C. § 103 over various combinations of Smolanoff et al. (U.S. Patent No. 6,117,279), Fu et al. (U.S. Patent No. 6,3065,265), Fukui et al. (U.S. Patent No. 5,755,938), and Le et al. (U.S. Application No. 2003/0077914). Specific rejections are further discussed below.

In making a rejection under 35 U.S.C. § 103(a), the Examiner must establish the three elements of a *prima facie* case of obviousness. MPEP § 2142. First, the Examiner must show that the prior art references teach all elements of the claims. Second, the Examiner must show that the prior art provides the reason or motivation to make the claimed combination. The mere fact that references can be combined does not create a *prima facie* case of obviousness. Moreover, the motivation to combine cannot come from the applicant's own disclosure but must come from the prior art itself. Additionally, no motivation to combine references exists where doing so would render one of the prior art references unsatisfactory for its intended purpose. Third , the Examiner must prove that there is a reasonable expectation of success in combining the prior art references. As further discussed below, the Examiner has not met this burden.

## I. Claims 2-4, 6-13, and 21-24 are allowable because the cited prior art does not collectively teach all of the elements of the claims.

Claims 2-6, 8, 10-13, and 21-24

The Examiner has rejected claims 8, 10-13, and 21 under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265). Claims 2-6 and 22-24 are rejected over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21 and further in view of Fukui et al. (5,755,938). Claim 21 has been amended to recite "a band rejection filter at a frequency of the bias power," which is substantially the limitation of claim 5. Claim 5 has been canceled.

As the Examiner states, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claim 21. (*See*, Office Action, page 5). As stated in the Declaration of Ernest Demeray filed with this amendment under 37 C.F.R. §1.132, the filter protecting the pulsed DC power supply from the RF power of the bias is an aspect of the claimed invention. The filter must pass the pulsed DC signal without unduly affecting the shape of that signal while rejecting the RF power. Therefore, the filter passes all frequencies except for the frequency of the bias power itself. As stated in the Declaration of Ernest Demeray, other filter designs resulted in a distortion of the pulsed DC signal or in leakage of RF power back to the pulsed DC power supply -- resulting in the catastrophic failure of the power supply.

The Examiner relies on Fukui for this element. However, Fukui does not teach a "band rejection filter at a frequency of the bias power." As stated in Fukui,

> [a]lso connected to the first electrode 20 is a dc power supply 28 through a band-pass filter 27 such as a low-pass filter for adjustment of impedance. The band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a dc power from the dc power supply 28.

(Fukui, col. 6, lines 31-36). Fukui teaches a band pass filter, specifically a low-pass filter, which would not protect the DC power supply from RF and which would unreasonably distort the pulsed-dc shape. Further, there is no indication that the band-pass filter of Fukui is related to the frequency of the bias power supply. A band pass filter, below at or above the frequency of the RF bias, will not protect the pulsed DC power supply from catastrophic failure as a result of the RF power. Further, a band pass filter does not allow the broad frequency range required for the square wave of the pulsed-DC supply to reach the substrate.

Therefore, as discussed above, claim 21 is allowable over Smollanoff, Fu, and Fukui. Claims 2-4, 6-13, 22-24, and new claims 40-41 depend from claim 21 and are therefore allowable for at least the same reasons as is claim 21.

Claims 7 and 9

The Examiner rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of Le et al. (2003/0077914). Claims 7 and 9 depend from claim 21. Le does not cure the defects in the teachings of Smolanoff , Fu, or Fukui.

## New Claims

Claims 42-50 have been added to this application. Claim 42 is similar in scope to claim 21 except for the limitation regarding conditioning the target. Claims 43-50 are similar to dependent claims from claim 21. Therefore, claims 42-50 are allowable over the cited art.

## Conclusion

In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 12, 2006

By:
Gary J. Edwards
Reg. No. 41,008

Attachment: Declaration of Dr. R.E. Demaray under 37 C.F.R. §1.132

**EXPRESS MAIL LABEL NO.**
**EV 860818108 US**

OIPE
JUN 12 2006

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al. ) Group Art Unit: 2823

Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS ) Confirmation No.: 6938

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

## Declaration of Dr. R. E. Demaray under 37 C.F.R. §1.132

**I, Dr. R. Ernest Demaray, declare as follows:**

1. I am currently the President and Chief Technology Officer of Symmorphix, Inc., and have served as the Chairman of the Board, the Chief Executive Officer, and the Chief Technology Officer during the history of Symmorphix, Inc. I have been with Symmorphix for the past eight years. I was previously employed at Applied Materials, Inc., of Santa Clara as General Manager and Managing Director of the PVD division of Applied Komatsu. Since receiving my B.S. in Physical Chemistry in 1972, I have worked in the semiconductor equipment field for more than 34 years. I received a Ph.D. in Chemical Physics from the University of California at Santa Cruz in 1977.

2. I am an inventor of U.S. Application Serial No. 10/101, 863. At Symmorphix, my co-inventors and I developed a pulsed-DC, RF-biased deposition apparatus and various deposition methods utilized in that apparatus for deposition of thin film oxides and dielectrics. To my knowledge, the combination of pulsed-DC with RF bias applied to the substrate of an RF power

applied to the deposition chamber had not been disclosed or demonstrated previous to my invention.

3. During development of the deposition chambers and methods claimed in this application, we damaged a number (more than six units) of pulsed-DC power supplies due to RF bias power coupling through the plasma into the pulsed-dc power supply. We utilized the Advanced Energy Pinacle Plus power supply, which produced a 10 kW square wave at a frequency of from 180 kHz to 300 KHz together with a pulse reverse time from 1.3 to 5.0 μsec. Utilizing a band-pass filter between the pulsed-DC power supply and the plasma, however, will not protect the pulsed-DC power supply from the RF bias and will also unduly distort the square-wave of the pulsed-DC power signal applied to the target, which detrimentally affects the deposition conditions.

4. My co-inventors and I developed the band-rejection filter described in the specification and claimed in U.S. Application Serial No. 10/101, 863 to overcome the problem of catastrophic failure of the pulsed-DC power supply output electrometer circuit during operation. We discovered that a band-rejection filter, which is a filter that passes all of the frequencies of the square wave power supply except within a narrow band centered on the RF frequency of the RF bias, protected the pulsed-DC power supply from the RF energy while not distorting the pulses generated by the pulsed-DC power supply applied to the target.

5. I have further studied the art cited by the Examiner, namely Smolanoff et al. (U.S. Patent No. 6,117,279) (Smolanoff), Fu et al. (U.S. Patent No. 6,306,265) (Fu), Fukui et al. (U.S. Patent No. 5,755,938) (Fukui), and Le et al. (U.S. Publication No. 2003/0077914) (Le). None of these references teach a pulsed-DC system that allows an RF bias in a fashion that would not damage the pulsed-DC power supply if actually implemented as shown and described. None of these references describe a band-rejection filter at a frequency of the bias power.

6. Smolanoff discloses a reactor where the target is coupled through a filter to a DC source. No description of the filter is provided. However, in the chamber described in Smolanoff, RF power can be supplied to the target, to a secondary plasma generated below the target, and to the

substrate itself. A pulsed-DC power supply without the protection disclosed in the present application would catastrophically fail under these conditions. .

7. Fu describes a PVD sputtering chamber with no pulsed-dc and no filter to protect a pulsed-dc power supply. Therefore, Fu also does not describe a band rejection filter centered at the frequency of an RF bias.

8. Fukui describes a band-pass filter (specifically a low pass filter) coupled between the pulsed-dc power supply and the filter. Again, a band-pass filter does not protect the pulsed-DC power supply, as is required, and will distort the pulsed-DC square wave. Further, Fukui indicates that "[t]he band-pass filter 27 serves to adjust the circuit impedance to have an infinite value so that no RF waves are superposed on a dc power from the dc power supply 28." (Fukui, col. 6, lines 33-36). This is quite the opposite of what occurs in our applications, where the RF signal is superimposed on the pulsed DC power signal in the plasma, to which the substrate is exposed. Therefore, Fukui does not teach a band-rejection filter at the frequency of the RF bias.

9. Le describes neither a biased power nor a filter and simply teaches an un-biased deposition process. Therefore, Le does not teach a band rejection filter.

10. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date June 7 2006

By: R E Demaray
R. Ernest Demaray

OIPE
JUN 12 2006

06-14-06

2823

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## NINTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Ninth Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

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01 FC:1806 180.00 DA

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: June 12, 2006

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 860818108 US**

OIPE
JUN 12 2006

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | **Complete if Known** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | *Application Number* | 10/101,863 |
| | | *Filing Date* | March 16, 2002 |
| | | *First Named Inventor* | ZHANG, Hongmei |
| | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | *Examiner Name* | ESTRADA, Michelle |
| Sheet 1 | of 2 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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| | | US 2006/0071592 A1 | 04-06-2006 | Narasimhan et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | JP 7-224379 A | 08-22-1995 | Ulvac Japan Ltd | | Abstract |
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|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | |
| *(Use as many sheets as necessary)* | | | |
| Sheet | 2 | of | 2 |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
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| | | Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated March 20, 2006 (Atty. Docket No. 9140.0030-00256). | |
| | | Office Action mailed April 19, 2006 in U.S. Application No. 10/851,542 (Attorney Docket No. 09140.0033-00). | |

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|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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(19) **JAPANESE PATENT OFFICE**

COPY

## PATENT ABSTRACTS OF JAPAN

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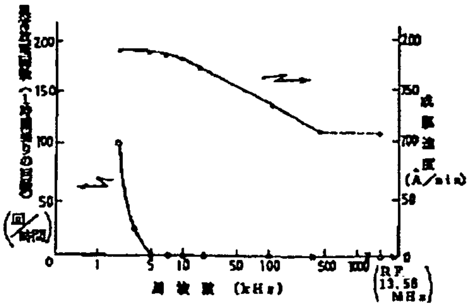
**KAWAMURA HIROAKI**
**SUZUKI IKUO**
**IKEDA SATOSHI**
**ISHIKAWA MICHIO**
**OTA YOSHIFUMI**
**MATSUMOTO MASAHIRO**

## (54) SPUTTERING METHOD AND DEVICE THEREFOR

(57) Abstract

PURPOSE: To form a film at a high rate without generating an abnormal discharge for a long time at the time of sputtering a conductive target in a gaseous reactant atmosphere by DC sputtering by applying a positive potential on a negative-potential target in the form of a pulse.

CONSTITUTION: A substrate and a conductive target are opposed in a vacuum treating chamber, and the target is sputtered in a gaseous reactant atmosphere by DC sputtering to form a thin film on the substrate. In this case, a device with a power source to apply a positive potential on a negative potential connected to the target is used, and a positive potential is applied on the negative-potential target in the form of a pulse at the frequency of 5-400kHz to conduct sputtering. The electron in the plasma is attracted by the positive potential to neutralize the plus ion accumulated on the insulator and high-resistance film, and the abnormal discharge due to an arc discharge is not generated.



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**特開平7－224379**

(43)公開日　平成7年(1995) 8月22日

| (51)Int.Cl.⁶ | 識別記号 | 庁内整理番号 | ＦＩ | 技術表示箇所 |
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| Ｃ２３Ｃ　14/34 | R | 8414－4K | | |
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| | M | 8414－4K | | |

審査請求　未請求　請求項の数4　ＯＬ　（全 5 頁）

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日電アネルバ(株)

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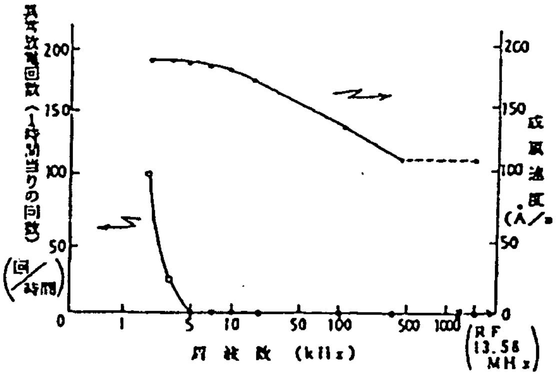
最終頁に続く

(54)【発明の名称】　スパッタ方法およびそのスパッタ装置

(57)【要約】

【目的】　反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行っても高速成膜が可能であり、かつ、長時間スパッタリングを行っても異常放電のないスパッタ成膜が出来るスパッタ方法。

【構成】　反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を一定の周波数でパルス状に印加しながらスパッタリングする。



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【特許請求の範囲】

【請求項１】　反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を周波数５～４００ｋＨｚでパルス状に印加しながらスパッタリングすることを特徴とするスパッタ方法。

【請求項２】　前記導電性ターゲットはＳｉ、Ａｌ、Ｔａ、Ｔｉ、Ｃ、ＩＴＯ、ＺｎＯ、$SnO_2$ またはこれらの合金であり、また、反応ガスは$N_2$、$O_2$、$H_2$、$NH_3$、ＣＯ、$CO_2$、$CH_4$、$C_2H_2$、$H_2O$のいずれか１つまたは２つ以上の混合ガスであることを特徴とする請求項第１項に記載のスパッタ方法。

【請求項３】　真空処理室内に基板と導電性ターゲットを対向させて設け、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ装置において、負電位に正電位を周波数５～４００ｋＨｚでパルス状に印加する電源を導電性ターゲットに接続したことを特徴とするスパッタ装置。

【請求項４】　前記導電性ターゲットはＳｉ、Ａｌ、Ｔａ、Ｔｉ、Ｃ、ＩＴＯ、ＺｎＯ、$SnO_2$ またはこれらの合金であり、また、反応ガスは$N_2$、$O_2$、$H_2$、$NH_3$、ＣＯ、$CO_2$、$CH_4$、$C_2H_2$、$H_2O$のいずれか１つまたは２つ以上の混合ガスであることを特徴とする請求項第３項に記載のスパッタ装置。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明はスパッタ方法およびそのスパッタ装置に関し、更に詳しくは、反応ガス雰囲気中で導電性ターゲットにスパッタリングを行うスパッタ方法およびそのスパッタ装置に関する。

【０００２】

【従来の技術】従来から、反応ガス雰囲気中で導電性ターゲットにスパッタリングを行って基板上に誘電体膜、光学膜、保護膜等の膜を成膜するスパッタ方法に用いられるスパッタ装置としては、真空処理室内に基板とターゲットカソードを対向して設け、該ターゲットカソードに導電性ターゲットを装着し、真空処理室内を所定の雰囲気とした状態でターゲットに所定電圧を印加してターゲットにスパッタリングを行う装置が知られている。

【０００３】そして、スパッタリング時の電源としては直流電源、または例えば13.56MHzの高周波電源を用いている。

【０００４】

【発明が解決しようとする課題】前記従来のスパッタ装置を用いて基板上に誘電体膜、光学膜、保護膜等の膜を成膜する際、高周波電源を用いるＲＦスパッタリングは長時間異常放電なしに成膜することが可能であるが、成膜速度が遅いという問題がある。

【０００５】また、前記従来のスパッタ装置を用いて基板上に誘電体膜、光学膜、保護膜等の膜を成膜する際、直流電源を用いるＤＣスパッタリングは成膜速度は速いが、スパッタリングの経時と共に、ターゲット表面に絶縁物や高抵抗膜が堆積するため、異常放電を起こすという問題がある。

【０００６】スパッタリング中に異常放電が発生すると欠陥のない均質な膜を成膜する上で致命的な悪影響を及ぼす。

【０００７】従って、従来のスパッタ装置では通常ＲＦスパッタリングを行っているが、高速成膜を必要とする場合は、ＤＣスパッタリングを行い、ターゲット表面に絶縁物や高抵抗膜が堆積しないようにターゲット全面に亘ってエロージョン化するようにしているが、異常放電を十分に除去することが出来ない。

【０００８】本発明はかかる問題点を解消し、反応ガス雰囲気中でスパッタリングを行っても高速成膜が可能であり、かつ、長時間スパッタリングを行っても異常放電のないスパッタ成膜の可能なスパッタ方法およびそれに用いるスパッタ装置を提供することを目的とする。

【０００９】

【課題を解決するための手段】本発明のスパッタ方法は、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ法において、負電位の導電性ターゲットに正電位を周波数５～４００ｋＨｚでパルス状に印加しながらスパッタリングすることを特徴とする。

【００１０】また、前記導電性ターゲットはＳｉ、Ａｌ、Ｔａ、Ｔｉ、Ｃ、ＩＴＯ、ＺｎＯ、$SnO_2$ またはこれらの合金とし、また、反応ガスは$N_2$、$O_2$、$H_2$、$NH_3$、ＣＯ、$CO_2$、$CH_4$、$C_2H_2$、$H_2O$のいずれか１つまたは２つ以上の混合ガスとしてもよい。

【００１１】本発明のスパッタ装置は、真空処理室内に基板と導電性ターゲットを対向させて設け、反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行って基板上に薄膜を形成するスパッタ装置において、負電位に正電位を周波数５～４００ｋＨｚでパルス状に印加する電源を導電性ターゲットに接続したことを特徴とする。

【００１２】また、前記導電性ターゲットはＳｉ、Ａｌ、Ｔａ、Ｔｉ、Ｃ、ＩＴＯ、ＺｎＯ、$SnO_2$ またはこれらの合金とし、また、反応ガスは$N_2$、$O_2$、$H_2$、$NH_3$、ＣＯ、$CO_2$、$CH_4$、$C_2H_2$、$H_2O$のいずれか１つまたは２つ以上の混合ガスとしてもよい。

【００１３】

【作用】反応ガス雰囲気中で導電性ターゲットに直流電源より直流電圧を印加し、スパッタリングを行うとターゲットはスパッタされて基板上に薄膜が形成される。

【００１４】長時間連続してスパッタリングを行うと、ターゲット上に堆積した絶縁物や高抵抗膜上に不活性ガスまたは反応ガスのプラス（＋）イオンが蓄積される。このプラス（＋）イオンの電荷がターゲット間、エロージョン部、アース電極等とアーク放電を引き起こして異常放電の原因となる。

【００１５】この異常放電でターゲット材、絶縁物、高抵抗膜が粒子状となって飛散し、基板上に付着し、成膜された薄膜の欠陥となる。

【００１６】ターゲットに直流電圧を印加してＤＣスパッタリングを行う際、負電位のターゲットに正電位を一定の周波数でパルス状に印加すると、正電位によりプラズマ中の電子を引き寄せ、ターゲット上に堆積した絶縁物、高抵抗膜上に蓄積するプラス（＋）イオンの電荷を中和し、アーク放電による異常放電を防止する。

【００１７】その際、ターゲットに印加する正電位の印加時間は負電位の時間に比べて極めて短くとも効果があるため、成膜速度は直流電流のみによる成膜速度より数％の減少となる程度であり、この成膜速度は高周波１３．５６ＭＨｚスパッタ時の成膜速度よりも高い。

【００１８】

【実施例】以下添付図面に従って本発明の実施例について説明する。

【００１９】図１は、スパッタ装置の１例を示すもので、図中、１は真空処理室を示す。

【００２０】真空処理室１を外部のクライオポンプのような真空ポンプ等の真空排気系２にバルブ３を介して接続し、該真空処理室１内の真空度を調節自在とすると共に、真空処理室１内に基板４とターゲットカソード５とを対向に配置し、該ターゲットカソード５の前面に導電性ターゲット６をロウ材でボンデングするようにしたまた、該真空処理室１内にガス導入管７を介してガスボンベ等のガス供給源８よりスパッタガスを導入するようにした。図示例ではガス導入管７を分岐し、一方の分岐管９ａにガス圧調節弁１０ａを介して不活性ガス（例えばアルゴンガス）のガス供給源８ａを接続し、他方の分岐管９ｂにガス圧調節弁１０ｂを介して反応ガス（例えば窒素ガス）のガス供給源８ｂを接続した。

【００２１】また、ターゲットカソード５に直流電源１１をパルスユニット１２を介して接続し、パルスユニット１２を調節して導電性ターゲット６に負電位と正電位を所定の周波数でパルス状に印加するようにした。

【００２２】また、ターゲットカソード５の背面側にマグネトロンスパッタのためのマグネット１３を配設して、ターゲットカソード５に取り付けられた導電性ターゲット６の表面にマグネトロンスパッタに必要な磁場を与えるようにした。

【００２３】次に、図１装置を用いて本発明のスパッタ方法の具体的実施例について説明する。

【００２４】実施例１

先ず、真空処理室１内に基板４と、ターゲットカソード５に導電性ターゲット６としてケイ素（Ｓｉ）製ターゲットを装着した。

【００２５】続いて、真空処理室１内を真空排気系２により $6.7\times10^{-5}$Pa（ $5\times10^{-7}$Torr）に排気した後、真空処理室１内にガス供給源８ａからのアルゴン（Ａｒ）ガスと、ガス供給源８ｂからの窒素（$N_2$）ガスとから成る反応ガスをガス導入管７を介して導入して、該真空処理室１内のスパッタ圧が $6.7\times10^{-1}$Pa（ $5\times10^{-3}$ Ｔｏｒｒ）となるようにした。次に基板４上に形成される窒化ケイ素（ＳｉＮｘ ）の屈折率が2.03となるようにＡｒガスと$N_2$ガスの流量をそれぞれ 100sccmと50sccmに調整した後、ＤＣマグネトロンスパッタ法により導電性ターゲット６に直流電源１１より直流電力３ｋＷを印加し、負電位のターゲット６に正電位をパルスユニット１２より周波数を2kHzから400kHzに変化させながらパルス状（図２参照）に印加し、スパッタリングを行って基板４上に膜厚 900Åの窒化ケイ素（ＳｉＮｘ ）膜を形成した。尚、負電位のターゲットにパルス状に印加する正電位の印加時間は周波数 10kHzまでの場合は10μsecとし、周波数 10kHzを超えて100kHzまでの場合は 5μsecとし、周波数100kHzを超えた場合は1μsec とした。また、ＤＣマグネトロンスパッタ時の磁場強度を 250Ｏｅとした。

【００２６】そして異常放電回数と成膜速度を負電位の導電性ターゲット６に印加する正電位の周波数毎に測定した。得られた測定結果を図３に示す。

【００２７】図３から明らかなように負電位に印加する正電位の周波数の増加に伴い、異常放電回数は減少し、周波数が5kHz以上ではその回数はほとんど０になり、これ以上の周波数で正電位を負電位のターゲットに印加すれば異常放電が発生しないことが分かる。また、負電位に印加する正電位の周波数が400kHz（時間1μsec ）の場合は、通常の高周波電源（13.56MHz）とほぼ同じ成膜速度となり、400kHz以上の周波数では正電位の印加は意味がない。従って、負電位のターゲットに印加する正電位の周波数範囲は 5～400kHzであることが確認された。

【００２８】また、周波数範囲 5～400kHzでの成膜速度は高周波電源（13.56MHz）よりも高い成膜速度である。

【００２９】反応ガス雰囲気中で直流スパッタ法により導電性ターゲットにスパッタリングを行うと、ターゲット上の非エロージョン部分に絶縁物または高抵抗膜が堆積し、従来の直流電源でターゲットに負の電位を放電し続けると、絶縁物上にプラス（＋）の電荷が蓄積し、ターゲット、エロージョン部、アース電極との間でアーク放電を起こし、電荷を放出する。その結果異常放電が発生することになるが、本発明では図２に示すように負電位に正電位を周期的に、即ち一定の周波数で印加することにより前記の電荷を補償して異常放電の発生を防止するようにしている。

【００３０】実施例２
反応ガスとして酸素（$O_2$）ガスを用い、スパッタ圧を $6.7\times10^{-1}$Ｐａ（$5\times10^{-3}$Torr）とし、直流電力を２ｋＷとし、基板上に形成される酸化ケイ素（ＳｉＯｘ）の屈折率が1.46となるように酸素流量を調整した以外は前記実施例１と同様の方法でＤＣマグネトロンスパッタ法によりターゲットにスパッタリングを行って基板上に膜厚1000Åの酸化ケイ素（ＳｉＯｘ）膜を形成した。

【００３１】そして異常放電回数を負電位のターゲットに印加する正電位の周波数毎に測定した。得られた測定結果を図４に示す。

【００３２】図４から明らかなように負電位に印加する正電位の周波数は約５ｋＨｚで異常放電をほぼ防止し得ることが分かる。

【００３３】尚、図４におけるＳｉＮx の測定結果（黒丸印）は前記実施例１の測定結果を参考のために記載したものである。

【００３４】実施例３
導電性ターゲットとしてグラファイト（Ｃ）を用い、反応ガスとしてメタン（$CH_4$）ガスを用い、スパッタ圧を $6.7\times10^{-1}$Ｐａ（$5\times10^{-3}$Torr）とし、直流電力を２ｋＷとした以外は前記実施例１と同様の方法でＤＣマグネトロンスパッタ法によりターゲットにスパッタリングを行って基板上に膜厚 200Åのダイヤモンドライクカーボン（ＤＬＣ）膜を形成した。

【００３５】そして異常放電回数を負電位のターゲットに印加する正電位の周波数毎に測定した。得られた測定結果を図４に示す。

【００３６】図４から明らかなように負電位に印加する正電位の周波数は約５ｋＨｚで異常放電をほぼ防止し得ることが分かる。

【００３７】前記実施例１，２，３の結果から、導電性ターゲット材料、放電状態によりプラス（＋）の電荷の蓄積量が異なるため、異常放電はターゲットに印加する周波数に大きく依存する。従って、周波数５ｋＨｚ以上であれば、種々のターゲット材料でもスパッタリング中の異常放電を大幅に減少することが出来ることになる。

【００３８】実施例４
導電性ターゲットとしてアルミニウム（Ａｌ）、チタン（Ｔｉ）、タンタル（Ｔａ）、またはこれらの合金例えばＡｌ－２at％Ｔｉを用い、反応ガスとして窒素（$N_2$）、酸素（$O_2$）、水素（$H_2$）、一酸化炭素（ＣＯ）、二酸化炭素（$CO_2$）、アンモニア（$NH_3$）、水（$H_2O$）を単独、或いは２種以上を用い、これらを種々組み合わせし、その他の条件を前記実施例１と同様にしてＤＣマグネトロンスパッタ法により基板上に酸化物、窒化物、炭化物のいずれかの薄膜を形成したが、負電位に印加する正電位が周波数５ｋＨｚ以上ではスパッタリング中に異常放電の発生は見られなかった。

【００３９】また、前記実施例１では導電性ターゲットにＳｉを用い、反応ガスとして窒素ガスを用いて基板上に窒化ケイ素（ＳｉＮx）膜を形成したが、導電性ターゲットとしてＳｉの代わりに$In_2O_3-SnO_2$焼結体（ＩＴＯ）、酸化亜鉛（ＺｎＯ）、酸化スズ（$SnO_2$）を用い、反応ガスとして窒素ガスの代わりに酸素（$O_2$）、一酸化炭素（ＣＯ）、二酸化炭素（$CO_2$）、水（$H_2O$）等の酸素を含むガス、またはそのガスに水素ガス（$H_2$）混合したガスを用い、負電位のターゲットに印加する正電位の周波数を５～４００ｋＨｚとした直流スパッタ法（ＤＣマグネトロンスパッタ法）により基板上に透明導電膜であるＩＴＯ、ＺｎＯ、$SnO_2$ の薄膜を形成することが出来る。

【００４０】図１装置では負電位に一定の周波数で正電位をパルス状に印加する電源装置として直流電源とパルス電源の組み合わせた装置としたが、これに限定されるものではなく、図２に示すような負電位に正電位が周期的（パルス状）に印加される一体型の電源装置としてもよい。

【００４１】

【発明の効果】本発明のスパッタ方法によるときは、反応ガス雰囲気中で、負電位の導電性ターゲットに正電位を一定の周波数でパルス状に印加しながらスパッタリングを行うようにしたので、スパッタリング中にターゲット上に堆積した絶縁物、高抵抗膜上に蓄積するプラスイオンの電荷を中和することが出来て、アーク放電による異常放電を防止しながら長時間に亘って速い成膜速度で基板上に欠陥のない均質な薄膜を形成することが出来る効果がある。

【００４２】また、本発明のスパッタ装置によるときは、導電性ターゲットに負電位に正電位を一定の周波数でパルス状に印加する電源を接続するようにしたので、アーク放電による異常放電を防止しながら長時間に亘って速い成膜速度で基板上に欠陥のない均質な薄膜を形成することが出来るスパッタ装置を提供する効果がある。

【図面の簡単な説明】

【図１】　本発明のスパッタ方法を実施するためのスパッタ装置の１例の概略截断側面図。

【図２】　図１装置による導電性ターゲットに印加される電位のモデル図。

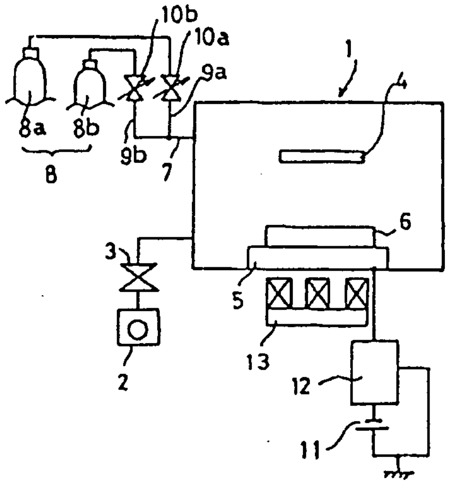
【図３】　本発明スパッタ方法の１実施例における成膜時の周波数と異常放電回数との関係、並びに周波数と成膜速度との関係を示す特性線図。

【図４】　本発明スパッタ方法の他の実施例における成膜時の周波数と異常放電回数との関係を示す特性線図。

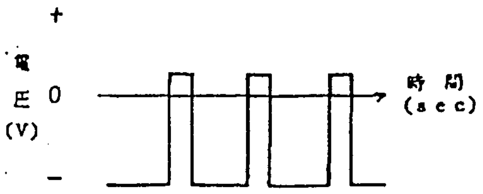
【符号の説明】

１　真空処理室、　２　真空排気系、　４　基板、６　導電性ターゲット、　７　ガス導入管、８　スパッタガス供給源、　１１　直流電源、１２　パルスユニット。

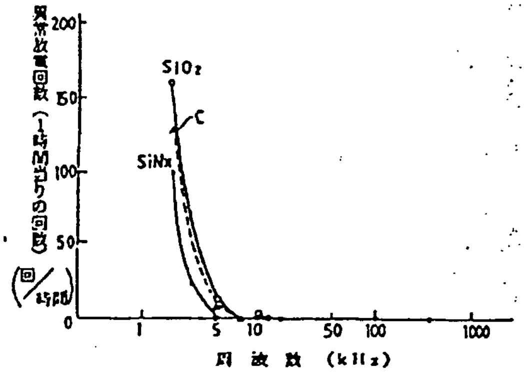
【図1】



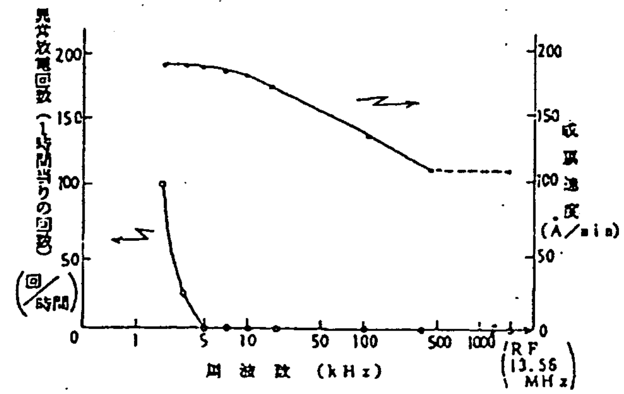
【図2】



【図4】



【図3】



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フロントページの続き

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RCE filed 2-24-06

PTO/SB/06 (12-04)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875 Effective December 8, 2004

Application or Docket Number: 10/101,863

## APPLICATION AS FILED – PART I

| FOR | (Column 1) NUMBER FILED | (Column 2) NUMBER EXTRA | SMALL ENTITY RATE ($) | SMALL ENTITY FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY FEE ($) |
|---|---|---|---|---|---|---|---|
| BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | 150.00 | | N/A | 300.00 |
| SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | $250 | | N/A | $500 |
| EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | $100 | | N/A | $200 |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X$ 25 = | | | X$50 = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X100 = | | OR | X200 = | |
| APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | +180= | | | +360= | |
| | | | TOTAL | | | TOTAL | |

* If the difference in column 1 is less than zero, enter "0" in column 2.

## APPLICATION AS AMENDED – PART II

**AMENDMENT A**

| 2-24-06 | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | SMALL ENTITY RATE ($) | ADDITIONAL FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| Total (37 CFR 1.16(i)) | * 17 | Minus | ** 39 | = | X$ 25 = | | OR | X$50 = | |
| Independent (37 CFR 1.16(h)) | * 2 | Minus | *** 5 | = | X100 = | | OR | X200 = | |
| Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | +180= | | OR | +360= | |
| | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

6-12-06

**AMENDMENT B**

| | (Column 1) CLAIMS REMAINING AFTER AMENDMENT | | (Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR | (Column 3) PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | OR | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|
| Total (37 CFR 1.16(i)) | * 27 | Minus | ** 39 | = — | X$ 25 = | — | OR | X$50 = | |
| Independent (37 CFR 1.16(h)) | * 3 | Minus | *** 5 | = — | X100 = | — | OR | X200 = | |
| Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | +180= | — | OR | +360= | |
| | | | | | TOTAL ADD'L FEE | — | OR | TOTAL ADD'L FEE | |

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

s collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the PTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, luding gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS DRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

# Index of Claims

Application No. 10/101863

Applicant(s)

Examiner

Art Unit

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| √ | Rejected | | – | (Through numeral) Cancelled | | N | Non-Elected | | A | Appeal |
| = | Allowed | | + | Restricted | | I | Interference | | O | Objected |

| Claim Final | Claim Original | Date 2/5/04 |
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U.S. Patent and Trademark Office

Part of Paper No. 02052004

07-17-06

2823

IFW

OIPE IAP25 JUL 13 2006 PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## TENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Tenth Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

07/18/2006 RMEBRAHT 00000101 060916 10101863
01 FC:1806 180.00 DA

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 13, 2006

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | *Complete if Known* |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | *Application Number* | 10/101,863 |
| | | | *Filing Date* | March 16, 2002 |
| | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of 2 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US 4,710,940 | 12-01-1987 | Sipes, Jr. | |
| | | US 4,785,459 | 11-15-1988 | Baer | |
| | | US 5,435,826 | 07-25-1995 | Sakakibara et al. | |
| | | US 5,512,147 | 04-30-1996 | Bates et al. | |
| | | US 5,569,520 | 10-29-1996 | Bates | |
| | | US 5,597,660 | 01-28-1997 | Bates et al. | |
| | | US 5,612,152 | 03-18-1997 | Bates | |
| | | US 6,168,884 B1 | 01-02-2001 | Neudecker et al. | |
| | | US 6,236,793 B1 | 05-22-2001 | Lawrence et al. | |
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| | | US 6,818,356 B1 | 11-16-2004 | Bates | |
| | | US 2001/0031122 A1 | 10-18-2001 | Lackritz et al. | |
| | | US 2003/0185266 A1 | 10-02-2003 | Henrichs | |
| | | US 2006/0134522 A1 | 06-22-2006 | Zhang et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

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| Sheet | 2 |
| of | 2 |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | COCORULLO, G. et al., "Amorphous silicon waveguides and light modulators for integrated photonics realized by low-temperature plasma-enhanced chemical-vapor deposition," *Optics Lett. 21*(24):2002-2004 (1996). | |
| | | Notice of Allowance mailed August 6, 2002, for US Patent No. 6,506,289 (Atty. Docket No. 09140.0002-01). | |
| | | Final Office Action mailed June 9, 2006 in U.S. Appl. No. 11/100,856 (Atty. Docket No. 09140.0015-01). | |
| | | Office Action issued on March 23, 2006, in U.S. Application No. 10/650,461 (Atty. Docket No. 09140-0025-00). | |
| | | Specification as filed September 2, 2005, for U.S. Appl. No. 11/218,652 (Atty. Docket No. 09140.0052-00000). | |

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| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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8-17-06

IFW 2823

OIPE IAP80
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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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| ZHANG, Hongmei et al. | ) | Group Art Unit: 2823 |
| | ) | |
| Application No.: 10/101,863 | ) | Examiner: ESTRADA, Michelle |
| | ) | |
| Filed: March 16, 2002 | ) | |
| | ) | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | ) | Confirmation No.: 6938 |
| | ) | |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## ELEVENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Eleventh Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 to Deposit Account No. 06-0916 as specified by Section 1.17(p).

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

English translations of the non-English language documents are enclosed.

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Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: August 15, 2006

By:
Gary J. Edwards
Reg. No. 41,008

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EV 746096525 US**

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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| Sheet 1 of 2 | | *Complete if Known* | |
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| | | *First Named Inventor* | ZHANG, Hongmei |
| | | *Art Unit* | 2823 |
| | | *Examiner Name* | ESTRADA, Michelle |
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| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

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|---|---|---|---|---|---|---|
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| | | JP 5-230642 A | 09/07/1993 | Nissin High Voltage Co., Ltd. | | Yes |
| | | WO 99/61674 A1 | 12/02/1999 | Universiteit Gent | | |
| | | WO 2006/063308 A2 | 06/15/2006 | Symmorphix, Inc. | | |

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| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
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| Examiner Signature | | Date Considered | |

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 2 | of | 2 |
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***Complete if Known***

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| | | Office Action issued on August 2, 2006, in U.S. Application No. 10/101,341 (Atty. Docket No. 09140-0017-00). | |
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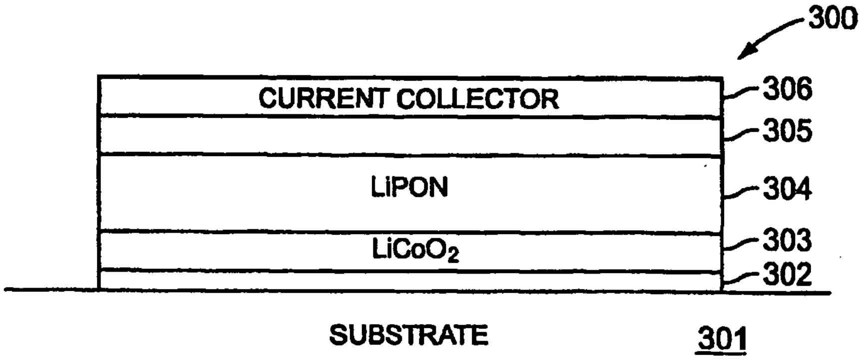
(54) Title: DEPOSITION OF LICoO2



(57) Abstract: In accordance with the present invention, deposition of $LiCoO_2$ layers in a pulsed-dc physical vapor deposition process is presented. Such a deposition can provide a low-temperature, high deposition rate deposition of a crystalline layer of $LiCoO_2$ with a desired <101> or <003> orientation. Some embodiments of the deposition addresses the need for high rate deposition of $LiCoO_2$ films, which can be utilized as the cathode layer in a solid state rechargeable Li battery. Embodiments of the process according to the present invention can eliminate the high temperature (>700°C) anneal step that is conventionally needed to crystallize the $LiCoO_2$ layer. Some embodiments of the process can improve a battery utilizing the $LiCoO_2$ layer by utilizing a rapid thermal anneal process with short ramp rates.

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# DEPOSITION OF $LICoO_2$

## RELATED APPLICATION

[001] The present application claims priority to Provisional Application No. 60/651,363, filed on February 8, 2005, by Hongmei Zhang and Richard E. Demaray, and to Provisional Application No. 60/634,818, filed on December 8, 2004, by the same inventors, each of which are herein incorporated by reference in their entirety.

## BACKGROUND

### 1. Field of the Invention

[002] The present invention is related to thin-film solid-state batteries and, in particular, the deposition of $LiCoO_2$ films and layers for battery manufacture.

### 2. Discussion of Related Art

[003] Solid-state thin-film batteries are typically formed by stacking thin films on a substrate in such a way that the films cooperate to generate a voltage. The thin films typically include current collectors, a cathode, an anode, and an electrolyte. The thin films can be deposited utilizing a number of deposition processes, including sputtering and electroplating. Substrates suitable for this application have conventionally been high temperature materials capable of withstanding at least one high temperature anneal process to at least 700 °C for up to about 2 hours in air so as to crystallize the $LiCoO_2$ film. Such a substrate can be any suitable material with appropriate structural and material properties, for example a semiconductor wafer, metallic sheet (e.g., titanium or zirconium), ceramic such as alumina, or other material capable of withstanding subsequent high temperature processing in

the presence of the $LiCoO_2$, which can experience significant interfacial reactions with most materials utilized in a battery during these temperature cycles.

[004] Other lithium containing mixed metal oxides besides $LiCoO_2$, including Ni, Nb, Mn, V, and sometimes also Co, but including other transition metal oxides, have been evaluated as crystalline energy storage cathode materials. Typically, the cathode material is deposited in amorphous form and then the material is heated in an anneal process to form the crystalline material. In $LiCoO_2$, for example, an anneal at or above 700°C transforms the deposited amorphous film to a crystalline form. Such a high temperature anneal, however, severely limits the materials that can be utilized as the substrate, induces destructive reaction with the lithium containing cathode material and often requires the use of expensive noble metals such as gold. Such high thermal budget processes (i.e., high temperatures for extended periods of time) are incompatible with semiconductor or MEM device processing and limit the choice of substrate materials, increase the cost, and decrease the yield of such batteries. The inventors are unaware of a process disclosed in the art that allows production of cathodic lithium films for a battery structure where a post-deposition anneal process has a low enough thermal budget to allow production of functional structures on low temperature materials such as stainless steel, aluminum, or copper foil.

[005] It is known that crystallization of amorphous $LiCoO_2$ on precious metals can be achieved. An example of this crystallization is discussed in Kim et al., where a conventional furnace anneal at 700°C for 20 minutes of an amorphous layer of $LiCoO_2$ on a precious metal achieves crystallization of the $LiCoO_2$ material, as shown by x-ray diffraction data. Kim, Han-Ki and Yoon, Young Soo, "Characteristics of rapid-thermal-annealed $LiCoO_2$, cathode film for an all-solid-state thin film microbattery," J. Vac. Sci. Techn. A 22(4), Jul/Aug 2004. In Kim et al., the $LiCoO_2$ film was deposited on a platinum film that was deposited on a high-temperature MgO/Si substrate. In Kim et al, it was shown that such

a crystalline film is capable of constituting the Li+ ion containing cathode layer of a functional all solid-state Li+ ion battery. However, it is of continuing interest for the manufacture of solid state Li+ ion batteries to further reduce the thermal budget of the post deposition anneal, both in time and in temperature, so as to enable the manufacture of such batteries without the need for expensive precious metal nucleation, barrier layers, or expensive high-temperature substrates.

[006] There are many references that disclose an ion beam assisted process that can provide a $LiCoO_2$ film that demonstrates some observable crystalline composition by low angle x-ray diffraction (XRD). Some examples of these are found in U.S. Patent Applications 09/815,983 (Publication No. US 2002/001747), 09/815,621 (Publication No. US 2001/0032666), and 09/815,919 (Publication No. US 2002/0001746). These references disclose the use of a second front side ion beam or other ion source side-by-side with a deposition source so as to obtain a region of overlap of the flux of ions with the flux of $LiCoO_2$ vapor at the substrate surface. None of these references disclose film temperature data or other temperature data of the film during deposition to support an assertion of low temperature processing.

[007] It is very difficult to form a uniform deposition either by sputtering a material layer or by bombardment with an ion flux. Utilization of two uniform simultaneous distributions from two sources that do not occupy the same position and extent with respect to the substrate enormously increases the difficulties involved in achieving a uniform material deposition. These references do not disclose a uniform materials deposition, which is required for reliable production of thin-film batteries. A well understood specification for material uniformity for useful battery products is that a 5% one-sigma material uniformity is standard in thin film manufacturing. About 86% of the films with this uniformity will be found acceptable for battery production.

[008] It is even more difficult to scale a substrate to manufacturing scale, such as 200 mm or 300 mm. Indeed, in the references discussed above that utilize both a sputtering deposition and an ion beam deposition, only small area targets and small area substrates are disclosed. These references disclose a single feasibility result. No method for achieving a uniform distribution from two separate front side sources has been disclosed in these references.

[009] Further, conventional materials and production processes can limit the energy density capacity of the batteries produced, causing a need for more batteries occupying more volume. It is specifically desirable to produce batteries that have large amounts of stored energy per unit volume in order to provide batteries of low weight and low volume.

[010] Therefore, there is a need for a low temperature process for depositing crystalline material, for example $LiCoO_2$ material, onto a substrate.

## SUMMARY

[011] In accordance with the present invention, deposition of $LiCoO_2$ layers in a pulsed-dc physical vapor deposition process is presented. Such a deposition can provide a low-temperature, high deposition rate deposition of a crystalline layer of $LiCoO_2$ with a desired <101> orientation. Some embodiments of the deposition address the need for high rate deposition of $LiCoO_2$ films, which can be utilized as the cathode layer in a solid state rechargeable Li battery. Embodiments of the process according to the present invention can eliminate the high temperature (>700 °C) anneal step that is conventionally needed to crystallize the $LiCoO_2$ layer.

[012] A method of depositing a $LiCoO_2$ layer according to some embodiments of the present invention includes placing a substrate in a reactor; flowing a gaseous mixture including argon and oxygen through the reactor; and applying pulsed-DC power to a target

formed of $LiCoO_2$ positioned opposite the substrate. In some embodiments, a $LiCoO_2$ layer is formed on the substrate. Further, in some embodiments the $LiCoO_2$ layer is a crystalline layer of orientation <101>.

[013] In some embodiments, a stacked battery structure can be formed. The stacked battery structure includes one or more battery stacks deposited on a thin substrate, wherein each battery stack includes: a conducting layer, a crystalline $LiCoO_2$ layer deposited over the conducting layer, a LiPON layer deposited over the $LiCoO_2$ layer; and an anode deposited over the LiPON layer. A top conducting layer can be deposited over the one or more battery stacks.

[014] In some embodiments, a battery structure can be formed in a cluster tool. A method of producing a battery in a cluster tool includes loading a substrate into a cluster tool; depositing a conducting layer over the substrate in a first chamber of the cluster tool; depositing a crystalline $LiCoO_2$ layer over the conducting layer in a second chamber of the cluster tool; depositing a LiPON layer over the $LiCoO_2$ layer in a third chamber of the cluster tool; depositing an anode layer over the $LiCoO_2$ layer in a fourth chamber; and depositing a second conducting layer over the LiPON layer in a fifth chamber of the cluster tool.

[015] A fixture for holding a thin substrate can include a top portion and a bottom portion, wherein the thin substrate is held when the top portion is attached to the bottom portion.

[016] These and other embodiments of the invention are further discussed below with reference to the following figures. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed. Further, specific explanations or theories regarding the deposition or performance of certain layers during deposition processes or in the performance of devices incorporating those layers are presented for explanation only and

are not to be considered limiting with respect to the scope of the present disclosure or the claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

[017] Figures 1A and 1B illustrate a pulsed-DC biased reactive deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[018] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A and 1B.

[019] Figure 3 illustrates a thin-film battery design according to some embodiments of the present invention.

[020] Figures 4A and 4B show an x-ray diffraction analysis of and an SEM photograph of a $LiCoO_2$ film deposited according to embodiments of the present invention.

[021] Figures 5A through 5F show SEM photographs of $LiCoO_2$ films according to some embodiments of the present invention.

[022] Figure 5G shows x-ray diffraction data corresponding to the depositions shown in Figures 5B-5F.

[023] Figure 6A illustrates a layer of $LiCoO_2$ deposited according to some embodiments of the present invention on a thin substrate.

[024] Figure 6B illustrates a layer of $LiCoO_2$ deposited according to some embodiments of the present invention over a conducting layer on a thin substrate.

[025] Figures 7A, 7B, 7C, and 7D illustrate a thin substrate mount and mask arrangement that can be utilized in the deposition of $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[026] Figure 8 illustrates a cluster tool that can be utilized to form batteries with $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[027] Figures 9A and 9B illustrate examples of stacked batter structures with $LiCoO_2$ layers deposited according to some embodiments of the present invention.

[028] Figures 10A through 10D illustrate deposition and anneal steps for $LiCoO_2$ deposited over an iridium layer on a silicon wafer.

[029] Figures 11A through 11D illustrate a single layer battery formed over an iridium layer according to some embodiments of the present invention.

[030] Figures 12A through 12L illustrate deposition of a crystalline LiCoO2 layer on a silicon or alumina substrate.

[031] Figures 13A through 13F illustrate rapid thermal anneal processes for $LiCoO_2$ layers deposited according to the present invention.

[032] Figures 14A through 14D illustrate several anneal processes utilized with a $LiCoO_2$ film deposited according to embodiments of the present invention.

[033] Figures 15A and 15B illustrate the effects of ramp-time in a rapid thermal anneal of $LiCoO_2$ films deposited according to the present invention.

[034] Figure 16 illustrates thickness uniformity of a LiCoO2 film deposited according to some embodiments of the present invention.

[035] Figure 17 illustrates battery charge and discharge profiles of a battery formed utilizing a $LiCoO_2$ film according to some embodiments of the present invention.

[036] In the figures, elements having the same designation have the same or similar functions.

## DETAILED DESCRIPTION

[037] In accordance with embodiments of the present invention, $LiCoO_2$ films are deposited on a substrate by a pulsed-dc physical vapor deposition (PVD) process. In contrast to, for example, Kim et al., $LiCoO_2$ films according to some embodiments of the present

invention provide a crystalline $LiCoO_2$ film as deposited on a substrate at a substrate temperature as low as about 220 °C during deposition, without the use of a metallic nucleation or barrier underlying film. The as-deposited crystalline $LiCoO_2$ films can be easily ripened to very high crystalline condition by anneal at about 700 °C for as little as 5 minutes without the use of an underlying precious metal film. In addition, the as deposited crystalline films, when positioned on a noble metal film can be annealed at much further reduced temperatures, for example as low as 400 to 500 °C, providing for deposition, annealing, and production of solid state batteries on lower temperature substrates.

[038] In the present application, a single, extended source is described which has been scaled to 400mm X 500mm for production achieving a $LiCoO_2$ uniformity of 3% one-sigma measured at 25 points at a deposition rate of 1.2 microns thickness an hour over an area of 2000 $cm^2$, without the need for secondary front side ion source or ion assistance.

[039] In one example process, a $LiCoO_2$ film was deposited utilizing a conductive ceramic $LiCoO_2$ target as described herein, with pulsed-dc power of 4 kW, no bias, with 60 sccm Ar and 20 sccm $O_2$ gas flows. A 3000 Angstrom layer of crystalline $LiCoO_2$ was deposited on a substrate area of 400 X 500 mm. As demonstrated in Figure 16, film thickness uniformity was located at about 25 locations spaced uniformly across the substrate using a felt marker pen to lift off a portion of the film in each location. High precision white-light interferometry was utilized to measure the film thickness in each location by measuring the step height from the substrate to film surface. All 25 thickness measurements demonstrated a 3% one-sigma uniformity in the film thickness over 400 X 500 mm substrate area. As shown in Figure 16, a film was deposited with average thickness of about 2.96 μm with a maximum of 3.09 μm and a minimum of 2.70 μm and standard deviation of 0.093. Thickness data was taken at points spaced 0.65 mm apart on the surface of the film. The film thickness therefore showed 3% one-sigma uniformity over the shown surface area.

[040] On other depositions utilizing this process, a temperature measurement of the substrate during deposition showed that the substrate remained at less than 224 °C. Temperature measurements were performed utilizing a temperature sticker purchased from Omega Engineering, Stamford, Ct (Model no. TL-F-390, active from 199-224 °C).

[041] Moreover, in some embodiments, films deposited according to the present invention can have a deposition rate of from about 10 to about 30 times higher than processes in conventional films. Deposition thicknesses and times of deposition for films deposited according to the present invention are illustrated in Table I. Furthermore, films according to the present invention can be deposited on wide area substrates having a surface area from 10 to 50 times the surface area of prior sputtering processes, resulting in much higher productivity and much lower cost of manufacture, thereby providing high-volume, low-cost batteries.

[042] Further, conventional deposition processes without ion sources are capable of depositing amorphous $LiCoO_2$ layers, but do not deposit crystalline $LiCoO_2$ layers. Surprisingly, depositions according to some embodiment of the present invention, deposit a $LiCoO_2$ layer with substantial crystallinity readily measured by x-ray diffraction techniques. In some embodiments, the crystallinity of the as-deposited $LiCoO_2$ layers is sufficient to be utilized in a battery structure with no further thermal processing. In some embodiments, crystallinity of the as-deposited $LiCoO_2$ layers are improved by thermal processes with low thermal budgets, which can be compatible with films deposited on low-temperature substrates.

[043] Further, as-deposited the stoichiometry of some $LiCoO_2$ layers deposited according to some embodiments of the present invention shows that this layer is sufficient for utilization in a battery. With the demonstrated ability to deposit a $LiCoO_2$ film with crystallinity and with sufficient stoichiometry, a battery utilizing as-deposited $LiCoO_2$ films

can be produced. Heat treating the $LiCoO_2$ layers may improve the crystallinity and lower the impedance.

[044] In some embodiments, a crystalline layer of $LiCoO_2$ with a <101> or a <003> crystalline orientation is deposited directly on the substrate. Deposition of crystalline material can eliminate or lessen the need of a subsequent high temperature anneal or precious-metal layers to crystallize and orient the film. Removing the high temperature anneal allows for formation of battery structures on light-weight and low temperature substrates such as stainless steel foil, copper foil, aluminum foil, and plastic sheet, reducing both the weight and the cost of batteries while retaining the energy density storage capabilities of Li-based batteries. In some embodiments, a crystalline $LiCoO_2$ layer can be deposited on a precious metal layer, such as platinum or iridium, resulting in a further significant lowering of the ripening thermal budget required to improve crystallinity.

[045] Deposition of materials by pulsed-DC biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002. Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films can be deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101863.

[046] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film. Apparatus 10 can also be a Phoenix Gen III PVD cluster tool made by Symmorphix, which is specifically designed for pulsed-dc processes such as is described herein.

[047] Apparatus 10 includes target 12 which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it from the pulsed DC power supply 14 and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[048] For pulsed reactive dc magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged and arcing is prevented. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality oxide films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[049] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 kHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics, and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[050] Filter 15 prevents the bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[051] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 14 and allow passage of the pulsed-dc power and frequency.

[052] Pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications such as barrier films and dielectric films, where high density is important, due to the boundaries between the columns. The columns act to lower the dielectric strength of the material, but may provide diffusion paths for transport or diffusion of electrical current, ionic current, gas, or other chemical agents such as water. In the case of a solid state battery, a columnar structure containing crystallinity as derived from processes according to the present invention is beneficial for battery performance because it allows better Li transport through the boundaries of the material.

[053] In the Phoenix system, for example, target 12 can have an active size of about 800.00 X 920.00 mm by 4 to 8 mm in order to deposit films on substrate 16 that have

dimension about 600 X 720 mm. The temperature of substrate 16 can be adjusted to between –50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm (in some embodiments, between 4.8 and 6 cm are used). Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 milliTorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the Phoenix reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 800 mm.

[054] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity, oxide film uniformity, or metallic film uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity, which is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity to the deposited film. In optimized processes, however, regions 52 and 24 may be coextensive.

[055] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[056] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface, and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater than or equal to the region of the film which is to have highly uniform electrical, mechanical, or optical properties such as index of refraction, stoichiometry, density, transmission, or absorptivity.

[057] Target 12 can be formed of any materials that provide the correct stoichiometry for $LiCoO_2$ deposition. Typical ceramic target materials include oxides of Li and Co as well as metallic Li and Co additions and dopants such as Ni, Si, Nb, or other suitable metal oxide additions. In the present disclosure, target 12 can be formed from $LiCoO_2$ for deposition of $LiCoO_2$ film.

[058] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 and 60 individual tiles. Tiles can be finished to a size so as to provide a margin of edge-wise non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[059] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further herein, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[060] Figure 3 shows a battery structure with a $LiCoO_2$ layer deposited according to some embodiments of the present invention. As shown in Figure 3, a metallic current collection layer 302 is deposited on a substrate 301. In some embodiments, current collection layer 302 can be patterned in various ways before deposition of a $LiCoO_2$ layer 303. Also according to some embodiments, $LiCoO_2$ layer 303 can be a deposited crystalline layer. In some embodiments of the invention, layer 303 is crystalline without the necessity of a crystallizing heat treatment. Therefore, substrate 301 can be a silicon wafer, titanium metal, alumina, or other conventional high temperature substrate, but may also be a low temperature material such as plastic, glass, or other material which could be susceptible to damage from the high temperature crystallizing heat treatment. This feature can have the great advantage of decreasing the expense and weight of battery structures formed by the present invention. The low temperature deposition of the $LiCoO_2$ allows for successive depositions of battery layers, one upon another. Such a process would have the advantage that successive layers of battery structure would be obtained in a stacked condition without the inclusion of a substrate

layer. The stacked layered battery would provide higher specific energy density as well as low impedance operation for charging and discharging.

[061] In some embodiments, an oxide layer can be deposited on substrate 301. For example, a silicon oxide layer can be deposited on a silicon wafer. Other layers can be formed between conducting layer 302 and substrate 301.

[062] As further shown in Figure 3, a LiPON layer 304 ($Li_xPO_yN_z$) is deposited over $LiCoO_2$ layer 303. LiPON layer 304 is the electrolyte for battery 300 while $LiCoO_2$ layer 303 acts as the cathode. A metallic conducting layer 305 can be deposited over the LiPON layer 304 in order to complete the battery. Metallic conducting layer 305 can include lithium adjacent to LiPON layer 304.

[063] An anode 305 is deposited over LiPON layer 304. Anode 305 can be, for example an evaporated lithium metal. Other materials such as, for example, nickel can also be utilized. A current collector 306, which is a conducting material, is then deposited over at least a portion of anode 305.

[064] A Li based thin film battery operates by transport of Li ions in the direction from current collector 306 to current collector 302 in order to hold the voltage between current collector 306 and current collector 302 at a constant voltage. The ability for battery structure 300 to supply steady current, then, depends on the ability of Li ions to diffuse through LiPON layer 304 and $LiCoO_2$ layer 303. Li transport through bulk cathode $LiCoO_2$ layer 303 in a thin film battery occurs by the way of grains or grain boundaries. Without being restricted in this disclosure to any particular theory of transport, it is believed that the grains with their planes parallel to substrate 302 will block the flow of Li ions while grains oriented with planes perpendicular to substrate 301 (i.e., oriented parallel to the direction of Li ion flow) facilitate the Li diffusion. Therefore, in order to provide a high-current battery

structure, $LiCoO_2$ layer 303 should include crystals oriented in the <101> direction or <003> direction.

[065] In accordance with the present invention, $LiCoO_2$ films can be deposited on substrate 302 with a pulsed-DC biased PVD system as was described above. In addition, an AKT 1600 PVD system can be modified to provide an RF bias, which is available in the Phoenix system, and an Advanced Energy Pinnacle plus 10K pulsed DC power supply can be utilized to provide power to a target. The pulsing frequency of the power supply can vary from about 0 to about 350 KHz. The power output of the power supply is between 0 and about 10 kW. A target of densified $LiCoO_2$ tiles having a resistivity in the range of about 3 to about 10 kΩ can be utilized with dc-sputtering.

[066] In some embodiments, $LiCoO_2$ films are deposited on Si wafers. Gas flows containing Oxygen and Argon can be utilized. In some embodiments, the Oxygen to Argon ratio ranges from 0 to about 50% with a total gas flow of about 80 sccm. The pulsing frequency ranges from about 200 kHz to about 300 kHz during deposition. RF bias can also be applied to the substrate. In many trials, the deposition rates vary from about 2 Angstrom/(kW sec) to about 1 Angstrom/(kW sec) depending on the $O_2$/Ar ratio as well as substrate bias.

[067] Table I illustrates some example depositions of $LiCoO_2$ according to the present invention. XRD (x-Ray Diffraction) results taken on the resulting thin films illustrate that films deposited according to the present invention are crystalline films, often with highly textured grain sizes as large as about 150 nm. The dominant crystal orientation appears to be sensitive to the $O_2$/Ar ratio. For certain $O_2$/Ar ratios (~10%), as-deposited films exhibit a preferred orientation in the <101> direction or the <003> direction with poorly developed <003> planes.

[068] Figures 4A and 4B illustrate an XRD Analysis and SEM cross section, respectively, of the $LiCoO_2$ film deposited as Example 15 in Table I. Such a $LiCoO_2$ film was deposited on Si wafer with 2kW of target power, a frequency of 300 kHz, with 60 sccm Ar and 20 sccm of $O_2$ for a substrate with an initial temperature of about 30°C. As shown in the XRD analysis of Figure 4A, a strong <101> peak is indicated showing a strong orientation of $LiCoO_2$ crystals in the desired <101> crystallographic direction. The SEM cross section shown in Figure 4B further shows the columnar structure of the film having the <101> direction and the grain boundaries of the resulting $LiCoO_2$ crystals.

[069] Figures 5A through 5F show SEM cross sections of further example depositions of $LiCoO_2$ crystals according to the present invention. In each of the examples, deposition of the $LiCoO_2$ film was performed on a Si wafer with target power of about 2 kW and frequency of about 250 kHz. The $LiCoO_2$ film shown in Figure 5A corresponds to the example deposition Example 1 in Table I. In the deposition of the $LiCoO_2$ film shown in Figure 5A, no bias power was utilized with an argon flow rate of about 80 sccm and an oxygen flow rate of about 0 sccm. A deposition rate of about 1.45 μm/hr was achieved over the full substrate area of 400 X 500 mm. Further, as is indicated in the cross section shown in Figure 5A, a <101> orientation of the $LiCoO_2$ was achieved.

[070] The rate of deposition of the $LiCoO_2$ layer shown in Figure 5A is very high, likely due to the relatively high conductivity or low resistivity of the ceramic $LiCoO_2$ oxide sputter target. A target resistance of 10 kOhms was measured by means of an Ohm meter over a distance of about 4 cm on the surface of target 12. This high rate allows the manufacture of the 3 micron or thicker $LiCoO_2$ layer required for the battery at high rate over a wide area in short times, resulting in very high productivity and very low cost. Target resistance on the order of about 500 kΩ over the same distance by the same measurement technique or higher would not allow for such a high sputter efficiency or high rate of

deposition at such a low target power. The resistance of conventional target materials can be unmeasurably high. A resistance of 100 kΩ over about 4 cm of surface will result in high sputter efficiency and high rate of deposition. Further, because deposition rates typically scale nearly linearly with target power, a deposition at 6 kW will yield a deposition rate of approximately 3 µm/hr, which is a very desirable rate of deposition for manufacturability of Li-based thin-film solid-state batteries on a surface area of 400 X 500 $mm^2$.

[071] The $LiCoO_2$ layer shown in Figure 5B is deposited under the conditions listed as Example 7 in Table I. Again, no bias was utilized in the deposition. An argon flow rate of about 72 sccm and an oxygen flow rate of about 8 sccm was utilized. The deposition rate was significantly reduced to about 0.85 µm/hr. Further, although a <101> crystallinity can be discerned, that <101> crystallinity is not as pronounced as that exhibited in the deposition of the film shown in Figure 5A.

[072] The $LiCoO_2$ film shown in Figure 5C was deposited according to Example 3 in Table I. In this deposition, 100 W of bias power is applied to the substrate. Further, an argon flow rate of 72 sccm, and an oxygen flow rate of 8 sccm was utilized. The deposition rate was about 0.67 µm/hr. Therefore, the application of bias in comparison with the $LiCoO_2$ film shown in Figure 5B further reduced the deposition rate (from 0.85 µm/hr of the example shown in Figure 5B to 0.67 µm/hr of the example shown in Figure 5C). Further, the desired <101> directionality of formed crystals appears to be further degraded.

[073] The $LiCoO_2$ film shown in Figure 5D corresponds to Example 4 in Table I. In this deposition, the $Ar/O_2$ ratio was increased. As is shown in Figure 5D, increasing the $Ar/O_2$ ratio improves crystallinity. With respect to the example illustrated in Figure 5C, the deposition illustrated in Figure 5D was performed with an argon flow of about 76 sccm and an oxygen flow of about 4 sccm as well as retaining the 100 W bias to the substrate. The

$LiCoO_2$ deposition rate was improved to 0.79 μm/hr from a rate of 0.67 μm/hr illustrated in Figure 5C.

[074] In the example deposition illustrated in Figure 5E corresponding to Example 5 in Table I. The substrate temperature was set at about 200°C while the bias power remained at about 100 W. The argon flow rate was set at about 76 sccm and the oxygen flow rate was set at about 4 sccm. The resulting deposition rate for the $LiCoO_2$ layer was about 0.74 μm/hr.

[075] In the example deposition illustrated in Figure 5F, which corresponds with Example 6 of Table I, the argon flow rate was set at about 74 sccm and the oxygen flow rate was set at about 6 sccm, resulting in a $LiCoO_2$ deposition rate of about 0.67 μm/hr. Therefore, increasing both argon and oxygen flow rate over the deposition illustrated in Figure 5E resulted in a lower deposition rate.

[076] Figure 5G illustrates XRD data corresponding to Figures 5F, 5D, 5C, 5E, and 5B, respectively. As illustrated in Figure 5G, as-deposited crystalline $LiCoO_2$ is deposited in these processes.

[077] The data show clearly that an as-deposited crystalline film of $LiCoO_2$ can be obtained under several of the process conditions, as shown in Table II. In particular, very high rates of deposition with low power are obtained along with the oriented crystalline structure for the process conditions according to embodiments of the present invention.

[078] Figure 6A illustrates a layer of $LiCoO_2$ 602 deposited on a thin substrate 601 according to some embodiments of the present invention. Higher lithium-ion mobilities can be achieved utilizing crystalline $LiCoO_2$ cathode films 602 deposited on a thin substrate 601 that has thickness comparable to that of the battery stack itself, rather than a thickness many or tens of times that of the battery stack. Such a film can lead to faster charging and discharging rates. Substrate 601 can be formed of a thin metallic sheet (e.g., aluminum,

titanium, stainless steel, or other suitable thin metallic sheet), can be formed of a polymer or plastic material, or may be formed of a ceramic or glass material. As shown in Figure 6B, if substrate 601 is an insulating material, a conducting layer 603 can be deposited between substrate 601 and $LiCoO_2$ layer 602.

[079] Depositing materials on a thin substrate involves holding and positioning the substrate during deposition. Figures 7A, 7B, 7C, and 7D illustrate a reusable fixture 700 for holding a thin film substrate. As shown in Figure 7A, reusable fixture 700 includes a top portion 701 and a bottom portion 702 that snap together. Thin substrate 601 is positioned between top portion 701 and bottom portion 702. As shown in Figure 7B, top portion 701 and bottom portion 702 are such that substrate 601 is brought into tension and subsequently clamped as top portion 701 is closed into bottom portion 702. Substrate 601 can be easily held by fixture 700 so that substrate 601 can be handled and positioned. In some embodiments, the corners of substrate 601, areas 703, are removed so that substrate 601 is more easily stretched by avoiding "wrap-around" corner clamping effects when top portion 701 is closed into bottom portion 702.

[080] As shown in Figure 7C, a mask 712 can be attached to fixture 700. In some embodiments, fixture 700 includes guides in order to align fixture 700 with respect to mask 712. In some embodiments, mask 712 may be attached to fixture 700 and travel with fixture 700. Mask 712 can be positioned at any desired height above substrate 601 in fixture 700. Therefore, mask 712 can function as either a contact or proximity mask. In some embodiments, mask 712 is formed of another thin substrate mounted in a fixture similar to fixture 700.

[081] As shown in Figure 7C and 7D, fixture 700 and mask 712 can be positioned relative to mount 710. Mount 710, for example, can be a susceptor, mount, or an electrostatic chuck of a processing chamber such as that shown in Figures 1A and 1B. Fixture 700 and

mask 712 can have features that allow for ready alignment with respect to each other and with respect to mount 710. In some embodiments, mask 712 is resident in the processing chamber and aligned with fixture 700 during positioning of fixture 700 on mount 710, as shown in Figure 7D.

[082] Utilizing fixture 700 as shown in Figures 7A, 7B, 7C, and 7D allows processing of a thin film substrate in a processing chamber. In some embodiments, thin film substrates can be about 10 μm or more. Further, thin film substrate 601, once mounted within fixture 700, can be handled and moved from process chamber to process chamber. Therefore, a multiprocessor chamber system can be utilized to form stacks of layers, including one or more layers of $LiCoO_2$ deposited according to embodiments of the present invention.

[083] Figure 8 illustrates a cluster tool 800 for processing thin film substrates. Cluster tool 800 can, for example, include load lock 802 and load lock 803, through which mounted thin film substrate 601 is loaded and a resultant device is removed from cluster tool 800. Chambers 804, 805, 806, 807, and 808 are processing chambers for depositions of materials, heat treatments, etching, or other processes. One or more of chambers 804, 805, 806, 807, and 808 can be a pulsed-DC PVD chamber such as that discussed above with respect to Figures 1A and 1B and within which a $LiCoO_2$ film deposited according to embodiments of the present invention may be deposited.

[084] Processing chambers 804, 805, 806, 807, and 808 as well as load locks 802 and 803 are coupled by transfer chamber 801. Transfer chamber 801 includes substrate transfer robotics to shuttle individual wafers between processing chambers 804, 805, 806, 807, and 808 and load locks 802 and 803.

[085] In production of a conventional thin-film battery, ceramic substrates are loaded into load lock 803. A thin metallic layer can be deposited in chamber 804, followed

by a $LiCoO_2$ deposition performed in chamber 805. The substrate is then removed through load lock 803 for an in-air heat treatment external to cluster tool 800. The treated wafer is then reloaded into cluster tool 800 through load lock 802. A LiPON layer can be deposited in chamber 806. The wafer is then again removed from cluster tool 800 for deposition of the lithium anode layer, or sometimes chamber 807 can be adapted to deposition of the lithium anode layer. A second metallic layer is deposited in chamber 808 to form a charge collector and anode collector. The finished battery structure is then off-loaded from cluster tool 800 in load lock 802. Wafers are shuttled from chamber to chamber by robotics in transfer chamber 801.

[086] A battery structure produced according to the present invention could utilize thin film substrates loaded in a fixture such as fixture 700. Fixture 700 is then loaded into load lock 803. Chamber 804 may still include deposition of a conducting layer. Chamber 805 then includes deposition of a $LiCoO_2$ layer according to embodiments of the present invention. A LiPON layer can then be deposited in chamber 806. Chamber 807 may still be adapted to deposition of a lithium rich material such as lithium metal and chamber 808 can be utilized for deposition of the conducting layer of the current collector. In this process, no heat treatment is utilized to crystallize the $LiCoO_2$ layer.

[087] Another advantage of a thin film battery process is the ability to stack battery structures. In other words, substrates loaded into cluster tool 800 may traverse process chambers 804, 805, 806, 807, and 808 multiple times in order to produce multiply stacked battery structures. Figures 9A and 9B illustrate such battery structures.

[088] Figure 9A illustrates a parallel coupled stacking. As shown in Figure 9A, a substrate 601, which for example can be a plastic substrate, is loaded into load lock 803. A conducting layer 603, for example about 2 μm of aluminum, copper, iridium or other material, acts as a bottom current collector. Conducting layer 603, for example, can be

deposited in chamber 804. A $LiCoO_2$ layer 602 is then deposited on conducting layer 603. $LiCoO_2$ layer 602 can be about 3-10 µm and can be deposited in chamber 805 according to embodiments of the present invention. The wafer can then be moved to chamber 806 where a LiPON layer 901 of thickness of about .5 to about 2 µm can be deposited. In chamber 807, an anode layer 902, for example a lithium metal layer of up to about 10 µm, can then be deposited in chamber 807. A second conducting layer 903 can then be deposited over anode layer 902. A second battery stack can then be deposited over the first battery stack formed by metal layer 603, LiCoO2 layer 602, LiPON layer 901, lithium layer 902, and current collection conduction layer 903. Over current collection conducting layer 903, another lithium layer 902 is formed. Another LiPON layer 901 is formed over lithium layer 902. Another LiCoO2 layer 602 is formed over LiPON layer 901 and finally another metal layer 603 is formed over LiCoO2 layer 602. In some embodiments, further stackings can be formed. In some embodiments, metal layers 603 and 903 differ in the mask utilized in deposition so that tabs are formed for electrical coupling of layers.

[089] As discussed above, any number of individual battery stacks can be formed such that parallel battery formations are formed. Such a parallel arrangment of battery stacking structure can be indicated as Current collector/LiCoO2/LiPON/Anode/current collector/Anode/LiPON/LiCoO2/current collector/LiCoO2 . . . /current collector. Figure 9B illustrates an alternative stacking corresponding to the battery structure current collector/LiCoO2/LiPON/anode/current collector/LiCoO2/LiPON/anode/current collector . . . /current collector. In this case, a series arrangement battery stacking structure is formed because the individual battery stacks share anodes.

[090] To form the structures shown in Figures 9A and 9B, substrates are rotated again through the chambers of cluster tool 800 in order to deposit the multiple sets of batteries. In general, a stack of any number of batteries can be deposited in this fashion.

[091] In some embodiments, stoichiometric $LiCoO_2$ can be deposited on iridium. Figures 10A through 10D illustrate an anneal procedure for Li-Co deposition over an iridium layer that has been deposited on a Si wafer. The $LiCoO_2$ deposition was accomplished as discussed above with a target power of 2 kW, no bias power, reverse time of 1.6 μs, a pulsing frequency of 300 kHz, with 60 sccm Ar flow and 20 sccm of $O_2$ flow, with no pre-heat for 7200 sec. As a result, a layer of $LiCoO_2$ of about 1.51 μm was deposited.

[092] Figures 10A through 10D show XRD analysis of both as-deposited and annealed layers of $LiCoO_2$ deposited as discussed above. The XRD analysis of the as-deposited layer demonstrates a shallow peak at $2\theta = 18.85°$ denoting a <003> orientation of crystalline $LiCoO_2$, a sharper peak at about $2\theta = 38.07°$ corresponding with the desired <101> crystallographic direction, and a peak at $2\theta = 40.57°$ corresponding to the <111> direction of iridium. However, the position of the <101> $LiCoO_2$ peak indicates that the <101> $LiCoO_2$ peak is nonstoichiometric $LiCoO_2$. In order to be useful as a battery layer, stoichiometric $LiCoO_2$ provides for the best Li transport. One of ordinary skill in the art will notice that careful adjustment of deposition parameters can provide stoichiometric $LiCoO_2$ of desired orientation.

[093] Figure 10B shows an XRD analysis of the sample shown in figure 10A after a 300°C anneal in air for 2 hours. As shown in Figure 10B, the XRD peak corresponding to <003> $LiCoO_2$ grows, indicating crystallization of $LiCoO_2$ into the <003> direction. Further, the <101> peak of $LiCoO_2$ shifts slightly to $2\theta = 38.53°$, indicating a more stoichiometric crystallization of the <101> $LiCoO_2$. However, the crystalline $LiCoO_2$ is still not stoichiometric after this anneal. One of ordinary skill in the art will notice that longer anneals and/or further adjustment of the deposited stoichiometry may result in usefully oriented stoichiometric $LiCoO_2$ layers with anneal temperatures at 300 °C or less. Consequently, low temperature materials such as polymers, glass, or metal may be utilized as the substrate.

[094] Figure 10C illustrates an XRD analysis from the sample after a subsequent 500°C anneal in air for 2 hours. As shown in Figure 10C, more of the $LiCoO_2$ crystalizes into the <003> layer. Further, the <101> $LiCoO_2$ peak shifts again to $2\theta = 39.08°$, indicating crystallization of a <012> layer of $LiCoO_2$. In this case, the <012> $LiCoO_2$ cyrstal is stoichiometric and therefore allows for efficient Li transport. One of ordinary skill in the art will notice that longer anneals and/or further adjustment of the deposited stoichiometry may result in usefully oriented stoichiometric $LiCoO_2$ layers with anneal temperatures at 500°C or less. Consequently, low temperature materials such as polymers, glass, or metal may be utilized as the substrate.

[095] Figure 10D illustrates an XRD analsysis of the sample after a subsequent anneal of 700°C in air for 2 hours. As shown in Figure 10D, the <003> $LiCoO_2$ peak disappears, but the <012> $LiCoO_2$ peak remains relatively the same as that shown in the 500° anneal illustrated in Figure 10C.

[096] Figures 10A through 10D demonstrate deposition of <101> $LiCoO_2$ at low temperature over an iridium layer. Subsequent anneals to 500°C may be desired to change the stoichiometry of the <101> $LiCoO_2$ layer, but anneals to 700 °C do not appear to be necessary. With anneal temperatures less than 500°C, depositions of a $LiCoO_2$ layer over a conducting iridium layer can be accomplished on glass, aluminum foil, plastic, or other low temperature substrate material. Anneal temperatures of less than 500°C but greater than 300°C or lengthening the time of lower temperature anneals may also result in desired orientations of stoichiometric crystalline $LiCoO_2$.

[097] Figures 11A through 11D illustrate formation of a single-layer battery according to some embodiments of the present invention. As shown in Figure 11A, a lift-off layer 1102 can be deposited on a substrate 1101. Further, an iridium layer 1103 can be

deposited over lift-off layer 1102. In some embodiments, substrate 1101 can be plastic, glass, Al foil, Si wafer, or any other material. Lift-off layer 1102 can be any lift off layer and can be a polymer layer such as polyimide, an inorganic layer such as $CaF_2$ or carbon, or an adhesive layer that loses its adhesion as a result of, for example, oxidation, heat, or light. Lift-off layers are well known. Iridium layer 1103 can be from about 500 Å or more.

[098] As shown in Figure 11B, a $LiCoO_2$ layer is deposited over iridium layer 1103 as was discussed above. In some embodiments, an anneal can be performed at this step. In some embodiments, further layers of the battery may be deposited before an anneal step is performed. In some embodiments, a stoichiometric $LiCoO_2$ layer of a useful crystalline orientation may result in the as-deposited $LiCoO_2$ with no further anneals necessary.

[099] Figure 11C illustrates deposition of a LiPON layer 1105 over the $LiCoO_2$ layer, deposition of a Li layer 1106 over LiPON layer 1105, and deposition of an electrode layer 1107 over Li layer 1106. In some embodiments, an anneal step of up to 500°C as discussed above may be performed here.

[0100] As shown in Figure 11D, the resulting single-layer battery formed from iridium layer 1103, $LiCoO_2$ layer 1104, LiPON layer 1105, Li layer 1106, and electrode layer 1107 can be "lifted off" from substrate 1101. Such a single-layer battery can be a free-standing battery of thickness about 5 μm or greater. Such a battery, without the requirement of a substrate 1101, is well known to have the potential of energy storage of greater than about 1 kW-hr/liter.

[0101] As an alternative to a lift-off process as described in Figures 11A through 11D, a substrate may be removed during anneal leaving a single-layer battery. Further, in some embodiments, substrate 1101 can be removed by a solvent, etching, or a photo process. Further, single-layer batteries may be combined or stacked in any fashion to provide a device of greater energy storage at a particular voltage.

[0102] Figures 12A through 12L illustrate the crystallinity of as-grown and post anneal $LiCoO_2$ layers according to samples 31 and 32 illustrated in Table I. Samples 31 and 32 were formed in the same deposition, utilizing a silicon substrate and an alumina substrate, respectively.

[0103] Figure 12A illustrates an XRD analysis of the as-deposited $LiCoO_2$ film on $Al_2O_3$ substrate (Example 32 in Table I). A broad <003> crystalline $LiCoO_2$ peak is observed. The remaining peaks in the analysis, which are not labeled in Figure 12A, result from the $Al_2O_3$ substrate. The <003> peak is characteristic of the layered structure in the as-deposited crystalline $LiCoO_2$ film according to embodiments of the present invention.

[0104] Figure 12B illustrates the crystallinity of the LiCoO2 film shown in Figure 12A after a 2 hr 700 °C anneal. As shown in Figure 12B, the <003> peak becomes sharper and higher, indicating better crystallinity. As shown in Figures 12G through 12J, in comparison with figures 12C through 12F, the columnar structure ripens with the anneal and the grain size becomes larger with anneal. Figure 12B also shows <012> and <006> crystallinity peaks.

[0105] Figure 12C through 12F show SEM photos of the granularity of the as-deposited film corresponding to Example 32 in Figure I. Figures 12G through 12J show SEM photos of the granularity of the annealed film, as illustrated in Figure 12B. A comparison of Figures 12C through 12F with 12G through 12J illustrate the increased granularity resulting from the anneal process.

[0106] Figure 12K illustrates a fracture cross-section SEM that illustrates the morphology of the as-deposited crystalline film corresponding to Example 31 in Table I. Figure 12L illustrate a similar cross-section SEM corresponding to the film grown according to Example 32 in Table I.

[0107] Figures 13A through 13J illustrate rapid thermal anneal processes applied to a $LiCoO_2$ layer as in Example 49 of Table I. In that example, $LiCoO_2$ is deposited on alumina with a 2 kW pulsed DC power with no bias. Argon flow as set to 60 sccm and oxygen flow was set to 20 sccm. The deposition parameters are nearly identical with those of Example 32 in Table I, therefore XRD data for the as-deposited films are shown in Figure 12A. Figure 13A shows XRD data after a 15 minute 700 °C anneal in an argon atmosphere. Ramp-up time (room temperature to 700 °C) is 45 sec and ramp-down time (700 °C to about 300 °C) occurred over 10 min. At 300 °C, the sample is removed from the rapid-thermal-anneal (RTA) oven and cooled in air to room temperature. As shown in Figure 13A, substantial crystallinity is obtained. Figure 13B shows XRD data after a RTA as described with Figure 13A in an argon/oxygen atmosphere. The argon/oxygen ratio was 3:1.

[0108] As shown in a comparison of Figures 13A and 13B, more crystallinity is observed in an argon only RTA than with a RTA performed in the presence of oxygen. This is further illustrated in a comparison of Figures 13C and 13D with Figures 13E and 13F. Figures 13C and 13D show the granularity of the $LiCoO_2$ film after the RTA illustrated in Figure 13A. Figures 13E and 13F show the granularity of the $LiCoO_2$ film after the RTA illustrated in Figure 13B. As is observed, the granularity shown in Figures 13C and 13D (which differ in magnification) is better than that shown in Figures 13E and 13F (which also differ in magnification).

[0109] Figures 14A through 14D illustrate several anneal processes with the Example 37 of Table I. In that example, LiCoO2 was deposited on alumina utilizing a pulsed-dc process with 2kW of power and 100 W of bias with an argon flow of 60 sccm and an oxygen flow of 20 sccm.

[0110] Figure 14A shows an SEM photo of an as-deposited $LiCoO_2$ film according to the process illustrated in Example 37 of Table I. Figure 14B shows an SEM photo of

$LiCoO_2$ film according to the process illustrated in Example 37 of Table I, annealed conventionally with a two-hour 700 °C anneal. Figures 14C and 14D show SEM photos of a $LiCoO_2$ film according to the process illustrated in Example 37 of Table I, annealed in an RTA process at 700 °C. The ramp-up and ramp-down times in the RTA process is illustrated above. Figure 14C shows an SEM photo of a $LiCoO_2$ film after an RTA process at 700 °C for five minutes whereas Figure 14D shows an SEM photo of a $LiCoO_2$ film after an RTA process at 700 °C for fifteen minutes. It is clear from a comparison of Figures 14C and 14D with Figure 14B, that much better granularity is achieved with the low thermal-budget RTA process rather than the conventional furnace anneal. A low thermal-budget RTA process allows for deposition of such films on low temperature substrates.

[0111] Figures 15A and 15B show SEM photos of a $LiCoO_2$ film that was annealed in an RTA process utilizing two different ramp-up times, illustrating the effects of the ramp time in the RTA process. A $LiCoO_2$ film was deposited on an alumina substrate according to the process described as Example 51 in Table I. The film shown in Figure 15A was annealed with a 45 sec ramp-up time (i.e., room temperature to 700 °C in 45 sec). The film shown in Figure 15B was annealed with a 240 sec ramp-up time. Both films were held at 700 °C for five minutes. As shown in a comparison between Figures 15A and 15B, it is clear that a short anneal ramp-up times yield better granularity than longer ramp-up times.

[0112] Figure 17 illustrates battery charge and discharge profiles of a battery structure formed utilizing $LiCoO_2$ films according to embodiments of the present invention. The $LiCoO_2$ film in the battery profiled in Figure 17 was deposited according to Example 54 in Table I. The $LiCoO_2$ film was deposited on an alumina substrate with a gold current collector. The $LiCoO_2$ film was annealed utilizing a fast-ramp (45 sec) RTA process as was described above. A 1.5 μm LiPON layer was then deposited with a standard RF deposition process without bias in a modified AKT reactor. A lithium anode and a nickel current collector were then deposited. Data was taken at 0.33 mA, 1.65 mA, 3.3 mA, 16.5 mA, 33 mA, and 66 mA. As observed, the battery was capable of storing an exceptional 25 mA/cm$^2$ at voltages greater than 2.0 V.

[0113] One skilled in the art will recognize variations and modifications of the examples specifically discussed in this disclosure. These variations and modifications are intended to be within the scope and spirit of this disclosure. As such, the scope is limited only by the following claims.

## TABLE I

| Example # | Target Power (kW) | Bias Power (W) | Reverse Time (µs) | Frequency (kHz) | Ar (sccm) | $O_2$ (sccm) | Initial Substrate Temperature (temperature during deposit) (°C) | Deposition Time (sec) | Film Thickness (µm) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 0 | 1,6 | 250 | 80 | 0 | 30 | 10000 | 3.9 |
| 2 | 2 | 0 |  | 250 | 72 | 8 | 30 | 7200 | 1.7 |
| 3 | 2 | 100 |  | 250 | 72 | 8 | 30 | 7200 | 1.34 |
| 4 | 2 | 100 |  | 250 | 76 | 4 | 30 | 7200 | 1.57 |
| 5 | 2 | 100 |  | 250 | 76 | 4 | 200 | 7200 | 1.3 |
| 6 | 2 | 100 |  | 250 | 74 | 6 | 200 | 7200 | 1.3 |
| 7 | 2 | 0 |  | 300 | 72 | 8 | 30 | 7200 | 1.58 |
| 8 | 2 | 0 |  | 300 | 74 | 6 | 30 | 7200 |  |
| 9 | 2 | 100 |  | 300 | 74 | 6 | 30 | 7200 |  |
| 10 | 2 | 100 |  | 300 | 72 | 8 | 30 | 7200 |  |
| 11 | 2 | 100 |  | 300 | 70 | 10 | 30 | 7200 |  |
| 12 | 2 | 0 |  | 300 | 70 | 10 | 30 | 7200 |  |
| 13 | 2 | 0 |  | 300 | 72 | 8 | 30 | 7200 | 1.58 |
| 14 | 2 | 0 |  | 300 | 74 | 6 | 30 | 7200 |  |
| 15 | 2 | 0 |  | 300 | 60 | 20 | 30 | 7200 |  |
| 16 | 2 | 0 |  | 300 | 50 | 30 | 30 | 7200 |  |
| 17 | 2 | 200 |  | 300 | 60 | 20 | 30 | 7200 |  |
| 18 | 2 | 50 |  | 300 | 60 | 20 | 30 | 7200 |  |
| 19 | 2 | 0 |  | 300 | 70 | 10 | 30 | 7200 |  |
| 20 | 2 | 0 |  | 300 | 65 | 15 | 30 | 7200 |  |
| 21 | 3 | 0 |  | 300 | 65 | 15 | 30 | 7200 |  |
| 22 | 2 | 0 | 1.6 | 250 | 60 | 20 | 30 | 7200 |  |
| 23 | 3 | 0 | 1.6 | 250 | 60 | 20 | 30 | 7200 |  |
| 24 | 2 | 0 | 1.6 | 250 | 60 | 20 | 30 (NPH) | 7200 |  |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 25 | 2 | 0 | 1.6 | 250 | 60 | 20 | 10min heat 30min coc | 7200 | |
| 26 | 2 | 0 | 1.6 | 250 | 60 | 20 | no preheat | 9000 | |
| 27 | 2 | 0 | | 300 | 60 | 20 | no preheat | 7200 | |
| 28 | 2 | 0 | | 300 | 60 | 20 | 15min heat, 10min | 7200 | |
| 29 | 2 | 0 | | 250 | 60 | 20 | no preheat | | |
| 30 | 2 | 0 | | 250 | 60 | 20 | 10min, 10min | | |
| 31 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30 (220) | 7200 | 4.81 |
| 32 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30 (220) | 7200 | 4.74 |
| 33 | 2 | 0 | 1.3 | 300 | 22.5 | 7.5 | 30 (220) | 7200 | 3.99 |
| 34 | 2 | 0 | 1.3 | 300 | 22.5 | 7.5 | 30 (220) | 7200 | 3.93 |
| 35 | 2 | 0 | 1.3 | 300 | 37.5 | 12.5 | 30 (220) | 7200 | 3.64 |
| 36 | 2 | 0 | 1.3 | 300 | 37.5 | 12.5 | 30 (220) | 7200 | 3.54 |
| 37 | 2 | 100 | 1.3 | 300 | 60 | 20 | 30 (220) | 7200 | 4.54 |
| 38 | 2 | 200 | 1.3 | 300 | 60 | 20 | 30 (220) | 7200 | 4.84 |
| 39 | 2 | 100 | 1.3 | 300 | 37.5 | 12.5 | 30 (220) | 7200 | 4.30 |
| 40 | 2 | 100 | 1.3 | 300 | 22.5 | 7.5 | 30 (220) | 7200 | 3.77 |
| 41 | 2 | 200 | 1.3 | 300 | 37.5 | 12.5 | 30 (220) | 7200 | 3.92 |
| 42 | 2 | 200 | 1.3 | 300 | 60 | 20 | 400 | 7200 | 3.77 |
| 43 | 2 | 0 | 1.3 | 300 | 22.5 | 7.5 | 30(220) | 7200 | 3.24 |
| 44 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30(220) | 7200 | 3.88 |
| 45 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30(220) | 3600 | 1.78 |
| 46 | 2 | 200 | 1.3 | 300 | 60 | 20 | 30(220) | 3600 | 1.87 |
| 47 | 2 | 200 | 1.3 | 300 | 22.5 | 7.5 | 30(220) | 3600 | 1.52 |
| 48 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30(220) | 6000 | 1.12 |
| 49 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30(220) | 10800 | 1.89 |
| 50 | 2 | 0 | 1.3 | 300 | 60 | 20 | 30(220) | 14400 | 2.52 |
| 51 | 2 | 100 | 1.3 | 300 | 60 | 20 | 30(220) | 10000 | 1.57 |
| 52 | 2 | 100 | 1.3 | 300 | 60 | 20 | 30(220) | 10000 | 2.11 |
| 53 | 2 | 100 | 1.3 | 300 | 60 | 20 | 30(220) | 6000 | 2.70 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 54 | 2 | 100 | 1.3 | 300 | 60 | 20 | 30(220) | 6000 | 2.70 |

**TABLE II**

| Example # | Phase | Lattice | Texture | $d_{101}$ [Å] | 2θ [°] | crystallite size [Å] |
|---|---|---|---|---|---|---|
| 15 | $LiCoO_2$ | rhombohedral | strong [101] | 2.376(1) | 37.83 | ~1300 |
| 16 | $LiCoO_2$ | Rhombohedral | strong [101] | 2.375(1) | 37.85 | ~750 |
| 17 | Co | cubic | random | -- | -- | <50 |
| 18 | Co | cubic | random | -- | -- | <50 |
| 19 | $LiCoO_2$ | rhombohedral | strong [101] | 2.370(1) | 37.93 | ~1400 |
| 20 | $LiCoO_2$ | rhombohedral | strong [101] | 2.372(1) | 37.90 | ~1500 |
| 21 | $LiCoO_2$ | rhombohedral | strong [101] | 2.370(1) | 37.92 | ~1700 |
| PDF | $LiCoO_2$ | Rhombohedral | random | 2.408(1) | 37.31 | -- |

WHAT IS CLAIMED IS:

1. A method of depositing a $LiCoO_2$ layer, comprising:

placing a substrate in a reactor;

flowing a gaseous mixture including argon and oxygen through the reactor; and

applying pulsed DC power to a target formed of $LiCoO_2$ positioned opposite the substrate,

wherein a crystalline layer of $LiCoO_2$ is deposited over the substrate.

2. The method of claim 1, further including applying an RF bias to the substrate.

3. The method of claim 1, wherein the crystalline layer is <101> oriented.

4. The method of claim 1, wherein the crystalline layer is <003> oriented.

5. The method of claim 1, wherein a grain size of the crystalline layer is between about 750 Å and about 1700 Å.

6. The method of claim 1 wherein the substrate is a material chosen from a set comprised of silicon, polymers, glasses, ceramics, and metals.

7. The method of claim 1, further including preheating the substrate to a temperature of about 200 °C.

8. The method of claim 1, wherein the substrate is a low temperature substrate.

9. The method of claim 8, wherein the low temperature substrate is one of a set of substrates including glass, plastic, and metal foil.

10. The method of claim 1, further including depositing an oxide layer on the substrate.

11. The method of claim 10, wherein the oxide layer is a silicon dioxide layer.

12. The method of claim 3, wherein the crystalline layer is deposited at a rate of greater than 1 μm per hour.

13. The method of claim 1 wherein the target is a ceramic $LiCoO_2$ sputter target with a resistance measured across about 4 cm of surface of less than about 500 kΩ.

14. The method of claim 1, further including depositing a metal layer on the substrate.

15. The method of claim 14, wherein the metal layer is iridium.

16. The method of claim 14, wherein the metal layer is platinum.

17. The method of claim 1, further including annealing the crystalline layer with a low thermal budget.

18. The method of claim 17, wherein annealing the crystalline layer includes annealing to 700°C in a rapid thermal anneal process for a period of time less than about 10 minutes.

19. The method of claim 14, further including annealing the $LiCoO_2$ layer at a temperature of less than or equal to about 500°C.

20. The method of claim 14, further including annealing the $LiCoO_2$ layer at a temperature of less than or equal to about 400°C.

21. A battery structure, comprising:

a crystalline $LiCoO_2$ layer deposited over a low-temperature substrate.

22. The structure of claim 21, further including a conducting layer deposited between the crystalline $LiCoO_2$ layer and the low-temperature substrate.

23. The structure of claim 22, wherein the conducting layer is an iridium layer.

24. The structure of claim 22, wherein the conducting layer is a platinum layer.

25. The structure of claim 21, further including a LiPON layer deposited over the $LiCoO_2$ layer.

26. The structure of claim 21, further including a second conducting layer deposited over the $LiCoO_2$ layer.

27. A stacked battery structure, comprising:

one or more battery stacks deposited on a thin substrate, wherein each battery stack comprises:

a conducting layer,

a $LiCoO_2$ layer deposited as a crystalline layer over the conducting layer,

a LiPON layer deposited over the crystalline $LiCoO_2$ layer,

an anode layer deposited over the LiPON layer; and

a top conducting layer deposited over the one or more battery stacks.

28. The stacked battery structure of claim 27, wherein the battery stacks form a parallel stacked battery structure.

29. The stacked battery structure of claim 27, wherein the battery stacks form a series stacked battery structure.

30. The stacked battery structure of claim 27, wherein the conducting layer is a metal layer deposited on a substrate.

31. The stacked battery structure of claim 30, wherein the metal layer is an iridium layer.

32. The stacked battery structure of claim 30, wherein the metal layer is a platinum layer.

33. The stacked battery structure of claim 30, wherein the substrate is a low temperature substrate.

34. The stacked battery structure of claim 27, wherein the conducting layer is a metallic foil.

35. The stacked battery structure of claim 34, wherein the metallic foil is formed of a metal from a group consisting of copper, gold, platinum, aluminum, stainless steel and other nickel or cobalt based super alloy.

36. A method of producing a battery, comprising:

loading a substrate into a cluster tool;

depositing a crystalline $LiCoO_2$ layer over a conducting layer in a chamber of the cluster tool with a pulsed-dc PVD process.

37. The method of claim 36, wherein depositing a crystalline $LiCoO_2$ layer includes depositing crystalline $LiCoO_2$ through a mask.

38. The method of claim 36, further including

depositing a conducting layer on the substrate.

39. The method of claim 36, further including depositing a LiPON layer over the $LiCoO_2$ layer.

40. The method of claim 39, further including deposition an anode over the LiPON layer.

41. The method of claim 40, further including depositing a conducting layer over the anode.

42. The method of claim 36, wherein the conducting layer is an iridium layer.

43. A fixture for holding a thin substrate, comprising:

a top portion; and

a bottom portion, wherein

the thin substrate is held when the top portion is attached to the bottom portion.

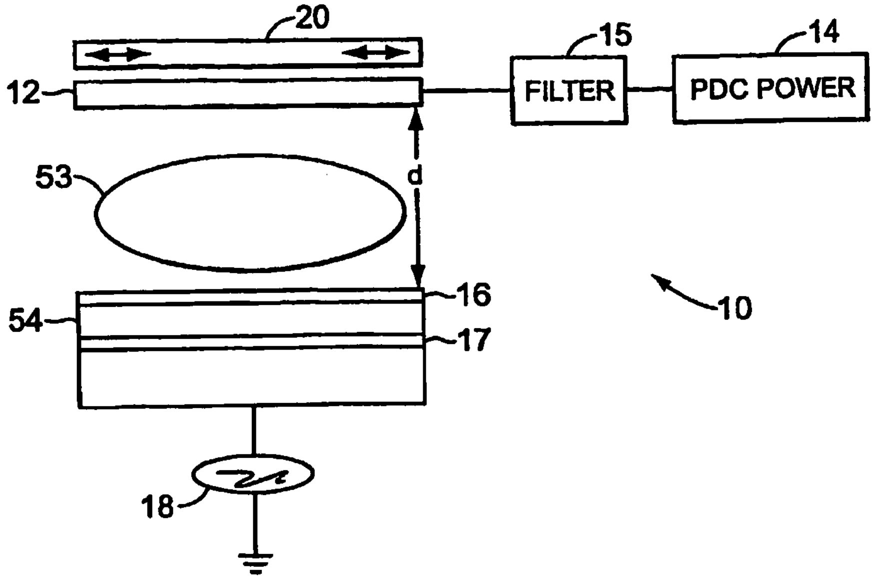

20
12
15
FILTER
14
PDC POWER
53
d
16
54
17
10
18

FIG. 1A

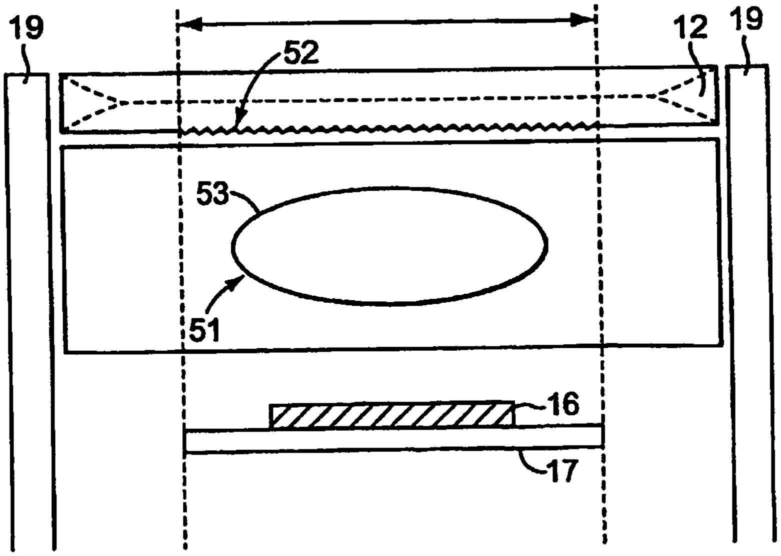

19
52
12
19
53
51
16
17

FIG. 1B

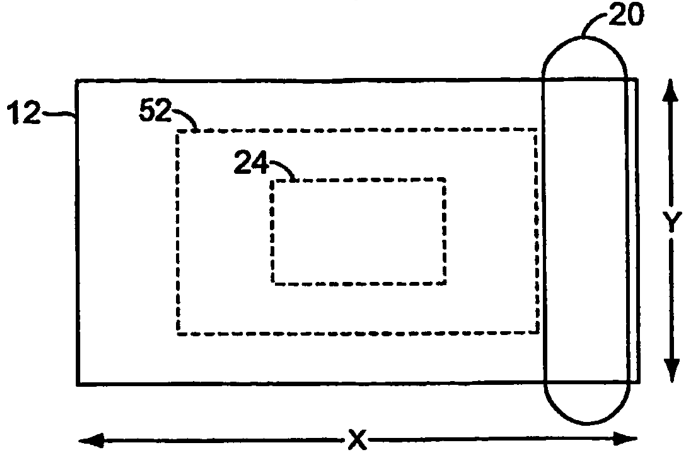


FIG. 2

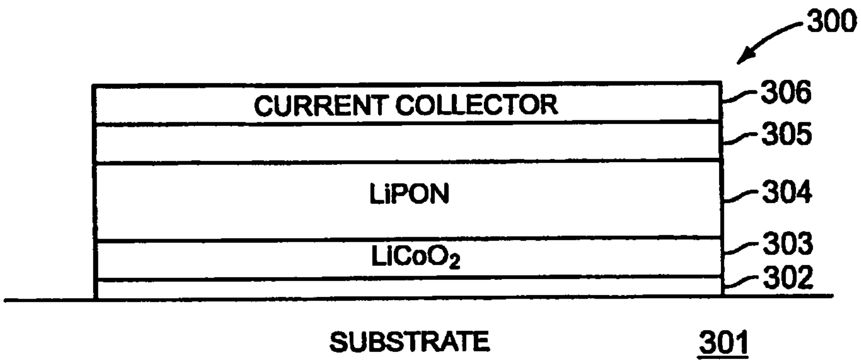


FIG. 3

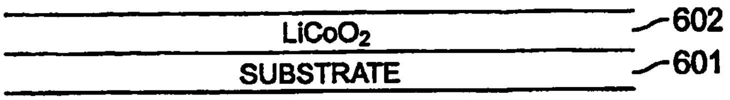


FIG. 6A

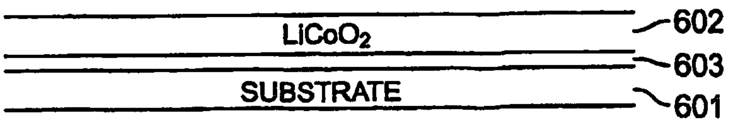


FIG. 6B

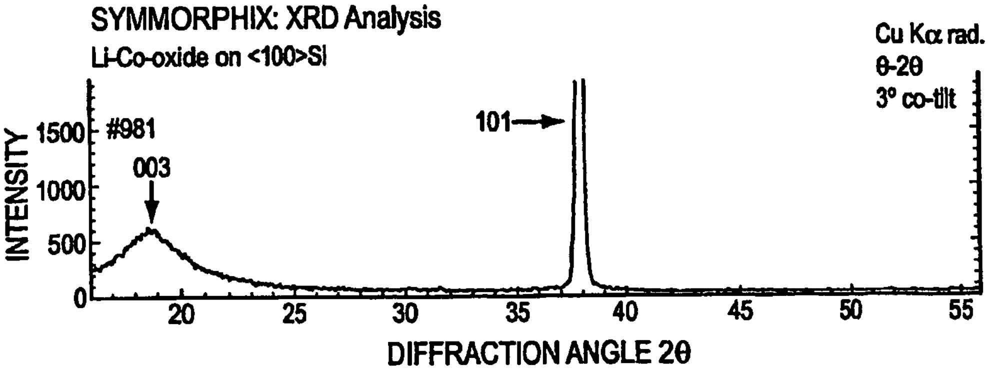


FIG. 4A

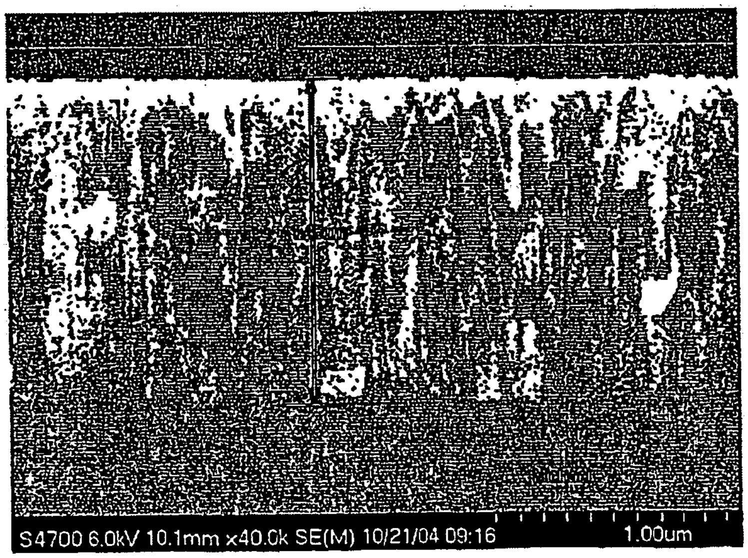


FIG. 4B

SUBSTITUTE SHEET (RULE 26)

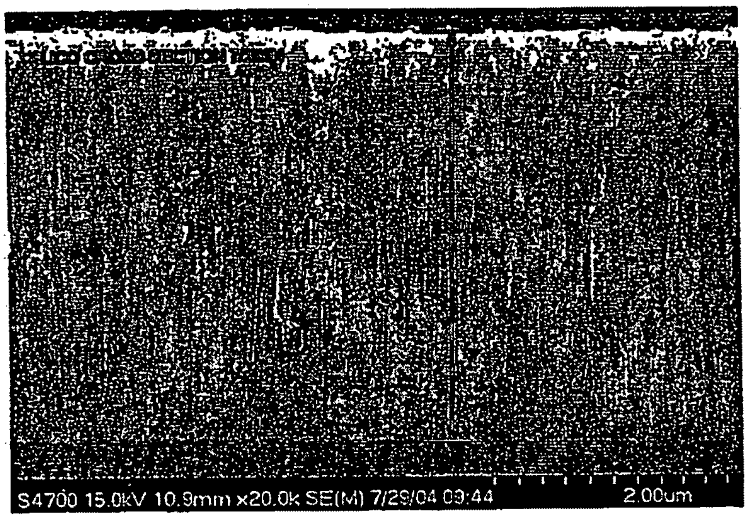
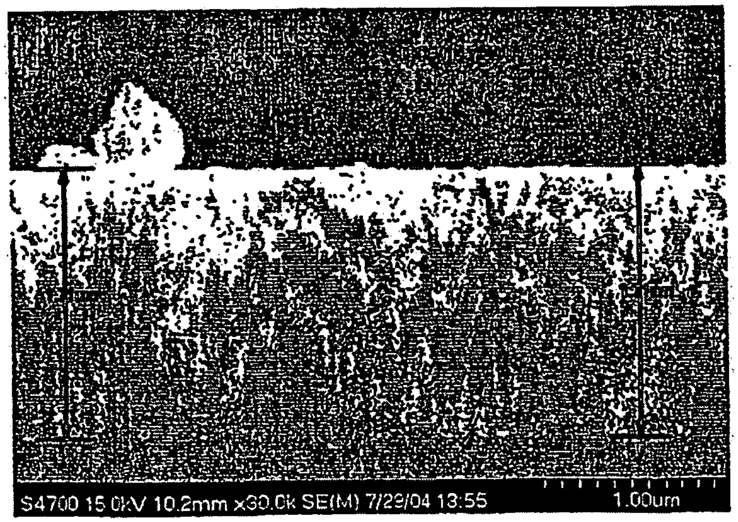

S4700 15.0kV 10.9mm x20.0k SE(M) 7/29/04 09:44
2.00um

FIG. 5A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1.00um

FIG. 5B

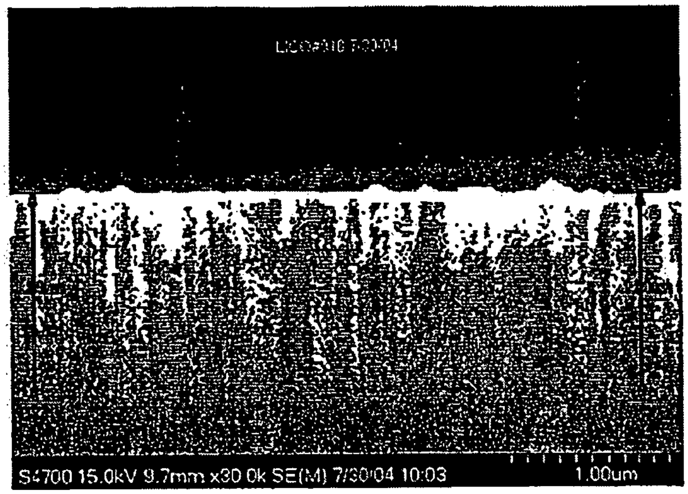
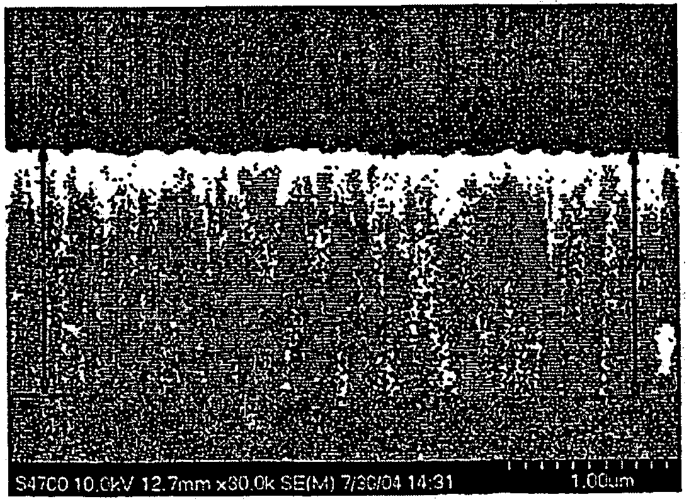

S4700 15.0kV 9.7mm x30.0k SE(M) 7/30/04 10:03
1.00um

FIG. 5C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1.00um

FIG. 5D

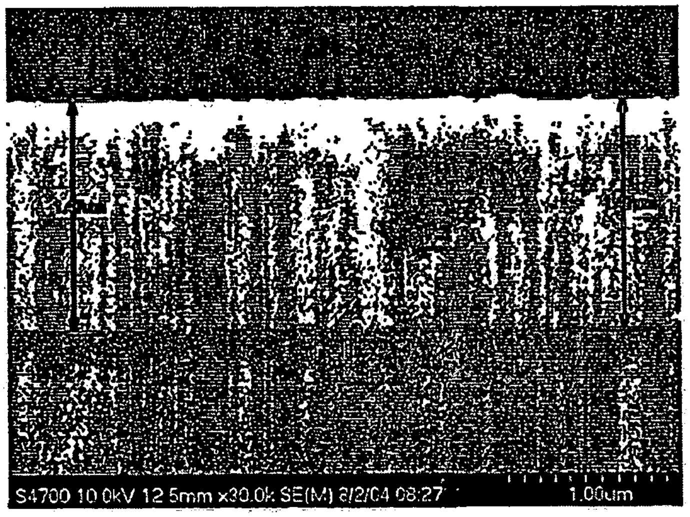

S4700 10.0kV 12.5mm x30.0k SE(M) 8/2/04 08:27
1.00um

FIG. 5E

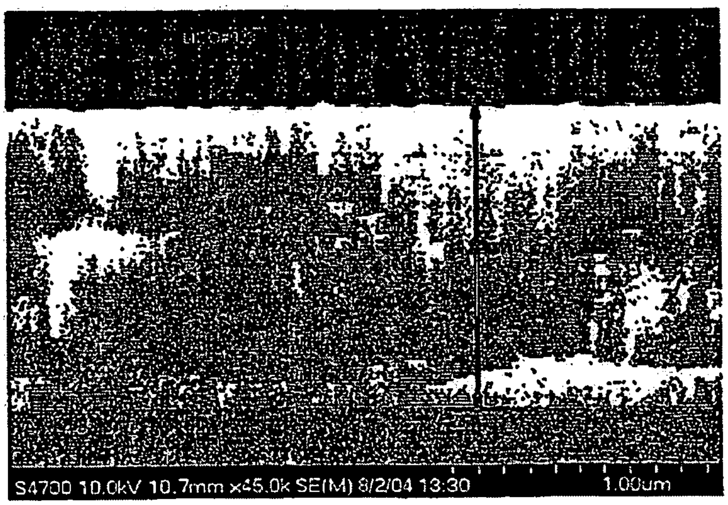

S4700 10.0kV 10.7mm x45.0k SE(M) 8/2/04 13:30
1.00um

FIG. 5F

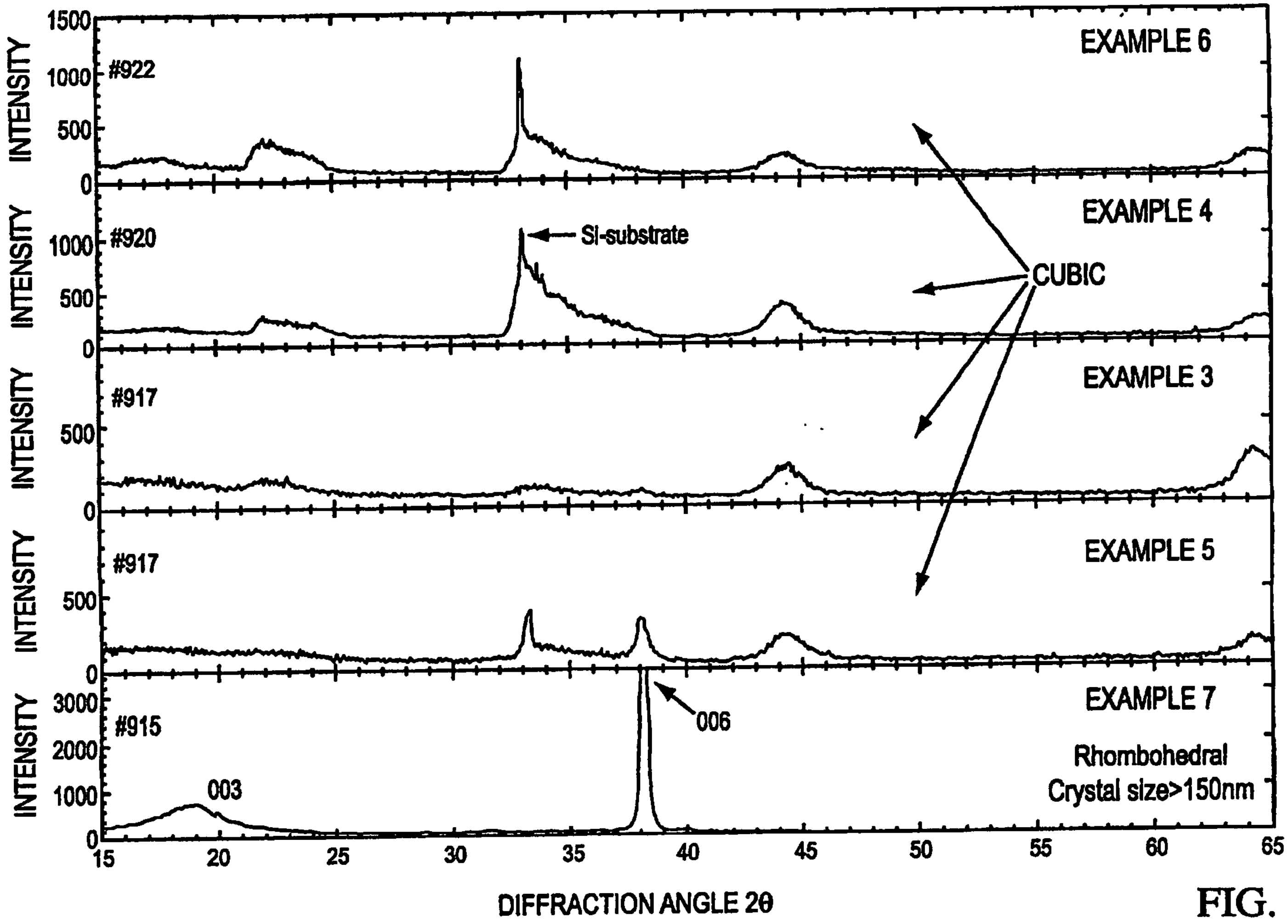

INTENSITY
1500
1000
500
0
#922
EXAMPLE 6
#920
Si-substrate
EXAMPLE 4
CUBIC
#917
EXAMPLE 3
#917
EXAMPLE 5
3000
2000
1000
#915
003
006
EXAMPLE 7
Rhombohedral
Crystal size>150nm
15
20
25
30
35
40
45
50
55
60
65
DIFFRACTION ANGLE 2θ

FIG. 5G

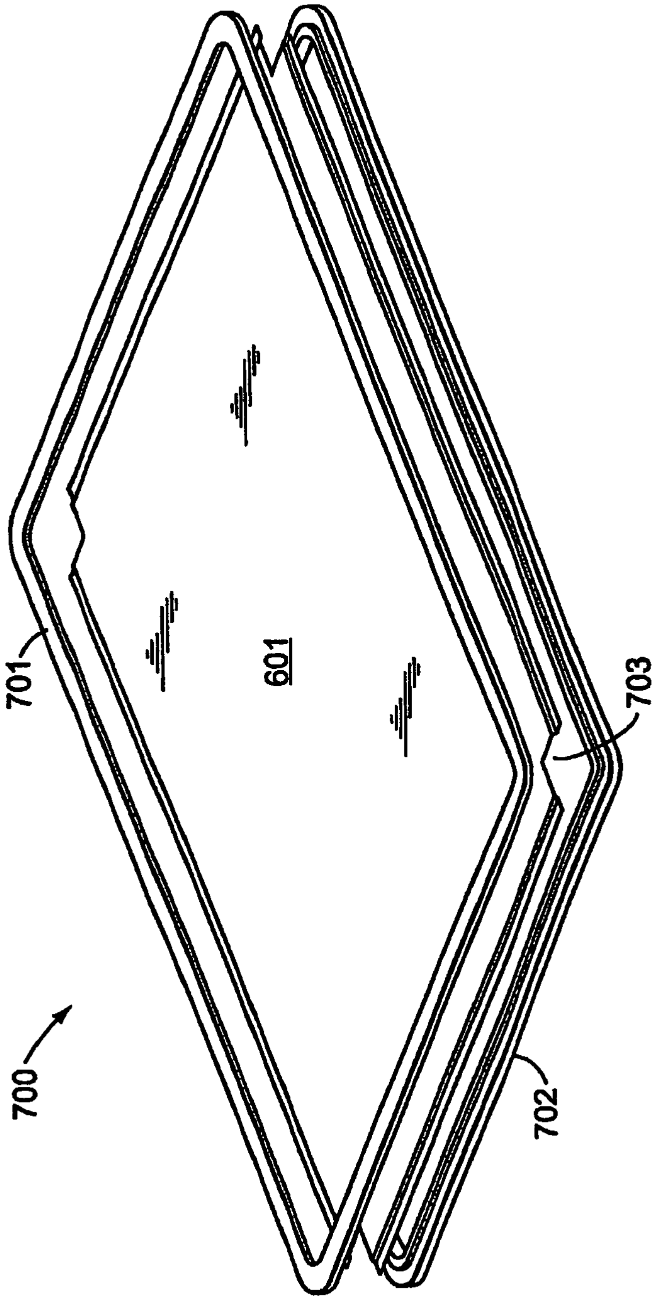


FIG. 7A

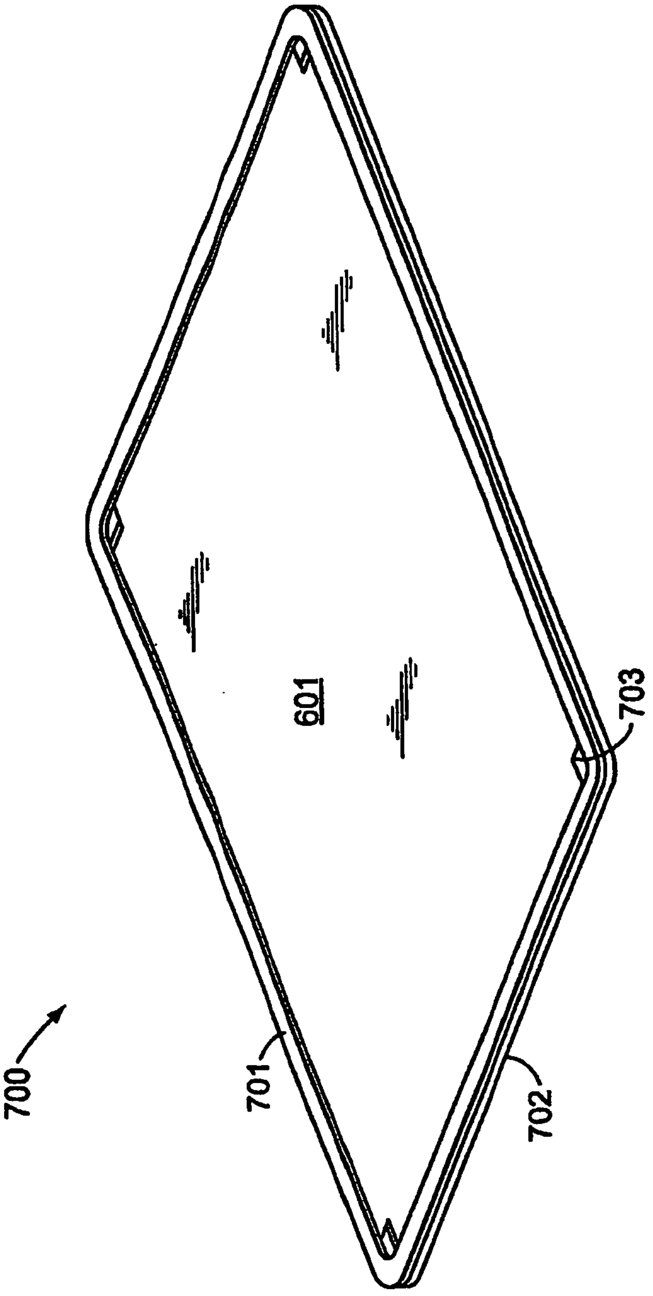


FIG. 7B

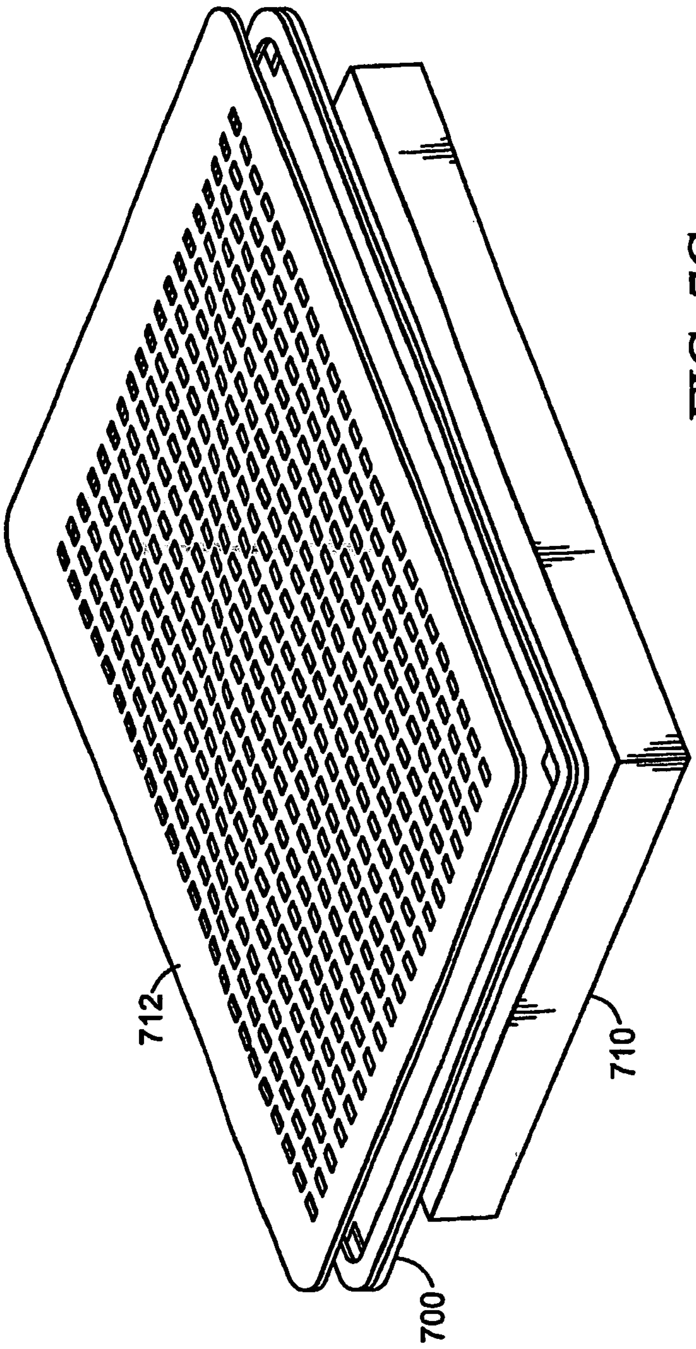


FIG. 7C

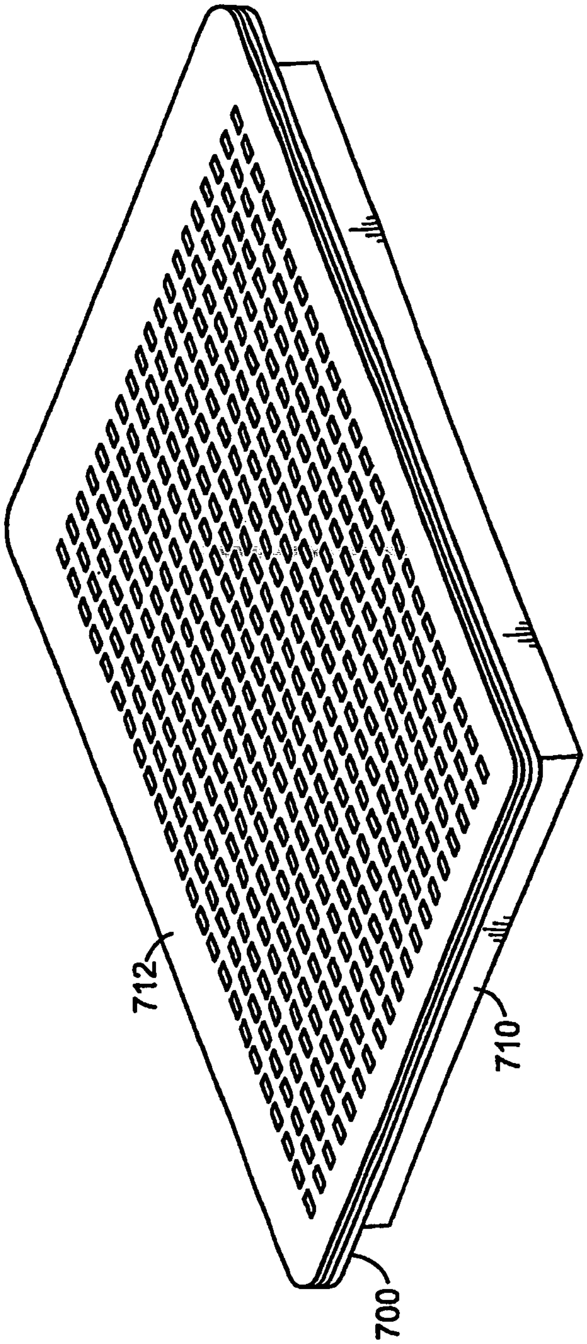


FIG. 7D

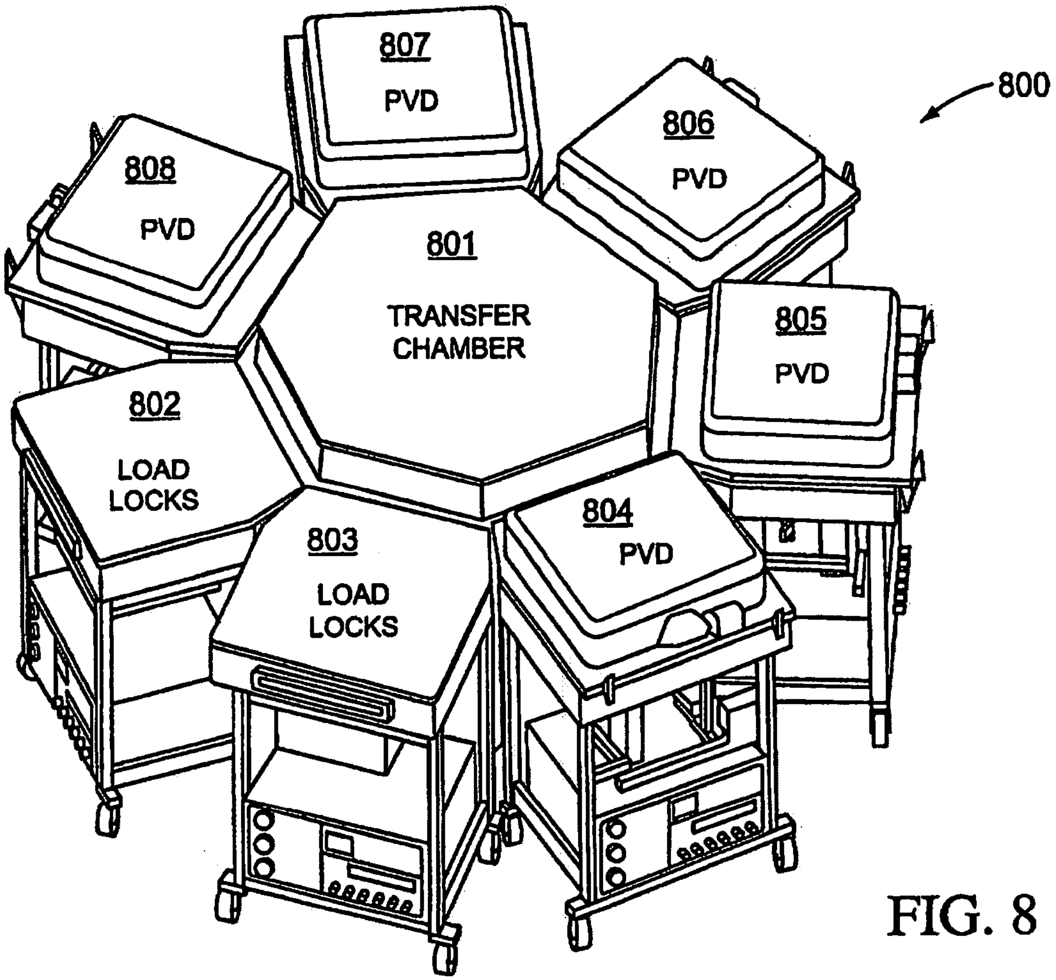

800
807
PVD
808
PVD
806
PVD
801
TRANSFER
CHAMBER
805
PVD
802
LOAD
LOCKS
803
LOAD
LOCKS
804
PVD

FIG. 8

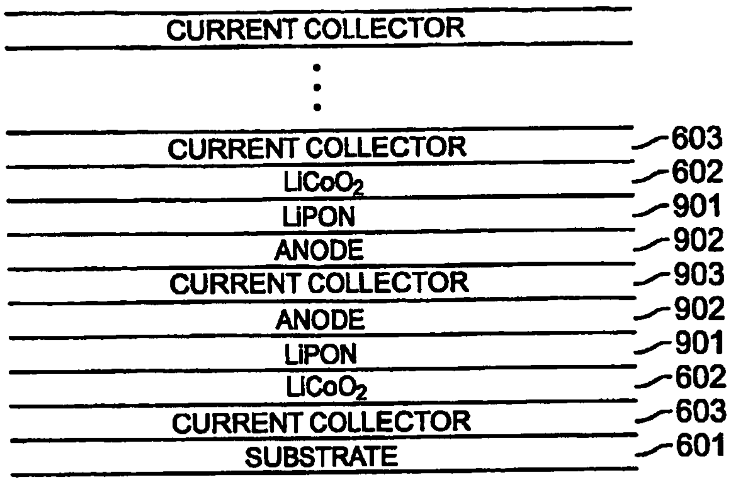

CURRENT COLLECTOR
CURRENT COLLECTOR
603
$LiCoO_2$
602
LiPON
901
ANODE
902
CURRENT COLLECTOR
903
ANODE
902
LiPON
901
$LiCoO_2$
602
CURRENT COLLECTOR
603
SUBSTRATE
601

FIG. 9A

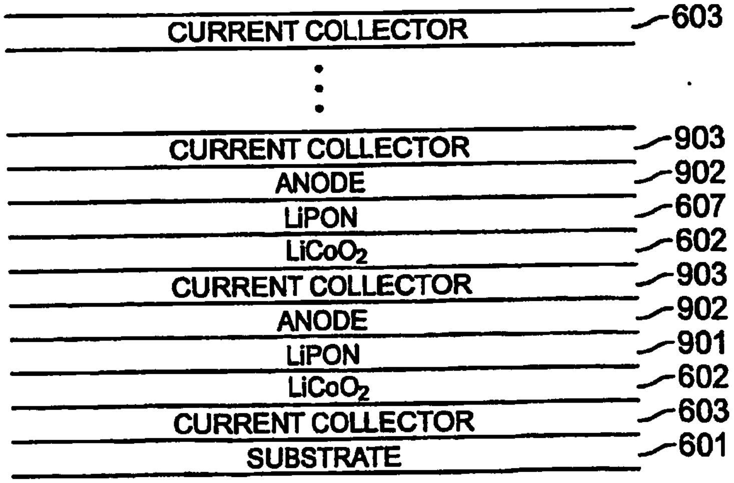

CURRENT COLLECTOR
603
CURRENT COLLECTOR
903
ANODE
902
LiPON
607
$LiCoO_2$
602
CURRENT COLLECTOR
903
ANODE
902
LiPON
901
$LiCoO_2$
602
CURRENT COLLECTOR
603
SUBSTRATE
601

FIG. 9B

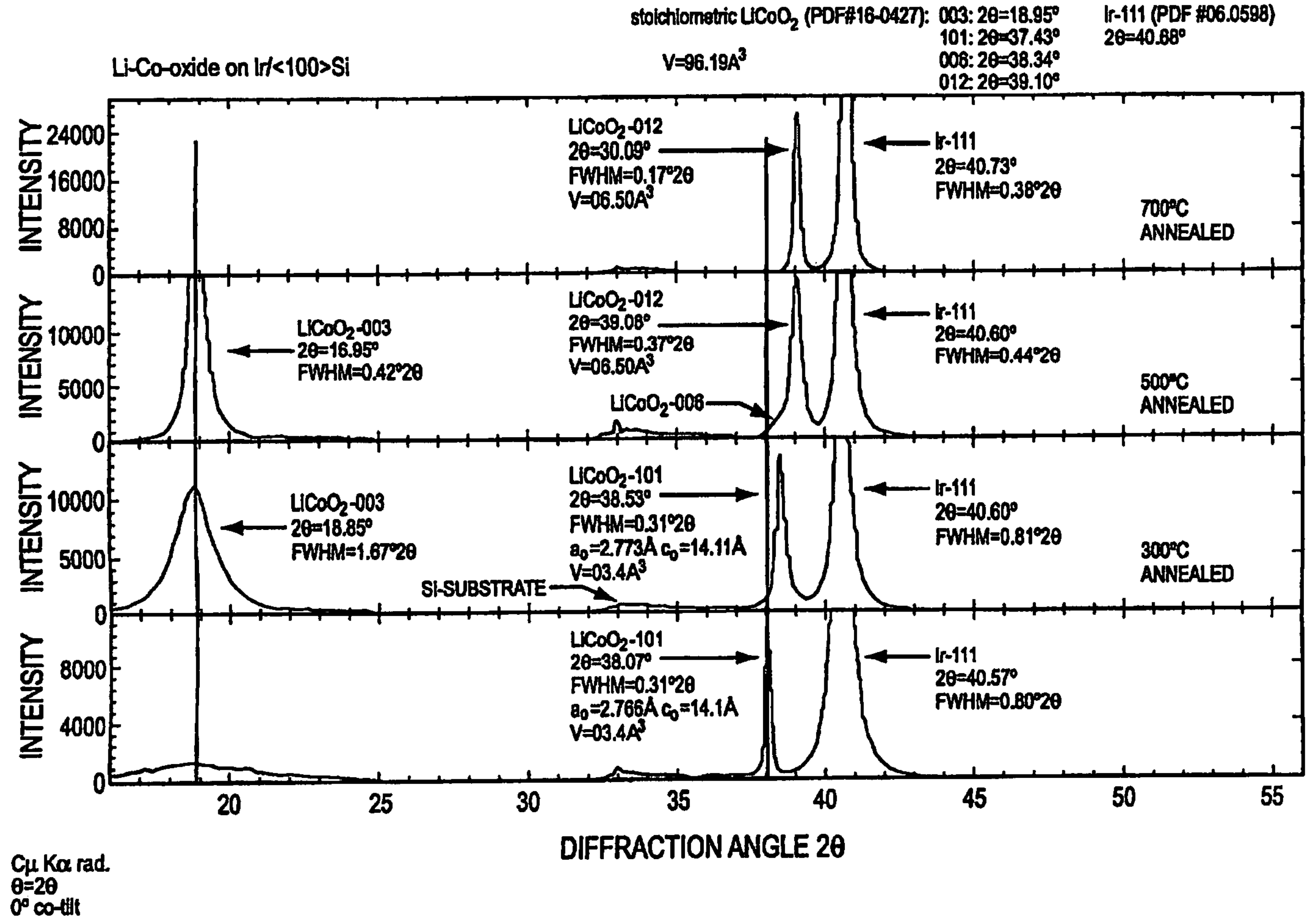


FIG. 10D

FIG. 10C

FIG. 10B

FIG. 10A

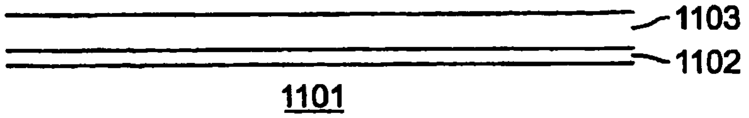


FIG. 11A

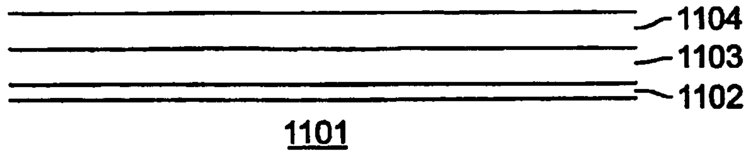


FIG. 11B

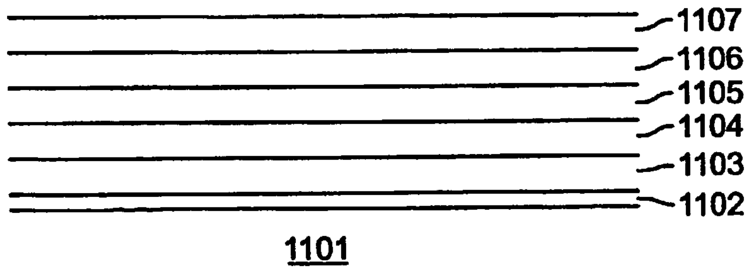


FIG. 11C

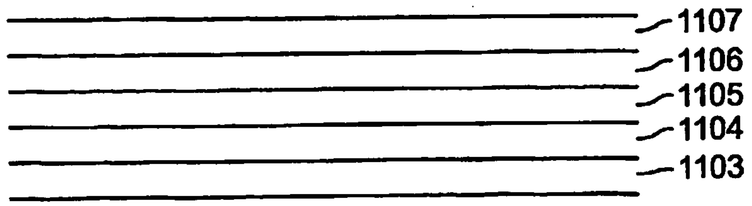
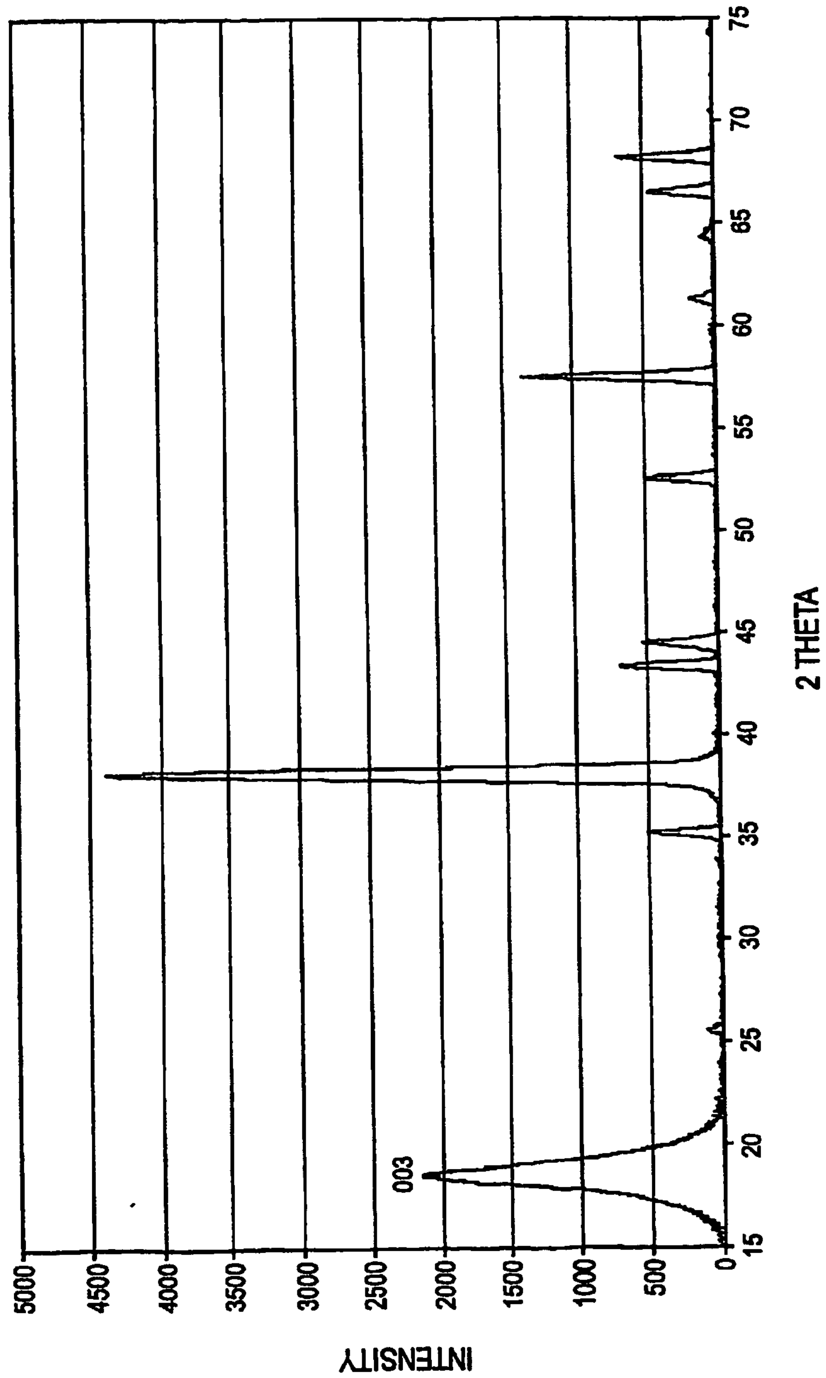


FIG. 11D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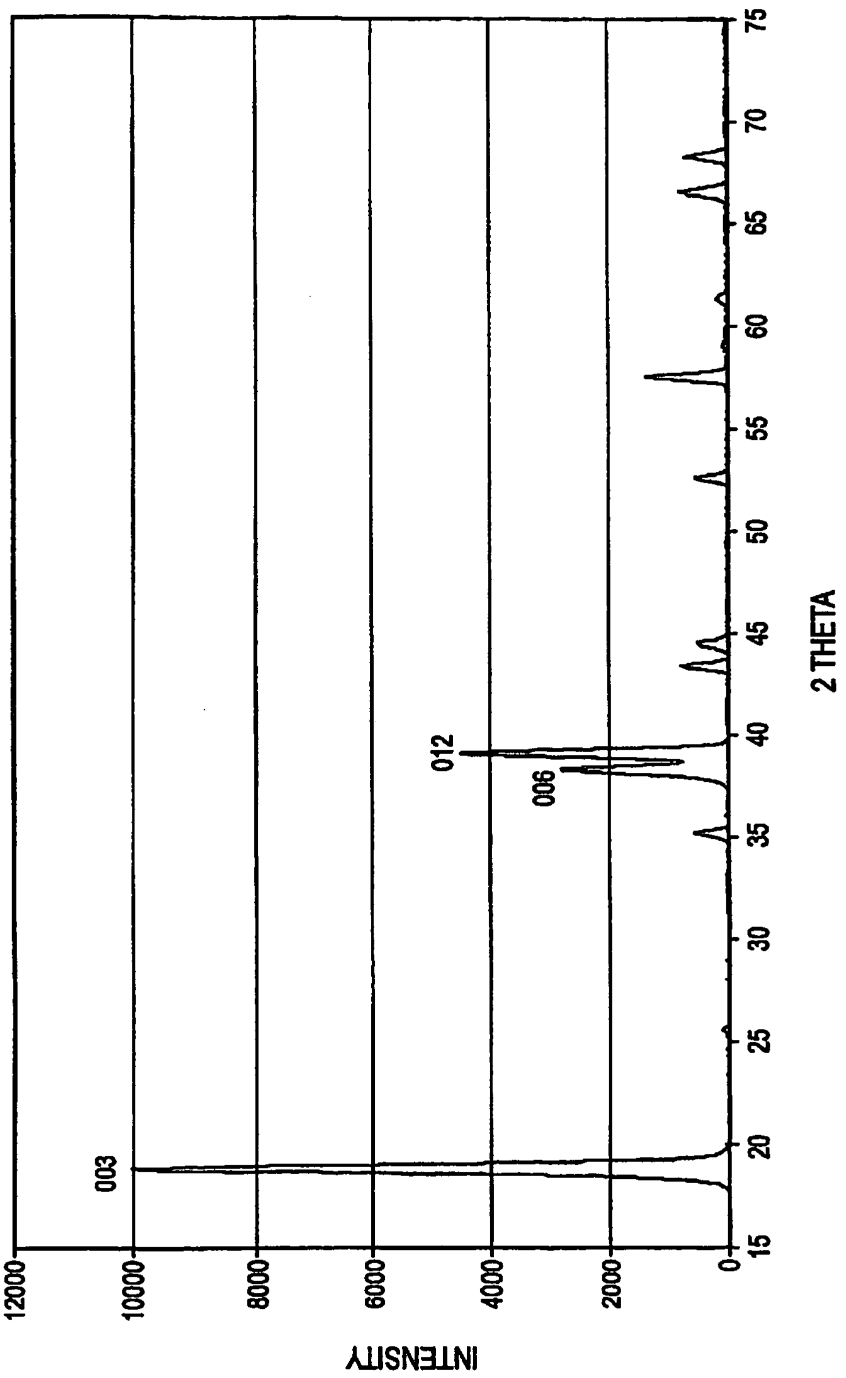
65
70
75
003
2 THETA

FIG. 12A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012
006

FIG. 12B

FIG. 12C

FIG. 12D

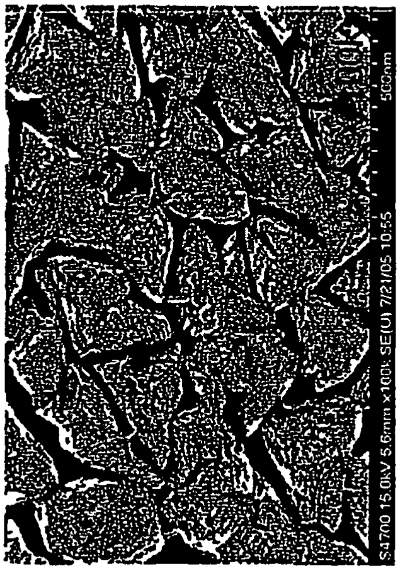


FIG. 12E

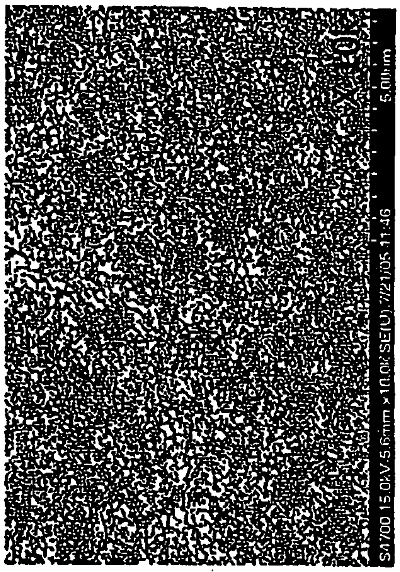


FIG. 12F

SUBSTITUTE SHEET (RULE 26)

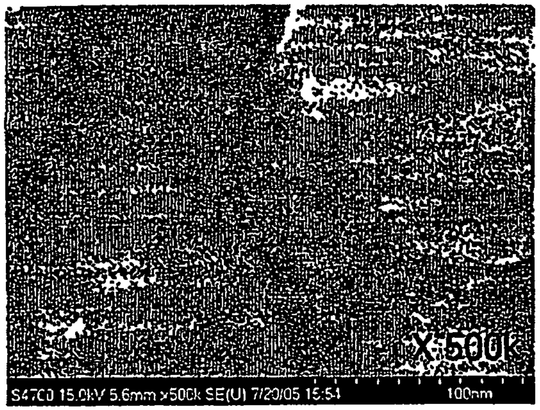


FIG. 12G

FIG. 12H

FIG. 12I

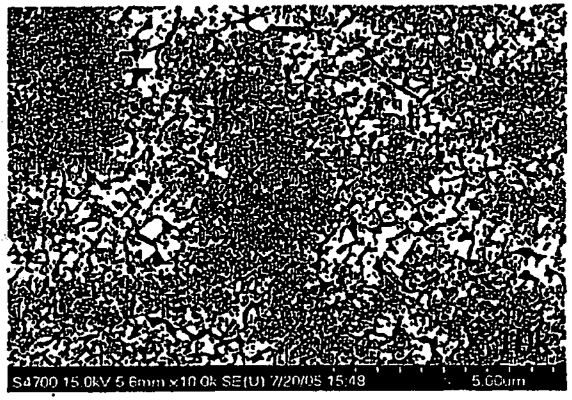
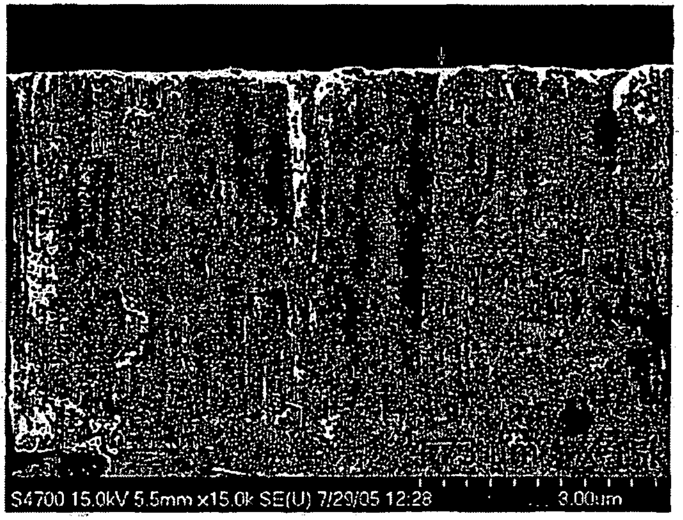


FIG. 12J

FIG. 12K

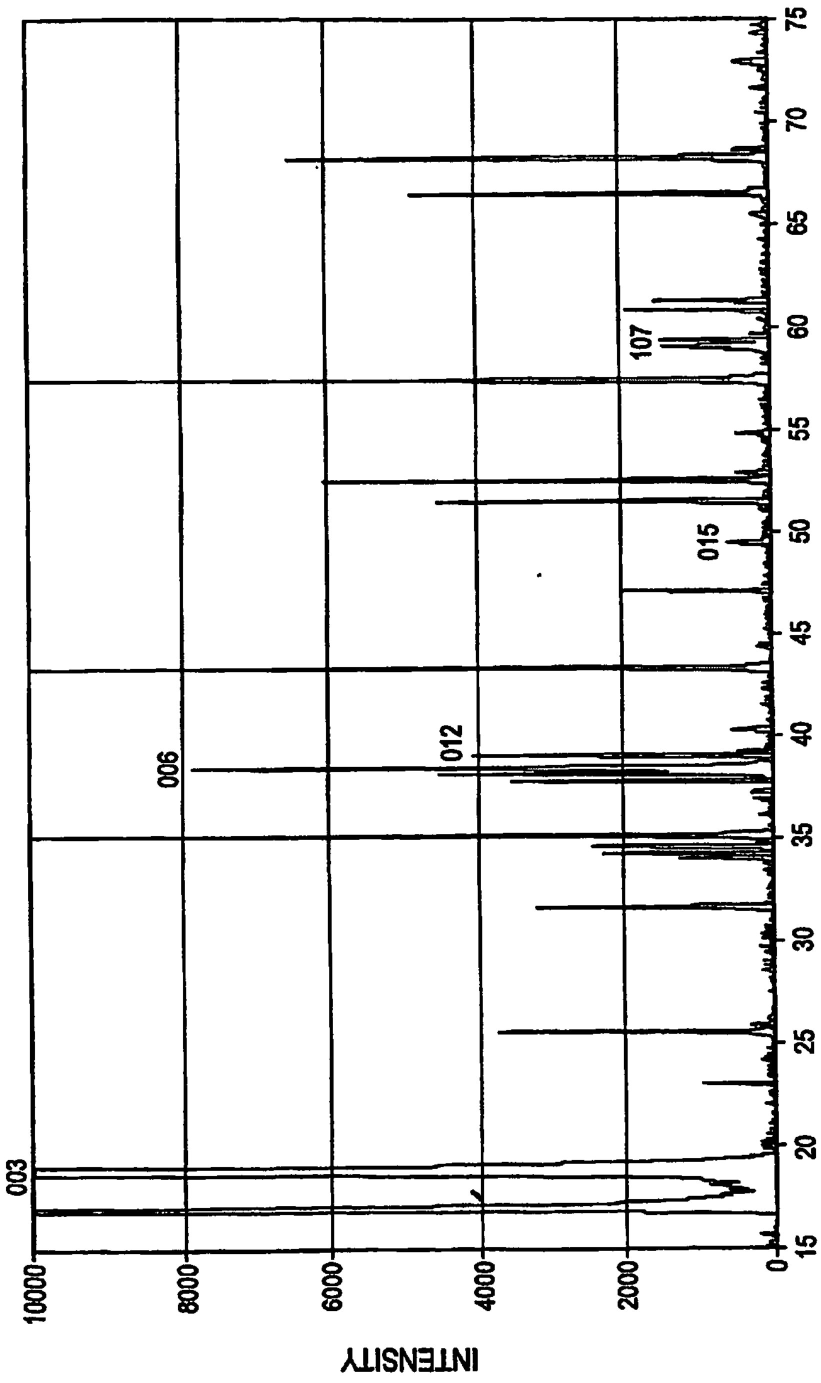
On Si

FIG. 12L



On alumina

BEST AVAILABLE COPY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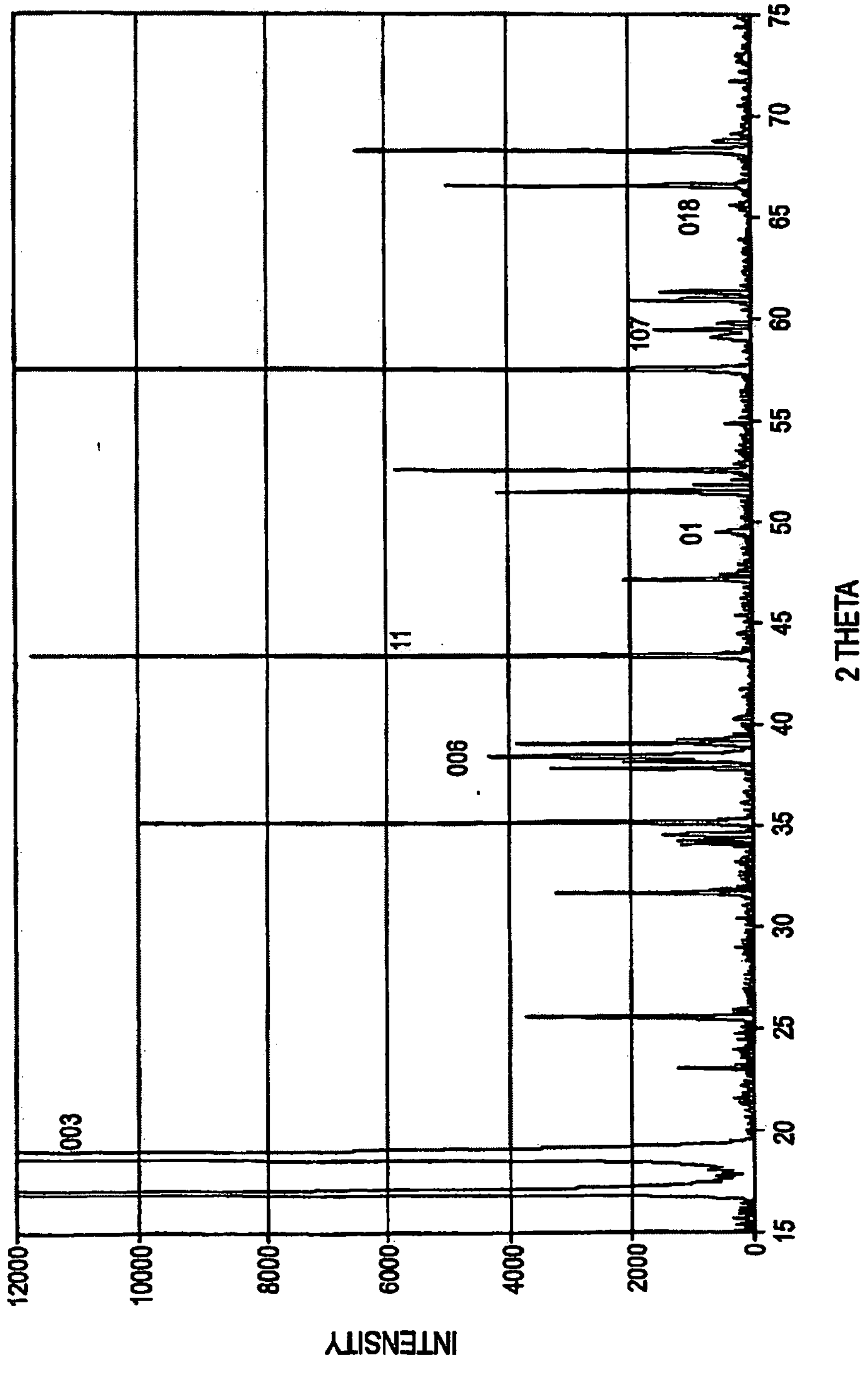
65
70
75
2 THETA

FIG. 13A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INTENSITY
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65
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75
2 THETA

FIG. 13B

FIG. 13C

FIG. 13E

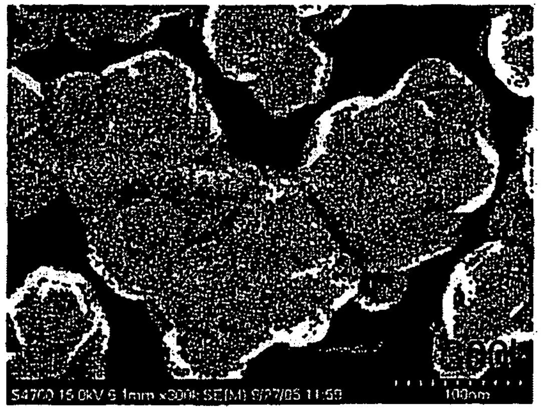
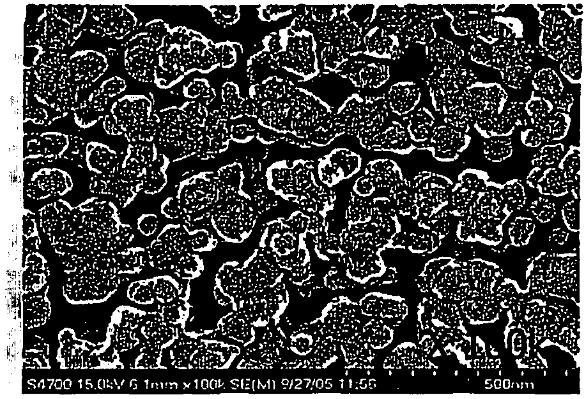


FIG. 13D

In Ar

FIG. 13F



In Ar/$O_2$ (3/1)

FIG. 14A

As deposited

FIG. 14B

700CX2h

FIG. 14C

RTA-5m

FIG. 14D

RTA-700C15m

FIG. 15A

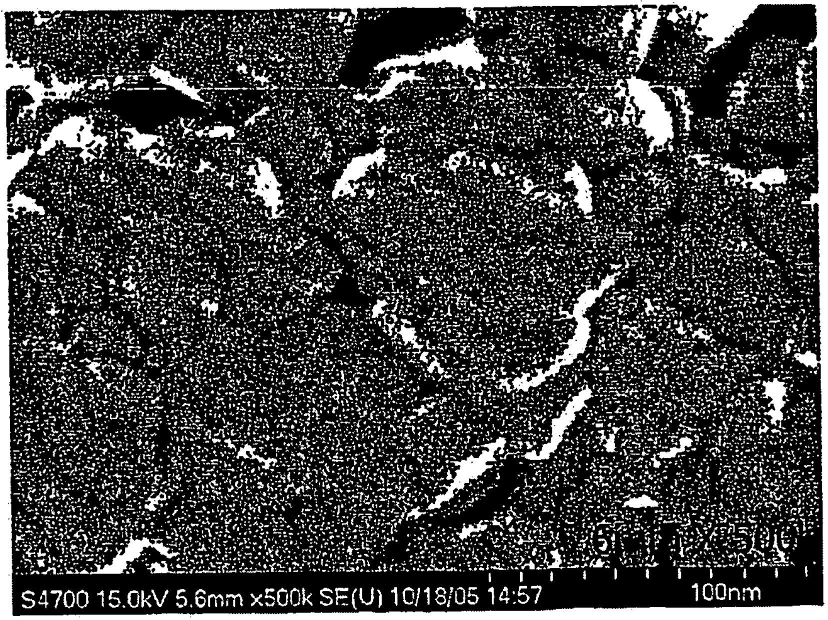
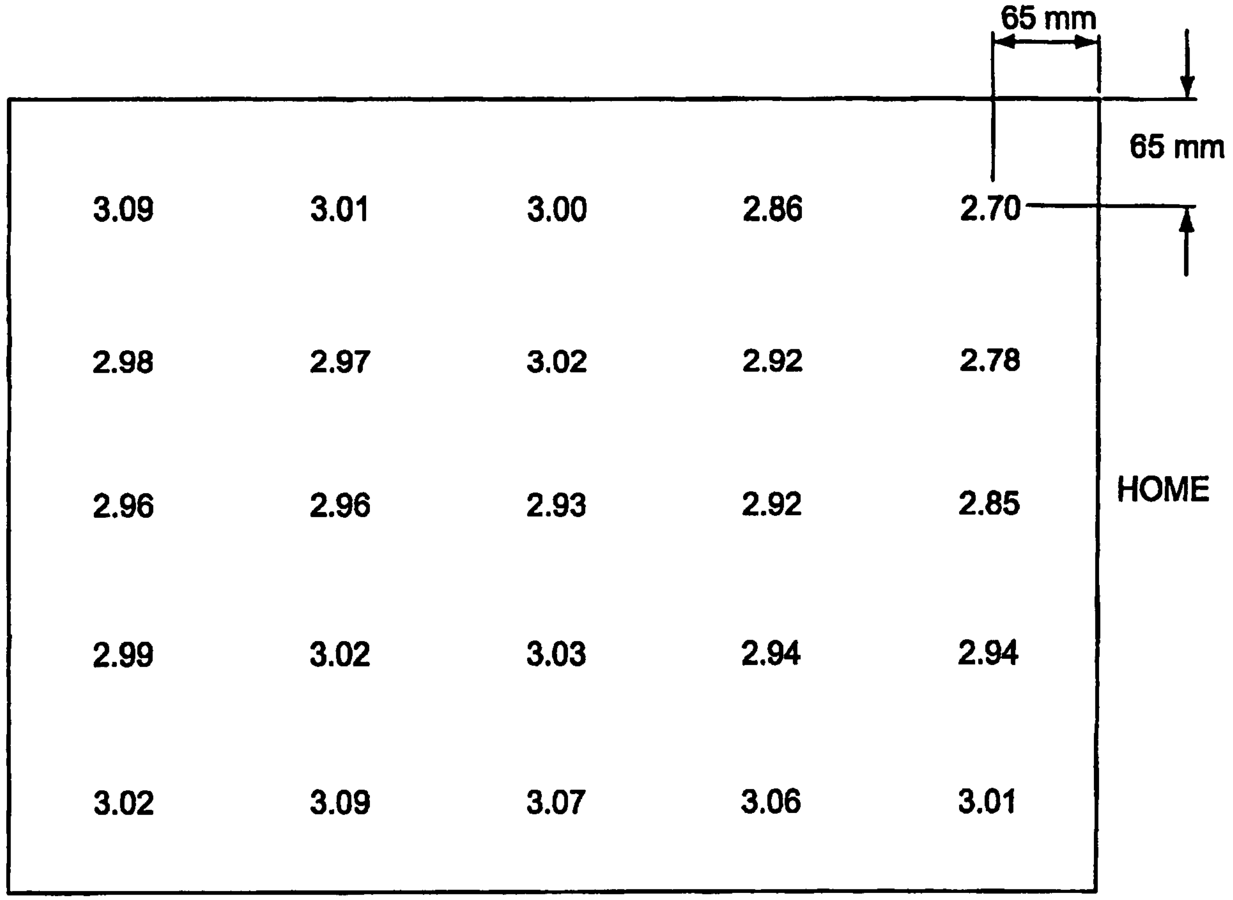


FIG. 15B



| | | | | |
|---|---|---|---|---|
| 3.09 | 3.01 | 3.00 | 2.86 | 2.70 |
| 2.98 | 2.97 | 3.02 | 2.92 | 2.78 |
| 2.96 | 2.96 | 2.93 | 2.92 | 2.85 |
| 2.99 | 3.02 | 3.03 | 2.94 | 2.94 |
| 3.02 | 3.09 | 3.07 | 3.06 | 3.01 |

FIG. 16

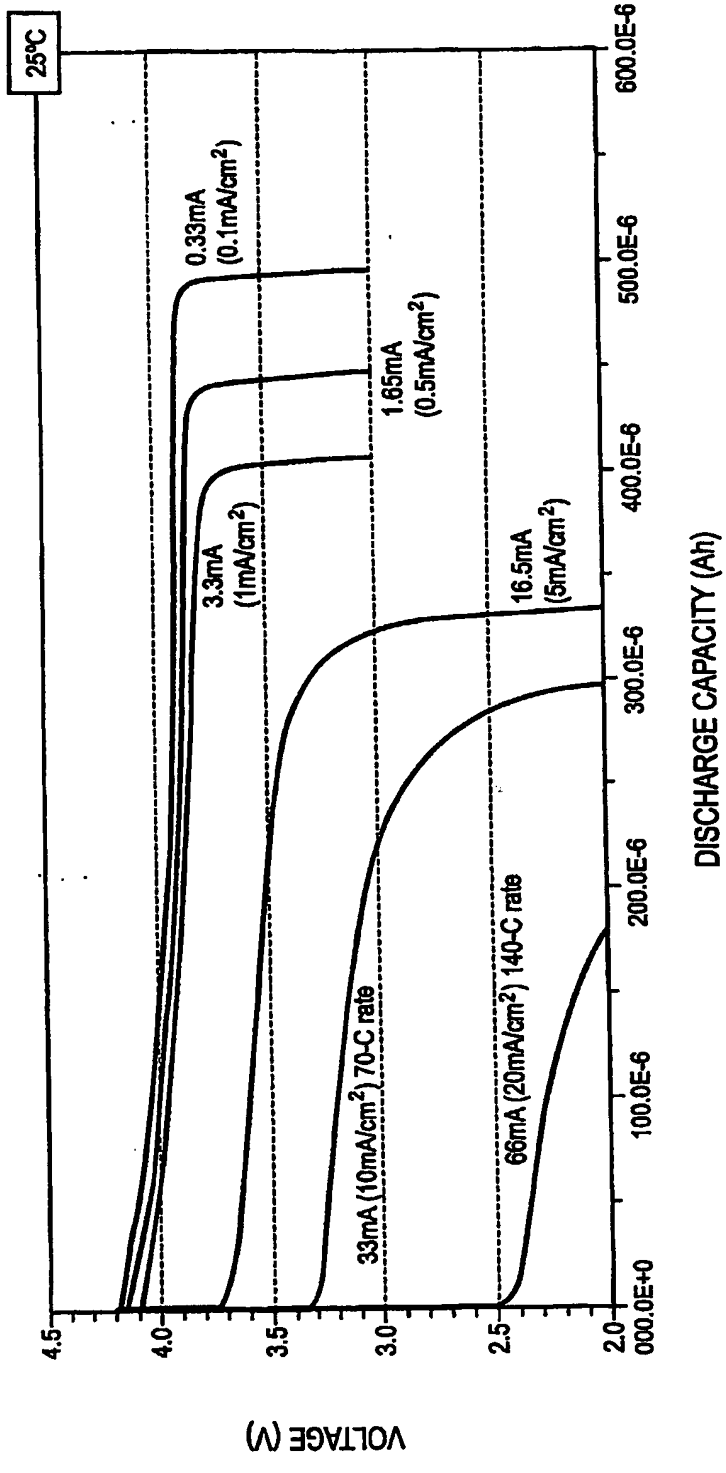

25°C
0.33mA
(0.1mA/cm$^2$)
1.65mA
(0.5mA/cm$^2$)
3.3mA
(1mA/cm$^2$)
16.5mA
(5mA/cm$^2$)
33mA (10mA/cm$^2$) 70-C rate
66mA (20mA/cm$^2$) 140-C rate
VOLTAGE (V)
4.5
4.0
3.5
3.0
2.5
2.0
DISCHARGE CAPACITY (Ah)
000.0E+0
100.0E-6
200.0E-6
300.0E-6
400.0E-6
500.0E-6
600.0E-6

FIG. 17

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**(72) Inventors; and**
**(75) Inventors/Applicants** *(for US only)*: HOSTE, Serge [BE/BE]; Gaverse steenweg 579, B-9280 Merelbeke (BE). PERSYN, Frans [BE/BE]; Oude boomgaardlaan 23, B-9080 Lochrist (BE). VAN DRIESSCHE, Isabel [BE/BE]; Wareslagstraat 94, B-9250 Waasmunster (BE).

**(74) Agents:** BIRD, William et al.; Bird Goën & Co., Termerestraat 1, B-3020 Winksele (BE).

**(81) Designated States:** JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

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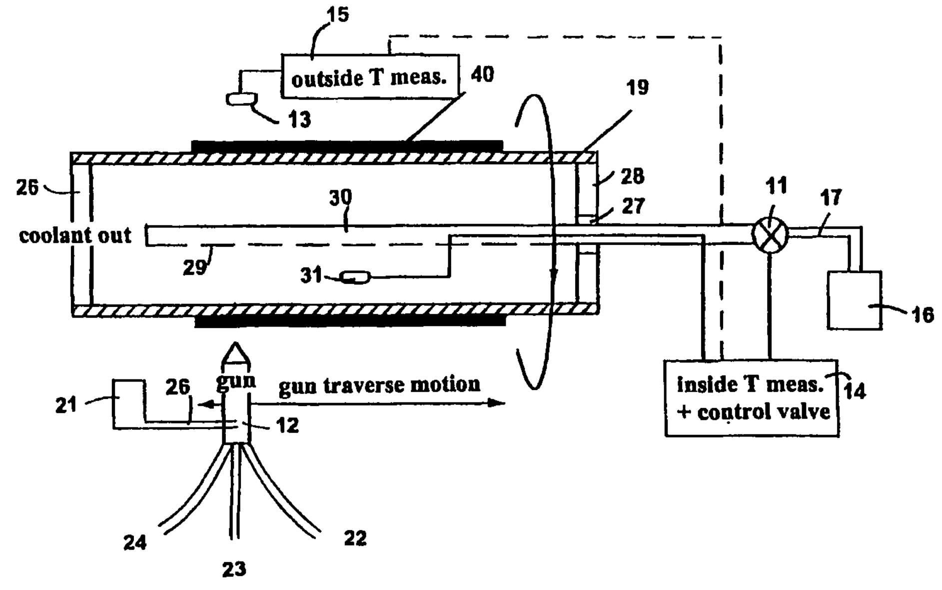
*With international search report.*

## (54) Title: SPRAYING METHOD TO FORM A THICK COATING AND PRODUCTS OBTAINED



(57) Abstract

A method and an apparatus for spraying materials onto a substrate to produce a coating thereon is described which allows very thick layers of complex metal oxides to be produced. The apparatus and method are particularly suitable for producing superconducting coatings.

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| SN | Senegal |
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# SPRAYING METHOD TO FORM A THICK COATING AND PRODUCTS OBTAINED

The present invention relates an apparatus and a method of spraying to form a coating on flat or curved substrates, for example, either as part of the direct formation of metallic or ceramic coatings such as superconductive or piezo-electric layers or for the production of targets for sputtering magnetrons having coatings which are precursors of such layers.

## TECHNICAL BACKGROUND

From EP-A-286 135 it is known to flame spray complex ceramic materials onto a substrate such as a tape to form a superconducting layer. It is suggested to pre-heat the substrate to temperatures above 540°C and to cool the coating slowly. It is further recommended to treat the coating in an atmosphere containing one of the components of the superconducting ceramic. An oxy-acetylene flame is used for the flame spraying. Thickness of up to 3 mm are described.

It is also known from US 5,196,400 to plasma spray a coating onto a target for use in a sputtering magnetron to sputter a Y-Ba-CuO superconductor coating. Deposition of only a thin target coating of 0.5 mm is reported.

The production of superconducting powders using flame spraying is reported in US 5,140,005. An oxy-acetylene flame is used. It is tacitly accepted that the high temperature of the flame changes the stoichiometric ratios of the components and that this has to be compensated by increasing the more volatile components in the original mixtures. US 5,045,365 describes a method of cooling a oxy-acetylene flame-sprayed substrate with water. Without special precautions, water cooling is unsuitable for superconductors due to the water vapour produced.

EP-A-355 736 describes production of flat targets with metal oxides up to a layer thickness of 3 mm. WO 98/0833 describes the production of < 20 micron thick layers of superconducting metal oxide mixtures.

The article by Murakami et. al. "Rapidly Solidified Thick Deposit Layers of Fe-C-Mo Alloys by Flame Spraying" describes up to 1.5 mm thick rapidly cooled thick layers of Fe-C-Mo alloys by flame spraying. Special precautions were taken to produce dense layers, e.g. direct application of cryogenic gas on the coating during application.

EP-A-586 809 describes the metal spraying application of a layer of relatively homogeneous material (nickel coated silicon) which is much easier to handle than the heterogeneous oxide mixtures contemplated by the present invention. Layer thicknesses of up to 8 mm are described but 3 to 5 mm is preferred. Various layers are proposed including a Ni-Al layer for improving adhesion between the deposited layer and the substrate. A Ni-Al adhesion promoter is known from DE-A-33 18 828.

Plasma spraying of superconducting materials is described in EP-A-288711 up to a thickness of 250 micron.

It is an object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a ceramic coating on flat or curved substrates.

It is a further object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a thick walled ceramic coating on flat or curved substrates which is structurally sound.

It is a further object of the present invention to provide an apparatus and a method of spraying to form a thick walled coating of a superconducting ceramic material.

It is still a further object of the present invention to provide an apparatus and a method of spraying suitable for forming a thick walled ceramic coating on flat or curved targets to be used in a sputtering magnetron.

It is still another object of the present invention to provide a method of producing a (magnetron) vacuum sputtering target as well as the target itself with improved thermal and electrical conductivity and high mechanical strength using a spraying process employing dedicated powder formulations.

## SUMMARY OF THE INVENTION

One aspect of the present invention is to provide a substrate with a coating of a combination of metal oxides having a thickness greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. Preferably, the coating is deposited by spraying, e.g. flame or plasma spraying. Preferably, the substrate is cylindrical and is more preferably is suitable as a cylindrical target substrate for a sputtering magnetron. The combination of oxides preferably comprises at least a superconductive precursor or a superconductor. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity of the composite preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical resistivity of the deposited layer is lower than $15 \times 10^{-6}$ Ohm.m, more preferably lower than $10 \times 10^{-6}$ and most preferably less than $5 \times 10^{-6}$ Ohm.m. Values below $1 \times 10^{-6}$ Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

The electrical , thermal and mechanical properties of the coating deposited in accordance with the present invention should be sufficient that the deposited layer can be applied to a suitable substrate by means of a sputtering magnetron preferably at a static sputtering deposition speed of at least 5 nm/minute, more preferably, at 20 nm/minute and most preferably at at least 40 nm/minute.

When a superconductor precursor or a superconductive material is deposited, at least 10% of the coating is in the superconducting phase, more preferably 15%. This may be assisted by a subsequent limited thermal treatment, e.g. 3 hours and 940°C, after deposition.

The present invention also includes a method of depositing by spraying a superconductor precursor layer onto a cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase. The present invention also includes a method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

In accordance with one aspect of the present invention a flame spraying apparatus is provided for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a burner for producing a flame; an inlet for feeding material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm.

Another aspect of the present invention is to provide a flame spraying apparatus for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a flame spraying gun; and a cooling system for the substrate, the cooling system including a device for bringing a cryogenic fluid into contact with the substrate. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. The input material for the sprayer may be a liquid solution of soluble compounds (e.g. nitrates) which decompose thermally into ceramic component oxides, liquid slurries of the ceramic components or metal powders, or dry metal or ceramic powders or precursors of the ceramic components, e.g. nitrates, of such powders.

The present invention may provide a method of flame spraying a combination of metal oxide materials onto a substrate to produce a coating thereon, comprising: generating a flame; feeding the material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides.

The present invention may also provide a method of flame spraying metal oxide combinations onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the materials; and cooling the substrate by bringing a cryogenic fluid into contact with the substrate.

The present invention may also provide a method of flame spraying a superconducting ceramic material or a precursor thereof onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the ceramic material; depositing the coating on the substrate; and during deposition of the coating, cooling the substrate so that the solidified coating thereon has a temperature between room temperature (~25°C) and 150°C, preferably room temperature (~25°C) and 100°C. Water or cryogenic fluid cooling are particularly preferred.

One linking concept between the above methods and apparatus is control of the total heat energy into the spraying/coating system. This can be achieved by careful control of parameters which influence the energy input such as spraying distance, spray head traverse speed, rotation speed of a cylindrical substrate, powder dwell time in the hot exit plume from the spray head, particle velocity exiting the spray head, cooling method and rate of cooling the substrate during coating deposition.

The present invention also includes a method of reconditioning a target for a sputtering magnetron by flame spraying or atmospheric plasma spraying as well as a reconditioned target as made in accordance with the method. The target material or coating is preferably a ceramic coating, in particular a superconducting or superconductor precursor coating.

The final coating is preferably a metallic or ceramic layer, in particular a superconducting or piezo-electric layer or a precursor thereof. The present invention includes a method of spray drying a liquid to form a powder suitable for flame spraying. The spray dried powder may be sintered. The present invention also includes a manufacturing method for depositing a coating on a substrate comprising the steps of: spray drying a precursor liquid to form a powder and flame spraying the powder to form a coating on a substrate. The substrate may be a target for a sputtering magnetron and the final coating may sputtered onto a final substrate in the sputtering magnetron. The ceramic powder may be sintered after the spray drying step. The flame of the flame spray gun preferably imparts a temperature to the powder to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. During flame spraying the target is preferably cooled by bringing a cryogenic fluid into contact with the target. In particular the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The present invention includes an apparatus for spray drying a liquid to form a powder suitable for flame spraying. The present invention may also include an apparatus for depositing a coating on a substrate comprising: a spray drier for drying a precursor liquid to a powder, and a flame sprayer for flame spraying the powder to form a coating on a substrate. The substrate may be a target for a magnetron. Additionally, a sputtering magnetron for sputtering the final coating onto the final substrate using the target may be provided. The flame of the flame spray gun preferably imparts a temperature to the powder to be sprayed of slightly above the melting point of the sprayed material. Preferably the temperature imparted is 1500°C or less, preferably 1200°C or less. Temperatures of 600 to 850 °C may be suitable for some metal oxides. In the flame sprayer a cooling system for the target is preferably provided, the cooling system including a device for bringing a cryogenic fluid into contact with the target. In particular the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The above methods may be used, for example, either as part of the direct formation of superconductive or piezo-electric layers on the substrate, e.g. a tape, or for the production of coatings on targets for use in a sputtering magnetron to sputter a superconducting layer onto a final substrate. The present invention may provide oxide sputtering targets supporting very high power dissipation thus enabling high sputter deposition rates of at least 50 nm/min.

The dependent claims describe additional individual embodiments of the present invention. The present invention will now be described with reference to the following drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of a flame spraying apparatus in accordance with one embodiment of the present invention.

Fig. 2 is a schematic representation of a flame spraying apparatus in accordance with another embodiment of the present invention.

Fig. 3 is a schematic representation of a spray drying apparatus in accordance with another embodiment of the present invention.

## DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

The present invention will be described with reference to certain specific embodiments and with reference to certain specific drawings but the invention is not limited thereto but only by the claims. In particular, the present invention will mainly be described with reference to the deposition of a superconductor precursor or superconductive coatings but the invention is not limited thereto but may be used advantageously with other heterogeneous coatings such as ceramic coatings, particularly those having special properties such as piezo-electric coatings and in particular coatings which contain components which can be degraded by high temperatures or which are more volatile than other components. More particularly the present invention will be described with reference to the manufacture of $YBa_2Cu_3O_7$ superconducting powders and coatings but the invention is not limited thereto but only by the claims. Further one way of carrying out the present invention will be described with reference to low temperature flame spraying but the present invention is not limited thereto. By carrying out the invention in accordance with the processing details and principles described below thick layer (greater than 3 mm, more preferably greater than 5 mm and most preferably greater than 8 mm) metal oxide combination coatings suitable for use as a sputtering magnetron target have been applied by oxy-acetylene flame spraying with water cooling or by atmospheric pressure or low-pressure plasma spraying to substrates including cylindrical substrates used in rotating cathode magnetrons. During plasma spraying gasses may be used such as argon or mixtures of argon and other gasses to shield the plasma spray. Also the present invention will mainly be described with reference to an input to the flame spraying head of spray dried powder. The present invention is not limited thereto but includes other forms of input materials such as a mixture of the metal oxides, including slurries thereof or mixtures of precursors of metal oxides such as metal nitrates as well as slurries and solutions thereof.

Fig. 1 is a schematic diagram of the flame spraying apparatus 10 in accordance with a first embodiment of the present invention. A flame spraying gun is represented schematically at 12. The gun 12 may be a commercially available flame spraying gun as for instance available from Sulzer Metco, Westbury, NY, USA or a high velocity oxy-fuel spraying gun available from the same company. The gun 12 may be provided with an air pincher. The gun 12 may be fed with fuel gas in pipe 22, oxygen in pipe 23 and gun cooling air in pipe 24. Additional gases may be supplied to the gun 12 as described for instance in US 5,273,957 or EP-A-413 296. Material to be coated is fed in powder or liquid form, e.g. a dry powder, a slurry of the powder and a liquid or in solution, to the gun via conduit 26 from hopper 21. Gun 12 is mounted on a drive (not shown) which provides the necessary movements of the gun 12 to coat the substrate 19. When substrate 19 is a cylindrical target, for instance, for a rotating cathode magnetron, this may be rotated and the movements of the gun 12 may be simple reciprocating movements parallel to the axis of the target 19. If the substrate 19 is a flat rectangular or circular plate, the movements may be provided by a suitable robot and may be complex, e.g. including rotational cycloidal motions. For rapid deposition several guns 12 may spray the same substrate 19 at the same time.

The fuel gas for the gun 12 may be selected from one of acetylene, propylene, hydrogen or similar fuels but the present invention is not necessarily limited thereto. Particularly preferred in one embodiment of the present invention is a fuel with a lower calorific value such as one of ethylene, natural or town gas, butane or propane as these provide a lower temperature flame than acetylene and butane is particularly preferred as it gives a stable easily controllable flame and is considered safer than acetylene if powders containing copper compounds are used. It is generally accepted that oxy-acetylene flames have temperatures of 2000 °C and more. It is preferred in accordance with an embodiment of the present invention if the flame of the flame spraying gun 12 imparts a temperature only sufficient to just melt the powder to be sprayed. Temperatures of 1500 °C or less and preferably 1200 °C or less are preferred and temperatures between 600 and 1000 °C may be more preferable. These low flame temperatures minimise decomposition of the ceramic powder components during flame spraying. Moreover, they limit the impact of evaporation of the materials to be flame sprayed and allow a deposition efficiency of more than 80%, i.e. more than 80% of the solid mass originally introduced into the gun 12, becomes attached to the substrate 19. Mechanically stable, scratch resistant flame sprayed coatings are produced with these low temperatures.

The gun 12 is preferably held at 7 to 15 cm from the substrate 19 to be coated but this depends upon the size of the flame. Similar coatings have been obtained using both oxy-acetylene flame spraying and plasma spraying. Attention must be paid to the energy taken up by the sprayed particles during the spraying and the transfer of this energy to the substrate. Intensive cooling of the substrate is preferred which may be on the side of the substrate remote from the deposited layer and/or on the same side. By altering the velocity of the particles in the flame or plasma the dwell time therein may be altered, thus limiting the energy uptake by the particles.

The material of substrate 19 preferably has a high melt temperature and a high thermal conductivity and when the substrate 19 is to be used as a target for a sputtering magnetron a good electrical conductivity is preferable. It is also preferred if the thermal expansion of the substrate material is similar to that of the ceramic coating to be applied. In accordance with embodiments of the present invention low temperature flame spraying and/or intense cooling of the substrate 19 allows the use of substrates 19 with a thermal expansion coefficient up to at least twice or down to at least a half of the thermal expansion coefficient of the ceramic coating. A non-limiting list of suitable materials may be steel, iron, stainless steel, copper or copper alloys, however the low temperature flame spraying process in accordance with the present invention, either independently or in combination with intense cryogenic cooling of the substrate 19, allows other materials to be used such as paper, cardboard or polymeric materials. Preferably, the substrate 19 should be free of grease and dry before deposition. Preferably, the outer surface of metals is sand blasted and then lapped with abrasive materials. Buffer layers between the substrate and the sprayed coating may be used such as Ni-Al or an In-alloy. These may be applied by flame or plasma spraying before application of the metal oxide coating. .

Where the substrate 19 is rigid it may be mounted in a suitable jig. For example, a cylindrical substrate 19 is preferably mounted in a rotating device such as a lathe. The substrate 19 may be held by rotatable chucks at each end thereof. The temperature of the solidified flame sprayed coating 40 on the surface of the substrate 19 is preferably measured by a temperature sensor 13, 15. The sensor head 13 is preferably a remote sensing optical head which is not in contact with the surface 40 of the flame sprayed coating. The temperature to be measured is of the solidified coating 40 and not that of the coating immediately on impacting the substrate 19 which may have a higher temperature. Hence, the temperature sensor 13 is preferably mounted so that it lags behind the impact position of the flame sprayed materials a little. In addition a temperature sensor 31 may be provided inside the substrate 19 for further control of the deposition process. Control of deposition temperature is an important aspect of the present invention. Control of temperature affects the amount of thermal stress in the coating, a low stress reducing the possibility of cracks forming in the coating.

In accordance with one embodiment of the present invention a means for intense cooling of the substrate 19 is provided. This is preferably a cryogenic cooler comprising a supply 16 of cryogenic fluid and a delivery system 11, 14, 17, 29, 30. The delivery system may be adapted to the form of the substrate 19. For example, for a cylindrical substrate 19 the cooling device may be a conduit 17 for supplying the cryogenic fluid to a control valve 11, a conduit 30 with regularly spaced holes 29 for distribution of the cryogenic fluid inside the substrate 19 and a control device 14 for receiving the output of the temperature sensor 13, 15 and for controlling the operation of the control valve 11 so as to maintain the surface temperature of the solidified coating 40 to within a certain range. Particularly preferred is a temperature range from room temperature (25 to 30°C) to 150 °C and more preferably room temperature to 100 °C. These low temperatures avoid thermal stresses between the coating 40 and the substrate 19 providing a good bond and good coating density, hardness and scratch resistance thus helping to ensure the long term stability of such a coating. Using a cryogenic fluid such as liquid nitrogen (77 °K) is quite advantageous and economical as it does not require the complication of perfectly sealed rotating inlets and outlets to the substrate 19 when water or other liquid coolants are used. Additionally, cryogenic fluids such as liquid nitrogen produce large temperature gradients, thus increasing the thermal sink-effect. Other liquid coolants such as water are not excluded from the present invention.

The cylindrical substrate 19 may be sealed by a seal 26 at one end and with a rotating seal 28 at the other. The seal 28 may be provided with a sealed feedthrough 27 for the supply of cryogenic fluid. If water cooling is used, rotating seals at both ends of the cylindrical substrate are considered very important to prevent escape of water vapour into the deposition environment. In accordance with an embodiment of the present invention it is preferred if the ends 26, 27 allow escape of a cryogenic fluid which then forms a shield gas around substrate 19 during the spraying process. Particularly preferred cryogenic fluids are liquid nitrogen, liquid oxygen and liquid air. With some complex ceramic materials, one or more components may be reduced in the spraying process. For such materials it may be advantageous to use a shield gas including oxygen, e.g. liquid air or liquid oxygen, which may help to reoxidise the reduced component. On the other hand with other complex ceramics it may be advantageous to reduce the contact time with oxygen at high temperatures, under which conditions liquid nitrogen would be preferred, or a reducing gas may be included such as hydrogen. It is preferable to control the atmosphere in the vicinity of the substrate 19 during coating deposition to prevent the presence of excessive water vapour and in particular to prevent condensation of water on the substrate 19. This may be achieved by generally air conditioning the air around the substrate 19 to reduce its dew point.

It is preferred if the deposition rate is selected in order to maintain the substrate surface temperatures mentioned above. Assuming the cylindrical substrate as shown in Fig. 1, the rotation speed of the substrate 19, the linear speed of the gun 12 and the rate of material exiting the gun 12 may be controlled to achieve the temperatures specified above. For instance, it has been found that when using cylindrical substrates made of stainless steel of 15 cm diameter and up to 40 cm long, a powder delivery of 5-10 g/min was suitable to produce 3 -10 mm coatings when depositing a $YBa_2Cu_3O_7$ layer. The rotational speed of the substrate 19 may be in the range 10 to 100 RPM with a surface speed in the range 1 to 40 m/min and the longitudinal feed of the gun 12 in the range 1-3 m/min, typically 2 m/min. The deposition rate per reciprocating pass of the gun 12 may be 10 to 50 micron thickness of the coating. About 10% to 15% of the deposited coating had maintained the lattice structure of the powder and exhibited superconducting properties. It will be appreciated by the skilled person that increasing the deposition speed, deposition thickness per pass or the flame temperature or reducing the thermal conductivity of the substrate material will increase the thermal load on the cooling system and adjustments of one or more of these parameters may be necessary to obtain satisfactory coatings. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical resistivity of the deposited layer is lower than $15 \times 10^{-6}$ Ohm.m, more preferably lower than $10 \times 10^{-6}$ and most preferably less than $5 \times 10^{-6}$ Ohm.m. Values below $1 \times 10^{-6}$ Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

Fig. 2 is a schematic representation of a further embodiment of the flame spraying process and apparatus in accordance with the present invention. Components in Fig. 2 with the same reference numbers as in Fig. 1 refer to equivalent items. The substrate 19 in accordance with this embodiment is a foil or sheet of metal, plastic or other flexible material which is wound from a pay-off spool 32 to a take-up spool 36. Where the final coating 40 cannot be spooled, the foil with coating 14 may be drawn linearly from the pay-off spool 32 and cut into lengths. The coating 40, which may be a superconducting layer, is flame sprayed with a flame spray gun 12 similar to the one described with respect to Fig. 1. In particular it is preferable to use a fuel with a lower calorific value than acetylene such as natural or town gas, butane or propane. Preferably, the temperature of the flame of the gun 12 imparts a temperature of 1500 °C or less, more preferably 1200 °C or less to the material being sprayed through the flame. This material may be in the form of powder either of finished components of the coating 40, e.g. oxides, or precursors thereof, e.g. nitrates, or may be in the form of a slurry of powders, e.g. oxides, or a solution, e.g. of nitrates. Gun 12 may be controlled by hand or more preferably by a robot to provide zigzag motions across the width of foil 19 thus applying an even coating 40. Preferably a layer of 10 to 50 micron thickness is applied in each pass.

The temperature of the coating 40 may be monitored by one or more optical sensors 13, 15. The temperature of the foil 19 is regulated by means of a cryogenic fluid supplied from a container 16 to a series of holes or jets 29 via conduit 17, a controllable valve 11 and a conduit 30. The valve 11 is controlled by a controller 14 to maintain the temperature of the foil as determined by the sensor 13, 15 to less than 400 °C, preferably less than 150 °C and most preferably between 50 and 100 °C. Such low temperatures allow a wide range of materials for substrate 19 including polymeric materials, cellulosic materials as well as metals. Although only one controller 14 is shown the present invention includes several controllers each with its own controllable cryogenic cooling device 11, 29, 30 for individually controlling the temperature of different parts of the foil 19 or coating 40. Optionally, an optical encoder 34 may be attached to a roller 35. The optical encoder may be read with an optical sensor 37, 38, the pulse frequency generated in the sensor 37, 38 being proportional to the linear speed of the foil 19. This value may also be used by the controller 14 to control the complete process to maintain the temperatures and coating thicknesses mentioned above.

When producing superconducting coatings 40, it is preferred if there is no condensation of water onto the coating 40 nor onto the foil 19 so it is preferred if the atmosphere around the deposition equipment is air conditioned to reduce the dew point to below ambient temperature. Preferably the coated substrates in accordance with this invention are preferably stored for long periods in a plastic bag filled with a dry inert gas such as dry nitrogen. One aspect of the present invention is the flame spraying of powders which already have superconducting properties in the powder form. Using the methods in accordance with the present invention it is possible to flame spray such coatings and retain 10% to 15% of superconducting property of the coating 40 produced without extensive post-heat treatments.

The superconducting and/or ceramic powder and/or metallic powder to be used for flame spraying is preferably homogeneous, exhibits the appropriate rheological properties and correct stoichiometry to generate the required properties in the final coating. Typical preferred densities for superconducting powders may lie in the range 4 to 5 g/cm$^3$. A non-limiting list of suitable materials which may be flame sprayed as powders, slurries or liquid solutions in accordance with the present invention are: superconducting materials such as $R_1Ba_2Cu_3O_y$ where R is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu; or $Bi_{2-x}Pb_xSr_2Ca_{n-1}Cu_nO_y$, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$; or $Ba_2Ca_{n-1}O_{2n+2}$, or $CaBa_2Ca_{n-1}Cu_nO_{2n+\delta}$; or cuprate high temperature superconductors of the general formula $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ where A, E, R are selected from various cations such as A= Bi, Tl, Hg, Pb, Cu or a lanthanide element, E = Ba or Sr and R = Ca or rare earth element; or piezo-electric ceramics, for example, with the general formula $M(Zr_xTi_{1-x})O_3$ where M = Pb, Ba or Sr; or refractory ceramic oxides, nitrides, carbides or phosphates, e.g. $Al_2O_3$, MgO, $Zr_xO_y$; or metals and their alloys.

In accordance with a further embodiment of the present invention a method is provided for production of suitable ceramic powders. By starting from aqueous solutions containing the salts of the metals in the correct proportions a reactive precursor powder can be obtained using commercially available spray drying equipment in batches of kilograms. The type of salt (mostly nitrates) should preferably be compatible with thermal decomposition to oxides in further processes such as sintering or flame spraying. In accordance with the present invention spray dried nitrate powders may be flame sprayed directly or the powders may first be sintered and then flame sprayed.

A spray drying system 50 in accordance with an embodiment of the present invention for the delivery of powder suitable for subsequent flame spraying is shown schematically in Fig. 3. The input liquid is drawn from a suitable source 53 via a peristaltic pump 54 to a spray head 71. Pressurised air 51 is drawn in through an air dryer and optional pre-heater 52 to the spray head 71 by a suction device such as a fan 63 at the end of the generally closed system. The liquid from source 53 enters the spray head 71 which is cooled by any suitable means 55 to prevent clogging due to early evaporation of the liquid. The liquid is atomised in a co-current two fluid nozzle 71 by the dry pressurised air 51 and discharged it into a chamber 56 where it dries to a powder. The liquid from source 53 may be a solution of suitable nitrates or a slurry of the relevant oxides with the addition of other agents such as binders.

Air 65 is drawn in by fan 63 over a heater 64 and introduced into chamber 56 via a ring orifice 72 which surrounds the outlet of the spray head 71. The air 65 also heats the spray head 71. The circumferential air flow 65 guides the evaporating liquid in chamber 56 and helps to prevent the powder sticking to the walls of the chamber 56. The air throughput of fan 63 is chosen so that powder of the correct grain size is swept from chamber 36 through an optional heater section 58 into a powder collector 59. Heavier particles settle out in trap 57 and are removed from the bottom of chamber 56.

The powder collector 59 may be any suitable device such as a cyclone, a bag filter or an electrostatic filter although a cyclone is preferred. The cyclone discharges the powder into a removable container 60 sealed to the bottom of the cyclone 59. Spent air is removed via the trap 61 and scrubbed in scrubber 12 to remove impurities. The final clean air is exhausted to atmosphere by the fan 63 which controls air flow through the system.

The control system 66 - 70 for the process functions as follows. The rotational speed of the centrifugal air pump 53, the temperature of the heating element 64 and the flow of the atomised air are set with controller 67, 70. Air flow is measured by gauge 68. The temperature of the hot air 65 and the air in the tube leading from the chamber 56 to the optional heater 58 is monitored using thermocouples 66, whereas final powder temperature is monitored by temperature sensor 69.

After spray drying, the powder may be sintered in a single step. For example, to produce a superconducting powder of the general formula $YBa_2Cu_3O_7$ with optional Ag, the required nitrates are dissolved in water in the correct stoichiometric proportions and spray dried as indicated above. The nitrates are then reduced to oxides by sintering at 920 - 960 °C for 40 to 60 hours. Optionally the nitrates may first be reduced by heating in air at 780 °C for 10 hours before sintering at the above temperatures and times. The $YBa_2Cu_3O_7$ powder produced by this procedure is superconducting. On aspect of the present invention is to produce powders with superconducting properties by spray drying and optional sintering and then to flame spray these superconductive powders at the lowest flame temperatures necessary to obtain melting of the powder and coating formation on the substrate while cooling the coating in the fastest possible way. By this procedure the crystal structure present in the superconducting powder is disturbed as little as possible by the flame spraying process. Of course, melting the powder during flame spraying causes complete loss of crystal organisation if the time in the melt is long. By lowering the flame temperature and shortening the time in the melt phase by cooling the coating very rapidly in accordance with the present invention, some local crystal organisation is kept in the final flame sprayed coating, e.g. about 10% of the final coating is in the superconducting phase, thus providing a coating on the substrate with an optimum starting condition for further heat processing to develop full superconducting properties. The addition of the metallic silver enhances the thermal and mechanical properties in later flame spraying and magnetron sputtering.

Alternatively, the powder for flame spraying may be spray dried from slurries of the relevant oxides in the correct stoichiometric proportions with the optional addition of silver in the above apparatus in accordance with the present invention. For instance, in the manufacture of a ceramic material the mixture of oxides may be produced by individually sieving them to 40 micron and then mixing in the correct proportions to obtain the stoichiometric proportions in the final coating. A quantity of deionised water is added of about 60% by weight of the powder as well as a quantity of an organic binder such as PVA (polyvinyl acetate) equal to about 2% by weight of the powder and then mixed into a slurry. The slurry is then spray dried as described above resulting in powder with a grain size from 30 to 50 micron. Generally, spray dried oxide slurries do not require sintering before flame spraying. The organic binder may be burnt out during flame spraying or in a special sintering step.

Spray drying of 10% by weight nitrate solutions generally produce grain sizes of 3 micron on average with at least 90% of the grains between 0.5 and 5 microns. In order to obtain the required grain size it is preferable to sinter as mentioned above. Light grinding and sieving of this sintered powder may produce a mass fraction of more than 80% with grain sizes between 40 and 80 micron. By the variation of appropriate concentrations of the solution of the aqueous media 53, and/or the addition of binders and/or the spray drying of slurries rather than solutions, allows control of the grain size in the final powder to between 2 and 100 microns. For example, the present invention includes the addition of organic binders such as polyvinyl acetate (PVA) to the liquid to be spray dried to control grain size in the final powder. Such binders may be burnt out in a later high temperature process such as sintering. An average grain size of 40 to 80 microns is preferred for good flame spray deposition. The final powder may be lightly milled and sieved to be improve the homogeneity of grain sizes.

One aspect of the present invention is the inclusion of silver metal in the final superconducting ceramic coating. This is achieved as mentioned above by inclusion of about 20% to 30% by weight of the ceramic materials of silver nitrate when nitrate solutions are spray dried and the flame sprayed or by addition of

$Ag_2O$ powder in an oxide slurry which is then spray dried and flame sprayed. The addition of silver in the flame sprayed material is beneficial for the inter-grain adhesion and heat dispersal during flame spraying thus yielding a strong and dense coating. The silver improves the thermal and electrical conductivity of the flame sprayed coating which is beneficial to the sputtering process when the substrate is used as a sputtering target. The improved conductivities allow higher power throughput for the magnetron than targets not containing silver.

The flame spraying process in accordance with the present invention allows the reconditioning of targets for sputtering magnetrons. It is well known that the presence of a static race-track plasma on a magnetron target during sputtering results in an erosion groove and poor target utilisation. Using the flame spraying process of the present invention such a worn target may be reconditioned by spraying the appropriate target material into the erosion groove and building up the target to its former thickness in these regions. By providing the intensive cryogenic cooling described above, the general target temperature may be kept below 400 °C, preferably below 150°C and most preferably between room temperature (~25°C) and 100°C. These low temperatures result in little damage to the existing target material while still providing a mechanically strong coating in the old erosion grooves. Such as process is particularly economic when the target material is expensive such as superconducting materials. The flame spraying gun 12 described above may be hand held and the contour of the erosion groove in the used target followed building up the lost material slowly, preferably 10 to 50 micron per pass. Preferably the gun 12 is controlled by a robot which is programmed to execute the correct motions with the gun 12 to fill up the erosion groove in the target.

While the invention has been shown and described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention as defined in the attached claims.

## CLAIMS

1. A composite comprising: a substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 5 mm, more preferably greater than 8mm, the coating comprising metal oxides.

2. The composite according to claim 1, wherein the coating comprises a superconductor precursor and at least 10% of the coating is in a superconductive phase

3. The composite according to claim 1 or 2, wherein the composite is a target for a sputtering magnetron.

4. The composite according to claim 3, wherein the target is cylindrical.

5. The target for a sputtering magnetron comprising: a cylindrical substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 3mm, more preferably at least 5 mm, most preferably greater than 8mm, the coating comprising a superconductor precursor and at least 10% of the coating is in a superconductive phase.

6. The target or a composite in accordance with any previous claim, wherein the coating has a thermal conductivity of between 1 and 5 $Wm^{-1}K^{-1}$.

7. The target or a composite in accordance with any previous claim, wherein the thermal conductivity of the composite or the target through the substrate and the coating is in the range 25 to 125 $Wm^{-1}K^{-1}$.

8. The target or a composite in accordance with any previous claim, wherein the coating has an electrical resistivity of lower than 15 x $10^{-6}$ Ohm.m, more preferably lower than 10 x $10^{-6}$ and most preferably less than 5 x $10^{-6}$ Ohm.m.

9. The target or a composite in accordance with any previous claim, wherein the coating can withstand impact of a 0.036 kg steel ball from a height of 1 metre, preferably from 1.5 metre.

10. The target or a composite in accordance with any previous claim, wherein the spraying is one of plasma spraying and flame spraying.

11. A method of depositing by spraying a superconductor precursor layer onto a cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase.

12. A method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

13. The method according to claim 11 or 12, wherein the spraying step is one of flame spraying and low-pressure or atmospheric pressure plasma spraying.

14. The method according to claim 13, wherein the spraying step includes spraying a material through a spraying head, the material being in the form of a powder, a slurry or a solution.

15. A method of reconditioning a used target for a sputtering magnetron having an erosion groove in the target material, comprising the step of: flame or atmospheric pressure plasma spraying target material into the erosion groove.

16. A reconditioned target for a sputtering magnetron, comprising:
an erosion groove in the target material; and target material flame sprayed or atmospheric plasma sprayed into said groove to restore the thickness of the target material to that of the unused material.

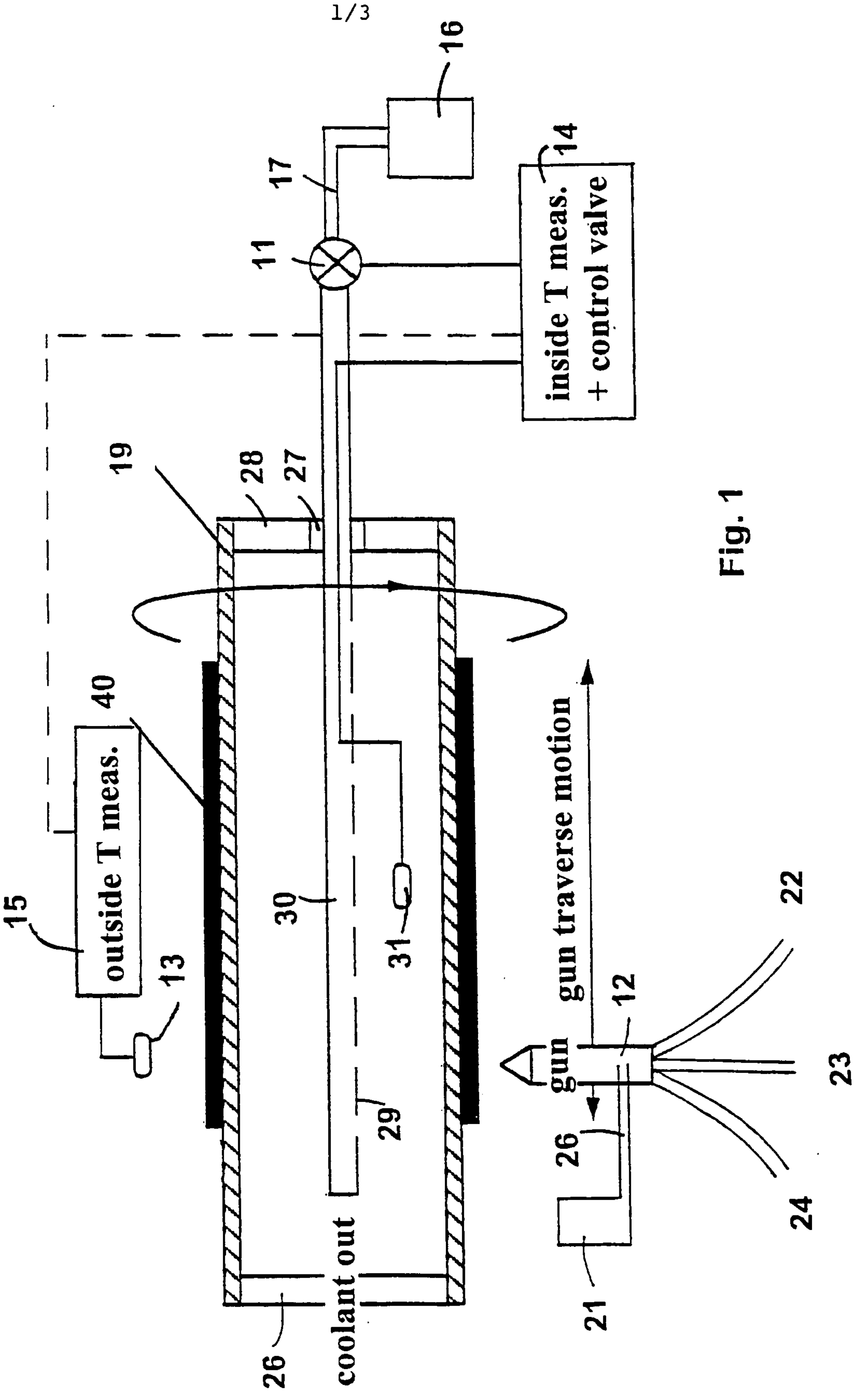
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Fig. 1

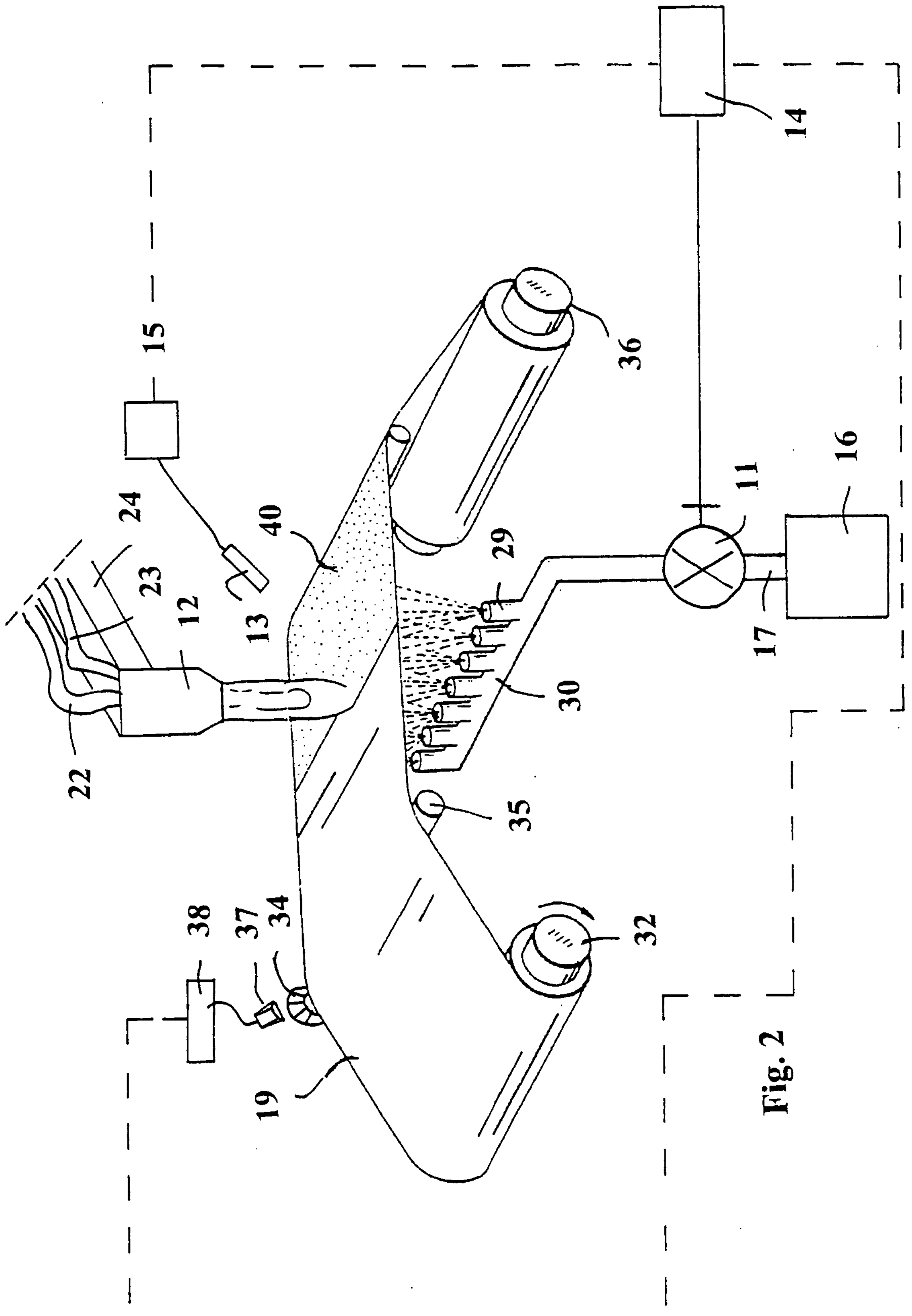

Fig. 2

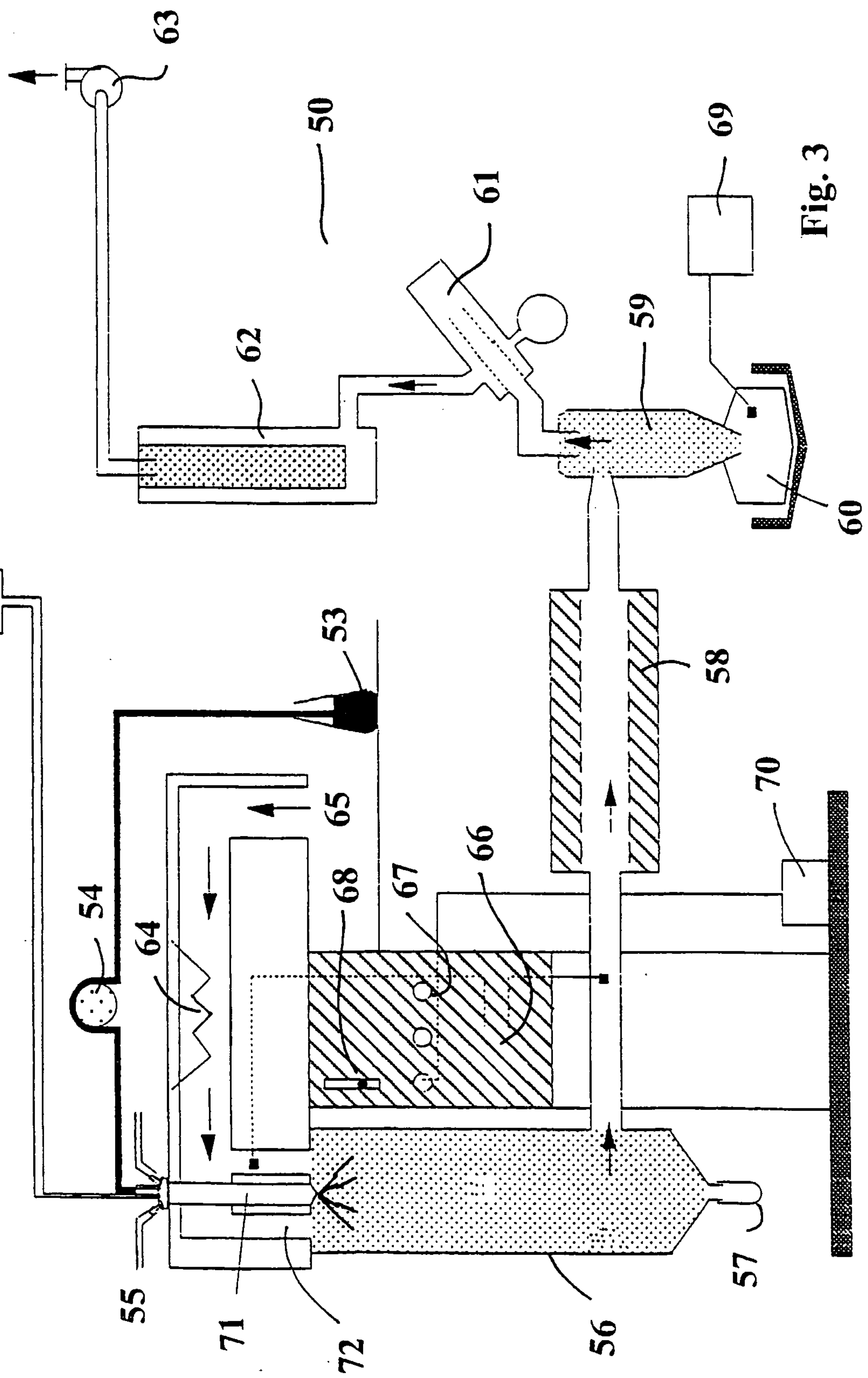

Fig. 3

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03599

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 C23C4/10 C23C4/12 C23C14/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 5 196 400 A (CHEN CHIOU T ET AL)<br>23 March 1993 (1993-03-23)<br>cited in the application<br>column 3, line 52 - column 4, line 16<br>--- | 1-5,<br>10-14 |
| X | EP 0 330 196 A (PERKIN ELMER CORP)<br>30 August 1989 (1989-08-30)<br>page 5, line 20 - line 25; claims 1,8<br>--- | 1,2,10,<br>12-14 |
| X | CH 648 358 A (CASTOLIN SA)<br>15 March 1985 (1985-03-15)<br>claim 1<br>--- | 1,10,<br>12-14 |
| X | DD 277 471 A (MANSFELD KOMBINAT W PIECK VEB) 4 April 1990 (1990-04-04)<br>page 2, line 21 - line 23<br>---<br>-/-- | 15,16 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>9 September 1999 | Date of mailing of the international search report<br>16/09/1999 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Patterson, A |

2

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03599

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DE 40 15 387 A (LEYBOLD AG)<br>21 November 1991 (1991-11-21)<br>the whole document<br>--- | 15,16 |
| A | EP 0 377 073 A (MITSUBISHI METAL CORP)<br>11 July 1990 (1990-07-11)<br>page 3, line 41 - line 57; table 2<br>page 7, line 7 - line 23; table 4<br>----- | 5-8 |

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

ernational application No.
PCT/EP 99/03599

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 9
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
SEE FURTHER INFORMATION SHEET

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

SEE FURTHER INFORMATION SHEET

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99/03599

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8,10-14

Claims for a composite comprising an oxide-containing coating deposited by spraying and having a certain minimum thickness, a sputter target having a layer of a superconductor precursor, also deposited by spraying and having a minimum thickness, and methods for producing each of these products, respectively.

2. Claims: 15,16

Reconditioned sputter target and method for its manufacture by flame or plasma spraying material into the sputtered erosion groove.

The only common concept linking subjects 1 and 2 is the application of spraying for depositing layers of material. Since this feature is known from many prior art documents (see for example search report) there is effectively no common concept to connect the two groups of claims. Furthermore, while subject 1 addresses the problem of producing relatively thick deposits of oxides by means of spraying, subject 2 solves the unrelated problem of spraying an unspecified material to repair local damage on a target.

Therefore there is a lack of unity between the two subjects.

Nevertheless, since the EPO has already searched the subject-matter of claims 15 and 16 in connection with the priority application EP98870120, an International search report is issued for both subjects.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99 /03599

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 9

Claim 9 relates to a product defined (inter alia) by reference to the following parameter:
the result of a test involving impact of a ball consisting of an unspecified steel, wherein both the weight of the ball and the height from which it is dropped are arbitrarily chosen.
The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the remaining claims

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03599

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TO:Mr. Gary Edwards COMPANY:

PTO 06-6046 German Patent No. DE 37 38 738 C1

# POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. AUGUST 2006
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GERMAN PATENT OFFICE
PATENT NO. DE 37 38 738 C1
(Patentschrift)

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| Int. Cl.$^4$: | B 22 F 7/00<br>H 01 L 21/203 |
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| Filing Date: | November 14, 1987 |
| Publication Date of Patent Grant: | January 26, 1989 |

# POWDER-METALLURGICAL PROCESS FOR THE PREPARATION OF TARGETS

[Pulvermetallurgisches Verfahren zur Herstellung von Targets]

| | |
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| Inventors: | Dr. Stephan Schittny et al. |
| Patent Holder: | Degussa AG |
| Publications Taken in Consideration For Judging Patentability: | DE 35 37 191 A1 |

## Claims

1. Process for the preparation of highly pure mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum, characterized in that the rare earths are inserted with the corresponding transition metals in the form of master alloys.

2. The process of Claim 1, characterized in that master alloys having a eutectic composition are inserted.

## Description

The invention pertains to a process for the preparation of highly pure, mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum

Targets are required in installations for cathode evaporation and for the vaporization of objects. With the aid of cathode evaporation (sputtering) and vaporization, a thin layer can be produced on a substrate, the applications for which span from functional layers in electronics and data systems engineering through corrosion-protective layers and anti-abrasion layers to optical layers for decorative and thermic purposes.

In cathode evaporation, an electrical gas discharge occurs between cathode (target) and counter electrode, during which impacting ions eject particles of atomic size from the target, which condense on substrates arranged in the area of the counter electrode.

Either inert gases such as argon or helium, or reactive gases, such as oxygen, nitrogen or acetylene are put in at low pressure as a gas discharge atmosphere.

In inert gas sputtering, the target commonly is composed of the material of which the layer to be formed shall be composed, while in reactive sputtering, ejected target particles react with the reaction gas and are condensed as a layer in the form of a reaction product.

In the vaporization process, the target material is thermally vaporized in a vacuum by means of electron beam heating or resistance heating and deposited as a thin layer on the substrate.

Targets commonly can be prepared using melting technology with corresponding secondary processing by means of non-cutting and tensioning processes or with powder metallurgy, by means of compressing and sintering corresponding powders or powder mixtures.

For target materials, which owing to their composition contain higher portions of brittle phases, preparation processes using melting technology prove to be problematic, since such targets when cooling after casting exhibit fissures owing to thermal stress and can crumble into pieces. In addition, such materials cannot for the most part be mechanically machined, such that certain desirable target geometries cannot be prepared.

Powder-metallurgical processes exhibit problems with those target materials containing higher portions of reaction-sensitive components and that react, e.g., with atmospheric oxygen. Due to the large specific surface area of the powder and the resulting reactivity, high-value target qualities having low oxygen content cannot be produced using powder metallurgy.

In addition, products prepared using powder metallurgy for the most part exhibit a partially open residual porosity, which is intolerable for oxygen sensitive target materials due to the potential oxidation of the entire target.

These preparation difficulties appear particularly for targets containing a predominance of rare earths and transition metals.

A powder-metallurgical process for the preparation of targets of rare earths and the transition metals iron, cobalt and nickel is known from DE-OS 35 37 191, for which a powder mixture of rare earths and the aforementioned transition metals is subjected to hot forming under decreased pressure and under inert gas at temperatures below the eutectic point, with a brittle intermetallic compound developing at the boundary between the rare earth metal and the transition metal. This process has the disadvantage that hot forming must be carried out expensively for a minimum of at least two hours, by means of which noticeable quantities of brittle intermetallic phases are formed, that powder preparation for rare earths is associated with difficulties and that the oxygen content in the powder of rare earths is still relatively high.

It was thus the problem of the present invention to develop a process for the preparation of highly pure, mechanically stable and dense targets of rare earths and the transition metals iron, cobalt and/or nickel for cathode evaporation and vaporization installations by means of the action of pressure and temperature on a corresponding powder mixture in an inert-gas atmosphere or under vacuum that without great technical expense supplies a product containing limited portions of and a fine distribution of brittle phases and as little oxygen as possible.

This problem is solved in accordance with the invention by means of the fact that the rare earths are inserted with the corresponding transition metals in the form of master alloys.

Preferably, master alloys having a eutectic composition are inserted.

Reaction sensitive rare earths are processed into powders and/or shavings not as such, but as master alloys of rare earths and the corresponding transition metals, which in comparison to pure components feature lower melting points, are well intermixed with powders and/or shavings of the transition metals and are compacted into targets. The compacting of said mixture can be carried out by means of sintering, hot-rolling, hot-pressing, hot-forging, high-temperature isostatic pressing or combinations thereof in a vacuum or under inert gas.

The conditions for compacting (temperature, pressure, time, degree of defurmation) are selected such that a mechanically stable compound material emerges, the grain structure of which, as a non-equilibrium state, features only limited portions of brittle equilibrium phases formed by means of diffusion at the boundaries of the rare earth phases and the transition metal phases. Through the use of master alloys between rare earths and transition metals, relatively low compacting temperatures and brief compacting times can be selected. This leads to a decreased technical expense and to a limited formation of diffusion zones of brittle non-equilibrium phases at the contact locations of the powder grains and in the grains.

Surprisingly, it has been shown that fundamentally simpler, highly pure and low-oxygen powders or shavings can be prepared out of master alloys of rare earths with corresponding transition metals rather than out of pure rare earths. These master alloys may be used to produce shavings and powders, e.g., by means of machining, such as milling or filing under protective gas, which is not possible without difficulty with pure rare earth metals, owing to their ductility, even with subsequent grinding. During the comminution process, the brittle phase portions of the most extremely fine grain structure of master alloys causes the formation of particles having a suitable grain shape and grain size distribution, enabling a powder preparation having a good yield and very low oxygen content (< 500 ppm).

Likewise in powder preparation by means of inert gas atomization, lower values of impurities and more limited oxygen content in the powder are achieved from lower melting master alloys owing to lower reaction rates with the crucible material and with the atmosphere at lower process temperatures and owing to the briefer residence time in the installation. Moreover, the atomization parameters (superheating, cooling rates, process gas pressure, etc.) can be optimized to a wide degree, such that the powder yield and the grain fraction can be adjusted more favorably in comparison to atomization of pure rare earths.

Surprisingly, the use of master alloys of rare earths and transition metals leads to compacting times considerably briefer in comparison to those with the use of pure rare earths, signifying a significant economic advantage of this process.

As a rule, compacting times are less than one hour and, more often than not, less than 30 minutes. Apart from this, targets prepared in accordance with the invention exhibit more favorable mechanical and magnetic properties in comparison to targets produced with powder metallurgy from pure metals. As has been shown, this is based on an advantageous distribution of portions present in the grain structure of free iron, cobalt and/or nickel, on the limited quantities of intermetallic phases and on the residual eutectic originating from the master alloys.

The following examples shall explain the process in accordance with the invention in greater detail:

1) In order to prepare highly pure, compact, mechanically stable sputter targets, first a master alloy of 80 atom% terbium and 20 atom% iron is prepared in a vacuum induction oven ($10^{-5}$ Pa). Subsequent pulverization and further processing is carried out exclusively under argon protective gas. With the aid of a wave-milling cutter, the ingot is machined to a coarse powder. A terbium-iron powder having an average grain size ≤ 105 μm and having a yield of 70-80% is obtained by means of subsequent grinding in a ball mill. The desired target composition of, e.g., 67 atom% iron, 25 atom% terbium and 8 atom% cobalt is regulated by means of a 20 minute mixing of the corresponding iron, cobalt and master alloy powder quantities in an asymmetric moved mixer.

The processes of high-temperature isostatic pressing (HIP), hot-rolling and hot-forging in a capsule were employed in order to compact the powder mixture into targets.

For high-temperature isostatic pressing, process parameters of 820°C final temperature, 200 Mpa pressure and 20 minute residence time at the final temperature were selected. Sheet steel cans were used as containers, which prior to being brought into the installation were evacuated at 300°C for over 3 hours. This produces mechanically stable, machinable molding bodies featuring a non-equilibrium grain structure of iron grains, zones of intermetallic phases and residual eutectic. The density is > 99% of the theoretical density, the oxygen content less than 1200 ppm. Longer residence times of, e. g., 1-2 hours at 820°C result in a wide reaching formation of large-surface zones of the intermetallic equilibrium phases, which causes an undesirable brittleness of the grain structure. It is for this reason that residence times as brief as possible are to be observed.

For compacting by means of hot-rolling, the powder mixture is filled in a sheet iron capsule, which is evacuated and welded shut. Conversion occurs at 650°C up to a degree of conversion of approximately 60% in several passes in a period of few minutes. After removal of the capsule material, a stable, highly pure target is yielded having a density of ≈ 99% of the theoretical density and an oxygen content of 1200 ppm The grain structure is of a form similar to that for compacting by means of high-temperature isostatic pressing.

For hot-forging, the powder mixture likewise is filled in a sheet steel can and evacuated. The forging process can be carried out at 800°C in a 200 ton forge. The achievable density is, at 60% conversion ≈ 99% of the theoretical density.

2. A different type of powder preparation is atomization of a melt in an inert-gas flow. For the use of low-melting point master alloys of the composition 66 atom% gadolinium, 18 atom% iron and 16 atom% cobalt having a melting temperature of approximately 620°C, an atomizing temperature of 700-800°C can be selected. This comparatively very low atomizing temperature enables, for extremely reactive rare earth materials, the preparation of low-oxygen, very pure master alloy powders, since the reaction of the melt with the crucible material and with the atmosphere is comparatively limited. Moreover, the master alloy melt exhibits a favorable viscosity and surface tension at these temperatures, such that the atomized powder features good yields of e.g., 80-90% at a grain size ≤ 88 μm. With the aid of the mixing and compacting processes described in Example 1, highly pure, compact, stable molding bodies having oxygen contents < 1000 ppm likewise are obtained. The non-equilibrium grain structures in turn are composed of iron grains, zones of intermetallic phases and residual eutectic.

Since the intermetallic phases are present in a fine distribution in the master alloys, and the grain structure is not very brittle, the blend portion of free iron can be reduced in comparison with the intermetallic phases by varying the composition of the master alloys, The magnetic properties of the targets, which are important for magnetron sputtering, can be improved by said means.

⑲ BUNDESREPUBLIK
DEUTSCHLAND

DEUTSCHES
PATENTAMT

⑫ **Patentschrift**
⑪ **DE 37 38 738 C1**

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DE 3738738 C1

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(56) Für die Beurteilung der Patentfähigkeit
in Betracht gezogene Druckschriften:
DE 35 37 191 A1

# (54) Pulvermetallurgisches Verfahren zur Herstellung von Targets

Zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets aus seltenen Erden und den Übergangsmetallen Eisen, Kobalt und Nickel auf pulvermetallurgischem Weg vermeidet man hohe Gehalte und ungünstige Verteilungen an spröden Phasen und größere Sauerstoffgehalte im Werkstoff durch Verwendung von Vorlegierungen aus seltenen Erden und den Übergangsmetallen anstelle reinen seltenen Erden.

DE 3738738 C1

BUNDESDRUCKEREI 12. 88 808 164/374 80

## Patentansprüche

1. Verfahren zur Herstellung von hochreinen mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum, **dadurch gekennzeichnet**, daß die Seltenen Erden in Form von Vorlegierungen mit den entsprechenden Übergangsmetallen eingesetzt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Vorlegierungen mit eutektischer Zusammensetzung eingesetzt werden.

## Beschreibung

Die Erfindung betrifft ein Verfahren zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum.

Targets werden in Anlagen zur Kathodenzerstäubung und zur Bedampfung von Gegenständen benötigt. Mit Hilfe der Kathodenzerstäubung (Sputtern) und des Bedampfens können dünne Schichten auf Substraten erzeugt werden, deren Anwendung von funktionalen Schichten in der Elektronik und Datentechnik über Korrosions- und Verschleißschutzschichten bis zu optischen Schichten für dekorative und wärmetechnische Zwecke reicht.

Beim Kathodenzerstäuben findet zwischen Kathode (Target) und Gegenelektrode eine elektrische Gasentladung statt, bei der von den aufprallenden Ionen aus dem Target Teilchen von atomarer Größe herausgeschlagen und auf Substraten, die im Bereich der Gegenelektrode angeordnet sind, niedergeschlagen werden.

Als Gasentladungsatmosphäre werden entweder inerte Gase, wie beispielsweise Argon oder Helium, oder reaktive Gase, wie z. B. Sauerstoff, Stickstoff oder Acetylen, bei geringem Druck eingesetzt.

Beim Inertgassputtern besteht das Target üblicherweise aus dem Material, aus dem die zu bildende Schicht bestehen soll, während beim Reaktivsputtern die herausgeschlagenen Targetteilchen mit dem Reaktionsgas reagieren und in Form eines Reaktionsproduktes als Schicht niedergeschlagen werden.

Bei den Bedampfungsverfahren wird das Targetmaterial im Vakuum durch Elektronenstrahl- oder Widerstandsbeheizung thermisch verdampft und als dünne Schicht auf dem Substrat abgeschieden.

Die Targets können üblicherweise schmelztechnisch hergestellt werden mit entsprechender Nachbearbeitung durch umformende und spannende Verfahren, oder pulvermetallurgisch durch Pressen und Sintern entsprechender Pulver bzw. Pulvergemische.

Bei Targetmaterialien, die aufgrund ihrer Zusammensetzung höhere Anteile an spröden Phasen enthalten, erweisen sich schmelztechnische Herstellverfahren als problematisch, da solche Targets beim Abkühlen nach dem Gießen aufgrund von thermischen Spannungen Risse aufweisen und in Stücke zerfallen können. Darüber hinaus sind solche Materialien meist nicht mechanisch bearbeitbar, so daß bestimmte wünschenswerte Targetgeometrien nicht herstellbar sind.

Pulvermetallurgische Verfahren zeigen bei denjenigen Targetmaterialien Probleme, die höhere Anteile an reaktionsempfindlichen Komponenten enthalten, und z. B. mit dem Luftsauerstoff reagieren. Wegen der großen spezifischen Oberfläche der Pulver und der daraus resultierenden Reaktionsfreudigkeit lassen sich keine hochwertigen Targetqualitäten mit niedrigem Sauerstoffgehalt pulvermetallurgisch herstellen.

Außerdem weisen pulvermetallurgisch hergestellte Produkte meist eine zum Teil offene Restporosität auf, die bei sauerstoffempfindlichen Targetmaterialien wegen der möglichen Oxidation des gesamten Targets nicht tolerierbar ist.

Diese Herstellungsschwierigkeiten treten insbesondere bei Targets auf, die überwiegend Seltene Erden und Übergangsmetalle enthalten.

Aus der DE-OS 35 37 191 ist ein pulvermetallurgisches Verfahren zur Herstellung von Targets aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und Nickel bekannt, bei dem ein Pulvergemisch aus Seltenen Erden und den genannten Übergangsmetallen unter vermindertem Druck und unter Inertgas bei Temperaturen unterhalb des eutektischen Punktes einer Warmverformung unterzogen wird, wobei sich eine spröde intermetallische Verbindung an der Grenzfläche zwischen dem Seltenen Erdmetall und dem Übergangsmetall ausbildet. Dieses Verfahren hat den Nachteil, daß die Warmverformung aufwendig mindestens zwei Stunden lang erfolgen muß, wodurch sich bemerkbare Mengen an spröden intermetallischen Phasen bilden, daß die Pulverherstellung bei den Seltenen Erden mit Schwierigkeiten verbunden ist und der Sauerstoffgehalt im Pulver der Seltenen Erden noch relativ hoch ist.

Es war daher Aufgabe der vorliegenden Erfindung, ein Verfahren zur Herstellung von hochreinen, mechanisch stabilen und dichten Targets für Kathodenzerstäubungs- und Bedampfungsanlagen aus Seltenen Erden und den Übergangsmetallen Eisen, Kobalt und/oder Nickel durch Einwirkung von Druck und Temperatur auf entsprechende Pulvergemische in Inertgasatmosphäre oder unter Vakuum zu entwickeln, das ohne großen technischen Aufwand ein Produkt liefert, das geringe Anteile und eine feine Verteilung an spröden Phasen und möglichst wenig Sauerstoff enthält.

Diese Aufgabe wird erfindungsgemäß dadurch gelöst, daß die Seltenen Erden in Form von Vorlegierungen mit den entsprechenden Übergangsmetallen eingesetzt werden.

Vorzugsweise werden Vorlegierungen mit eutektischer Zusammensetzung eingesetzt.

Die reaktionsempfindlichen Seltenen Erden werden nicht als solche, sondern als Vorlegierungen aus Seltenen Erden und den entsprechenden Übergangsmetallen, die im Vergleich zu den reinen Komponenten niedrigere Schmelzpunkte aufweisen, zu Pulvern und/oder Spänen verarbeitet, mit Pulvern und/oder Spänen der Übergangsmetalle gut durchmischt und zu Targets kompaktiert. Die Kompaktierung dieser Mischung kann durch Sintern, Warmwalzen, Heißpressen, Warmschmieden, Heißisostatische Preßverfahren oder Kombinationen daraus im Vakuum oder unter Inertgas erfolgen.

Die Kompaktierungsbedingungen (Temperatur, Druck, Zeit, Umformungsgrad) werden so gewählt, daß ein mechanisch stabiles Verbundmaterial entsteht, dessen Gefüge als Ungleichgewichtszustand nur geringe Anteile an spröden Gleichgewichtsphasen aufweist, die durch Diffusion an den Grenzflächen der Seltenen Erd-Phasen und der Übergangsmetallphasen gebildet werden. Durch die Verwendung von Vorlegierungen zwischen Seltenen Erden und Übergangsmetallen können relativ niedrige Kompaktierungstemperaturen und kurze Kompaktierungszeiten ausgewählt werden. Das führt zu einem verminderten technischen Aufwand und zu einer geringen Ausbildung von Diffusionszonen aus spröden Ungleichgewichtsphasen an den Berührungsstellen der Pulverkörner und in den Körnern.

Es hat sich überraschenderweise gezeigt, daß aus Vorlegierungen der Seltenen Erden mit den entsprechenden Übergangsmetallen wesentlich einfacher, hochreine und sauerstoffarme Pulver oder Späne herstellbar sind als aus den reinen Seltenen Erden. Aus diesen Vorlegierungen lassen sich z. B. durch spanende Bearbeitung, wie Fräsen oder Feilen, unter Schutzgas Späne und Pulver erzeugen, was bei den reinen Seltenen Erd-Metallen auf Grund ihrer Duktilität auch mit nachfolgendem Mahlen nicht ohne Schwierigkeiten möglich ist. Die spröden Phasenanteile des äußerst feinen Gefüges der Vorlegierungen bewirken beim Zerkleinerungsvorgang die Bildung von Partikeln mit geeigneter Kornform und Korngrößenverteilung, so daß eine Pulverherstellung mit guter Ausbeute und sehr niedrigem Sauerstoffgehalt (< 500 ppm) möglich ist.

Ebenso werden bei der Pulverherstellung durch Inertgasverdüsen aus den niedriger schmelzenden Vorlegierungen aufgrund der bei den tieferen Prozeßtemperaturen geringeren Reaktionsgeschwindigkeiten mit dem Tiegelmaterial und mit der Atmosphäre und aufgrund der kürzeren Verweilzeit in der Anlage, niedrigere Werte an Verunreinigungen und geringere Sauerstoffgehalte im Pulver erzielt. Desweiteren lassen sich hier die Verdüsungsparameter (Überhitzung, Abkühlrate, Prozeßgasdruck usw.) in weiten Maßen optimieren, so daß die Pulverausbeute und die Kornfraktion im Vergleich zur Verdüsung der reinen Seltenen Erden günstiger eingestellt werden können.

Die Verwendung von Vorlegierungen aus Seltenen Erden und Übergangsmetallen führt im Vergleich zur Verwendung der reinen Seltenen Erden überraschenderweise zu wesentlich kürzeren Kompaktierungszeiten, was einen bedeutenden wirtschaftlichen Vorteil dieses Verfahrens bedeutet.

Die Kompaktierungszeiten liegen in der Regel unterhalb einer Stunde, meist unterhalb von 30 Minuten. Darüber hinaus zeigen die erfindungsgemäß hergestellten Targets im Vergleich zu Targets, die pulvermetallurgisch aus den reinen Metallen hergestellt wurden, günstigere mechanische und magnetische Eigenschaften. Dies beruht, wie sich gezeigt hat, auf einer vorteilhaften Verteilung der im Gefüge vorhandenen Anteile an freiem Eisen, Kobalt und/oder Nickel, an den geringen Mengen intermetallischer Phasen und an dem aus den Vorlegierungen stammenden Resteutektikum.

Die folgenden Beispiele sollen das erfindungsgemäße Verfahren näher erläutern:

1) Zur Herstellung von hochreinen, kompakten, mechanisch stabilen Sputtertargets wird zuerst eine Vorlegierung aus 80 Atom% Terbium und 20 Atom% Eisen in einem Vakuuminduktionsofen ($10^{-5}$ Pa) hergestellt. Die anschließende Pulverisierung und Weiterverarbeitung erfolgt ausschließlich unter Argon-Schutzgas. Mit Hilfe eines Wellenfräsers wird der Gußblock zu grobem Pulver zerspant. Durch anschließendes Mahlen in einer Kugelmühle erhält man ein Terbium-Eisenpulver mit einer mittleren Korngröße ≤ 105 µm und mit einer Ausbeute von 70–80%. Die gewünschte Targetzusammensetzung von z. B. 67 Atom% Eisen, 25 Atom% Terbium und 8 Atom% Kobalt wird durch 20 minütiges Mischen der entsprechenden Eisen-, Kobalt- und Vorlegierungspulvermengen in einem Taumelmischer eingestellt.

Zum Kompaktieren der Pulvermischung zu Targets wurden die Verfahren des Heißisostatischen Pressens (HIP) des Warmwalzens und des Heißschmiedens in einer Kapsel angewendet.

Beim Heißisostatischen Pressen werden als Prozeßparameter 820°C Endtemperatur, 200 MPa Druck und 20 min Haltezeit bei Endtemperatur gewählt. Als Behälter wurden Stahlblechkannen verwendet, die vor Einbringen in die Anlage bei 300°C über 3 Stunden evakuiert wurden. Man erhält auf diese Weise mechanisch stabile, bearbeitbare Formkörper, die ein Ungleichgewichtsgefüge aus Eisenkörnern, Zonen von intermetallischen Phasen und Resteutektikum aufweisen. Die Dichte ist >99% der theoretischen Dichte, der Sauerstoffgehalt liegt unterhalb 1200 ppm. Längere Haltezeiten von z. B. 1–2 Stunden bei 820°C haben eine weitgehende Ausbildung von großflächigen Zonen der intermetallischen Gleichgewichtsphasen zur Folge, was eine unerwünschte Versprödung des Gefüges bedingt. Es sind daher möglichst kurze Haltezeiten einzuhalten.

Für das Kompaktieren durch Warmwalzen wird das Pulvergemisch in eine Eisenblechkapsel eingefüllt, die evakuiert und zugeschweißt wird. Die Umformung erfolgt bei 650°C bis zu einem Umformgrad von ca. 60% in mehreren Stichen in einem Zeitraum von wenigen Minuten. Nach Entfernen des Kapselmaterials ergibt sich ein stabiles, hochreines Target mit einer Dichte von ≈99% der theoretischen Dichte und einem Sauerstoffgehalt von 1200 ppm. Das Gefüge ist ähnlich ausgebildet wie bei der Kompaktierung durch Heißisostatisches Pressen.

Beim Heißschmieden wird die Pulvermischung ebenfalls in eine Blechkanne gefüllt und evakuiert. Der Schmiedevorgang kann bei 800°C in einer 200 to Schmiede durchgeführt werden. Die erzielbare Dichte beträgt bei 60% Umformung ≈99% der theoretischen Dichte.

2. Eine andere Art der Pulverherstellung ist das Verdüsen einer Schmelze im Inertgasstrom. Bei Benutzung von niedrigschmelzenden Vorlegierungen der Zusammensetzung 66 Atom% Gadolinium, 18 Atom% Eisen und 16 Atom% Kobalt mit einer Schmelztemperatur von ca. 620°C kann eine Verdüsungstemperatur von 700–800°C gewählt werden. Diese vergleichsweise sehr niedrige Verdüsungstemperatur ermöglicht bei den extrem reaktionsfreudigen Seltenen Erd-Materialien die Herstellung von sauerstoffarmen, sehr reinen Vorlegierungspulvern, da die Reaktion der Schmelze mit dem Tiegelmaterial und der Atmosphäre vergleichsweise gering ist. Des weiteren zeigt die Vorlegierungsschmelze bei dieser Temperatur eine günstige Viskosität und Oberflächenspannung, so daß die verdüsten Pulver gute Ausbeuten von z. B. 80–90% bei einer Korngröße ≤88 µm aufweisen. Mit Hilfe der in Beispiel 1 beschriebenen Misch- und Kompaktierungsverfahren erhält man ebenfalls hochreine, kompakte, stabile Formkörper mit Sauerstoffgehalten <1000 ppm. Die Ungleichge-

wichtsgefüge bestehen wiederum aus Eisenkörnern, Zonen von intermetallischen Phasen und Resteutektikum.

Da die intermetallischen Phasen in den Vorlegierungen fein verteilt vorliegen, und das Gefüge nicht sehr verspröden, lassen sich die Mengenanteile an freiem Eisen im Vergleich zu den intermetallischen Phasen durch Variation der Zusammensetzung der Vorlegierungen reduzieren. Die magnetischen Eigenschaften der Targets, die für das Magnetronsputtern wichtig sind, lassen sich hierdurch verbessern.

# MACHINE-ASSISTED TRANSLATION (MAT):

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|---|---|
| (19)【発行国】<br>日本国特許庁（ＪＰ） | **(19)[ISSUING COUNTRY]**<br>Japan Patent Office (JP) |
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| (54)【発明の名称】<br>スパッタ・ターゲット | **(54)[TITLE OF THE INVENTION]**<br>Sputter target |
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|---|---|
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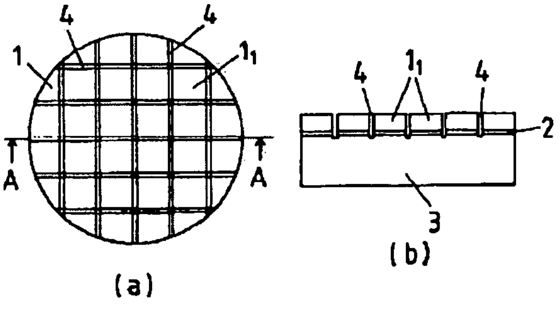
| (57)【要約】 | **(57)[ABSTRACT OF THE DISCLOSURE]** |
| 【目的】<br>ターゲット材の加熱による割れを防止すること。 | **[PURPOSE]**<br>Prevent the crack by heat of a target material. |
| 【構成】<br>所要の元素を含むターゲット材１はボンディング材２によってバッキングプレート３に固着されている。ターゲット材１にスリ割り溝（或いは切り込み、カッティングによる溝）４を設け、ターゲット材１を多数の小区画$1_1$に分割する。ターゲット材の厚さ方向位置での伸びの差等が小さくなり、ターゲット材の割れを防ぐことができる。予め作っておいたターゲット材の小片をバッキングプレートに貼り付けても良い。 | **[CONSTITUTION]**<br>The target material 1 containing a required element adheres to the backing plate 3 by the bonding material 2.<br>It provides the offset rate slot (or an incision, the slot by cutting) 4 in a target material 1, and partitions a target material 1 into many subsection $1_1$.<br>The difference of the elongation in the thickness direction position of a target material etc. becomes smaller, it can prevent the crack of a target material.<br>It is sufficient to bond on a backing plate the fragment of the target material made beforehand. |



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| 【特許請求の範囲】 | **[CLAIMS]** |
| 【請求項１】<br>バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又はターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを特徴とするスパッタ・ターゲット。 | **[CLAIM 1]**<br>A sputter target, in which the target material which adhered to the backing plate is partitioned into many subsections by the offset rate slot, or many fragments of a target material adhere to the backing plate in the shape of a tile sticking. |
| 【請求項２】<br>請求項１のスパッタ・ターゲットを備えていることを特徴とするスパッタ型イオン源。 | **[CLAIM 2]**<br>A sputter type ion source, which has the sputter target of Claim 1. |
| 【発明の詳細な説明】 | **[DETAILED DESCRIPTION OF THE INVENTION]** |
| 【０００１】 | **[0001]** |
| 【産業上の利用分野】<br>本発明は、加熱によるターゲット材の割れを防いだスパッタ型イオン源等に用いるスパッタ・ターゲットに関する。 | **[INDUSTRIAL APPLICATION]**<br>This invention relates to the sputter target which is used for the sputter type ion source which prevents the crack of the target material by heat. |
| 【０００２】 | **[0002]** |
| 【従来の技術】<br>スパッタ型イオン源、イオンビームスパッタリング装置等におけるスパッタ・ターゲットは、 | **[PRIOR ART]**<br>As shown in the front elevation of FIG.4(a), and sectional drawing of said (b) in the A-A, the sputter target in a sputter type ion source, an |

図４（ａ）の正面図、そのＡ－Ａ線での同（ｂ）の断面図に示すように、プラズマイオン、イオンビームでスパッタされる所要の元素を含む板状のターゲット材１をボンディング材２によってバッキングプレート３に固着して構成されている。ターゲット材１はスパッタ時、周囲のプラズマとプラズマイオン、或いはイオンビームの衝撃により加熱されるから、その冷却のためにバッキングプレート３は冷却ホルダーに取り付けられている。

ion-beam-sputtering apparatus, etc. adheres to a backing plate 3, and the bonding material 2 comprises the tabular target material 1 containing the required element by which a sputter is carried out from a plasma ion and an ion beam.

A target material 1 is heated by the shock of the surrounding plasma, a plasma ion, or an ion beam at the time of a sputter, therefore

The backing plate 3 is attached to the cooling holder for the cooling.

【０００３】

**[0003]**

【発明が解決しようとする課題】

かかるスパッタ・ターゲットのサイズが直径５０ｍｍ程度の大きさのものになると、ターゲット材１が熱伝導の悪い材質の場合には、スパッタ時、ターゲット材１の厚み方向位置での熱膨張による伸びに大きな差が生じる等の理由により、ターゲット材が割れてしまうことがある。

**[PROBLEM TO BE SOLVED BY THE INVENTION]**

When the size of this sputter target becomes the size which is diameter 50 mm degree and a target material 1 is the bad material of a heat conduction, a target material may break for the reasons of a big difference arising on the elongation by the thermal expansion in the thickness direction position of a target material 1 at the time of a sputter.

【０００４】

本発明は、プラズマやイオンによる加熱で、ターゲット材が割れることを防止したスパッタ・ターゲットの提供を目的とするものである。

**[0004]**

This invention aims to provide the sputter target which prevents the crack of a target material by heating by the plasma or an ion.

【０００５】

[0005]

【課題を解決するための手段】本発明は、スパッタ・ターゲットにおいて、バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又は、ターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを主たる特徴とするものであり、そして、かかるスパッタ・ターゲットをスパッタ型イオン源に用いたことを特徴とするものでる。

**[MEANS TO SOLVE THE PROBLEM]**
As for this invention, in a sputter target, the target material which adhered to the backing plate is partitioned into many subsections by the offset rate slot, or many fragments of a target material adhere to a backing plate in the shape of a tile sticking.
And this sputter target is used for the sputter type ion source.
It is characterized by the above-mentioned.

【０００６】

[0006]

【作用】ターゲット材がスリ割り或いは小片のタイル貼り形式により、小さく分割されているから、各分割域における加熱による熱膨張が他の分割域に波及することがないから、ターゲット材の厚み方向位置での伸びの差等が小さく抑えられ、スパッタ・ターゲットの割れが生じない。そして、かかるターゲットをスパッタ型イオン源に用いることにより、イオンビームが安定して引出せる。

**[OPERATION]**
The target material is small partitioned according to an offset rate or the tile sticking form of a fragment, therefore
Since the thermal expansion by the heat in each partition region does not affect another partition region, the difference of the elongation in the thickness direction position of a target material etc. is restrained small, the crack of a sputter target does not arise.
And it can pull out an ion beam with stability by using this target for a sputter type ion source.

【０００７】

[0007]

【実施例】
本考案の実施例について図面を参照して説明する。図１（ａ）、（ｂ）はスリ割り形式によるスパッタ・ターゲットの正面図及びそのＡ－Ａ線での断面図である。バッキングプレート３にボンディング材２で固着されたターゲット材１に、碁盤の目状にスリ割り溝（スリ割りないし切り込み、カッティングによる溝）４を設け、ターゲット材１を一辺が１０ｍｍ程度の多数の小区画$1_1$に小分割する。スリ割り溝４は、少なくともターゲット材部分に形成されていれば充分であるが、図１（ｂ）ではバッキングプレート３にまで達しているものを示している。

**[EXAMPLES]**

With reference to drawing, it demonstrates the Example of this design.

FIG. 1 (a), (b) is the front elevation of the sputter target by offset rate form, and sectional drawing in the A-A.

It provides the offset rate slot (an offset rate or an incision, slot by cutting) 4 in the target material 1 which adhered to the backing plate 3 by the bonding material 2 in a grid pattern, and one side small-partitions a target material 1 into many subsection $1_1$ which are 10 mm level.

If the offset rate slot 4 is formed in the target material part at least, it is enough.

However, FIG.1(b) shows what has reached even the backing plate 3.

【０００８】
図２（ａ）、（ｂ）はタイル貼り形式のスパッタ・ターゲットの正面図とそのＡ－Ａ線での断面図であり、予めターゲット材を一辺が１０ｍｍ程度の小片$1_2$に分割しておき、かかる多数のターゲット材の小片$1_2$をボンディング材２によって、タイル貼り形式でバッキングプレート３に固着する。

**[0008]**

FIG. 2 (a), (b) is the front elevation and sectional drawing in an A-A of the sputter target of tile sticking form.

One side partitions the target material into fragment $1_2$ which is 10 mm level beforehand, and it adheres fragment $1_2$ of the target material of these many to a backing plate 3 in tile sticking form by the bonding material 2.

【０００９】
このように、ターゲット材１は、何れも一辺が１０ｍｍ程度の小区画ないしは小片$1_1$、$1_2$に分

**[0009]**

Thus, the target material 1 is partitioned into the subsection whose one side is all 10 mm level or fragment $1_1$, and $1_2$, therefore

割されているから、ターゲット材１のスパッタ時に発熱、加熱が生じても、ターゲット材等の熱膨張は、各小区画、小片１$_1$、１$_2$内に限定されて、他の部分には波及せず、各小区画、小片１$_1$、１$_2$の厚み方向位置での伸びの差は小さく抑えられるから、ターゲット材に割れが発生しない。

Even if heat generation and heat arise at the time of the sputter of a target material 1, thermal expansion, such as a target material, is limited in each subsection, fragment $1_1$, and $1_2$, it does not affect the other part but the difference of the elongation in the thickness direction position of each subsection, fragment $1_1$, and $1_2$ is restrained small, therefore

A crack does not occur in a target material.

【００１０】

プラズマ・スパッタ型負イオン源では、スパッタ・ターゲット表面で発生した負イオンをイオン源の出口にビームとして集束させるために、スパッタ・ターゲットの表面を球面状にえぐった形とする場合がある。このようにすると、ターゲット材の周辺部では、その厚みは５ｍｍ程度に達し、スパッタ材が割れる可能性が高くなる。図３（ａ）及び（ｂ）は、かかる負イオン源のスパッタ・ターゲットにスリ割りを実施したものの正面図と、そのＡ－Ａ線での断面図である。図１に示したものと同様に、表面が球面状にえぐられたターゲット材１をボンディング材２によってバッキングプレート３に固着しておき、スリ割り溝４を形成することによって、ターゲット材１を多数の小区画に分割する。加熱によるスパッタ・ターゲットの割れが防止で

**[0010]**

In the source of a plasma sputter type negative ion, in order to converge as a beam the negative ion generated on the sputter target surface on the outlet of an ion source, it may make the surface of a sputter target into the form scooped out to the spherical shape.

If it does in this way, in the periphery part of a target material, the thickness will amount to 5 mm level, possibility that a sputter material will break becomes higher.

Although FIG.3(a) and (b) implemented the offset rate at the sputter target of this source of a negative ion, they are a front elevation and sectional drawing in the A-A.

It partitions a target material 1 into many subsections by the surface's adhering to the backing plate 3 the target material 1 scooped out by the spherical shape by the bonding material 2 like what was shown in FIG. 1, and forming the offset rate slot 4.

It can prevent the crack of the sputter target by heat, therefore

It becomes possible to pull out a beam more stably than an ion source.

きるから、イオン源より安定にビームを引出すことが可能になる。図２と同様に、タイル貼り形式を実施してもよい。

It is sufficient to implement tile sticking form like FIG. 2.

【００１１】

**[0011]**

## 【発明の効果】

## [ADVANTAGE OF THE INVENTION]

本発明は以上説明したように、ターゲット材が小さく分割されているから、スパッタ時に、ターゲット材における厚み方向の熱膨張による伸びの差等を小さく抑えることができ、ターゲット材の割れを防止することができる。

As for this invention, as explained above, the target material is partitioned small, therefore At the time of a sputter, it can restrain small the difference of the elongation by the thermal expansion of the thickness direction in a target material etc., and can prevent the crack of a target material.

【００１２】

**[0012]**

そして、本発明によるスパッタ・ターゲットをイオン源に用いることにより、イオンビームを安定に引出すことができ、特に表面が球面状にえぐられたスパッタ・ターゲットの場合に効果的である。

And in the case of the sputter target with which it could pull out the ion beam stably, and particularly the surface was scooped out by the spherical shape, it is effective by using the sputter target by this invention for an ion source.

## 【図面の簡単な説明】

## [BRIEF DESCRIPTION OF THE DRAWINGS]

【図１】

**[FIG. 1]**

本発明の実施例の正面図及び断面図である。

It is the front elevation and sectional drawing of an Example of this invention.

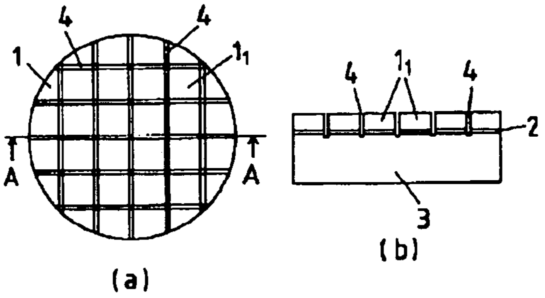
【図２】

**[FIG. 2]**

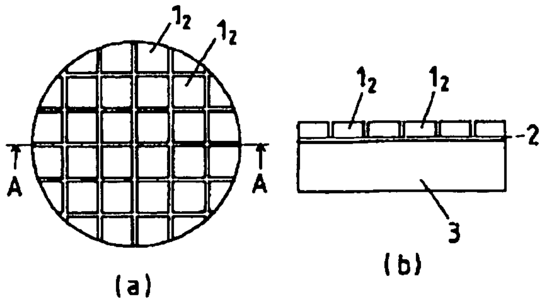
他の実施例の正面図及び断面図である。

It is the front elevation and sectional drawing of another Example.

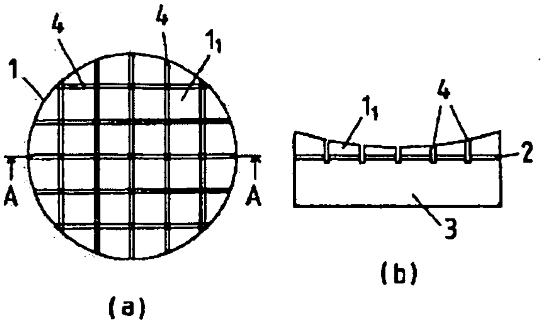
| | |
|---|---|
| 【図３】 | **[FIG. 3]** |
| 更に他の実施例の正面図及び断面図である。 | Furthermore, it is the front elevation and sectional drawing of another Example. |
| 【図４】 | **[FIG. 4]** |
| 従来のスパッタ・ターゲットの正面図及び断面図である。 | It is the front elevation and sectional drawing of a sputter target of the past. |
| 【符号の説明】 | **[DESCRIPTION OF SYMBOLS]** |
| $1, 1_1, 1_2$　ターゲット材 | $1, 1_1, 1_2$ target material |
| 2　ボンディング材 | 2 Bonding material |
| 3　バッキングプレート | 3 Backing plate |
| 4　スリ割り溝 | 4 Offset rate slot |
| 【図１】 | **[FIG. 1]** |



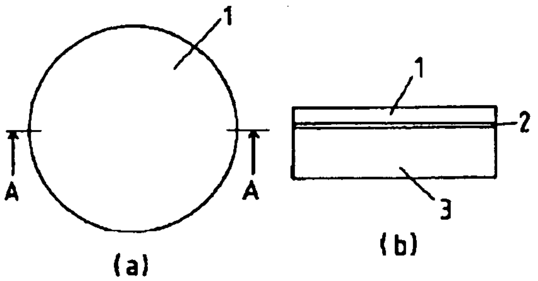
| | |
|---|---|
| 【図２】 | **[FIG. 2]** |



【図３】 [FIG. 3]



【図４】 [FIG. 4]



## THOMSON SCIENTIFIC TERMS AND CONDITIONS

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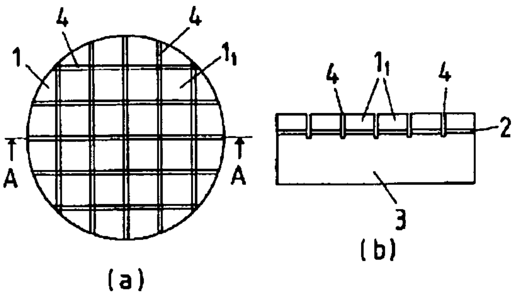
# (54)【発明の名称】　スパッタ・ターゲット

(57)【要約】

【目的】　ターゲット材の加熱による割れを防止すること。

【構成】　所要の元素を含むターゲット材1はボンディング材2によってバッキングプレート3に固着されている。ターゲット材1にスリ割り溝（或いは切り込み、カッティングによる溝）4を設け、ターゲット材1を多数の小区画$1_1$に分割する。ターゲット材の厚さ方向位置での伸びの差等が小さくなり、ターゲット材の割れを防ぐことができる。予め作っておいたターゲット材の小片をバッキングプレートに貼り付けても良い。



【特許請求の範囲】

【請求項１】　バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又はターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを特徴とするスパッタ・ターゲット。

【請求項２】　請求項１のスパッタ・ターゲットを備えていることを特徴とするスパッタ型イオン源。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、加熱によるターゲット材の割れを防いだスパッタ型イオン源等に用いるスパッタ・ターゲットに関する。

【０００２】

【従来の技術】スパッタ型イオン源、イオンビームスパッタリング装置等におけるスパッタ・ターゲットは、図４（ａ）の正面図、そのＡ－Ａ線での同（ｂ）の断面図に示すように、プラズマイオン、イオンビームでスパッタされる所要の元素を含む板状のターゲット材１をボンディング材２によってバッキングプレート３に固着して構成されている。ターゲット材１はスパッタ時、周囲のプラズマとプラズマイオン、或いはイオンビームの衝撃により加熱されるから、その冷却のためにバッキングプレート３は冷却ホルダーに取り付けられている。

【０００３】

【発明が解決しようとする課題】かかるスパッタ・ターゲットのサイズが直径５０mm程度の大きさのものになると、ターゲット材１が熱伝導の悪い材質の場合には、スパッタ時、ターゲット材１の厚み方向位置での熱膨張による伸びに大きな差が生じる等の理由により、ターゲット材が割れてしまうことがある。

【０００４】本発明は、プラズマやイオンによる加熱で、ターゲット材が割れることを防止したスパッタ・ターゲットの提供を目的とするものである。

【０００５】

【課題を解決するための手段】本発明は、スパッタ・ターゲットにおいて、バッキングプレートに固着されたターゲット材がスリ割り溝によって多数の小区画に分割されているか、又は、ターゲット材の多数の小片がタイル貼り状にバッキングプレートに固着されていることを主たる特徴とするものであり、そして、かかるスパッタ・ターゲットをスパッタ型イオン源に用いたことを特徴とするものでる。

【０００６】

【作用】ターゲット材がスリ割り或いは小片のタイル貼り形式により、小さく分割されているから、各分割域における加熱による熱膨張が他の分割域に波及することがないから、ターゲット材の厚み方向位置での伸びの差等が小さく抑えられ、スパッタ・ターゲットの割れが生じない。そして、かかるターゲットをスパッタ型イオン源に用いることにより、イオンビームが安定して引出せる。

【０００７】

【実施例】本考案の実施例について図面を参照して説明する。図１（ａ）、（ｂ）はスリ割り形式によるスパッタ・ターゲットの正面図及びそのＡ－Ａ線での断面図である。バッキングプレート３にボンディング材２で固着されたターゲット材１に、碁盤の目状にスリ割り溝（スリ割りないし切り込み、カッティングによる溝）４を設け、ターゲット材１を一辺が１０mm程度の多数の小区画$1_1$に小分割する。スリ割り溝４は、少なくともターゲット材部分に形成されていれば充分であるが、図１（ｂ）ではバッキングプレート３にまで達しているものを示している。

【０００８】図２（ａ）、（ｂ）はタイル貼り形式のスパッタ・ターゲットの正面図とそのＡ－Ａ線での断面図であり、予めターゲット材を一辺が１０mm程度の小片$1_2$に分割しておき、かかる多数のターゲット材の小片$1_2$をボンディング材２によって、タイル貼り形式でバッキングプレート３に固着する。

【０００９】このように、ターゲット材１は、何れも一辺が１０mm程度の小区画ないしは小片$1_1$、$1_2$に分割されているから、ターゲット材１のスパッタ時に発熱、加熱が生じても、ターゲット材等の熱膨張は、各小区画、小片$1_1$、$1_2$内に限定されて、他の部分には波及せず、各小区画、小片$1_1$、$1_2$の厚み方向位置での伸びの差は小さく抑えられるから、ターゲット材に割れが発生しない。

【００１０】プラズマ・スパッタ型負イオン源では、スパッタ・ターゲット表面で発生した負イオンをイオン源の出口にビームとして集束させるために、スパッタ・ターゲットの表面を球面状にえぐった形とする場合がある。このようにすると、ターゲット材の周辺部では、その厚みは５mm程度に達し、スパッタ材が割れる可能性が高くなる。図３（ａ）及び（ｂ）は、かかる負イオン源のスパッタ・ターゲットにスリ割りを実施したものの正面図と、そのＡ－Ａ線での断面図である。図１に示したものと同様に、表面が球面状にえぐられたターゲット材１をボンディング材２によってバッキングプレート３に固着しておき、スリ割り溝４を形成することによって、ターゲット材１を多数の小区画に分割する。加熱によるスパッタ・ターゲットの割れが防止できるから、イオン源より安定にビームを引出すことが可能になる。図２と同様に、タイル貼り形式を実施してもよい。

【００１１】

【発明の効果】本発明は以上説明したように、ターゲット材が小さく分割されているから、スパッタ時に、ターゲット材における厚み方向の熱膨張による伸びの差等を小さく抑えることができ、ターゲット材の割れを防止することができる。

【0012】そして、本発明によるスパッタ・ターゲットをイオン源に用いることにより、イオンビームを安定に引出すことができ、特に表面が球面状にえぐられたスパッタ・ターゲットの場合に効果的である。

【図面の簡単な説明】

【図１】本発明の実施例の正面図及び断面図である。

【図２】他の実施例の正面図及び断面図である。

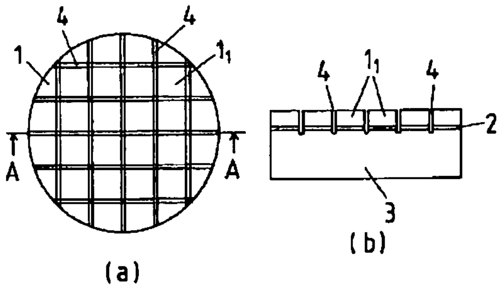
【図３】更に他の実施例の正面図及び断面図である。

【図４】従来のスパッタ・ターゲットの正面図及び断面図である。

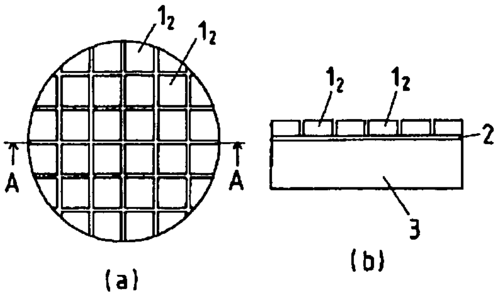
【符号の説明】

| | |
|---|---|
| $1, 1_1, 1_2$ | ターゲット材 |
| 2 | ボンディング材 |
| 3 | バッキングプレート |
| 4 | スリ割り溝 |

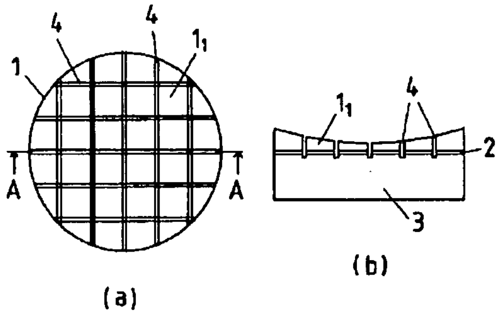
【図1】



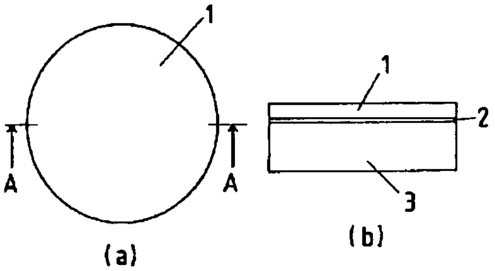
【図2】



【図3】



【図4】



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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | M-12245 US | 6938 |

22852 7590 09/06/2006

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| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| **ART UNIT** | **PAPER NUMBER** |
| 2823 | |

DATE MAILED: 09/06/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 10/03)

| Office Action Summary | Application No. | Applicant(s) |
|---|---|---|
| | 10/101,863 | ZHANG ET AL. |
| | **Examiner** | **Art Unit** |
| | Michelle Estrada | 2823 |

*-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --*

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

1)☒ Responsive to communication(s) filed on 12 June 2006.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

4)☒ Claim(s) 2-4,6-14 and 21-50 is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☒ Claim(s) 14 is/are allowed.

6)☒ Claim(s) 2-4,6-13 and 21-50 is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

**Application Papers**

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date 8/15/06,6/12/06.

4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application

6) ☐ Other: _____.

## DETAILED ACTION

The Declaration under 37 CFR 1.132 filed June 12, 2006 is insufficient to overcome the rejection of claims 21 and 43 based upon Smolanoff et al. in view of Fu et al. as set forth in the last Office action because: using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation "the filter is a band rejection filter at a frequency of the bias power" is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved.

Applicant's arguments with respect to claims 21 and 43 have been considered but are moot in view of the new ground(s) of rejection.

### *Claim Rejections - 35 USC § 103*

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21 and 40-45 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claims 21, 40 and 43, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation "the filter is a band rejection filter at a frequency of the bias power" is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 8, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12 and 49, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

## *Allowable Subject Matter*

Claim 14 is allowed.

## *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Michelle Estrada
Primary Examiner
Art Unit 2823

ME
September 5, 2006

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(*Use as many sheets as necessary*)

O I P E

AUG 15 2006

PATENT & TRADEMARK OFFICE

| | | | | |
|---|---|---|---|---|
| Sheet | 1 | of | 2 | |

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.¹ | Document Number<br>Number-Kind Code² *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| ME | | US 5,433,835 | 07/18/1995 | Demaray | |
| ME | | US 6,288,835 B1 | 09/11/2001 | Nilsson et al. | |
| ME | | US 6,452,717 B1 | 09/17/2002 | Endo | |
| ME | | US 2002/0014406 A1 | 02/07/2002 | Takashima | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.¹ | Foreign Patent Document<br>Country Code³ Number⁴ Kind Code⁵ *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation⁶ |
|---|---|---|---|---|---|---|
| ME | | DE 37 38 738 C1 | 01/26/1989 | Degussa AG | | Yes |
| ME | | JP 5-230642 A | 09/07/1993 | Nissin High Voltage Co., Ltd. | | Yes |
| ME | | WO 99/61674 A1 | 12/02/1999 | Universiteit Gent | | |
| ME | | WO 2006/063308 A2 | 06/15/2006 | Symmorphix, Inc. | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.¹ | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation⁶ |
|---|---|---|---|
| ME | | AGRAWAL, G.P., in: Fiber-Optic Communication Systems, 2nd Edition, John Wiley & Sons, New York, pp. 361-399 and 415 (1997). | |
| ME | | ASM Handbook, Formerly Ninth Edition, Metals Handbook, Volume 15, Casting, Davis et al. (Eds.), ASM International, pp. 372-373, 376-383, and 410-411 (1988). | |
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|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 8/28/06 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 2 | of | 2 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michel |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Signature | Michelle Estrada | Date Considered | 8/28/06 |

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JUN 12 2006

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

Sheet 1 of 2

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

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|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 8/28/04 |

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*(Use as many sheets as necessary)*

| Sheet | 2 | of | 2 |
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| *Complete if Known* | |
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| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
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| Examiner Signature | Michelle Estrada | Date Considered | 8/28/06 |

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# Index of Claims

| | | |
|---|---|---|
| Application No.<br>10/101863 | Applicant(s) | |
| Examiner | Art Unit | |

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 9140.0016-00 | 6938 |

22852 7590 01/23/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

EXAMINER
ESTRADA, MICHELLE

| ART UNIT | PAPER NUMBER |
|---|---|
| 2823 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 01/23/2007 | PAPER |

**Please find below and/or attached an Office communication concerning this application or proceeding.**

PTOL-90A (Rev. 10/06)

| *Interview Summary* | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. | |
|---|---|---|---|
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 | |

All participants (applicant, applicant's representative, PTO personnel):

(1) Michelle Estrada. (3) Richard Demaray.

(2) Gary Edwards. (4) Hongmei Zhang.

Date of Interview: 18 January 2007.

Type: a)☒ Telephonic b)☐ Video Conference
c)☐ Personal [copy given to: 1)☐ applicant 2)☐ applicant's representative]

Exhibit shown or demonstration conducted: d)☐ Yes e)☒ No.
If Yes, brief description: _____.

Claim(s) discussed: 21 and 43.

Identification of prior art discussed: Smolanoff et al..

Agreement with respect to the claims f)☒ was reached. g)☐ was not reached. h)☐ N/A.

Substance of Interview including description of the general nature of what was agreed to if an agreement was reached, or any other comments: Applicants explained the basis of the invention and the difference over Smolanoff reference with respect to the pulsed DC power. Applicants will amend claims 21 and 43 to further clarify the invention. Further consideration and search would be needed for the new limitations in the claims.

(A fuller description, if necessary, and a copy of the amendments which the examiner agreed would render the claims allowable, if available, must be attached. Also, where no copy of the amendments that would render the claims allowable is available, a summary thereof must be attached.)

THE FORMAL WRITTEN REPLY TO THE LAST OFFICE ACTION MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a reply to the last Office action has already been filed, APPLICANT IS GIVEN A NON-EXTENDABLE PERIOD OF THE LONGER OF ONE MONTH OR THIRTY DAYS FROM THIS INTERVIEW DATE, OR THE MAILING DATE OF THIS INTERVIEW SUMMARY FORM, WHICHEVER IS LATER, TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW. See Summary of Record of Interview requirements on reverse side or on attached sheet.

Michelle Estrada
MICHELLE ESTRADA
PRIMARY EXAMINER

Examiner Note: You must sign this form unless it is an Attachment to a signed Office action.

Examiner's signature, if required

02-08-07

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PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al.

Application No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: ESTRADA, Michelle

Confirmation No.: 6938

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed September 6, 2006, and the Interview Summary, mailed January 23, 2007, the period for response having been extended to February 6, 2007, by a request for extension of one month with authorization for the Commissioner to charge the fee to Deposit Account No. 06-0916, Applicants propose that this application be amended as follows:

**Amendments to the Claims** are reflected in the listing of claims in this paper beginning on page 2.

**Remarks/Arguments** follow the amendment sections of this paper beginning on page 6.

## AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 µs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Currently amended): The method of Claim 21, wherein ~~the film is an upper cladding layer of a waveguide structure and~~ the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously Presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14.-20. (Cancelled).

21. (Currently amended): A method of depositing [[a]] an oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target through a filter such that the target voltage oscillates between positive and negative voltages to create a plasma and deposit the oxide film,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface, and

wherein the filter is a band rejection filter at a frequency of the bias power.

22. (Previously Presented ): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously Presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously Presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (Previously presented): The method of claim 21, wherein the band rejection filter is a

narrow band-pass filter.

41. (Previously presented): The method of claim 21, wherein a bandwidth of the band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing [[a]] an oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power such that the target voltage oscillates between positive and negative voltages and an oxide film is deposited on the substrate.

44. (Previously presented): The method of claim 43, wherein a bandwidth of the band rejection filter is about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (Previously presented): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (New): A method of depositing an oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages; and

filtering the pulsed DC power through a narrow band rejection filter at a frequency of the bias power,

wherein the oxide film is deposited on the substrate.

52. (New): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, $N_2$, $O_2$, $C_2F_6$, $CO_2$, CO, $NH_3$, NO, and halide containing gasses.

53. (New): The method of claim 51, wherein the target is a metallic target.

54. (New): The method of claim 51, wherein the target is an intermetllic target.

55. (New). The method of claim 51, further including sweeping the target with a magnetic field.

56. (New): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (New): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (New) The method of claims 21, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (New) The method of claim 43, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about

350 kHz.

60. (New) The method of claim 51, wherein applying pulsed DC power through the filter includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

## REMARKS

Claims 2-4, 6-14, and 21-50 are pending in this application. The Examiner has allowed claim 14 and rejected claims 2-4, 6-13, and 21-50. Applicants have canceled claim 14, amended claims 21 and 43, and added new claims 51-60.

## Examiner's Interview

Applicants wish to thank the Examiner for spending her time in an interview on January 18, 2007. In attendance at the Interview were Examiner Michelle Estrada, Applicant's counsel, Gary J. Edwards, and Inventors R. Ernest Demaray and Hongmei Zhang. Applicants substantially agree with the Examiner's Summary of the Interview mailed on January 23, 2007, and provide further discussion of the material discussed below.

During the interview, the inventors described to the Examiner the development of the invention, including the development of applicant's pulsed-DC processing technology, and the teachings of the cited references. In particular, the Smolanoff reference was discussed with respect to independent claims 21 and 43. Applicants discussed amending the claims to further clarify the distinctions between the claimed invention and the teachings of Smolanoff and other cited art. Those amendments are reflected in the amended claims above and in the newly added claims. The distinctions between the claimed invention and the cited prior art is further discussed below.

As pointed out to the Examiner during the interview, and as further discussed in the specification (see, e.g., Par. [0049]), the historical difficulty in deposition of insulating oxide layers is the formation of insulating layers on the target, which build up charges with the ultimate result of unwanted arcing. The arcing results in damaged power supplies and deposition of particulate matter, which degrades the properties of the resulting films deposited on the substrate.

Some embodiments of pulsed DC processing, as defined in the present application, can substantially eliminate this problem. As discussed, for example, in paragraph [0053] of Applicant's application, pulsed DC sputtering refers to a sputtering technique where the pulsed DC power supply oscillates between positive and negative potentials, driving the voltage of the target alternately to positive and negative potentials. Claims 21 and 43 of the present application have been amended to explicitly recite that "the target voltage oscillates between positive and negative voltages." New claim 51 also recites that "the target voltage oscillates between positive and negative voltages." The claims have also been amended to recite that the deposited films are oxide films. Applicants reserve the right to pursue allowable claims to the subject matter disclosed in the present application in continuation applications.

In order to further improve the quality of the deposited film, Applicant's apply a combination of pulsed DC power to the target and RF bias to the substrate. As is discussed, for example, in paragraph [0057] of the specification, application of RF bias to the substrate results in a densification of the deposited film. In order to supply both a pulsed DC power to the target and an RF bias to the substrate, a narrow band rejection filter is coupled between the pulsed DC power supply and the target. The band rejection filter is arranged to reject RF power at the frequency of the RF bias to the substrate. Applicants discovered that the use of pulsed DC power to the target and RF bias to the substrate resulted in catastrophic failure of the pulsed DC power supply due to transmission of the RF power into the pulsed DC power supply. However, a conventional high or low pass filter blocks a portion of the pulsed DC frequency to the target and therefore the benefits of using pulsed DC power are lost. Applicants discovered that a narrow band rejection filter, an embodiment of which is described in the specification at paragraph [0056], both protects the DC power supply from the RF bias power and passes the pulsed DC frequencies which form the square pulse of the pulsed DC power to the target so that the benefits of pulsed DC deposition with RF bias can be realized. The elimination of a narrow band of frequencies about a single frequency in a narrow band rejection filter has a small effect on the square shape of the pulsed DC pulse. However, elimination of either all higher frequencies or all lower frequencies from the single frequency effectively destroys the shape of the square pulse and eliminates control of both the magnitude and duration of the positive portion of the pulse.

During prosecution of this application, several prior art publications have been raised, including Smolanoff (U.S. Patent 6,117,279) and Le (U.S. Publication No. 2003/0077914). Smolanoff was discussed during the Interview. Both publications are discussed below in particular. Neither of these references, either separately or in combination, teaches the combination of pulsed-DC deposition, where the target voltage oscillates between positive and negative voltages, and an RF bias. As a summary, Smolanoff teaches sputtering of a conducting or metallic layer and does not teach deposition of an "oxide layer," as is recited in each of claims 21, 43, and 51 above. Additionally, Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in each of claims 21, 43 and 51. Further, although Smolanoff teaches a filter between a DC power supply and the target, Smolanoff does not teach a "narrow band rejection filter" as is recited in each of claims 21, 43, and 51.

Le does not cure the defects in the teachings of Smolanoff. Le teaches "a method of depositing a titanium oxide layer on a substrate" utilizing pulsed DC voltage. (Le, Abstract) However, Le does not teach applying an RF bias to the substrate or a band rejection filter coupled between the pulsed DC power supply and the target. Further, one skilled in the art would not be motivated to combine the teachings of Smolanoff, which is directed toward deposition of metallic layers, with the teachings of Le, which is directed toward deposition of a titanium oxide layer.

As is further discussed below, claims 2-13, 21-24, and 40-60 are allowable over the cited prior art.

## Claim Rejections under 35 U.S.C. § 103[1]

The Examiner has rejected claims 2-4, 6-13, and 21-50 over combinations of Fu and Le with Smolanoff. As discussed below, claims 2-4, 6-13, and 21-50, as amended, are allowable over the cited references.

### Claims 10-13, 21, and 40-45

The Examiner has rejected claims 10-13, 21, and 40-45 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,117,279 ("Smolanoff et al.") in view of U.S. Patent No. 6,306,265 ("Fu et al."). However, Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Additionally, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Further, Smolanoff does not teach deposition of "an oxide film," as is recited in claims 21 and 43.

### I. Smolanoff does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43.

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[1] The Examiner has made multiple characterizations of the claims, the cited art, and application of legal principles to those characterizations. Applicants shall not be deemed to agree with or to acquiesce in the Examiner's statements by not specifically addressing these characterizations in this response.

Smolanoff teaches that "[t]he target power supply 21 is usually a source of constant or pulsed DC power and is connected between the cathode assembly 17 and some element such as the chamber wall 13 which is at ground potential and serves as the system anode." (Smolanoff, col. 5, lines 51-54). Additionally, Smolanoff teaches that "[p]ower from the steady or pulsed DC power supply 21 and/or RF generator 24 produces a negative potential on the target 16." (Smolanoff, col. 5, line 66, through col. 6, line 1).

Applicants have explicitly defined pulsed DC power to refer to power that oscillates between positive and negative voltages. (*See*, application, par. [0053]). As described in the specification, the positive voltage period allows an insulating layer deposited on the target to discharge, resulting in an arc free deposition process. (*See,* application, par. [0053]). However, a second definition of "pulsed DC power" was also in use at the time, and the second definition is apparently the definition utilized in Smolanoff. In this second definition, which is also referred to as unipolar pulsed DC, the DC power supplied to the target is grounded on occasion, either periodically or when an impending discharge is detected. The DC power can be shunted to ground so that the voltage on the target was brought from a high negative voltage to near ground voltage until the arc condition was dissipated, while the negative voltage power supply was protected from the discharge. This process was also referred to as "pulsed DC power," but, in Smolanoff, the target remains at a negative voltage throughout the deposition.[2]

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[2] Applicant has submitted three articles that explain various aspects of pulsed-dc technology in the Information Disclosure Statement that accompanies this amendment: *See, e.g.,* Richard A. Scholl, "Power Systems for Reactive Sputtering of Insulating Films," Advanced Energy Industries, Inc., While Paper, September, 2001, page 3, paragraph 3; *See also,* Richard A. Scholl, "Advanced Supplies for Pulsed Plasma Technologies: State-Of-The-Art and Outlook," Advanced Energy Industries, Inc., White Paper, 1999; ; and A. Belkind, et al., "Pulsed-DC Reactive

(continued...)

The process of pulsed DC power as claimed in claims 21 and 43, where "the target voltage oscillates between positive and negative voltages," then, differs from the teachings of Smolanoff at least in that Smolanoff teaches that the target remains at a negative potential. Such pulses occur only, generally, when an impending discharge from the target is sensed and may not be periodic. Therefore, Smolanoff does not teach "that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43.

## II. Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43.

Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Smolanoff teaches that "[t]he power supply 21 preferably is connected to the cathode assembly 17 through an RF filter 22." (Smolanoff, col. 5, lines 56-58). However, no further description of filter 22 is provided. Therefore, Smolanoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43.

The Examiner has commented that "using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies." (OA, page 2). Additionally, the Examiner commented that "the limitation 'the filter is a band rejection filter at a frequency of the bias power' is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved." (OA, page 2). Applicants disagree.

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(...continued)
Sputtering of Dielectrics: Pulsing Parameter Effects," Society of Vacuum Coaters 43rd Annual Technical Conference Proceedings, Denver, CO, April 15-20, 2000.

Although it is true that "the filter is going to work at certain frequencies," as suggested by the Examiner, the recited "band rejection filter" works at the frequency of the RF bias supply and blocks only a narrow band of frequencies around the frequency of the RF bias supply. This allows the square wave pulse of the DC power, which is formed of all frequencies both higher and lower than the biased frequency, to be transmitted through the filter to the target. Otherwise, the pulse that would reach the target is distorted so that the benefits of the pulsed DC power are not realized. Therefore, utilization of a band rejection filter at the frequency of the bias power is neither taught nor obvious from the teachings of Smolanoff. Furthermore, use of a band rejection filter at the frequency of the bias power places a distinct limitation on the claim.

Therefore, Smolanoff does not teach "applying pulsed DC power to the target through a filter . . . wherein the filter is a band rejection filter at a frequency of the bias power," as is recited in claims 21, or "applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power," as is recited in claim 43.

### III. Smolanoff teaches deposition of metallic films and does not teach "an oxide film," as is recited in claims 21 and 43.

Smolanoff teaches "a sputter coating apparatus" that is generally directed to deposition of conducting films. In particular, Smolanoff "relates to sputter coating, and more particularly, to the Ionized Physical Vapor Deposition (IPVD) of coating material onto substrates." (Smolanoff, col. 1, lines 6-8). Smolanoff teaches that

> For some sputtering processes, such as those used for coating contacts at the bottoms of high aspect ratio holes and other features on the substrate 15 and for metallizing such holes by filling them with sputtered conductive material, it is highly preferred in VLSI semiconductor device manufacturing that the particles impinge onto the substrate 15 in a narrow angular distribution around the

> normal to the substrate so that they can proceed directly into the features and onto the feature bottoms without striking or being shadowed by the feature sides.

(Smolanoff, col. 6, lines 34-43).

As stated in Smolanoff,

> The present invention is further predicated in part upon a principle that a substantial loss of positive ions from a secondary plasma and a resulting reduction in the ionization fraction of sputtered ions by the secondary plasma, are prevented when electrically conductive shields employed in ionized physical deposition processes on the periphery of the secondary plasma used for the ionization of the puttered material are prevented from developing a substantial negative DC potential. The invention is further predicated in part upon the concept that the existence of conductive shields or chamber walls bounding the secondary plasma, if prevented from developing a strongly negative DC potential or if kept far from the center of the chamber, will reduce the steering of positive ions from the secondary plasma into the walls or shields, and decrease the width of the plasma sheath. The invention is particularly predicated on the concept of providing these effects while maintaining an RF shield that will allow effective and efficient coupling of energy into the secondary plasma.

Further, Smolanoff teaches that

> For sputter processing, the gas from the supply 40 is typically an inert gas such as argon. For reactive processes, additional gases, such as nitrogen, hydrogen, ammonia, oxygen or other gas, can be introduced through auxiliary flow controllers.

(Smolanoff, col. 7, lines 23-26). Further, Smolanoff teaches that "[a] metal shield positioned inside of the window shields the window from the deposition of conductive sputtered material thereon which, if permitted to accumulate on the window, would isolate the chamber from the coil." (Smolanoff, col. 4, lines 19-22). Additionally, Smolanoff teaches that

> While the window 60 itself is not electrically conductive, it is susceptible to the accumulation of a coating of conductive material sputtered from the target 16. . . .
>
> To prevent such buildup of conductive sputtered material on the window 60, a shield 70 is provided in the vacuum of the

> chamber 12 between the space 11 and the window 60, in close proximity to the inside surface of the window 60.

(Smolanoff, col. 7, line 61, -col. 8, line 9).

As indicated in Smolanoff, and discussed above, the shield taught in Smolanoff can not be made insulating and must remain electrically conducting in order for the Smolanoff invention to function. Any deposition of insulating material, which would occur during deposition of an oxide material, would cause the invention taught in Smalanoff to become nonfunctional. Smolanoff, therefore, teaches away from deposition of dielectric materials such as oxide materials. Therefore Smolanoff teaches sputtering of conductive materials and does not teach deposition of oxide materials.

## IV. Fu does not cure the defects in the teachings of Smolanoff.

As discussed above, Smolanoff teaches deposition of conducting films and does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Additionally, Smolonoff does not teach "a band rejection filter at a frequency of the bias power," as is recited in claims 21 and 43. Fu does not cure the defects in the teachings of Smolonoff.

Fu teaches "sputtering of materials." (Fu, col. 1, line 13). As shown in Figure 1, Fu teaches applying DC power to the target. (*See*, Fu, Fig. 1; col. 1, lines 30-32). However, Fu does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages," as is recited in claims 21 and 43. Therefore, Fu does not teach the combination of "applying pulsed DC power to the target through a filter . . . wherein the filter is a band rejection filter at a frequency of the bias power," as is recited in claim 21, or "applying pulsed DC power to a target through a band rejection filter at a frequency of the bias power," as is recited in claim 43. Although Fu mentions that oxygen can be supplied to the reactor to produce oxides such as $Al_2O_3$ (*See*, Fu, col. 1, lines 39-40), Fu concentrates on ionized metal deposition (*See, e.g.,* Fu, title).

Therefore, claims 21 and 43 are allowable over the combination of Fu and Smolanoff. Claims 10-13 and 40-42 depend from claim 21 and are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 21. Claims 44-45 depend from claim 43 and are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 43.

**Claims 2-4, 5, and 22-24**

The Examiner has rejected claims 2-4, 6, and 22-24 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of the Examiner's comments.

However, claims 2-4, 6, and 22-24 depend from claim 21, which is allowable over the combination of Fu and Smolanoff as discussed above. Therefore, claims 2-4, 6, and 22-24 are allowable over the combination of Fu and Smolanoff for at least the same reasons as is claim 21.

The Examiner's comments regarding the prima facie obviousness of claiming different ranges are not appropriate with regard to claims 2-4, 6, and 22-24 because the recited ranges are directed to the process claimed, which as discussed above is allowable over the cited prior art. Therefore, the recited ranges in claims 2-4, 6, and 22-24 are not related to the ranges provided in the prior art, which is directed towards different processes.

**Claims 7 and 9**

The Examiner has rejected claims 7 and 9 under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13, and 21, and further in view of U.S. Application No. 2003/0077914 ("Le et al.").

As discussed above with respect to claim 21, the combination of Smolanoff and Fu does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages" and "a band rejection filter at a frequency of the bias power," as is recited in claims 21. Le does not cure the defects in the teachings of Smolanoff and Fu.

Le teaches "a method of depositing a titanium oxide layer on a substrate" utilizing pulsed DC voltage. (Le, Abstract) However, Le does not teach applying an RF bias to the substrate or a band rejection filter coupled between the pulsed DC power supply and the target. Therefore, Le does not teach "applying pulsed DC power to the target . . . such that the target voltage oscillates between positive and negative voltages" and "a band rejection filter at a frequency of the bias power," as is recited in claims 21.

Further, one skilled in the art would not be motivated to combine the teachings of Smolanoff, which is directed toward deposition of metallic layers, with the teachings of Le, which is directed toward deposition of a titanium oxide layer. In fact, as discussed above, Smolanoff teaches away from the deposition of oxide layers because deposition of an oxide layer on the shield, which would occur during deposition of an oxide layer, would cause the Smolanoff invention to not function.

Therefore, claims 7 and 9, which depend from claim 21, are allowable for at least the same reason as is claim 21.

## New Claims

Applicants have added new claims 51-60. Independent claim 51 includes the limitations of "an oxide film," "applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages," and "filtering the pulsed DC power through a narrow band rejection filter at a frequency of the bias power," which are the limitations that were discussed with the Examiner during the Interview of January 18, 2007. Claim 51 includes limitations similar to those recited in claims 21 and 43 and discussed above. Therefore, claim 51 is allowable over the cited prior art. Claims 52-57 and claim 60, which depend from claim 51, are therefore allowable over the cited prior art for at least the same reasons as is claim 51. Claim 58 depends from claim 21 and is therefore allowable over the prior art for at least the same reasons as is claim 21. Claim 59 depends from claim 43 and is allowable over the prior art for at least the same reasons as is claim 43.

Support for claims 51-60 can be found throughout the specification. Claim 51 includes limitations similar to claims 21 and 43. Claim 52 is disclosed, for example, in paragraph [0015] and paragraph [0073]. Claims 53 and 54 are disclosed, for example, in paragraph [0062]. Claim 55 is similar to claim 12. Claim 56 includes limitations from claim 3. Claim 57 is similar to claim 4. Claims 58-60 include limitations from claim 3.

## Conclusion

In view of the foregoing remarks, Applicants submit that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicants therefore request the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

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PATENT
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Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al.

Application No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: ESTRADA, Michelle

Confirmation No.: 6938

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## TWELFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed foreign and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By:____________________
Gary J. Edwards
Reg. No. 41,008

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | ***Complete if Known*** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Application Number* | 10/101,863 |
| | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of | 3 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
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| | | US-6,154,582 | 11-28-2000 | Bazylenko et al. | |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | KR 2003-0088236 | 11-19-2003 | Hyundai Motor Co Ltd | | Abstract |
| | | WO 01/82297 A1 | 11-01-2001 | Koninklijke Philips Electronics N.V. | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | BELKIND, A. et al., "Pulsed-DC Reactive Sputtering of Dielectrics: Pulsing Parameter Effects," 43rd Annual Technical Conference Proceedings-Denver: 86-90 (April 15-20, 2000). | |
| | | SCHOLL, R., "Power Supplies for Pulsed Plasma Technologies: State-Of-The-Art And Outlook," Advances Energy Industries, Inc., pages 1-8 (1999). | |
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| | | Final Office Action dated October 12, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Response to Final Office Action dated November 3, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Office Action dated December 1, 2006, in U.S. Application No. 10,291,179 (Attorney | |

| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**

*(Use as many sheets as necessary)*

| Sheet | 2 | of | 3 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| | | | |
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| | | Docket No. 9140.0001-00). | |
| | | Amendment dated October 19, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Office Action dated December 18, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Response to Office Action dated September 11, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
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| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.
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**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**

*(Use as many sheets as necessary)*

| Sheet | 3 | of | 3 |
|---|---|---|---|

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|---|---|
| ***Complete if Known*** | |
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

| | | **NON PATENT LITERATURE DOCUMENTS** | |
|---|---|---|---|
| | | Response to Office Action dated January 26, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |
| | | Preliminary Amendment dated July 21, 2006, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00). | |
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| | | Continuation application and Preliminary Amendment dated December 13, 2006 (Attorney Docket No. 9140.0042-01). | |
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| | | PCT International Search Report and Written Opinion for Application No. PCT/US05/44781 dated October 3, 2006 (Attorney Docket No. 9140.0042-00304). | |

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|---|---|---|---|
| Examiner Signature | | Date Considered | |

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**EXPRESS MAIL LABEL NO.
EV 955594467 US**

Derwent WPI

0014040325
WPI Acc no: 2004-222504/200421
**Flywheel for radiating heat and increasing rigidity**
Patent Assignee: HYUNDAI MOTOR CO LTD (HYUN-N)
Inventor: SONG J H
Patent Family: 2 patents, 1 countries

| Patent Number | Kind | Date | Application Number | Kind | Date | Update | Type |
|---|---|---|---|---|---|---|---|
| **KR 2003088236** | **A** | **20031119** | **KR 200226187** | **A** | **20020513** | **200421** | **B** |
| KR 507142 | B | 20050809 | KR 200226187 | A | 20020513 | 200662 | E |

Priority Applications (no., kind, date): KR 200226187 A 20020513

Patent Details

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| KR 2003088236 | A | KO | 1 | 10 | | |
| KR 507142 | B | KO | | | Previously issued patent | KR 2003088236 |

**Alerting Abstract** KR A
NOVELTY - A flywheel for radiating and reinforcing is provided to prevent crack by absorbing burst force with elastic force and radiating friction heat in operating the clutch because the flywheel is divided into plural portions and manufactured with different materials.
DESCRIPTION - A flywheel(10) is composed of a support plate(10a) combined with a crankshaft with pressing and fitting a ring gear(11); a cover plate(10b) fixed to the support plate and bent to form the storage space; an insert plate(10c) fastened inside the cover plate; and a friction plate(10d) contacted to the insert plate and inserted to the cover plate to receive clamping load from a clutch plate in operating the clutch. The durability is improved by preventing crack from burst force in the flywheel and radiating friction heat from clamping load.

# (19)대한민국특허청(KR)
# (12) 공개특허공보(A)

**(51) 。Int. Cl.⁷**
**F16F 15/30**

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**(43) 공개일자** **2003년11월19일**

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심사청구 : 있음

## (54) 방열과 강성 강화용 플라이 휠

요약

본 발명은 방열과 강성 강화용 플라이 휠에 관한 것으로, 플라이휠을 서로 결합되는 여러 부분으로 분리해 제작하면서 그 재질을 달리해 버스트포스를 자체적인 탄성을 통해 흡수하면서 클러치의 조작에 의한 마찰열의 방열성도 향상시켜 균열을 방지함에 그 목적이 있다.

상기와 같은 목적을 달성하기 위한 본 발명은, 플라이휠(10)이 링기어(11)가 외주 측에 압입되면서 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 일단이 고정되면서 절곡된 내부로 수용공간을 형성하는 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 고정되는 인서트플레이트(10c) 및 이 인서트플레이트(10c)에 접촉됨과 더불어 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작에 따라 클러치플레이트(22)로부터 클램핑 로드(F')를 받는 마찰플레이트(10d)로 이루어진 것을 특징으로 한다.

대표도

도 4

명세서

도면의 간단한 설명

도 1은 일반적인 엔진의 구성도

도 2는 종래에 따른 플라이 휠부위의 구성도

도 3은 종래에 따른 플라이휠의 구성 단면도

도 4는 본 발명에 따른 플라이휠의 구성 단면도

<도면의 주요부분에 대한 부호의 설명>

1 : 실린더 2 : 피스톤

3 : 커넥팅 로드 5 : 크랭크축

6 : 워터펌프 7 : 밸브기구

8 : 크랭크풀리 9 : 타이밍 기어

10 : 플라이휠 10a : 지지플레이트

10b : 커버플레이트 10c : 인서트플레이트

10d : 마찰플레이트 10d' : 슬롯

11 : 링기어 20 : 클러치어셈블리

21 : 클러치커버 22 : 클러치플레이트

H : 휠하우징

F' : 클램핑로드 K : 갭

## 발명의 상세한 설명

### 발명의 목적

### 발명이 속하는 기술 및 그 분야의 종래기술

본 발명은 방열과 강성 강화용 플라이 휠에 관한 것으로, 보다 상세하게는 엔진의 회전력에 의한 균열을 방지하도록 강성을 강화함과 더불어 클러치와의 마찰에 의한 마찰열의 방열성도 향상할 수 있도록 된 방열과 강성 강화용 플라이휠에 관한 것이다.

일반적으로 엔진은 도 1에 도시된 바와 같이 실린더(1) 내에서 혼합 가스가 폭발하여 피스톤(2)이 왕복 운동되고, 상기 피스톤(2)과 커넥팅 로드(3)로 연결된 크랭크축(5)이 회전 운동되면서 회전 동력이 발생하게 된다.

또한, 상기 크랭크축(5)에는 그 선단측에 워터펌프(6) 및 밸브기구(7)를 작동하기 위한 크랭크풀리(8) 및 타이밍기어(9)가 설치되어 있고, 반대쪽에는 하우징(H)내로 수용되어 엔진의 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)가 외주 측에 열 박음으로 압입되면서 클러치와 변속기에 회전 동력을 전달하는 플라이휠(10)이 설치되어 있다.

여기서, 상기 플라이휠(10)은 도 2에 도시된 바와 같이, 링기어(11)가 압입된 반대측으로 클러치페달에 의해 플라이휠(10)과 마찰되는 클러치플레이트(22)를 감싸는 클러치커버(21)로 이루어져 엔진과 변속기사이의 회전 전달을 분리 · 연결하는 클러치어셈블리(20)가 구비되어진다.

이러한 플라이휠(10)은 엔진의 4행정 중에서 폭발행정에서 얻어진 토크(Torque)를 흡입· 압축· 배기 행정에 고르게 분배하여 승차감 및 차량 출발성에 맞춘 형상으로 설계됨은 물론 엔진과 변속기를 연결하는 역할로 클러치의 용량에 맞게 설계됨은 물론이다.

그러나, 이와 같은 플라이휠(10)은 도 3에 도시된 바와 같이 크랭크축(5)에 보울트등을 매개로 고정된 상태에서 엔진의 회전력을 변속기로 전달하기 위해 고속으로 회전하면서, 또한 클러치의 조작에 따라 클러치플레이트(22)와 서로 강하게 마찰되면서 엔진의 회전력을 단속하는데 이에 따라, 포트(Port)형 클러치인 경우에는 클러치플레이트(22)의 취부면과 플라이휠(10)좌면 사이의 노치(C : Notch)부위가 회전에 따른 버스트 포스(Burst Force)에 의해 균열(Crack)이 발생될 소지가 있는 문제가 있게 된다.

또한, 트럭과 버스와 같이 대형 디젤엔진을 사용하는 경우에는 플라이휠(10)의 형상도 이너시아(Inertia)값이 매우 큰 형상으로 주철로 제조되는데 특히, 이와 같은 경우에는 빈번하면서 장시간동안 클러치를 조작하는 경우 클러치에서 발생되는 약 250 - 300℃ 정도의 고온에 의해 플라이휠(10)의 열변형을 가져오고 이에 따른 강도 저하는 물론 균열을 발생시킬 수 있는 문제가 있게 된다.

## 발명이 이루고자 하는 기술적 과제

이에 본 발명은 상기와 같은 점을 감안하여 발명된 것으로, 플라이휠을 서로 결합되는 여러 부분으로 분리해 제작하면서 그 재질을 달리해 버스트포스를 자체적인 탄성을 통해 흡수하면서 클러치의 조작에 의한 마찰열의 방열성도 향상시켜 균열을 방지함에 그 목적이 있다.

상기와 같은 목적을 달성하기 위한 본 발명은, 플라이휠이 링기어가 외주 측에 압입되면서 크랭크축에 결합되는 지지플레이트와, 이 지지플레이트에 일단이 고정되면서 절곡된 내부로 수용공간을 형성하는 커버플레이트, 이 커버플레이트의 안쪽에서 고정되는 인서트플레이트 및 이 인서트플레이트에 접촉됨과 더불어 커버플레이트내에 삽입· 고정되어 클러치 조작에 따라 클러치플레이트로부터 클램핑 로드를 받는 마찰플레이트로 이루어진 것을 특징으로 한다.

## 발명의 구성 및 작용

이하 본 발명의 실시예를 첨부된 예시도면을 참조로 상세히 설명한다.

도 4는 본 발명에 따른 플라리휠의 구성 단면도를 도시한 것인바, 본 발명은 피스톤(2)의 왕복 운동을 회전운동으로 변환하는 크랭크축(5)에 결합되면서 클러치어셈블리(20)가 장착되는 플라이휠(10)이 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)가 외주 측에 열 박음으로 압입됨과 더불어 보울트등의 고정부재를 통해 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 보울트등의 고정부재를 통해 고정된 일단으로부터 서로 간격을 두도록 절곡되어 그 내부로 수용공간을 형성하는 컵 형상의 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 보울트등의 고정부재를 통해 고정되는 인서트플레이트(10c) 및 이 인서트플레이트(10c)에 접촉됨과 더불어 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작 시 클러치어셈블리(20)의 클러치플레이트(22)와 접촉되어 클램핑로드(F')가 작용되는 마찰플레이트(10d)로 이루어진다.

여기서, 상기 지지플레이트(10a)와 인서트플레이트(10c)는 주철로 이루어지는 반면, 상기 커버플레이트(10b)는 강(Steel)재질로 이루어져 플라이휠(10)에 작용하는 버스트 포스(F)를 자체적인 탄성력을 통해 흡수· 완화시켜주게 된다.

또한, 상기 인서트플레이트(10c)는 클러치 조작에 따라 마찰플레이트(10d)에서 발생되는 마찰열의 전달시 열팽창에 의해 커버플레이트(10b)와의 간섭을 방지하도록 약 1.00 - 1.50mm 정도의 갭(K)을 유지하게 된다.

그리고, 상기 마찰플레이트(10d)는 클러치 조작에 따른 클러치플레이트(22)와의 마찰열을 외부로 발산하도록 그 측면 테두리를 따라 다수의 슬럿(10d')이 형성되어진다.

이하 본 발명의 작동을 첨부된 도면을 참조로 상세히 설명한다.

본 발명은 플라이휠(10)이 일체로 이루어지는 대신 여러 부품들로 이루어지는데 즉, 지지플레이트(10a)에 초기 시동시에 스타트 모터의 피니언 기어와 맞물려 회전력을 전달받는 링기어(11)를 열 박음으로 압입시킨 상태에서 커버플레이트(10b)의 안쪽으로 보울트등의 고정부재를 이용해 인서트플레이트(10c) 와 마찰플레이트(10d) 순차적으로 고정한 후, 상기 커버플레이트(10b)와 지지플레이트(10a)를 보울트등의 고정부재를 매개로 결합시킨 상태에서 크랭크축(5)에 결합하여 플라이휠(10)을 조립하게 된다.

이때, 상기 지지플레이트(10a)와 크랭크축(5)사이에는 파이롯 베어링(Pilot Bearing)이 개재됨은 물론이다.

이어, 상기 플라이휠(10)에 클러치어셈블리(20)를 결합하여 클러치 조작시 클러치플레이트(22)에 의해 플라이휠(10)의 마찰플레이트(10d)쪽으로 강하게 작용하는 클램핑로드(F')를 통해 엔진과 변속기사이의 회전력을 단속하게 된다.

이때, 본 발명의 플라이휠(10)은 클러치의 조작에 따라 야기되는 엔진의 회전에 의해 플라이휠(10)에 발생되는 버스트 포스(F)가 강재질로 이루어진 커버플레이트(10b)의 탄성력에 의해 흡수· 완화되거나 또는 제거되고 이로 인해, 상기 커버플레이트(10b)의 모서리부위인 노치 부위로 집중되는 버스트 포스(F)에 의한 균열의 발생을 예방할 수 있게 된다.

또한, 본 발명의 플라이휠(10)은 클러치의 빈번한 조작에 의한 클램핑로드(F')에 의해 클러치플레이트(22)와 마찰플레이트(10d)사이에서 마찰열이 발생되면, 상기 마찰플레이트(10d)에 접촉된 인서트플레이트(10c)로 전달됨과 더불어 마찰플레이트(10d)의 측면 테두리를 따라 형성된 다수의 슬랏(10d')을 통해 보다 빠른 열의 방출이 이루어지게 된다.

이때, 상기 인서트플레이트(10c)로 전달된 마찰열이 방열되는 것보다 적층되는 것이 클 경우에는 인서트플레이트(10c)가 팽창하게 되지만, 이때 상기 인서트플 레이트(10c)가 이를 수용한 커버플레이트(10b)내에서 약 1.00 - 1.50mm 정도의 갭(K)을 유지하므로 열팽창에 의한 커버플레이트(10b)와의 간섭을 방지할 수 있게 됨은 물론이다.

## 발명의 효과

이상 설명한 바와 같이 본 발명에 의하면, 플라이휠이 링기어가 외주 측에 압입되면서 크랭크축에 결합되는 부분과 클러치 조작에 따라 클러치플레이트로부터 클램핑 로드를 받는 부분으로 분리 제작한 후 서로 조립· 결합시켜, 플라이휠이 적용되는 차종에 관계없이 플라이휠에서 발생되는 버스트포스에 의한 크랙과 클램핑로드에 따른 마찰열의 방열성을 향상시킬 수 있어 내구성을 강화할 수 있는 효과가 있게 된다.

## (57) 청구의 범위

### 청구항 1.

링기어(11)가 압입되어 크랭크축(5)에 결합되는 지지플레이트(10a)와, 이 지지플레이트(10a)에 고정된 일단으로부터 절곡되어 그 내부로 수용공간을 형성하는 커버플레이트(10b), 이 커버플레이트(10b)의 안쪽에서 보고정되는 인서트플레이트(10c) 및 상기 커버플레이트(10b)내에 삽입· 고정되어 클러치 조작 시 클러치어셈블리(20)의 클러치플레이트(22)와 접촉되어 마찰력을 발생하는 마찰플레이트(10d)로 이루어진 방열과 강성 강화용 플라이 휠.

### 청구항 2.

제 1항에 있어서, 상기 지지플레이트(10a)와 인서트플레이트(10c)는 주철로 이루어지는 반면, 상기 커버플레이트(10b)는 탄성을 갖는 강재질로 이루진 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

### 청구항 3.

제 1항에 있어서, 상기 인서트플레이트(10c)는 열팽창에 의해 커버플레이트(10b)와의 간섭을 방지하도록 갭(K)을 형성하는 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

### 청구항 4.

제 3항에 있어서, 상기 갭(K)은 약 1.00 - 1.50mm 정도인 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

### 청구항 5.

제 1항에 있어서, 상기 마찰플레이트(10d)는 클러치 조작에 따른 클러치플레이트(22)와의 마찰열을 외부로 발산하도록 그 측면 테두리를 따라 다수의 슬랏(10d')이 형성되어진 것을 특징으로 하는 방열과 강성 강화용 플라이 휠.

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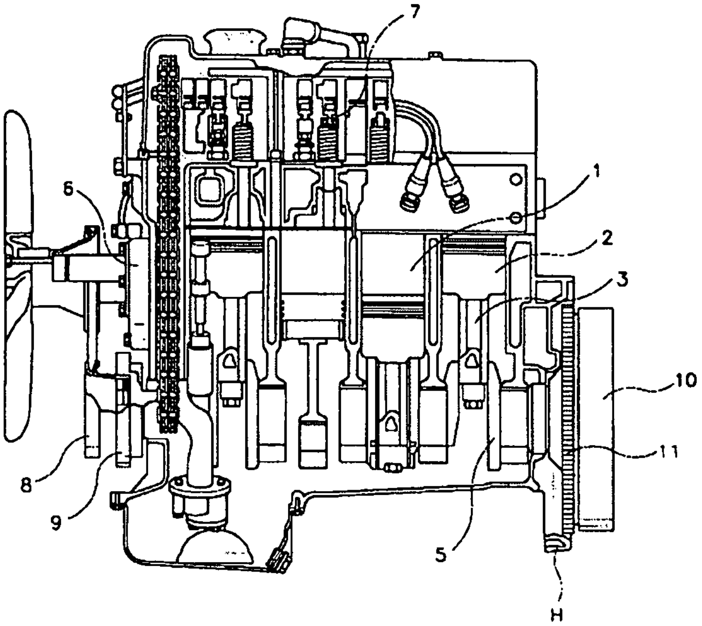

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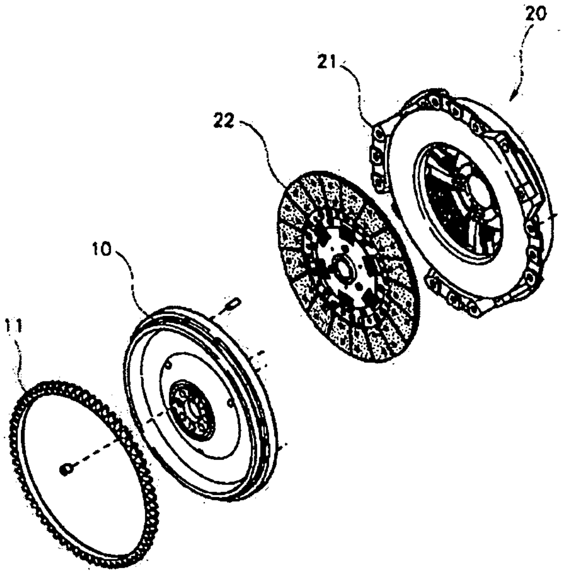

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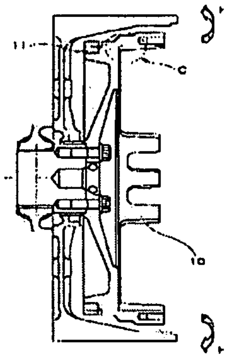

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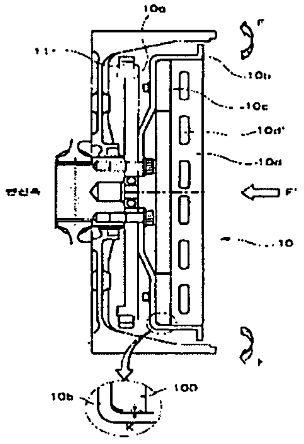

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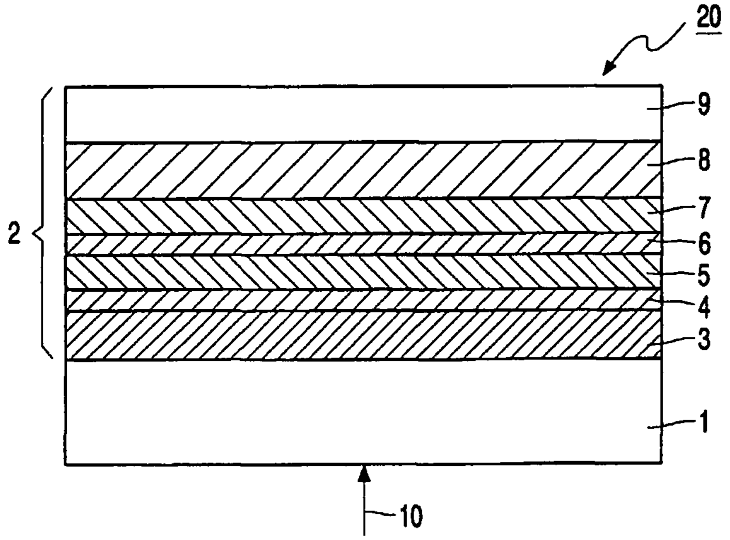
**(54) Title:** OPTICAL RECORDING MEDIUM AND USE OF SUCH OPTICAL RECORDING MEDIUM



**(57) Abstract:** The optical recording medium (20) has a substrate (1) and a stack (2) of layers provided thereon. A phase change recording layer (5), having a melting point $T_{mp}$ is sandwiched between a first (3) and a second (7) dielectric layer. A crystallization-accelerating layer (4, 6) is being interposed in contact with the recording layer (5). Further a reflective layer (8) is present and an optional cover layer (9). The crystallization-accelerating layer (4, 6) consists of a binary metal alloy or a semiconductor and has a melting point $T_{mg}$ at least 250 °C higher than the melting point $T_{mp}$ of the recording layer (5) and has a crystal structure similar to the crystalline state of the recording layer (5).

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# Optical recording medium and use of such optical recording medium

The invention relates to an optical recording medium having a substrate and a stack of layers provided thereon, the stack comprising a recording layer, having a melting point $T_{mp}$ and being able to change between an amorphous and a crystalline state, sandwiched between a first and a second dielectric layer, the first being adjacent to the substrate, a crystallization accelerating layer being interposed in contact with the recording layer, and a reflective layer.

The invention also relates to the use of such an optical recording medium.

An optical recording medium of the type mentioned in the opening paragraph is known from Japanese patent application JP-09161316 A. In the known medium the state of the recording layer locally changes from crystalline to amorphous when data are optically recorded.

Optical data storage based on the phase change principle is attractive, because it combines the possibilities of direct overwrite (DOW) and high storage density with easy compatibility with read-only optical data storage systems. Phase-change optical recording involves the formation of submicrometer-sized amorphous recording marks in a crystalline film using a focused relatively high power laser-light beam. During recording information, the medium is moved with respect to the focused laser-light beam that is modulated in accordance with the information to be recorded. Due to this, quenching takes place in the phase-change recording layer and causes the formation of amorphous information bits in the exposed areas of the recording layer that remains crystalline in the unexposed areas. Erasure of written amorphous marks is realized by recrystallizing through heating with the same laser at an intermediate power level, without melting the recording layer. The amorphous marks represent the data bits, which can be read, e.g. via the substrate, by a low-power focused laser-light beam. Reflection differences of the amorphous marks with respect to the crystalline recording layer bring about a modulated laser-light beam which is subsequently converted by a detector into a modulated photocurrent in accordance with the recorded digital information.

One of the most important demands in phase-change optical recording is a high data rate, which means that data can be written in and read from the medium with a rate of at least 30Mbits/s. A high data rate requires the recording layer to have a high crystallization rate, i.e. a short crystallization time. To ensure that the previously recorded amorphous marks can be crystallized during direct overwrite, the recording layer should have a proper crystallization time to match the velocity of the medium relative to the laser-light beam. If the crystallization speed is not high enough to match the velocity of the medium relative to the laser-light beam the amorphous marks from the previous recording, representing old data, cannot be completely erased, meaning recrystallized, during DOW. This causes a high noise level. A high crystallization speed is particularly required in high-density recording and high data rate applications, such as disc-shaped DVD+RW, DVR-red and blue which are abbreviations of new generation high density Digital Versatile Disc+RW, where RW refers to the rewritability of such discs, and Digital Video Recording optical storage discs, where red and blue refer to the used laser wavelength. For these new discs the complete erasure time (CET) has to be at most 60 ns. CET is defined as the minimum duration of the erasing pulse for complete crystallization of a written amorphous mark in a crystalline environment, which is measured statically. For DVD+RW, which has a 4.7 GB recording density per 120 mm disk, a user data bit rate of 33 Mbits/s is needed, and for DVR-red said rate is 35 Mbits/s. For rewritable phase change optical recording systems such as DVR-blue, a user data rate higher than 50 Mbits/s is required.

The known medium of the phase-change type comprises a disc-shaped substrate carrying a stack of layers consisting, in succession, of a first dielectric layer, a $Sb_2Te_3$ layer as crystallization accelerating layer, a Sb layer as a composition correcting layer, a recording layer of a phase-change $Sb_{72}Te_{28}$ alloy, a second dielectric layer and a metal reflective layer. Such a stack of layers can be referred to as an INP'PIM structure, wherein M represents a reflective or mirror layer, I represents a dielectric layer and P represents a phase-change recording layer while P' represents a composition correction layer which mixes with the recording layer at first recording. A crystallization accelerating layer N of $Sb_2Te_3$, has been arranged between the first dielectric layer and the correction and the recording layer to achieve a fast crystallization of the medium during erasing information in the medium by means of a laser-light beam. In the known recording medium the N layer has a melting point of 618°C, only 68°C higher than the melting point 550°C of the P layer. The melting point of the known N layer is relatively close to the melting point of the P layer causing the N layer to dissolve in the correction and recording layer P'P after one or at best a few recording/erasure cycles, whereafter the crystallization accelerating layer N is no longer present and its crystallization-accelerating action is lost.

For complete erasure of an amorphous mark, two processes occur, i.e. nucleation and grain (crystallite) growth. An investigation of the known recording medium has revealed that the known crystallization-accelerating layer N is merely a nucleation-promoting layer.

It is a disadvantage of the known medium that its crystallization accelerating layer only functions for at most a few recording and erasing cycles. This is not sufficient for modern erasable media, which require a stable performance for at least a thousand of recording and erasing cycles.

It is an object of the invention to provide an optical recording medium of the kind described in the opening paragraph, which is suitable for high speed rewritable optical recording, having a CET-value of at most 60 ns.

It is another object of the invention to provide an optical recording medium of the kind described in the opening paragraph, which is suitable for rewritable optical recording, having a stable performance for at least $10^3$ recording and erasing cycles.

This object is achieved in accordance with the invention by an optical recording medium as described in the opening paragraph, which is characterized in that the crystallization accelerating layer

- comprises a material selected from the group consisting of binary metal alloys, semiconductors elements and semiconductor alloys and
- has a melting point $T_{mg}$ at least 250°C higher than the melting point $T_{mp}$ of the recording layer and
- has a crystal structure similar to the crystalline state of the recording layer.

The crystallization accelerating layer according to the invention, which will also be abbreviated as G, yields a high crystallization speed of the recording layer because the amorphous marks of the recording layer are in contact with the G-layer. This accelerates the crystallite growth process, leading to a higher crystallization speed. Especially because the crystal structure of the G-layer is similar to, or even the same as, the structure of the crystalline state of the recording layer the crystallization rate of amorphous marks is advantageously increased. The crystal structure of the G-layer then serves as a very good grain growth initialization or nucleation layer for crystallite growth in the recording layer.

The G-layer is always present adjacent to a thermally isolating layer, here the first or second dielectric layer, because a stack having a G-layer between the recording layer and the substrate or the reflection layer cannot realize the desired thermal properties.

An advantage of the G-layer, comprising a material selected from the group consisting of binary metal alloys, semiconductors and semiconductor alloys, is that it has a high melting point. This counteracts dissolving of the G-layer in the recording layer and maintenance of the crystalline structure for a large number of recording and erasing cycles. During recording, the maximum temperature in the recording layer is about 800°C, which is about 1.4 times $T_{mp}$ for a recording layer with a $T_{mp}$ of 550°C. This may be deduced from a temperature calculation based on the presented laser energy during recording and the physical properties of the stack. The melting temperature $T_{mg}$ of the G-layer has to be above this maximum temperature so that the G-layer remains in crystalline state when the recording layer is melted.

Therefore, the melting temperature difference between recording layer and G-layer should be 250°C or larger, but preferably 300°C or larger, taking into consideration a safety margin.

Preferred materials, which may be used as G-layer, are PbTe, $Ag_2Te$, CrTe, Ge and Si.

In an embodiment of the recording medium the G-layer is arranged between the recording layer and the second dielectric layer. The thickness of the G-layer may be chosen between 0.1 and 10 nm. The thermal conductivity of the crystallization-accelerating layer is generally comparable to that of the recording layer, which is an alloy of metals. However this only has a small effect on the thermal behaviour of the stack because the thickness of the G-layer is generally relatively small compared to the other layers in the stack. This facilitates the thermal design of the stack.

In another embodiment the crystallization time is reduced further in that a second G-layer is arranged between the recording layer and the first dielectric layer. Thus a G-layer is arranged on both sides of the recording layer. The second G-layer may be of a material similar or identical to the material of the other G-layer. The crystallization time is reduced because now a crystalline layer, which accelerates the crystallite growth process, is present against the recorded amorphous mark on both sides. The thicknesses of the G-layers are between 0.1 and 10nm, preferably lower than 5 nm.

In a specific embodiment the two G-layers present on either side of the recording layer are substantially equal both in thickness and in composition. Equal in thickness means to within 10% of each other. The equality of the thicknesses is advantageous in the manufacturing of the medium. In general the stack is deposited by evaporation or by sputtering in a vacuum chamber, where substrates move stepwise along a series of stations having targets of different compositions. The dwell time at each station is about equal, and the thickness of the layer deposited at a station is determined in part by switching the deposition process on and off. Consequently, the deposition of a relatively thin layer may require less time than available at a station, whereas the deposition of a relatively thick layer may even require two adjacent stations having the same target. It is therefore advantageous to choose to replace a relatively thick layer and a relatively thin layer by two layers of about equal thickness and composition, thereby reducing the number of deposition stations and the manufacturing time of a stack.

In a specific embodiment the recording layer comprises an alloy of Q, In, Sb and Te, wherein Q is selected from the group consisting of Ag and Ge.

The preferred composition comprises $Q_a In_b Sb_c Te_d$ (in atomic percentages), wherein Q is selected from the group consisting of Ag and Ge;

$2 \leq a \leq 9$

$0 < b \leq 6$

$55 \leq c \leq 80$

$16 \leq d \leq 30; a + b + c + d = 100.$

In another specific embodiment the recording layer comprises a compound of Ge, Sb and Te. The preferred composition of this compound is defined by the formula

$Ge_{50x}Sb_{40-40x}Te_{60-10x}$ (in atomic percentages), wherein $0.166 \leq x \leq 0.444$;

the recording layer having a thickness of 5 to 35 nm;

This composition exists on a part of the line connecting the compounds GeTe and $Sb_2Te_3$ in the triangular Ge-Sb-Te composition diagram and includes the stoichiometric compounds $Ge_2Sb_2Te_5$ ($x = 4/9$), $GeSb_2Te_4$ ($x = 2/7$) and $GeSb_4Te_7$ ($x = 1/6$). Especially these ternary stoichiometric compounds are preferred, because these materials crystallize rapidly since no segregation is required during crystallization.

The first and second dielectric layers are preferably made of a mixture of ZnS and $SiO_2$, e.g. $(ZnS)_{80}(SiO_2)_{20}$. The layers may alternatively be made of $SiO_2$, $TiO_2$, $Ta_2O_5$, ZnS, AlN and/or $Si_3N_4$. The dielectric layer through which the laser light enters the stack preferably has a thickness of 70 to $(70+\lambda/2n)$ nm wherein n is the refractive index of the first dielectric layer and $\lambda$ is the wavelength of the read/write laser-light beam. If the total thickness is smaller than 70 nm, the cyclability is reduced considerably. The cyclability is measured by the relative change of the optical contrast $M_0$ after a large number of DOW-cycles, e.g. $10^3$. The optical contrast $M_0$ is defined as $|R_C-R_A|/R_C$, where $R_C$ and $R_A$ are the reflections of the recording material in the crystalline and amorphous state respectively. Another way to define cyclability is related to jitter increase of the medium. Jitter is a measure of the distortion of the shape of a recording mark, and is measured as a time shift of rising and falling edges in the information signal. The jitter of the medium should be at a low, constant level during at least $10^3$ DOW-cycles.

As mentioned above the total thickness of the first dielectric layer is preferably smaller than $(70+\lambda/2n)$ nm. A larger total thickness does not further increase the cyclability and is more expensive to make. If for example the wavelength is equal to 630 nm and the refractive index is 1.5, the thickness range extends from 70 nm to 280 nm.

The dielectric layer, which is closest to the reflective layer, has a thickness of 10 to 40 nm. Preferably the thickness of the dielectric layer adjacent to the reflective layer is larger than or equal to 15 nm. A smaller thickness results in an increased cooling rate of the recording layer and, consequently, an undesirable increase in the write power. The thickness is preferably smaller than 40 nm. A larger thickness decreases the thermal contact between the recording layer and the reflective layer too much, resulting in too low a cooling rate of the recording layer and a worse recording performance.

The reflective layer may comprise metals such as Al, Ti, Au, Ni, Cu, Ag and Cr, and alloys of these metals. The reflective layer preferably has a thickness of 60 to 120 nm.

Both the reflective layers and the dielectric layers generally have been provided by vapour deposition or sputtering.

Optionally an outermost layer may be present on the stack as a cover layer that protects the underlying layers from the environment. The cover layer is made of, for example, an UV light-cured poly(meth)acrylate.

Another specific embodiment is characterized in that the reflective layer is present between the substrate and the first dielectric layer. Optionally a cover layer, that is transparent for laser-light and has a surface which allows optical recording of information into and reading of information from the underlying recording layer with a focused laser-light beam is present on top of the stack. Thus in this embodiment the optical recording medium is written in and read out through the cover layer. This method is used in the new DVR discs that were mentioned above. The cover layer of a DVR disc has a thickness of about 100 micrometers. This cover layer allows the use, in optical disc recorders, of a read/write lens with a high numerical aperture that is necessary for high density recording and reading. Because the laser light enters the medium through the cover layer it may be necessary to adjust the thicknesses of the layers of the stack in order to optimize for optimal optical contrast between recorded and unrecorded areas.

The term high-speed recording, which was mentioned above, is to be understood to mean in this context a linear velocity of the medium relative to the laser-light beam of at least 7.2 m/s, which is six times the speed according to the Compact Disc standard. The use of an optical recording medium according to the invention is therefore advantageous because the crystallization rate is fast enough to permit at least this recording velocity. The important parameter is the CET (in ns), which is defined above. The CET is inversely proportional to the crystallization rate.

The substrate of the information medium generally is transparent to the laser wavelength, and is made, for example, of polycarbonate, polymethyl methacrylate (PMMA), amorphous polyolefin or glass. In a typical example, the substrate is disc-shaped and has a diameter of 120 mm and a thickness of 1.2 mm, 0.6 mm or 0.1 mm for respectively low, medium and high information density applications.

Alternatively, the substrate may be in the form of a synthetic resin flexible tape, made e.g. from a polyester film. This flexible tape, with a stack of layers deposited thereon, is called an optical tape and can be suited for use in an optical tape recorder, which is for example based on a fast spinning polygon. In such a device the reflected laser-light beam scans transversely across the tape surface.

The surface of the disc-shaped substrate on the side of the recording layer is, preferably, provided with a servotrack that can be scanned optically. This servotrack is often constituted by a spiral-shaped groove and is formed in the substrate by means of a mould during injection moulding or pressing. This groove can be alternatively formed in a replication process in a synthetic resin layer, for example, of an UV light-cured layer of acrylate, which is separately provided on the substrate. In high-density recording such a groove has a pitch e.g. of 0.5 - 0.8 μm and a width of about half the pitch.

High-density recording and erasing can be achieved by using a short-wavelength laser, e.g. with a wavelength of 675 nm or shorter (red to blue).

The phase change recording layer as well as the G-layer can be applied by vapour depositing or sputtering of a suitable target. The recording layer thus deposited is amorphous and exhibits a low reflection. In order to constitute a suitable recording layer having a high reflection, this layer must first be completely crystallized, which is commonly referred to as initialization. For this purpose, the recording layer can be heated in a furnace to a temperature just above the crystallization temperature of the e.g. Ge-In-Sb-Te or Ge-Sb-Te compound, e.g. 200°C. A synthetic resin substrate, such as polycarbonate, to which a high temperature may cause damage, can alternatively be heated by a laser-light beam of sufficient power. This can be realized, e.g. in a recorder, in which case a laser beam scans the moving recording layer. The amorphous layer is then locally heated to the temperature required for crystallizing the layer, without the substrate being subjected to a disadvantageous heat load.

If desired, an additional, optically transparent, metal layer M' can be interposed in the stack, thereby forming a so called MIRIM'-structure, wherein R represents a layer stack comprising a recording layer and at least one crystallization accelerating layer according to the present invention. Although the structure becomes more complicated, the additional metal layer increases the cooling rate of the recording layer as well as the optical contrast $M_0$.

Embodiments of the optical recording medium of the invention will be described with reference to the drawings.

In the drawings:

Fig. 1 shows a schematic cross sectional view of a first embodiment of the optical recording medium.

Fig. 2. shows a view as shown in FIG.1 of a second embodiment.

Fig. 3 shows a view as in FIG.2 of a third embodiment.

In Fig. 1 the optical recording medium 20 has a substrate 1 and a stack 2 of layers provided thereon. The substrate 1 may be made of, for example, a sheet of plastic, e.g. polycarbonate, or glass. In Fig. 1 the stack 2 comprises a phase change recording layer 5, having a melting point $T_{mp}$ and being able to change between an amorphous and a crystalline state, that is sandwiched between a first 3 and a second 7 dielectric layer, the first 3 being adjacent to the substrate 1. In this embodiment both the first dielectric layer 3 and the second dielectric layer 7 are made of the material $(ZnS)_{80}(SiO_2)_{20}$ and have a thickness of 125 nm and 20 nm respectively. A crystallization accelerating layer 6, abbreviated as G-layer, is interposed in contact with the recording layer 5, which comprises an alloy of Q, In, Sb and

Te, wherein Q is selected from the group consisting of Ag and Ge. A reflective layer 8 is present on top of the stack 2. Reflective layer 8 is a 100 nm layer of Al or an aluminium alloy, e.g. AlCr or AlTi. The crystallization accelerating layer 6 comprises a binary metal alloy or a semiconductor element or semiconductor alloy and has a melting point $T_{mg}$ at least 250°C higher than the melting point $T_{mp}$ of the recording layer 5. The crystal structure of these materials is similar to the crystalline state of the recording layer 5. In this embodiment the recording layer 5 is made of $Ge_{6.2}In_{3.2}Sb_{71.1}Te_{19.6}$, which has a thickness of 12 nm. The embodiment shown has a cover layer 9 that may be made of an organic material, e.g. a UV-cured resin. A focused laser-light beam with a wavelength $\lambda$=405 nm enters the medium through the substrate 1. This beam is diagrammatically illustrated by means of an arrow 10 in Fig. 1.

In this embodiment, when using PbTe as G-layer, which has a thickness of 3 nm, the CET has been measured to be equal to 40 ns, which is sufficiently short to allow high-speed recording. When no G-layer is present a minimal CET value of 48 ns can be obtained. Other preferred materials as G-layer are $Ag_2Te$, CrTe, Ge or Si. The melting points $T_{mg}$ of bulk PbTe, $Ag_2Te$, CrTe, Ge and Si are 914, 960, 1292, 936 and 1414°C respectively. The write power for the medium is relatively low and is 9 mW at the entrance face of the medium at a relative speed between the radiation beam and the medium of 7.2 m/s. The $R_A$ and $R_C$ are measured to be 4.3% and 23% respectively.

The cyclability is measured as the number of rewrite cycles where the jitter has increased to 12% of the clock time $T_C$. The jitter is the standard deviation of the difference between the rising and falling edges in the information signal and the data clock recovered from the information signal. As an example, for a standard CD format written with the so-called EFM code at the CD speed of 1.2 m/s and clock time of 230 ns, the jitter should be lower than 28 ns. The number of overwrite cycles before deterioration of the medium becomes noticeable, e.g. the jitter has increased to 12% of the clock time, is larger than $10^3$. The jitter of a pattern read from the medium as a function of the overwrite cycle does not show a large overshoot.

During writing, the recording layer 5 of $Ge_{6.2}In_{3.2}Sb_{71.1}Te_{19.6}$ is heated to a temperature of about 750°C, well above its melting temperature, which is about 550°C. The temperature during recording is below the melting temperature of the G-layer 6 comprising PbTe. The high melting temperature of the material used for the G-layer neighbouring the recording layer 5 therefore results in an increased cyclability of the recording medium.

In application JP-09161316 A the crystallization accelerating layer N of $Sb_2Te_3$, which has a melting point of 618°C, is thus heated above its melting temperature, causing the atoms in the layer to become mobile. These atoms are then able to diffuse into the recording layer. The properties of the recording layer are affected by the influx of foreign atoms, resulting in a deterioration of the recording process.

In Fig. 2 and Fig. 3 corresponding reference numerals denote the same layers as in Fig. 1.

In Fig. 2 a second crystallization accelerating layer 4 similar to the crystallization accelerating layer 6 is arranged between the recording layer 5 and the first dielectric layer 3. Now G-layers 4, 6 are present on both sides adjacent to the recording layer 5. The G-layer 6 is made of PbTe and has a thickness of 1.5 nm. The second G-layer 4 is substantially equal both in thickness and in composition to the G-layer 6. The recording layer 5 has a thickness of 10 nm. Further the characteristics of the stack 2 are the same as in Fig. 1. The CET is measured to be 36 ns. The CET in this embodiment is smaller than in the embodiment with only one G-layer. The $R_A$ and $R_C$ are measured to be 4.6% and 22% respectively.

In Fig. 3 the reflective layer 8 is present between the substrate 1 and the first dielectric layer 3. In this embodiment the laser light 10 is entering the stack 2 through the cover layer 9 which has a thickness of 100 μm. The cover layer 9 has a uniform thickness, thereby improving the optical read and write performance in underlying recording layers when the read or write laser beam passes through said cover layer 9. For example a 100 μm cover layer 9 is used for the new 60 mm radius Digital Video Recording (DVR) disc. This disc is recorded in and read out through this cover layer 9, which therefore has to be of good optical quality. Preferably, the cover layer 9 is 100+/-3 μm thick up to radius 58.5 mm. The cover layer 9 is made from a UV-cured resin. Dielectric layer 3 and 7 have a thickness of 20 nm and 125 nm respectively and are made of the same dielectric material as in Fig. 1. G-layer 4, 6 are made of the same material as in Fig. 2 and both have a thickness of 1.5 nm. Recording layer 5 has a thickness of 10 nm. For characteristics that are not specifically mentioned reference is made to the description of Fig. 1.

Preferably, for all embodiments, the surface of the disc-shaped substrate 1 on the side of the stack 2 is provided with a servotrack that can be scanned optically. This servotrack is often constituted by a spiral-shaped groove and is formed in the substrate by means of a mould during injection moulding or pressing. This groove can be alternatively formed in a replication process in a synthetic resin layer, for example, of an UV light-cured layer of acrylate, which is separately provided on the substrate 1. In high-density recording such a groove has a pitch e.g. of 0.5 - 0.8 μm and a width of about half the pitch.

In a modification of the recording medium of Fig. 3, the recording layer 5 comprises an alloy of Ge, Sb and Te, e.g. $Ge_2Sb_2Te_5$.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. The word "comprising" does not exclude the presence of elements or steps other than those listed in a claim. The word "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

According to the invention an optical recording medium is provided, which is suitable for high speed recording, e.g. with a possible data rate higher than 50 Mbits/s, and which is suitable for direct overwrite for a least $10^3$ times.

CLAIMS:

1. An optical recording medium (20) having a substrate (1) and a stack (2) of layers provided thereon, the stack comprising a recording layer (5), having a melting point $T_{mp}$ and being able to change between an amorphous and a crystalline state, sandwiched between a first (3) and a second (7) dielectric layer, the first (1) being adjacent to the substrate (1), a crystallization accelerating layer (4, 6) being interposed in contact with the recording layer (5), and a reflective layer (8), characterized in that the crystallization accelerating layer (4, 6)

- comprises a material selected from the group consisting of binary metal alloys, semiconductors elements and semiconductor alloys and
- has a melting point $T_{mg}$ at least 250°C higher than the melting point $T_{mp}$ of the recording layer (5) and
- has a crystal structure similar to the crystalline state of the recording layer (5).

2. An optical recording medium (20) as claimed in Claim 1 characterized in that the crystallization accelerating layer (4, 6) comprises a material selected from the group consisting of PbTe, $Ag_2Te$, CrTe, Ge and Si.

3. An optical recording medium (20) as claimed in any of Claims 1 or 2, characterized in that the crystallization accelerating layer (6) is arranged between the recording layer (5) and the second dielectric layer (7).

4. An optical recording medium (20) as claimed in Claim 3, characterized in that a second crystallization accelerating layer (4) similar to the crystallization accelerating layer (6) is arranged between the recording layer (5) and the first dielectric layer (3).

5. An optical recording medium (20) as claimed in Claim 4, characterized in that the second crystallization accelerating layer (4) is substantially equal both in thickness and in composition to the crystallization accelerating layer (6).

6. An optical recording medium (20) as claimed in Claim 1, characterized in that the recording layer (5) comprises an alloy of Q, In, Sb and Te, wherein Q is selected from the group consisting of Ag and Ge

7. An optical recording medium (20) as claimed in Claim 1, characterized in that the recording layer (5) comprises an alloy of Ge, Sb and Te.

8. An optical recording medium (20) as claimed in Claim 1, characterized in that the reflective layer (8) is present between the substrate (1) and the first dielectric layer (3).

9. The use of an optical recording medium (20), which medium is claimed in any one of the preceding claims, characterized in that the linear velocity of the medium relative to a laser-light beam (10) is at least 7.2 m/s.

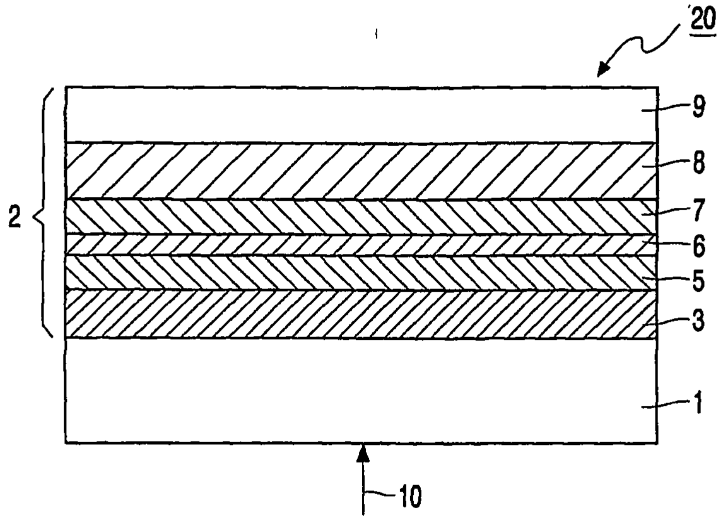

FIG. 1

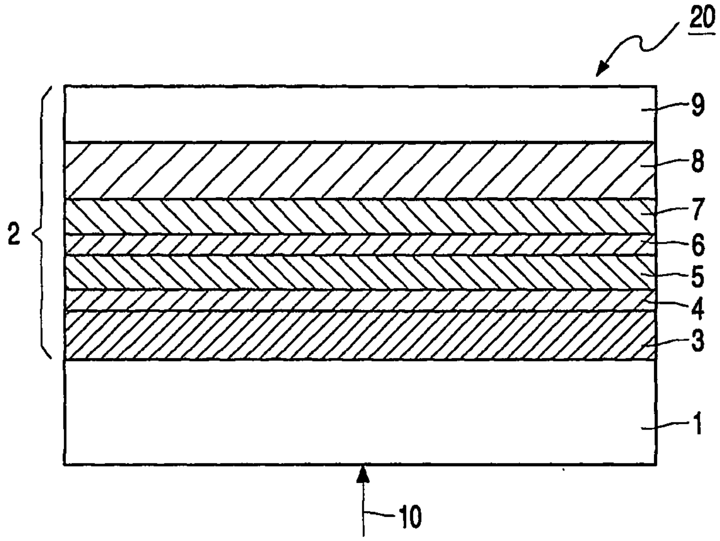

FIG. 2

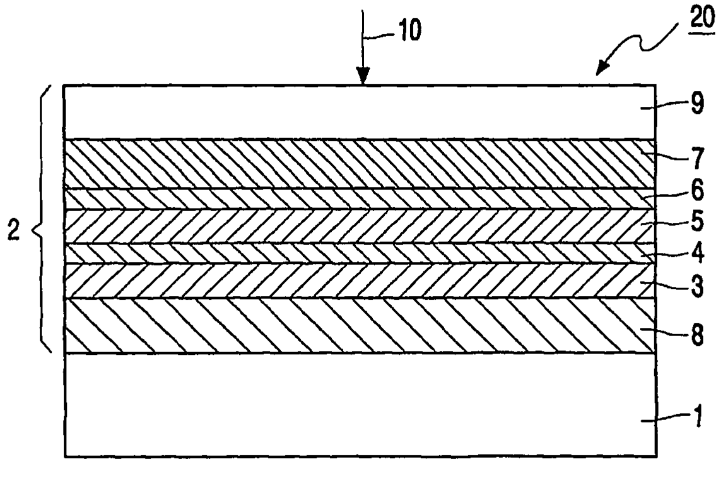

FIG. 3

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/04028

|  |
|---|
| **A. CLASSIFICATION OF SUBJECT MATTER**<br>IPC 7 G11B7/24 |
| According to International Patent Classification (IPC) or to both national classification and IPC |
| **B. FIELDS SEARCHED** |
| Minimum documentation searched (classification system followed by classification symbols)<br>IPC 7 G11B |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)<br>EPO-Internal, PAJ, WPI Data |

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 980 068 A (ASAHI CHEMICAL IND)<br>16 February 2000 (2000-02-16)<br>abstract<br>paragraph ‘0012! - paragraph ‘0019!<br>paragraph ‘0038!; figure 1 | 1,2,7 |
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| A |  | 3,4,9 |
| Y | EP 0 431 489 A (HITACHI LTD)<br>12 June 1991 (1991-06-12)<br>column 16, line 28 - line 56; figure 18 | 8 |
|  | -/-- |  |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

|  |  |
|---|---|
| Date of the actual completion of the international search<br>8 August 2001 | Date of mailing of the international search report<br>16/08/2001 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Annibal, P |

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/04028

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 945 860 A (MATSUSHITA ELECTRIC IND CO LTD) 29 September 1999 (1999-09-29)<br>abstract<br>paragraph '0017!<br>paragraph '0018!<br>paragraph '0034!<br>paragraph '0035!<br>paragraph '0050!<br>paragraph '0084!; figures 1,2 | 1,3-7,9 |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 018, no. 552 (P-1815),<br>20 October 1994 (1994-10-20)<br>& JP 06 195747 A (NEC CORP),<br>15 July 1994 (1994-07-15)<br>abstract | 1,7,9 |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 017, no. 384 (P-1575),<br>19 July 1993 (1993-07-19)<br>-& JP 05 062249 A (MATSUSHITA ELECTRIC IND CO LTD), 12 March 1993 (1993-03-12)<br>abstract | 1,7,9 |
| X | EP 0 843 874 A (PHILIPS ELECTRONICS NV)<br>27 May 1998 (1998-05-27)<br>column 25, line 10 -column 26, line 38;<br>examples 10,11 | 1,7 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 01/04028

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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FEB 06 2007
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS ) Confirmation No.: 6938
)

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## PETITION FOR EXTENSION OF TIME

Applicant petitions for a two month extension of time to reply to the Office action of September 9, 2006. The Commissioner is hereby authorized to charge the fee of $450.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 6, 2007

By: Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 955594467 US**

02/12/2007 EFLORES 00000096 060916 10101863
01 FC:1252 450.00 DA

PTO/SB/06 (07-06)
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| | | | |
|---|---|---|---|
| **PATENT APPLICATION FEE DETERMINATION RECORD**<br>Substitute for Form PTO-875 | Application or Docket Number<br>10/101,863 | Filing Date<br>03/16/2002 | ☐ To be Mailed |

APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY ☒ | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | RATE ($) | FEE ($) | | RATE ($) | FEE ($) |
| ☐ BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | X $ = | |
| ☐ APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| ☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | | | | | |
| | | | TOTAL | | | TOTAL | |

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

| | | (Column 1) | | (Column 2) | (Column 3) | SMALL ENTITY | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|---|---|---|
| AMENDMENT | **02/06/2007** | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
| | Total (37 CFR 1.16(i)) | * 36 | Minus | ** 39 | = 0 | X $25 = | 0 | OR | X $ = | |
| | Independent (37 CFR 1.16(h)) | * 3 | Minus | ***5 | = 0 | X $100 = | 0 | OR | X $ = | |
| | ☐ Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | ☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | | | OR | | |
| | | | | | | TOTAL ADD'L FEE | **0** | OR | TOTAL ADD'L FEE | |

| | | (Column 1) | | (Column 2) | (Column 3) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| AMENDMENT | | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
| | Total (37 CFR 1.16(i)) | * | Minus | ** | = | X $ = | | OR | X $ = | |
| | Independent (37 CFR 1.16(h)) | * | Minus | *** | = | X $ = | | OR | X $ = | |
| | ☐ Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | ☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | | | OR | | |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
Stella Little

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
ZHANG, Hongmei et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS ) Confirmation No.: 6938
)

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## TWELFTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed non-patent literature documents are attached. A copy of the U.S. patent publications is not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

03/21/2007 EEKUBAY1 00000028 060916 10101863
01 FC:1806 180.00 DA

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 19, 2007

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

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| | | | | | |
|---|---|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO<br>**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**<br>*(Use as many sheets as necessary)* | | | | ***Complete if Known*** | |
| | | | | *Application Number* | 10/101,863 |
| | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of | 1 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-2001/0034106 A1 | 10-25-2001 | Moise et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action and Terminal Disclaimer dated March 1, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Response to Office Action dated March 1, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Office Action dated March 14, 2007, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
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| | | Office Action dated March 6, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Notice of Allowance dated February 21, 2007, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00). | |
| | | Notice of Allowance dated February 22, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |

| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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**EV 977728611 US**

04-02-07

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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|  |  |  |
|---|---|---|
| In re Application of: | ) |  |
|  | ) |  |
| ZHANG, Hongmei et al. | ) | Group Art Unit: 2823 |
|  | ) |  |
| Application No.: 10/101,863 | ) | Examiner: ESTRADA, Michelle |
|  | ) |  |
| Filed: March 16, 2002 | ) |  |
|  | ) |  |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | ) | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## FOURTEENTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicant brings to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), the Commissioner is hereby authorized to charge the fee of $180.00 as specified by Section 1.17(p) to Deposit Account No. 06-0916.

Copies of the listed non-patent literature documents are attached. Copies of the U.S. patent and patent publication are not enclosed.

Applicant respectfully requests that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicant determines that the cited documents do not constitute "prior art" under United States law, Applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicant further reserves the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: March 30, 2007

By:____________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EV 977728497 US**

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MAR 3 0 2007
PATENT & TRADEMARK

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|---|---|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | **Complete if Known** |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Application Number* | 10/101,863 |
| | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of | 1 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-6,391,166 B1 | 05-21-2002 | Wang | |
| | | US-20070053139 A1 | 03-08-2007 | Zhang et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action dated March 19, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Response to Office Action dated March 30, 2007, 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Notice of Allowance dated March 26, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| | | Supplemental Notice of Allowance dated March 15, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |
| | | Voluntary Amendment dated March 8, 2007, in TW Appl. No. 93114518 (Attorney Docket No. 9140.0033-00270). | |
| | | Application filed March 22, 2007 (Attorney Docket No. 9140.0033-01). | |

| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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**UNITED STATES DEPARTMENT OF COMMERCE**
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www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 9140.0016-00 | 6938 |

22852 7590 05/02/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |

| ART UNIT | PAPER NUMBER |
|---|---|
| 2823 | |

| MAIL DATE | DELIVERY MODE |
|---|---|
| 05/02/2007 | PAPER |

**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

PTOL-90A (Rev. 04/07)

| | | | |
|---|---|---|---|
| **Office Action Summary** | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. | |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 | |

***-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --***

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

1)☒ Responsive to communication(s) filed on *06 February 2007*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

4)☒ Claim(s) *2-13,21-24 and 40-60* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *2-13,21-24 and 40-60* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

**Application Papers**

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date *2/6/07,3/30/07,3/19/07*.

4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application

6) ☐ Other: _____.

## DETAILED ACTION

### *Claim Rejections - 35 USC § 103*

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21, 40-45 and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265).

With respect to claims 21, 40, 43 and 52, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13) such that the target voltage opscillates between positive and negative voltages; and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, the limitation “the filter is a band rejection filter at a frequency of the bias power” is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claims 8 and 52, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12, 49 and 55, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claims 56-60, One of ordinary skill in the art would have been led to the recited time pulse, bias power and frequency to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of time pulse, bias power and frequency, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233

(CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed time pulse, bias power and frequency or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen time pulse, bias power and frequency or upon another variable recited in a claim, the Applicant must show that the chosen time pulse, bias power and frequency are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. as applied to claims 8, 10-13 and 21 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

## *Response to Arguments*

Applicant's arguments filed 2/6/07 have been fully considered but they are not persuasive. Applicant argues that Smolanoff et al. do not disclose a target voltage that oscillates between positive and negative voltages. However, Smolanoff is using and RF bias power, which will make the voltage to oscillate between positive and negative voltages, it doesn't matter if they are using just the negative voltage it will oscillate.

Applicant argues that Smolanoff et al. is directed to deposit conducing layers. However, Applicant claim is directed to an oxide, it doesn't say it can't be a conducting oxide. Therefore, the process suggested by Smolanoff et al. with the remaining references is encompassed by the instant claims.

## *Conclusion*

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL.** See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
April 30, 2007

OIPE
FEB 0 6 2007
PATENT & TRADEMARK OFFICE

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|---|---|---|
| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | **Complete if Known** | |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | *Application Number* | 10/101,863 |
| | *Filing Date* | March 16, 2002 |
| | *First Named Inventor* | ZHANG, Hongmei |
| | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | *Examiner Name* | ESTRADA, Michelle |
| Sheet 1 of 3 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-6,088,492 | 07-11-2000 | Kaneko et al. | |
| | | US-6,154,582 | 11-28-2000 | Bazylenko et al. | |
| | | US-2002/0191916 A1 | 12-19-2002 | Frish et al. | |
| | | US-2003/0044118 A1 | 03-06-2003 | Zhou et al. | |
| | | US 2003/0143853 A1 | 07-31-2003 | Celii et al. | |
| | | US 2005/0175287 A1 | 08-11-2005 | Pan et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | KR 2003-0088236 | 11-19-2003 | Hyundai Motor Co Ltd | | Abstract |
| | | WO 01/82297 A1 | 11-01-2001 | Koninklijke Philips Electronics N.V. | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | BELKIND, A. et al., "Pulsed-DC Reactive Sputtering of Dielectrics: Pulsing Parameter Effects," 43rd Annual Technical Conference Proceedings-Denver: 86-90 (April 15-20, 2000). | |
| | | SCHOLL, R., "Power Supplies for Pulsed Plasma Technologies: State-Of-The-Art And Outlook," Advances Energy Industries, Inc., pages 1-8 (1999). | |
| | | SCHOLLI, R., "Power Systems for Reactive Sputtering of Insulating Films," Advances Energy Industries, Inc., pages 1-8 (August 2001). | |
| | | Final Office Action dated October 12, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Response to Final Office Action dated November 3, 2006, in U.S. Application No. 10,291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Office Action dated December 1, 2006, in U.S. Application No. 10,291,179 (Attorney | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 4/26/07 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

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|---|---|---|---|
| Sheet | 2 | of | 3 |

| ***Complete if Known*** | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| | | | |
|---|---|---|---|
| | | Docket No. 9140.0001-00). | |
| ME | | Amendment dated October 19, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Office Action dated December 18, 2006, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Response to Office Action dated September 11, 2006 in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Office Action dated December 1, 2006, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Office Action dated October 31, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Response to Office Action dated December 6, 2006, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/228,834 (Attorney Docket No. 9140.0016-02). | |
| | | Supplemental Preliminary Amendment dated February 6, 2007, in U.S. Application No. 11/191,643 (Attorney Docket No. 9140.0016-04). | |
| | | Final Office Action dated October 19, 2006, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Voluntary Amendment dated July 26, 2006 in TW Appl. No. 92123625 (Attorney Docket No. 9140.0025-00270). | |
| | | Response to Final Office Action dated August 3, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00). | |
| | | Notice of Allowance dated October 23, 2006, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00). | |
| | | Office Action dated October 12, 2006, for U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| ME | | Response to Office Action dated December 21, 2006, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| no translation | | ~~Office Action dated September 22, 2006 from Korean Patent Office in Appl. No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202).~~ | |
| ME | | Response to Office Action dated November 8, 2006, to the Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202). | |
| | | Response to Office Action from Singapore Patent Office in Appl. No. 200505388-9, dated August 11, 2006 (Attorney Docket No. 9140.0030-00256). | |
| ME | | Final Office Action dated October 26, 2006, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 4/26/07 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EV 955594467 US**

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 3 | of | 3 |
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| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## NON PATENT LITERATURE DOCUMENTS

| | | | |
|---|---|---|---|
| ME | | Response to Office Action dated January 26, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |
| | | Preliminary Amendment dated July 21, 2006, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00). | |
| | | Supplemental Preliminary Amendment, Substitute Specification with Markings, Substitute Specification without Markings, and Replacement Drawing Sheets dated December 6, 2006 in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00). | |
| | | Continuation application and Preliminary Amendment dated December 13, 2006 (Attorney Docket No. 9140.0042-01). | |
| | | Voluntary Amendment dated August 15, 2006 in TW Appl. No. 94143175 (Attorney Docket No. 9140.0042-00270). | |
| ME | | PCT International Search Report and Written Opinion for Application No. PCT/US05/44781 dated October 3, 2006 (Attorney Docket No. 9140.0042-00304). | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 4/26/07 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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IDS Form PTO/SB/08: Substitute for form 1449A/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 1 |
|---|---|---|---|

| Complete if Known | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| /ME/ | | US-6,391,166 B1 | 05-21-2002 | Wang | |
| /ME/ | | US-20070053139 A1 | 03-08-2007 | Zhang et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| /ME/ | | Response to Office Action dated March 19, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| /ME/ | | Response to Office Action dated March 30, 2007, 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| /ME/ | | Notice of Allowance dated March 26, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| /ME/ | | Supplemental Notice of Allowance dated March 15, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |
| /ME/ | | Voluntary Amendment dated March 8, 2007, in TW Appl. No. 93114518 (Attorney Docket No. 9140.0033-00270). | |
| /ME/ | | Application filed March 22, 2007 (Attorney Docket No. 9140.0033-01). | |

| | | | |
|---|---|---|---|
| Examiner Signature | /Michelle Estrada/ | Date Considered | 04/26/2007 |

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EV 977728497 US**

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO<br>**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**<br>*(Use as many sheets as necessary)* | | | | ***Complete if Known*** |
| | | | *Application Number* | 10/101,863 |
| | | | *Filing Date* | March 16, 2002 |
| | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | *Art Unit* | 2823 |
| | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 1 | of 1 | *Attorney Docket Number* | 9140.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-2001/0034106 A1 | 10-25-2001 | Moise et al. | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action and Terminal Disclaimer dated March 1, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Response to Office Action dated March 1, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Office Action dated March 14, 2007, in Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Response to Office Action dated February 20, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Office Action dated March 6, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Notice of Allowance dated February 21, 2007, in U.S. Application No. 10/789,953 (Attorney Docket No. 9140.0030-00). | |
| | | Notice of Allowance dated February 22, 2007, in U.S. Application No. 10/851,542 (Attorney Docket No. 9140.0033-00). | |

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|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 4/26/07 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EV 977728611 US**

| Index of Claims | Application/Control No.<br>10101863 | Applicant(s)/Patent Under Reexamination<br>ZHANG ET AL. |
|---|---|---|
|  | Examiner<br>Estrada, Michelle | Art Unit<br>2823 |

|  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | Rejected | - | Cancelled | N | Non-Elected | A | Appeal |
| = | Allowed | ÷ | Restricted | I | Interference | O | Objected |

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

| CLAIM |  | DATE |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 |  |  |  |  |  |  |  |  |
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U.S. Patent and Trademark Office

Part of Paper No. : 20070430

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|---|---|---|
| ***Index of Claims*** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | **Rejected** | - | **Cancelled** | N | **Non-Elected** | A | **Appeal** |
| = | **Allowed** | ÷ | **Restricted** | I | **Interference** | O | **Objected** |

☐ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

| **CLAIM** | | **DATE** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 | | | | | | | | |
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OCT 0 2 2007
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al.

Application No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: ESTRADA, Michelle

Confirmation No.: 6938

**MAIL STOP RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), Applicants bring to the attention of the Examiner the document on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application.

Copies of the listed foreign document and non-patent literature documents are attached.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claim in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: ______________________
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.
EM 100825487 US**

10-04-07 RCE & IDS

# REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL

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PATENT & TRADEMARK OFFICE

Address to:
**Mail Stop RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

| | |
|---|---|
| Application Number: 10/101,863 | Confirmation Number: 6938 |
| Filing Date: March 16, 2002 | |
| First Named Inventor: ZHANG, Hongmei | |
| Group Art Unit: 2823 | |
| Examiner: ESTRADA, Michelle | |
| Attorney Docket Number: 10655.0016-00 | |

**This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of the above-identified application.**

Request for Continued Examination (RCE) practice under 37 C.F.R. § 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application.

1. **Submission required under 37 C.F.R. § 1.114: Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment.**

   a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

      i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on __________.

      ii. ☐ Other ________________________________

   b. ☐ **DO NOT ENTER** the amendment(s) previously filed on _________. An alternate submission is attached.

   c. ☒ Enclosed submission: .

      i. ☒ Amendment/Reply

      ii. ☐ Affidavit(s)/Declaration(s)

      iii. ☒ Information Disclosure Statement

      iv. ☐ Other ______________

2. Miscellaneous

   a. ☐ Suspension of action on the above-mentioned application is requested under 37 C.F.R. § 1.103(c) for a period of [number] months. (Period of suspension shall not exceed 3 months; fee under 37 C.F.R. § 1.17(i) required.)

   b. ☐ Other ________________________________

3. Fees

   a. ☒ The filing fee is calculated as follows:

      i. ☒ $810.00 RCE fee required under 37 C.F.R. § 1.17(e)

      ii. ☒ Petition for extension of time for (2 Months) $460.00

      iii. ☐ Other ________________________________

   b. ☒ The Commissioner is hereby authorized to charge the fee of $1,270.00 to deposit account no. 06-0916.

   c. ☒ The Commissioner is authorized to charge any deficiencies in the filing fees, and/or credit any overpayments to Deposit Account 06-0916.

**Signature of Applicant, Attorney, or Agent Required**

| | |
|---|---|
| Name: Gary J. Edwards | Reg. No.: 41,008 |
| Signature: Gary J. Edwards | Date: October 2, 2007 |

**EXPRESS MAIL LABEL NO.**
**EM 100825487 US**

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PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | ) |
| | ) |
| ZHANG, Hongmei et al. | ) Group Art Unit: 2823 |
| | ) |
| Application No.: 10/101,863 | ) Examiner: ESTRADA, Michelle |
| | ) |
| Filed: March 16, 2002 | ) |
| | ) |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | ) Confirmation No.: 6938<br>) |

**MAIL STOP RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## PETITION FOR EXTENSION OF TIME

Applicants petition for a two-month extension of time to reply to the Final Office Action of May 2, 2007. The Commissioner is hereby authorized to charge the fee of $460.00 to Deposit Account No. 06-0916.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

10/05/2007 TNGUYEN2 00000052 060916 10101863
02 FC:1252 460.00 DA

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

**EXPRESS MAIL LABEL NO.**
**EM 100825487 US**

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OCT 0 2 2007
PATENT & TRADEMARK OFFICE

**RESPONSE UNDER 37 C.F.R. § 1.116**
**EXPEDITED PROCEDURE REQUESTED**
**EXAMINING GROUP 2820**
PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al.

Application No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REATIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: ESTRADA, Michelle

Confirmation No.: 6938

**MAIL STOP RCE**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## AMENDMENT

This response is being filed with a Request for Continued Examination and is in reply to the Final Office Action mailed May 2, 2007, the period for response having been extended to October 2, 2007, by a request for extension of two months with authorization for the Commissioner to charge the fee to Deposit Account No. 06-0916. Applicant amends the application as follows:

**Amendments to the Claims** are reflected in the listing of claims in this paper beginning on page 2.

**Remarks/Arguments** follow the amendment sections of this paper beginning on page 7.

## AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Cancelled)

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the

substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14.-20. (Cancelled).

21. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target ~~through a filter~~ such that ~~the~~ a target voltage oscillates between positive and negative voltages to create a plasma and deposit the oxide film; and

band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target,

wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in poisonous mode to prepare the surface~~, and~~

~~wherein the filter is a band rejection filter at a frequency of the bias power~~.

22. (Previously presented ): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25.-39. (Canceled).

40. (Currently amended): The method of claim 21, wherein band rejection filtering utilizes the band rejection filter is a narrow band-pass filter.

41. (Currently amended): The method of claim 21, wherein a bandwidth of the narrow band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; ~~and~~

applying pulsed DC power to a target ~~through a band rejection filter at a frequency of the bias power~~ such that ~~the~~ a target voltage oscillates between positive and negative voltages and an oxide film is deposited on the substrate; and

band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target.

44. (Previously presented): The method of claim 43, wherein band rejection filtering the DC power includes utilizing a band rejection filter with a bandwidth of ~~the band rejection filter is~~ less than about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

47. (Previously presented): The method of Claim 43, further including holding the temperature

of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (Currently amended): A method of depositing an oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that ~~the~~ a target voltage oscillates between positive and negative voltages; and

narrow band rejection filtering the pulsed DC power ~~through a narrow band rejection filter~~ at a frequency of the bias power before applying pulsed DC power to the target,

wherein the oxide film is deposited on the substrate.

52. (Previously presented): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, $N_2$, $O_2$, $C_2F_6$, $CO_2$, CO, $NH_3$, NO, and halide containing gasses.

53. (Previously presented): The method of claim 51, wherein the target is a metallic target.

54. (Previously presented): The method of claim 51, wherein the target is an intermetllic target.

55. (Previously presented). The method of claim 51, further including sweeping the target with a magnetic field.

56. (Previously presented): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (Previously presented): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (Currently amended) The method of claims 21, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (Currently amended) The method of claim 43, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

60. (Currently amended) The method of claim 51, wherein applying pulsed DC power ~~through the filter~~ includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

## **REMARKS**

Claims 2-13, 21-24, and 40-60 are pending in this application. The Examiner has rejected claims 2-13, 21-24, and 40-60. Applicants herein have amended claims 21, 40, 43-44, 51, and 58-60 in order to further clarify the invention. No new matter has been added in this Amendment.

## **Claim Rejections Under 35 U.S.C § 103(a)1**

To establish a *prima facie* case of obviousness the prior art reference (or references when combined) must teach or suggest all the claim limitations. *See* MPEP § 2142, 8th Ed., Rev. 5 (August 2006). Moreover, "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed." USPTO Memorandum from Margaret A. Focarino, Deputy Commissioner of Patent Operations, May 3, 2007, page 2. As further discussed below, the Examiner has not established a *prima facia* case of obviousness at least because the prior art fails to teach all of the elements of each of the rejected claims.

### ***Claims 10-13, 21, 40-45, and 51-60***

Claims 10-13, 21, 40-45, and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 6,117,279 to Smolanoff et al. ("Smolanoff") in view of U.S.

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1 The Examiner has made multiple characterizations of the claims, the cited art, and the application of legal principles to those characterizations. Applicants shall not be deemed to agree with or to acquiesce in the Examiner's statements by not specifically addressing these characterizations in this response.

Patent No. 6,306,265 to Fu et al. ("Fu"). Claims 21, 43, and 51 are independent claims. Applicants herein traverse these rejections.

1. Neither Smolanoff nor Fu teach applying pulsed DC power to the target so that the target voltage oscillates between positive and negative voltages.

Claims 21 and 51 each recite "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages . . ." Claim 43 recites "applying pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages . . . ." Therefore, each of the independent claims requires applying pulsed DC power to the target such that the target voltage oscillates between positive and negative voltages. Neither Smolanoff nor Fu teach this limitation. In fact, both Smolanoff and Fu teach away from this feature in that both teach that the target voltage must be at a negative potential so that the target functions as a cathode.

The Examiner states that "Smolanoff et al. discloses . . . wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13) such that the target voltage opscillates [sic] between positive and negative voltages . . ." (Office Action, page 2). However, Smolanoff teaches away from the target voltage going positive. In fact, the Examiner's cited reference states exactly the opposite of the Examiner's assertion. that Smolanoff teaches that the target voltage oscillates between positive and negative voltages Smolanoff states that "[t]his main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16**, thereby ejecting particles of coating material from the target 16." (Smolanoff, col. 6, lines 8-13).

Smolanoff teaches in its background section that "[t]he plasma is typically generated by maintaining the target, either constantly or intermittently, **at a negative potential** so that the target functions as a cathode to supply electrons that excite the gas in the chamber and form a plamsa adjacent to the target surface." (Smolanoff, col. 1, lines 33-37) (emphasis added). Further, in operation "[t]he gas ions accelerate toward the target, **which is negatively biased**, to collide with the target surface and eject from the target surface atoms and atomic clusters or particles of target material, as well as secondary electrons, which play a role in sustaining the plasma." (Smolanoff, col. 1, lines 41-46) (emphasis added).

Further, in describing Smolanoff's apparatus, as shown in Figure 1, Smolanoff teaches that "[t]he magnet structure 20 preferably includes magnets that produce a closed magnetic tunnel over the surface of the target 16 that traps electrons given off into the chamber 12 by the cathode assembly 17 **when the cathode assembly 17 is <u>electrically energized to a negative potential</u> as is familiar to one skilled in the art.**" (Smolanoff, col. 5, lines 39-44) (emphasis added).

In particular, Smolanoff teaches that the target is always negative:

> Power from the steady or pulsed DC power supply 21 and/or RF generator 24 **produces a negative potential on the target 16**. The negative potential accelerates ions towards the surface of the target which, upon impact, cause electrons to be emitted from the surface of the target 16. These electrons become trapped over the surface of the target 16 by the magnetic field generated by the magnet pack 20, until, eventually, the electrons strike and thereby ionize atoms of process gas in close proximity to the surface of the target 16, forming a main plasma in a region 23 of the volume 11 adjacent to the surface of the target 16. This main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16**, thereby ejecting particles of coating material from the target 16.

(Smolanoff, col. 6, line 66, through col. 6, line 12) (emphasis added).

Therefore, repeatedly Smolanoff teaches that the target must be negative in order to create the plasma. Smolanoff never teaches that the target is at a positive voltage, which according to the teachings of Smolanoff would not work because the positive ions of the plasma would not then be attracted to the target. Smolanoff therefore teaches away from applying a positive voltage to the target. At a minimum, the Examiner can not maintain that Smolanoff teaches "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43.

Further Fu also teaches away from the target having a positive voltage. As taught in Fu, in describing a conventional PVD reactor, "[a] selectable DC power supply 22 **negatively biases the target 14 to about -600 VDC** with respect to the shield 20." (Fu, col. 1, lines 31-33) (emphasis added). Further, as was similarly taught in Smolanoff, "[w]hen the argon is admitted into the chamber, the DC voltage between the target 14 and the shield 20 ignites the argon into a plasma, and the **positively charged argon ions are <u>attracted to the negatively charged target 14</u>**." (Fu, col. 1, lines 51-54) (emphasis added). Therefore, Fu, like Smolanoff, teaches that the target must be negative and therefore teaches away from a positive target voltage. At a minimum, the Examiner can not maintain that Fu teaches "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43.

In responding to the remarks of Applicant's Amendment filed on February 6, 2007, the Examiner remarks that

> Applicant argues that Smolanoff et al. do not disclose a target voltage that oscillates between positive and negative voltages. However, Smolanoff is using and [sic] RF bias power, which will make the voltage to oscillate between positive and negative voltages, it doesn't matter if they are using just the negative voltage it will oscillate.

(Office Action, page 7). First, applying an RF bias to the substrate has negligible if any effect on the target voltage in a PVD deposition apparatus. Further, as seen in the discussion above, even if an RF voltage is applied to the target, the target achieves and maintains a negative voltage and never goes positive, as is well know in the art. Further, as is discussed in both Fu and Smolanoff, applying an RF bias to the substrate causes the substrate to become negative so as to attract the positive ions in the plasma. (*See* Smolanoff, col. 6, lines 51-63, "Such attraction of the positive ions of sputtered material toward the substrate 15 can be achieved, for example, **by applying a negative bias to the substrate 15 through the operation of the bias power supply 27**. Such bias attracts the positive sputtered ions . . . . For silicon semiconductor wafers, **this bias power supply 27 is preferably an RF generator** that operates in the range of from about 0.05 to 80 MHz." (emphasis added); Fu, col. 2, lines 36-45, "[t]he **pedestal 18** of FIG. 1, even if it is left electrically floating, **develops a DC self-bias**, which attracts ionized sputtered particles from the plasma across the plasma sheath adjacent to the pedestal 18 and deep into the hole 40 in the dielectral layer 42. **The effect can be accentuated with additional DC or RF biasing** of the pedestal electrode 18 to additionally accelerate the [positively] ionized particles extracted across the plasma sheath towards the wafer 16, thereby controlling the directionality of sputter deposition." (emphasis added)).

Therefore, neither Smolanoff nor Fu teach "applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages" as is recited in claims 21 and 51 or "applying a pulsed DC power to a target such that a target voltage oscillates between positive and negative voltages" as is recited in claim 43. In fact, both Smolanoff and Fu teach away from a positive voltage on the target.

2. Neither Smolanoff nor Fu teach "band rejection filtering the pulsed DC power"

The Examiner identifies filter 22 shown in Figure 1 of Smolanoff as teaching the band rejection filter recited in independent claims 21, 43, and 51. Further, the Examiner comments that "using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies." (Office Action, page 2) The Examiner further comments that "the limitation 'the filter is a band rejection filter at a frequency of the bias power' is a structural limitation in a method claim, so no matter what filter is used, as long as the same result is achieved, as explained above." (Office Action, page 2).

Claims 21, 43, and 51 have been amended such that the filtering is now a method step. Claims 21 and 43 now recite "band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target." Claim 51 now recites "narrow band rejection filtering the pulsed DC power at a frequency of the bias power before applying pulsed DC power to the target." Therefore, this limitation is now a method limitation and not a structural limitation.

Further, Smolanoff only refers to filter 22 once, and then only to identify it as "an RF filter 22." (Smolanoff, col. 5, line 58). Smolanoff does not teach that filter 22 performs the step "band rejection filtering the DC power at a frequency of the bias power" or "narrow band rejection filtering the pulsed DC power at a frequency of the bias power" as is recited in independent claims 21, 43, and 51.

Additionally, in order for the pulsed DC power applied to the target to be useful, the pulsed DC power must include substantially all of its Fourier constituents, and therefore only a band rejection filter that filters out a specific narrow band of filters can be utilized. Further, in order that the pulsed DC power be protected from the RF bias power supply, the band rejection filter must be set to filter out the frequency of the RF bias power supply. A low pass filter, which is commonly utilized in systems such as Smolanoff, would destroy all of the low frequency components of the pulses. With a band rejection filter, all of the pulsed DC power except that within the rejected band passes to the target. Therefore, far from not mattering which filter is used, as the Examiner opines, it is extremely important that the filter be a band rejection filter that filters out the frequency of the RF bias power, as is recited in claims 21, 43, and 51. For at least this reason, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu.

### 3. Neither Smolanoff nor Fu teach deposition of an oxide film

Each of claims 21, 43, and 51 recite deposition of an "oxide film." Both Smolanoff and Fu are directed towards deposition of metallic films. Smolanoff teaches away from deposition of insulating materials, as deposition of insulating materials would cause Smolanoff's reactor to become non-functional for its intended purpose.

As stated in Smolanoff, "[t]hose positive ions of sputtered material that are positively charged are capable of being electrically accelerated toward the substrate, for example, by application of a negative bias to the substrate." (Smolanoff, col. 2, lines 3-6). Smolanoff also explains this feature at col. 6, lines 51-63. Similarly, Fu teaches this same operable process in col. 2, lines 37-48. As Fu states, the substrate bias "attracts ionized sputter particles from the plasma." As is well known to those skilled in the art, when oxygen is introduced to the plasma, which is necessary to forming an oxide film, the oxygen reacts with the positive ions to form neutral particles of oxide, which are not attracted to the substrate by the RF bias on the substrate.

Both Smolanoff and Fu teach processes for ionized metal deposition or ionized metal plating (*see* Fu, col. 2, lines 47-48) and do not teach formation of oxide films on the substrate. Therefore, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu for at least this reason.

### 4. Conclusion

For at least the reasons stated above, claims 21, 43, and 51 are allowable over the combination of Smolanoff and Fu. Claims 10-13 and 40-42 depend from claim 21 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 21. Claims 44-45 depend from claim 43 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 43. Claims 52-60 depend from claim 51 and are allowable for at least the same reasons as is claim 51.

### ***Claims 2-4, 6, and 22-24***

Claims 2-4, 6, and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff in view of Fu, as applied to claims 8, 10-13, and 21. As discussed above, claim 21 is allowable over the combination of Smolanoff and Fu. Claims 2-4, 6, and 22-24 depend from claim 21 and are allowable over the combination of Smolanoff and Fu for at least the same reasons as is claim 21.

### ***Claims 7 and 9***

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff and Fu, as applied to claims 8, 10-13, and 21, and in view of U.S. Patent Publication No.

2003/0077914 to Le et al. ("Le"). Claim 21 is allowable over the combination of Smolanoff and Fu.

Le teaches deposition of oxides using pulsed DC processes without substrate bias. Le does not teach at least "band rejection filtering the DC power at a frequency of the bias power" or "narrow band rejection filtering the pulsed DC power at a frequency of the bias power" as is recited in independent claims 21, 43, and 51. Additionally, Le does not teach the combination of pulsed DC power and a RF bias to the substrate.

Further, one skilled in the art would not find a reason to combine Le with Smolanoff or Fu. Le is directed to deposition of oxide materials. Both Smolanoff and Fu are directed to deposition of ionized metal ions. One skilled in the art would realize that the introduction of oxygen, a reactive gas, to the processes disclosed in Smolanoff and Fu would render those processes non-functional for their intended purpose.

Therefore, claims 7 and 9 are allowable over the combination of Smolanoff, Fu, and Le.

## Conclusion

This Amendment is being filed with a Request for Continued Examination. In view of the foregoing remarks, Applicant submits that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicant therefore requests the entry of this Amendment, the Examiner's reconsideration and reexamination of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: October 2, 2007

By: Gary J. Edwards
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## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.$^1$ | Foreign Patent Document<br>Country Code$^1$ Number$^2$ Kind Code$^3$ *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation$^4$ |
|---|---|---|---|---|---|---|
| | | WO 2007/027535 A2 | 03-08-2007 | Symmorphix, Inc. | | |

## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.$^1$ | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation$^6$ |
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| | | Office Action dated September 22, 2006, from Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202). | Yes |
| | | Office Action mailed May 21, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00). | |
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| | | Notice of Non-Compliant Amendment mailed April 12, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
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| | | PCT International Preliminary Report on Patentability mailed June 21, 2007, in PCT Application No. PCT/US2005/044781 (Attorney Docket No. 9140.0042-304). | |

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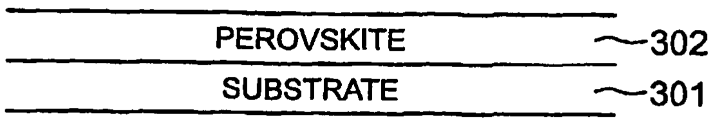
**(54) Title:** DEPOSITION OF PEROVSKITE AND OTHER COMPOUND CERAMIC FILMS FOR DIELECTRIC APPLICATIONS



**(57) Abstract:** In accordance with the present invention, deposition of perovskite material, for example barium strontium titanite (BST) film, by a pulsed-dc physical vapor deposition process or by an RF sputtering process is presented. Such a deposition can provide a high deposition rate deposition of a layer of perovskite. Some embodiments of the deposition address the need for high rate deposition of perovskite films, which can be utilized as a dielectric layer in capacitors, other energy storing devices and micro-electronic applications. Embodiments of the process according to the present invention can eliminate the high temperature (>700 °C) anneal step that is conventionally needed to crystallize the BST layer.

# Deposition of Perovskite and Other Compound Ceramic Films for Dielectric Applications

## FIELD OF THE INVENTION

[001] The present invention is related to production and application of dielectric thin-films and, in particular, the deposition of perovskites such as Barium Strontium Titanate (BST) films and other ceramic oxides for dielectric applications.

## DISCUSSION OF RELATED ART

[002] Perovskite films, for example Barium Strontium Titanate (BST) films, are one of the attractive materials to use in capacitors for high density device applications because of its relatively high dielectric constant, low leakage current density, high dielectric breakdown strength, and ferroelectric perovskite phase that does not exhibit fatigue. However, electric properties of the perovskite films are greatly dependent on the deposition process, the substrate, the post-processing, and the related film structure. For all of the potential, thin film perovskites have rarely been utilized in manufacture primarily because of difficulties in controlling physical and chemical properties of the crystalline and amorphous phases of perovskite thin-film materials and their interactions with metallic and conductive electrodes.

[003] Solid-state thin-film devices are typically formed by stacking thin films of metal and dielectric on a substrate. The thin films typically include two metallic electrodes with a dielectric layer in between. The thin films can be deposited utilizing a number of deposition processes, including sputtering, electroplating, chemical vapor deposition, sol gel, or oxidation. Substrates suitable for these applications have conventionally been high temperature materials capable of withstanding at least one high temperature anneal process to at least 650-750 °C so as to crystallize the perovskite dielectric film in order to increase its

dielectric constant. Such a substrate can be any suitable material with appropriate structural and material properties, for example a semiconductor wafer, refractory metallic sheet (e.g., titanium, zirconium, or stainless steel), ceramic such as alumina, or other material capable of withstanding subsequent high temperature processing.

[004] However, conventional materials and production processes can limit the types of materials that can be used in device manufacture. Typically, the dielectric material is deposited in amorphous form and then the material is heated in an anneal process to form the crystalline material. Conventional formation of perovskite layers, for example, require an anneal at or above 650°C to transform the deposited amorphous film to a crystalline form. Such a high temperature anneal, however, severely limits the materials that can be utilized as the substrate, and often requires the use of expensive noble metals such as platinum to protect the substrate from reaction with the electrode material. Such high heat-treat temperatures are incompatible with standard semiconductor or MEM device processing, and limit the choice of substrate materials on which the layers can be formed, increasing the cost, and decreasing the yield of such devices formed with the layers.

[005] Therefore, there is a need for a low temperature process for depositing crystalline material, for example perovskite material and other ceramic oxides, onto a substrate.

## SUMMARY

[006] In accordance with the present invention, deposition of layers in a pulsed-DC physical vapor deposition process from a conductive ceramic target is presented. In some embodiments, the deposition can provide a low-temperature, high deposition-rate deposition of a dense amorphous layer of BST from a conductive BST target, which can be annealed at much lower temperature to yield crystalline BST. Some embodiments of the deposition address the need for low temperature, high rate deposition of perovskite films, for example

BST films, which can be utilized as the dielectric layer in high specific capacitance devices as, for example, de-coupling capacitors, energy storage devices, voltage tunable capacitors, or other micro-electronic devices.

[007] A method of depositing a perovskite or ceramic oxide layer according to some embodiments of the present invention includes placing a substrate in a reactor; flowing a gaseous mixture, for example argon and oxygen, through the reactor; and applying pulsed-DC power to a target formed of conductive perovskite or ceramic oxide material, such as BST, positioned opposite the substrate.

[008] In some embodiments the perovskite layer can be formed utilizing radio frequency (RF) sputtering. The perovskite is deposited by RF sputtering of a wide area target in the presence of a sputtering gas under a condition of uniform target erosion. The substrate is positioned opposite a planar target formed of perovskite, for example BST, the area of the target being larger than the area of the substrate. A central area of the target of the same size as the substrate and overlying the substrate is exposed to a uniform plasma condition, which provides a condition of uniform target erosion. A uniform plasma condition can be created without magnetic enhancement, termed diode sputtering, or by providing a time-averaged uniform magnetic field by scanning a magnet across the target in a plane parallel to the plane of the target.

[009] A film produced utilizing a pulsed dc, bias PVD process with a conductive ceramic target can be deposited at much higher rates than an insulating ceramic process, which requires an RF sputtering process. Further, deposition occurs with much less oxygen present in the gas flow to provide a fully oxidized film as opposed to a metallic target. The resulting film is much higher density than the low rate films. The films can be stoichiometric, uniform, highly dense, with low sintering temperatures and resulting high dielectric properties.

[010] In some embodiments, the substrate is preheated. The substrate can be heated to a temperature of about 400°C or below during deposition for low temperature perovskite deposition, or to higher temperatures for perovskite deposition on substrates capable of withstanding such temperature regime. Substrates suitable for low temperature perovskite deposition include glass, plastic, metal foil, stainless steel, and copper. A perovskite layer of thickness up to several microns thick can be deposited, although layers of any thickness can be formed.

[011] In some embodiments the perovskite layer formed on the substrate is later annealed. The anneal temperature can be as low as 400°C for low temperature anneal, and higher for perovskite deposition on substrates capable of withstanding such higher temperature regime. In some embodiments the perovskite target can be doped with transition metal dopants, for example manganese, transition elements, lanthanides (including the rare earth ions) and/or amphoteric elements.

[012] In some embodiments, a stacked capacitor structure can be formed. The stacked capacitor structure includes one or more capacitor stacks deposited on a thin substrate, wherein each capacitor stack includes: a bottom electrode layer, a perovskite, for example BST, dielectric layer deposited over the bottom electrode layer; and a top electrode layer deposited over the dielectric layer. A top conducting layer can be deposited over the capacitor stacks.

[013] In some embodiments, a capacitor structure can be formed in a cluster tool. An exemplary method of producing a capacitor in a cluster tool includes loading a substrate into the cluster tool; depositing an electrode layer over the substrate in a first chamber of the cluster tool; depositing a perovskite dielectric layer over the electrode layer in a second chamber of the cluster tool; depositing a second electrode layer over the dielectric layer in a

third chamber. In some embodiments the first and the second electrode layers can be deposited in the same chamber.

[014] A fixture for holding a thin substrate can include a top portion; and a bottom portion, wherein the thin substrate is held when the top portion is attached to the bottom portion.

[015] In some embodiments, the ceramic layer can be deposited on a substrate coated with iridium or other refractory conductive material to provide a low temperature anneal processed capacitive structure.

[016] These and other embodiments of the invention are further discussed below with reference to the following figures. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed. Further, specific explanations or theories regarding the deposition or performance of materials according to the present invention are presented for explanation only and are not to be considered limiting with respect to the scope of the present disclosure or the claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

[017] Figures 1A and 1B illustrate a pulsed-DC biased reactive deposition apparatus that can be utilized in the methods of depositing according to the present invention.

[018] Figure 1C illustrates an RF sputtering deposition apparatus.

[019] Figure 2 shows an example of a target that can be utilized in the reactor illustrated in Figures 1A, 1B, and 1C.

[020] Figures 3A and 3B illustrate a thin-film capacitor design according to some embodiments of the present invention.

[021] Figures 4A, 4B, 4C, and 4D illustrate a thin substrate mount and mask arrangement that can be utilized in the deposition of dielectric perovskite layers, for example BST films, deposited according to some embodiments of the present invention.

[022] Figure 5 illustrates a cluster tool that can be utilized to form batteries with dielectric perovskite layers deposited according to some embodiments of the present invention.

[023] Figure 6 illustrates an example of stacked capacitor structure with dielectric perovskite layers deposited according to some embodiments of the present invention.

[024] In the figures, elements having the same designation have the same or similar functions.

## DETAILED DESCRIPTION

[025] In accordance with embodiments of the present invention, dielectric perovskite films or other ceramic oxide films are deposited on a substrate by a pulsed-DC physical vapor deposition (PVD) process utilizing a conductive ceramic target. In some embodiments, the film can be deposited by RF sputtering.

[026] In some embodiments, a dielectric perovskite layer, for example BST material, is deposited directly on the substrate with only low temperature anneal, eliminating the need of a subsequent high temperature anneal to crystallize the film. Removing the high temperature anneal allows for formation of capacitor structures on light-weight, low temperature, and low cost substrates such as copper foil and plastic sheet, reducing both the weight and the cost of capacitors while maintaining the high dielectric constant of the perovskite, for example BST, high-density dielectric film.

[027] Deposition of materials by pulsed-DC, RF biased reactive ion deposition is described in U.S. Patent Application Serial No. 10/101,863, entitled "Biased Pulse DC Reactive Sputtering of Oxide Films," to Hongmei Zhang, et al., filed on March 16, 2002.

Preparation of targets is described in U.S. Patent Application Serial No. 10/101,341, entitled "Rare-Earth Pre-Alloyed PVD Targets for Dielectric Planar Applications," to Vassiliki Milonopoulou, et al., filed on March 16, 2002. U.S. Patent Application Serial No. 10/101,863 and U.S. Patent Application Serial No. 10/101,341 are each assigned to the same assignee as is the present disclosure and each is incorporated herein in their entirety. Deposition of oxide materials by RF sputtering has also been described in U.S. Patent No. 6,506,289, which is also herein incorporated by reference in its entirety. Transparent oxide films can be deposited utilizing processes similar to those specifically described in U.S. Patent No. 6,506,289 and U.S. Application Serial No. 10/101,863.

[028] Figure 1A shows a schematic of a reactor apparatus 10 for sputtering material from a target 12 according to the present invention. In some embodiments, apparatus 10 may, for example, be adapted from an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu or an AKT-4300 (600 X 720 mm substrate size) system from Applied Komatsu, Santa Clara, CA. The AKT-1600 reactor, for example, has three deposition chambers connected by a vacuum transport chamber. These AKT reactors can be modified such that pulsed DC power is supplied to the target and RF power is supplied to the substrate during deposition of a material film.

[029] Apparatus 10 includes target 12, which is electrically coupled through a filter 15 to a pulsed DC power supply 14. In some embodiments, target 12 is a wide area sputter source target, which provides material to be deposited on a substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when power is applied to it from the pulsed DC power supply 14 and is equivalently termed a cathode. Application of power to target 12 creates a plasma 53. Substrate 16 is capacitively coupled to an electrode 17 through an insulator 54. Electrode 17 can be coupled to an RF power supply 18. A magnet 20 is scanned across the top of target 12.

[030] For pulsed reactive DC magnetron sputtering, as performed by apparatus 10, the polarity of the power supplied to target 12 by power supply 14 oscillates between negative and positive potentials. During the positive period, the insulating layer on the surface of target 12 is discharged. To obtain arc free deposition, the pulsing frequency exceeds a critical frequency that can depend on target material, cathode current and reverse time. High quality films can be made using reactive pulse DC magnetron sputtering as shown in apparatus 10.

[031] Pulsed DC power supply 14 can be any pulsed DC power supply, for example an AE Pinnacle plus 10K by Advanced Energy, Inc. With this DC power supply, up to 10 kW of pulsed DC power can be supplied at a frequency of between 0 and 350 kHz. The reverse voltage can be 10% of the negative target voltage. Utilization of other power supplies can lead to different power characteristics, frequency characteristics and reverse voltage percentages. The reverse time on this embodiment of power supply 14 can be adjusted between 0 and 5 μs.

[032] Filter 15 prevents the RF bias power from power supply 18 from coupling into pulsed DC power supply 14. In some embodiments, power supply 18 can be a 2 MHz RF power supply, for example a Nova-25 power supply made by ENI, Colorado Springs, Co.

[033] In some embodiments, filter 15 can be a 2 MHz sinusoidal band rejection filter. In some embodiments, the band width of the filter can be approximately 100 kHz. Filter 15, therefore, prevents the 2 MHz power from the bias to substrate 16 from damaging power supply 14 while allowing the full bandwidth of the pulsed DC power supply to pass filter 15.

[034] Pulsed DC deposited films are not fully dense and may have columnar structures. Columnar structures can be detrimental to thin film applications such as barrier films and dielectric films, where high density is important, due to the boundaries between the

columns. The columns act to lower the dielectric strength of the material, but may provide diffusion paths for transport or diffusion of electrical current, ionic current, gas, or other chemical agents such as water.

[035] In the AKT-1600 based system, for example, target 12 can have an active size of about 675.70 X 582.48 by 4 mm in order to deposit films on substrate 16 that have dimension about 400 X 500 mm. The temperature of substrate 16 can be adjusted to between –50 °C and 500 °C. The distance between target 12 and substrate 16 can be between about 3 and about 9 cm. Process gas can be inserted into the chamber of apparatus 10 at a rate up to about 200 sccm while the pressure in the chamber of apparatus 10 can be held at between about .7 and 6 milliTorr. Magnet 20 provides a magnetic field of strength between about 400 and about 600 Gauss directed in the plane of target 12 and is moved across target 12 at a rate of less than about 20-30 sec/scan. In some embodiments utilizing the AKT 1600 reactor, magnet 20 can be a race-track shaped magnet with dimensions about 150 mm by 600 mm.

[036] In some embodiments of the present invention a perovskite layer is deposited by RF sputtering with a wide area target and a condition of uniform target erosion. An example apparatus 30 for RF sputtering is illustrated schematically in FIG. 1C. Apparatus 30 includes an RF power supply 60 coupled to wide area sputter source target 12 which provides material to be deposited on substrate 16. Substrate 16 is positioned parallel to and opposite target 12. Target 12 functions as a cathode when RF power is applied to it and is equivalently termed the cathode. In the present disclosure, target 12 can be formed from a perovskite material, for example BST, for deposition of dielectric perovskite film. Substrate 16 is a solid, smooth surface. Substrate 16 typically is supported on a holder or carrier sheet 17 that may be larger than substrate 16.

[037] In some embodiments, a feature of the RF sputtering method is that the area of wide area target 12 is greater than the area on the carrier sheet on which physically and

chemically uniform deposition is accomplished. Secondly, a central region on target 12, overlying the substrate 16, can be provided with a very uniform condition of sputter erosion of the target material. Uniform target erosion is a consequence of a uniform plasma condition. In the following discussion, all mention of uniform condition of target erosion is taken to be equivalent to uniform plasma condition. Uniform target erosion is evidenced by the persistence of film uniformity throughout an extended target life. A uniform deposited film is defined as a film having a nonuniformity in thickness, when measured at representative points on the entire surface of a substrate wafer, of less than about 5%. Thickness nonuniformity is defined, by convention, as the difference between the minimum and maximum thickness divided by twice the average thickness. If films deposited from a target from which more than about 20% of the weight of the target has been removed under constant process conditions continue to exhibit thickness uniformity, then the sputtering process is judged to be in a condition of uniform target erosion for all films deposited during the target life.

[038] Thus, a uniform plasma condition can be created in the region between the target and the substrate overlying the substrate. The region of uniform plasma condition is indicated in the exploded view of FIG. 1B. A plasma is created in the region denoted 51, which extends under the entire target 12. The central region of the target 52 experiences the condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 will have uniform film thickness.

[039] In addition, the region in which deposition provides uniform film thickness is larger than the area in which deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In the present invention the target can be planar or approximately planar for the formation of a film on a planar substrate which is to be coated with the material of the target. In practice, planarity of the target means

that all portions of the target surface in region 52 are within a few millimeters of an ideal planar surface, typically within 0.5 mm.

[040] Figure 2 illustrates an example of target 12. A film deposited on a substrate positioned on carrier sheet 17 directly opposed to region 52 of target 12 has good thickness uniformity. Region 52 is the region shown in Figure 1B that is exposed to a uniform plasma condition. In some implementations, carrier 17 can be coextensive with region 52. Region 24 shown in Figure 2 indicates the area below which both physically and chemically uniform deposition can be achieved, for example where physical and chemical uniformity provide refractive index uniformity. Figure 2 indicates region 52 of target 12 that provides thickness uniformity, which is, in general, larger than region 24 of target 12 providing thickness and chemical uniformity to the deposited film. In optimized processes, however, regions 52 and 24 may be coextensive.

[041] In some embodiments, magnet 20 extends beyond area 52 in one direction, for example the Y direction in Figure 2, so that scanning is necessary in only one direction, for example the X direction, to provide a time averaged uniform magnetic field. As shown in Figures 1A and 1B, magnet 20 can be scanned over the entire extent of target 12, which is larger than region 52 of uniform sputter erosion. Magnet 20 is moved in a plane parallel to the plane of target 12.

[042] The combination of a uniform target 12 with a target area 52 larger than the area of substrate 16 can provide films of highly uniform thickness. Further, the material properties of the film deposited can be highly uniform. The conditions of sputtering at the target surface, such as the uniformity of erosion, the average temperature of the plasma at the target surface and the equilibration of the target surface with the gas phase ambient of the process are uniform over a region which is greater than or equal to the region to be coated with a uniform film thickness. In addition, the region of uniform film thickness is greater

than or equal to the region of the film which is to have highly uniform optical properties such as index of refraction, density, transmission, or absorption.

[043] In the present disclosure, target 12 can be formed from perovskite material, such as BST, for deposition of dielectric perovskite film. In some embodiments of the present invention the perovskite target is doped with transition metal dopants, for example Manganese, transition elements, lanthanides (including the rare earth ions) and/or amphotaric elements. In some embodiments of the present invention the percentage of the dopant in the perovskite target is from 0.1 to several percent.

[044] In some embodiments of the invention, material tiles are formed. These tiles can be mounted on a backing plate to form a target for apparatus 10. A wide area sputter cathode target can be formed from a close packed array of smaller tiles. Target 12, therefore, may include any number of tiles, for example between 2 and 20 individual tiles. Tiles can be finished to a size so as to provide a margin of non-contact, tile to tile, less than about 0.010" to about 0.020" or less than half a millimeter so as to eliminate plasma processes that may occur between adjacent ones of tiles 30. The distance between tiles of target 12 and the dark space anode or ground shield 19 in Figure 1B can be somewhat larger so as to provide non contact assembly or to provide for thermal expansion tolerance during process chamber conditioning or operation.

[045] As shown in Figure 1B, a uniform plasma condition can be created in the region between target 12 and substrate 16 in a region overlying substrate 16. A plasma 53 can be created in region 51, which extends under the entire target 12. A central region 52 of target 12 can experience a condition of uniform sputter erosion. As discussed further below, a layer deposited on a substrate placed anywhere below central region 52 can then be uniform in thickness and other properties (i.e., dielectric, optical index, or material concentrations). In addition, in region 52 the deposition provides uniformity of deposited film that can be larger

than the area in which the deposition provides a film with uniform physical or optical properties such as chemical composition or index of refraction. In some embodiments, target 12 is substantially planar in order to provide uniformity in the film deposited on substrate 16. In practice, planarity of target 12 can mean that all portions of the target surface in region 52 are within a few millimeters of a planar surface, and can be typically within 0.5 mm of a planar surface.

[046] Reactive gases that provide a constant supply of oxygen to keep the target surface oxidized can be provided to expand the process window. Some examples of the gases that can be utilized for controlling surface oxidation are $O_2$, water vapor, hydrogen, $N_2O$, fluorine, helium, and cesium. Additionally, a feedback control system can be incorporated to control the oxygen partial pressure in the reactive chamber. Therefore, a wide range of oxygen flow rates can be controlled to keep a steady oxygen partial pressure in the resulting plasma. Other types of control systems such as target voltage control and optical plasma emission control systems can also be utilized to control the surface oxidation of the target. In some embodiments, power to target 12 can be controlled in a feedback loop at supply 14. Further, oxygen partial pressure controller 20 can control either oxygen or argon partial pressures in plasma 53. In some embodiments of the present invention, oxygen flow or partial pressure can be utilized to maintain a constant voltage of discharge from target 12.

[047] Figures 3A and 3B show a capacitor structure with a dielectric perovskite layer deposited according to some embodiments of the present invention. As shown in Figure 3A, a dielectric perovskite layer 302 is deposited on a substrate 301. In some embodiments, the dielectric layer 302 can be patterned in various ways before deposition of a substrate 301. In some embodiments, a first electrode layer 303 can be deposited on the substrate and the dielectric layer 302 is deposited over the first electrode layer. The second electrode layer 304 is then deposited over the dielectric layer 302. In some embodiments of

the invention, the dielectric perovskite layer 302 is crystalline and has sufficiently high dielectric constant without the necessity of a high temperature anneal. Therefore, substrate 301 can be a silicon wafer, titanium metal, alumina, or other conventional high temperature substrate, but may also be a low temperature material such as plastic, glass, or other material that may be susceptible to damage from the high temperature anneal. This feature can have the great advantage of decreasing the expense and weight of capacitor structures formed by the present invention. The low temperature deposition of perovskite material allows for successive depositions of perovskite and electrode layers, one upon another. Such a process would have the advantage that successive layers of capacitor structure would be obtained in a stacked condition without the inclusion of a substrate layer. The stacked layered capacitor would provide higher capacitance and higher energy storage than single layer devices with a smaller surface area. Additionally, a capacitor with a lower inductance can be obtained.

[048] In accordance with the present invention, perovskite films can be deposited on substrate 302 with a pulsed-DC biased PVD system as was described above. In particular, an AKT 1600 PVD system can be modified to provide an RF bias and an Advanced Energy Pinnacle plus 10K pulsed DC power supply can be utilized to provide power to a target. The pulsing frequency of the power supply can vary from about 0 to about 350 KHz. The power output of the power supply is between 0 and about 10 kW.

[049] A target of Barium Strontium Titanate with resistivity in the range of less than about megaohms can be utilized with high rate pulsed-dc sputtering. As discussed above, the target can be mounted on a monolithic backing plate as described in U.S. Provisional Application {**Attorney Docket No. 09140.6013**}, filed on August 26, 2005, which is also herein incorporated by reference in its entirety.

[050] In general, target 12 can be a dielectric material having a resistivity of less than about a megaohm, and therefore can be described as a conducting ceramic target. Target

12, which is formed of a dielectric perovskite material that may not be inherently conducting, is made conducting by formulation so as to contain an excess of metallic composition or by addition of a dopant that provides sufficient conductivity. Examples of suitable dopants include boron, antimony, arsenic, phosphorous, or other dopants. In the example of a BST target, the sintering process can be conducted in the presence of a reducing ambient to achieve a sufficiently conductive target material. Utilization of a conducting ceramic target material can be sputtered at high rates utilizing reactive pulsed-DC techniques so as to form dense stoichiometric dielectric films.

[051] Gas flows containing Oxygen and Argon can be utilized. In some embodiments, the Oxygen to Argon ratio ranges from 0 to about 50% with a total gas flow of between about 60 to about 80 sccm. The pulsing frequency ranges from about 200 kHz to about 350 kHz during deposition. RF bias can also be applied to the substrate. In many trials, the deposition rates varied from about 2 Angstrom/(kW sec) to about 1 Angstrom/(kW sec) depending on the $O_2$/Ar ratio as well as substrate bias.

[052] Figure 3A illustrates a layer of perovskite material 302 deposited on a thin substrate 301 according to some embodiments of the present invention. Substrate 301 can be formed of a thin metallic sheet (e.g., copper, titanium, stainless steel, or other suitable thin metallic sheet), can be formed of a high temperature plastic material, or may be formed of a ceramic, glass, or polymer material.

[053] Depositing materials on a thin substrate involves holding and positioning the substrate during deposition. Figures 4A, 4B, 4C, and 4D illustrate a reusable fixture 400 for holding a thin film substrate. As shown in Figure 4A, reusable fixture 400 includes a top portion 401 and a bottom portion 402 that are fastened together to secure the substrate. Thin substrate 301 is positioned between top portion 401 and bottom portion 402. As shown in Figure 7B, top portion 701 and bottom portion 702 are such that substrate 301 is brought into

a planar condition and subsequently clamped as top portion 401 is closed into bottom portion 402. Substrate 301 can be easily held by fixture 400 so that substrate 301 can be handled and positioned. In some embodiments, the corners of substrate 301, areas 403, are removed so that substrate 301 is more easily stretched by avoiding "wrap-around" corner clamping effects when top portion 401 is closed into bottom portion 402.

[054] As shown in Figure 4C, a mask 412 can be attached to fixture 400. In some embodiments, fixture 400 includes guides in order to align fixture 400 with respect to mask 412. In some embodiments, mask 412 may be attached to fixture 400 and travel with fixture 400. Mask 412 can be positioned at any desired height above substrate 301 in fixture 400. Therefore, mask 412 can function as either a contact or proximity mask. In some embodiments, mask 412 is formed of another thin substrate mounted in a fixture similar to fixture 400.

[055] As shown in Figure 4C and 4D, fixture 400 and mask 412 can be positioned relative to mount 410. Mount 410, for example, can be a susceptor, mount, or an electrostatic chuck of a processing chamber such as that shown in Figures 1A and 1B. Fixture 400 and mask 412 can have features that allow for ready alignment with respect to each other and with respect to mount 410. In some embodiments, mask 412 is resident in the processing chamber and aligned with fixture 400 during positioning of fixture 400 on mount 410, as shown in Figure 4D.

[056] Utilizing fixture 400 as shown in Figures 4A, 4B, 4C, and 4D allows processing of a thin film substrate in a processing chamber. In some embodiments, thin film substrates can be about 1 μm or more. Further, thin film substrate 301, once mounted within fixture 400, can be handled and moved from process chamber to process chamber. Therefore, a multiprocessor chamber system can be utilized to form stacks of layers,

including one or more layers of perovskite film deposited according to embodiments of the present invention.

[057] Figure 5 illustrates a cluster tool 500 for processing thin film substrates. Cluster tool 500 can, for example, include load lock 502 and load lock 503, through which mounted thin film substrate 301 is loaded and a resultant device is removed from cluster tool 500. Chambers 504, 505, 506, 507, and 508 are processing chambers for depositions of materials, heat treatments, etching, or other processes. One or more of chambers 504, 505, 506, 507, and 508 can be a pulsed-DC or RF PVD chamber such as discussed above with respect to Figures 1A, 1B, and 1C and within which a dielectric perovskite film may be deposited according to embodiments of the present invention.

[058] Processing chambers 504, 505, 506, 507, and 508 as well as load locks 502 and 503 are coupled by transfer chamber 501. Transfer chamber 501 includes substrate transfer robotics to shuttle individual wafers between processing chambers 504, 505, 506, 507, and 508 and load locks 502 and 503.

[059] In production of a thin-film capacitor, substrates are loaded into load lock 503. An electrode layer can be deposited in chamber 504, followed by a perovskite deposition performed in chamber 505. The substrate can then be removed through load lock 503 for an in-air heat treatment external to cluster tool 500. The treated wafer can then be reloaded into cluster tool 500 through load lock 502. The wafer can then again be removed from cluster tool 500 for deposition of a second electrode layer, or sometimes chamber 506 can be adapted to deposition of the second electrode layer. The process can be repeated to form a capacitor stack. The finished capacitor structure is then off-loaded from cluster tool 500 in load lock 502. Wafers are shuttled from chamber to chamber by robotics in transfer chamber 501.

[060] A capacitor structure produced according to the present invention could utilize thin film substrates loaded in a fixture such as fixture 400. Fixture 400 is then loaded into

load lock 503. Chamber 504 may still include deposition of the electrode layer. Chamber 505 then includes deposition of a perovskite layer according to embodiments of the present invention. A second electrode layer can then be deposited in chamber 506. In this process, only low temperature anneal is utilized to increase crystallinity and the dielectric constant of the perovskite layer.

[061] Another advantage of a thin film capacitor process is the ability to stack capacitor structures. In other words, substrates loaded into cluster tool 500 may traverse process chambers 504, 505, 506, 507, and 508 multiple times in order to produce multiply stacked capacitor structures. Figures 6A and 6B illustrate such structures.

[062] Figure 6A illustrates a parallel coupled stacking. As shown in Figure 6A, a substrate 301, which for example can be a high temperature plastic substrate, such as polyimide, is loaded into load lock 503. Electrode layer 303, for example, can be deposited in chamber 504. A dielectric perovskite layer 302 is then deposited on electrode layer 303. Perovskite layer 302 can be about 0.1 to 1 μm and can be deposited in chamber 505 according to embodiments of the present invention. The wafer can then be moved to chamber 506 where the next electrode layer 304 of thickness of about 0.1 μm or more is deposited. A second capacitor stack can then be deposited over the first capacitor stack formed by first electrode layer 303, perovskite layer 302, and second electrode layer 304. This capacitor stack includes second perovskite layer 305 and third electrode layer 306. In some embodiments, further stacks can be formed. In some embodiments, metal layers 303, 304, and 306 differ in the mask utilized in deposition so that tabs are formed for electrical coupling of layers.

[063] As discussed above, any number of individual capacitor stacks can be formed such that parallel capacitor formations are formed. Such a parallel arrangement of capacitor

stacking structure can be formed of alternating layers of electrode and perovskite dielectric layers and can have any number of dielectric layers.

[064] To form the structures shown in Figure 6, substrates are rotated again through the chambers of cluster tool 500 in order to deposit the multiple sets of capacitors. In general, a stack of any number of capacitors can be deposited in this fashion.

[065] Tables I and II illustrate some examples depositions of perovskite material, for example BST, according to the present invention. In these examples, the BST film is deposited using an AKT-1600 PVD (400 X 500 mm substrate size) system from Applied Komatsu. The power supply is an ENI 13.56 MHz RF power supply with a ENI matchbox. The target material is BST with resistivity in the range of kΩs or less. The target material can, for example, be sintered. Silicon wafers are used for initial experiments. 0.1-1 microns of BST films are deposited on Si wafers with various bottom electrode materials such as: n++ Si, Ir, Pt, $IrO_2$ and also $Ti_4O_7$, $Ti_3O_5$, Nb, Os. The Oxygen to Argon ratio ranges from 0 to 50%. Process pressure ranges from 3-10 mT. RF bias is applied to substrates for some of the examples. The dielectric constant of as deposited film range from 13 to 123 and increases after post-deposition anneal to more than 1000.

[066] One skilled in the art will recognize variations and modifications of the examples specifically discussed in this disclosure. These variations and modifications are intended to be within the scope and spirit of this disclosure. As such, the scope is limited only by the following claims.

TABLE 1

| Example # | Film Thickness (nm) | Target Power (W)r | Bias Power (W) | $Ar/O_2$ Ratio | Vbd | Ebd | C (PF) | Dielectric Constant |
|---|---|---|---|---|---|---|---|---|
| BST 2 | 3679 | 1500 | 100 | 50/50 | 157 | 4.267464 | 167 | 13.35 |
| BST 3 | 3736 | 1500 | 100 | 50/50 | 150 | 4.014989 | 168 | 13.64 |
| BST3-N++ 550c | 3736 | 1500 | 100 |  | 40 | 1.070664 | 1670 | 135.57 |
| BST-Pt-1 | 2282 | 1500 | 100 | 50/25 | 47 | 2.059597 | 299.5 | 14.85 |
| BST Pt-1 550C | 2282 | 1500 | 100 |  | 16 | 0.701139 | 5722 | 283.74 |
| BST-n++-4 | 2282 | 1500 | 100 | 50/25 | 120 | 5.258545 | 274 | 13.59 |
| BST-n++550c | 2282 | 1500 | 100 |  | 30 | 1.314636 | 1970 | 97.69 |
| BST-IrO2-1 | 2310 | 1500 | 100 | 50/25 | 100 | 4.329004 | 296.2 | 14.87 |
| BST-IrO2-1 750C | 2310 |  |  | 50/25 | 2.4 | 0.103896 | 17700 | 888.46 |
| BST-Pt-2 | 2310 | 1500 | 100 | 50/25 | 100 | 4.329004 | 319 | 16.01 |
| BST-Pt-2 650C | 2310 |  |  |  | 9.4 | 0.406926 | 9750 | 489.41 |
| BST-Pt-3 | 2199 | 1500 | 100 | 75/25 | 7 | 0.318327 | 2580 | 123.28 |
| BST-Pt-3 550 | 2199 | 1500 | 100 | 75/25 | 11.2 | 0.509322 | 10740 | 513.20 |
| BST IrO2-2 | 2199 | 1500 | 100 | 75/25 | 16.7 | 0.759436 | 378 | 18.06 |
| BST IrO2-2 550 | 2199 | 1500 | 100 | 75/25 | 1.4 | 0.063665 | 10400 | 496.95 |
| BST IrO2-2 650 | 2199 | 1500 | 100 | 75/25 | 6.9 | 0.313779 | 11000 | 525.62 |
| BST IrO2-2 750 | 2199 |  |  | 75/25 | 1.4 | 0.063665 | 21950 | 1048.85 |
| BST Pt 1 step | 2918 | 2000 | 0 | 50/50 |  |  | 1239 | 78.56 |
| BST Ir 1 step | 2918 | 2000 | 0 | 50/50 |  |  | 1180 | 74.82 |
| BST IrO2 1 step | 2918 | 2000 | 0 | 50/50 |  |  | 567 | 35.95 |
| BST Pt 2 steps | 1689 | 2000 | 0 | 100/0-50/50 |  |  | 1220 | 44.78 |
| BST Ir 2 steps | 1689 | 2000 | 0 | 100/0-50/50 |  |  | 1230 | 45.14 |
| BST IrO2 2 steps | 1689 | 2000 | 0 | 100/0-50/50 |  |  | 684 | 25.10 |

## Table II

| Sample# | thickness | target power | bias power | Ar/O2 | dep time (sec) | Vbd | Ebd | C(PF) | Dielectric Constant, k | Vbd (V) | | C(PF) | Dielectric Constant, k (after 500C° anneal) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ALDOEN++-1 | 840.4 | | | | | 70 | 8.329367 | 380 | 6.939418 | | | | |
| | 840.4 | | | | | | | 377 | 6.884633 | | | | |
| ALDOEN++-2 | 5767.2 | | | | | | | 60.5 | 7.581825 | | | | |
| | | | | | | | | 1200 | 0 | | | | |
| experiment 109 | 1000 | | | | | | | 1200 | 26.07562 | | | | |
| | 840 | | | | | 75 | 8.928571 | 405 | 7.392438 | | | | |
| ebonex,BST (A) | 1140 | 900 | 100 | | 3600 | | 0 | | 0 | | | | |
| Ir Coated #2 | 2220 | 900 | 0 | 50/50 | 5400 | | 0 | 508 | 24.50587 | | | 16800 | 810.4302 |
| | | | | | | | | | | | | 5000 | |
| | 2220 | | | | | | | | | | | 21530 | 1038.605 |
| IrO2 Coated #2 | 2220 | 900 | 0 | 50/50 | 5400 | | 0 | 365 | 17.60756 | 9 | 0.405 | 22000 | 1061.278 |
| | 2220 | | | | | | 0 | | | | | 20000 | 964.7979 |
| | | | | | | | | | | | | 19000 | |
| | | | | | | | | | | | | 9000 | |
| N++(1) | 2220 | 900 | 0 | | 5400 | 12 | 0.540541 | 290 | 13.98957 | 12 | | 2512 | 121.1786 |
| N++(2) | 840 | 900 | 100 | 50/50 | 5400 | 10 | 1.190476 | 982 | 17.92438 | 10 | | 2675 | 48.8266 |
| N++(3) | can't meas | 900 | 200 | | 5400 | | | 377 | | | | | |
| N++(4) | 1490 | 900 | 100 | 50/25 | 5400 | | 0 | 242 | 7.835289 | | | 537 | 17.38657 |
| Ti4O7 (A) | 910 | 900 | | 50/50 | | | 0 | 3030 | 59.91525 | | | 450 | 8.898305 |
| | 910 | | | | | | | 2962 | 58.57062 | | | | |
| | 910 | | | | | | | 2860 | 56.55367 | | | | |
| Ti4O7 (B) | 1490 | | | 50/25 | | | 0 | 1988 | 64.36593 | | | 314 | 10.16645 |
| | 1490 | | | | | | | 2048 | 66.30856 | | | | |
| Ir # 3 | 650 | 900 | 1000 sec no bias/ 4400sec bias 80W | 50/50 | 5400 | | | very leaky | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ir #4 | 870 | 900 | 500 sec no bias/ 4900 sec 50w bias | 50/50 | 5400 | | | very leaky | | | | | |
| Ir #5 | 2000 | 900 | 1500sec no bias/5700 sec 50W bias | 50/50 | 7200 | | | very leaky | | | | | |
| IrO2 (Tsub=450c) | 2000 | 900 | no bias | 50/50 | 5400 | 10 | 0.5 | 1390 | 60.40852 | 10 | | 5972 | 259.5393 |
| | 2000 | | | | | | | | | | | 6021 | 261.6688 |
| n++ (6)(Tsub=450c) | 934 | 900 | 75 w bias | 50/50 | 7200 | 12 | 1.284797 | 870 | 17.65711 | 12 | | 2857 | 57.98431 |
| n++ (7) (room) | 2541 | 900 | no bias | 50/50 | 5400 | | | 219 | | 13 | 0.512 | 2210 | 122.0254 |
| n++(8) (room) | 2504 | 900 | 75 w bias | 50/50 | 7200 | | | 224 | 12.18809 | 22 | 0.879 | 2218 | 120.6839 |
| n++ (9) (room) | 10000 | | 75 w bias | 50/50 | 28800 | | | 58 | 12.60322 | 55 | 0.55 | 954.7 | 207.4533 |
| n++ (10) (room) | 5000 | | 75w bias | 50/50 | 14400 | | | | | | | | |

WHAT IS CLAIMED IS:

1. A method of depositing a perovskite layer on a substrate, comprising:

   placing the substrate into a reactor;

   flowing a gaseous mixture through the reactor; and

   providing power to a target formed of a perovskite material positioned opposite the substrate.

2. The method of claim 1, wherein providing power to the conducting target includes applying pulsed-DC power to the conducting target.

3. The method of claim 2 further including filtering the pulsed-DC power to protect a pulsed DC power supply from a bias power while allowing passage of the pulsed DC power through the filter.

4. The method of claim 2, further including supplying an RF bias power to the substrate.

5. The method of claim 1, wherein providing power to the conducting target includes applying RF power to the conducting target.

6. The method of claim 1, wherein a perovskite layer is formed on the substrate.

7. The method of claim 6, wherein the perovskite layer is a barium strontium titanite (BST) layer.

8. The method of claim 6, wherein the formed perovskite layer is more than about 0.1 micron thick.

9. The method of claim 6 wherein the formed perovskite layer is less than about 1 micron thick.

10. The method of claim 6, further comprising annealing the perovskite layer formed on the substrate.

11. The method of claim 10 wherein annealing the perovskite layer includes heating the perovskite layer to an anneal temperature of between about 500°C and about 800°C.

12. The method of claim 1, further comprising preheating the substrate before applying power to the conducting target.

13. The method of claim 12, wherein preheating the substrate including heating the substrate to a temperature of about 400 °C for low temperature perovskite deposition.

14. The method of claim 1, wherein the substrate is a low temperature substrate.

15. The method of claim 14, wherein the low temperature substrate is one of a set of substrates including glass, plastic, metal foil, copper, and stainless steel.

16. The method of claim 1 wherein the conducting target is doped with a transition metal dopant, transition element, lanthanide, and/or amphotaric elements.

17. The method of claim 16 wherein the target is doped with Manganese.

18. The method of claim 17 wherein a level of Manganese in the target is at least 0.1%.

19. The method of claim 1, wherein the perovskite target is a conductive target.

20. A capacitor structure, comprising:

a first conducting electrode layer;

a dielectric perovskite layer deposited over the first conducting electrode layer; and

a second conducting electrode layer deposited over the dielectric perovskite layer.

21. The capacitor of claim 20, wherein the first conducting layer is a copper sheet.

22. A stacked capacitor structure, comprising:

one or more capacitor stacks deposited on a substrate, wherein each capacitor stack comprises:

a bottom electrode layer,

a dielectric perovskite layer deposited over the electrode layer, and

a top electrode layer deposited over the one or more capacitor stacks.

23. The stacked capacitor structure of claim 22, wherein the capacitor stacks form a parallel stacked capacitor structure.

24. The stacked capacitor structure of claim 22, wherein the capacitor stacks form a series stacked capacitor structure.

25. A method of producing a capacitor, comprising:

loading a substrate into a cluster tool;

depositing a dielectric perovskite layer over a substrate in a chamber of the cluster tool.

26. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing perovskite film with a pulsed-DC PVD process.

27. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing perovskite film with an RF sputtering PVD process.

28. The method of claim 25, wherein depositing the dielectric perovskite layer includes depositing the perovskite material through a mask.

29. The method of claim 25, further including

depositing a bottom electrode layer on the substrate wherein the dielectric perovskite layer is .deposited over the bottom electrode layer.

31. The method of claim 25, further including depositing a top electrode layer over the dielectric perovskite layer.

32. A fixture for holding a thin substrate, comprising:

a top portion; and

a bottom portion, wherein

the thin substrate is held when the top portion is attached to the bottom portion.

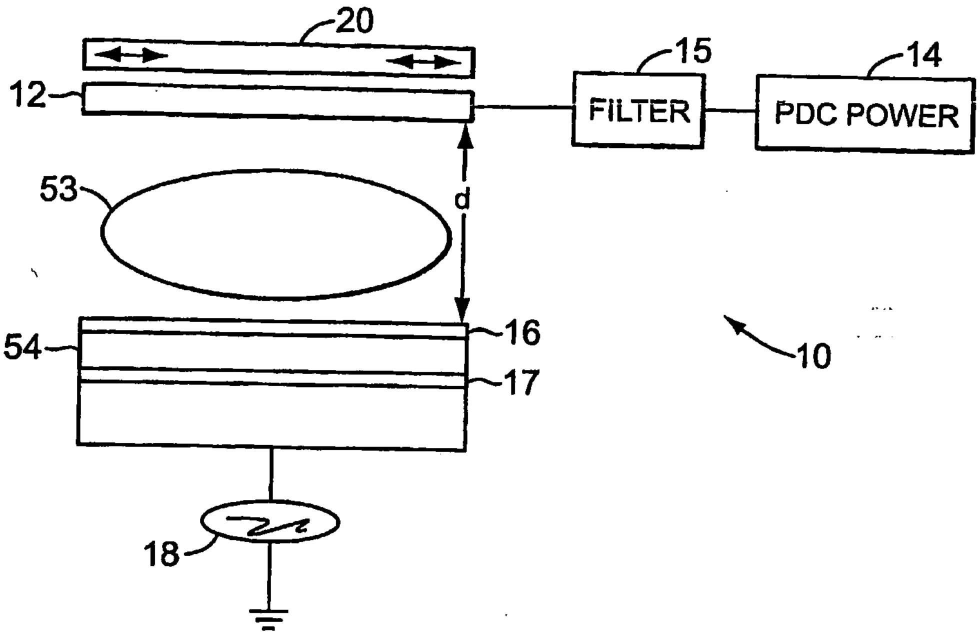

20
15
14
12
FILTER
PDC POWER
53
d
54
16
17
10
18

FIG. 1A

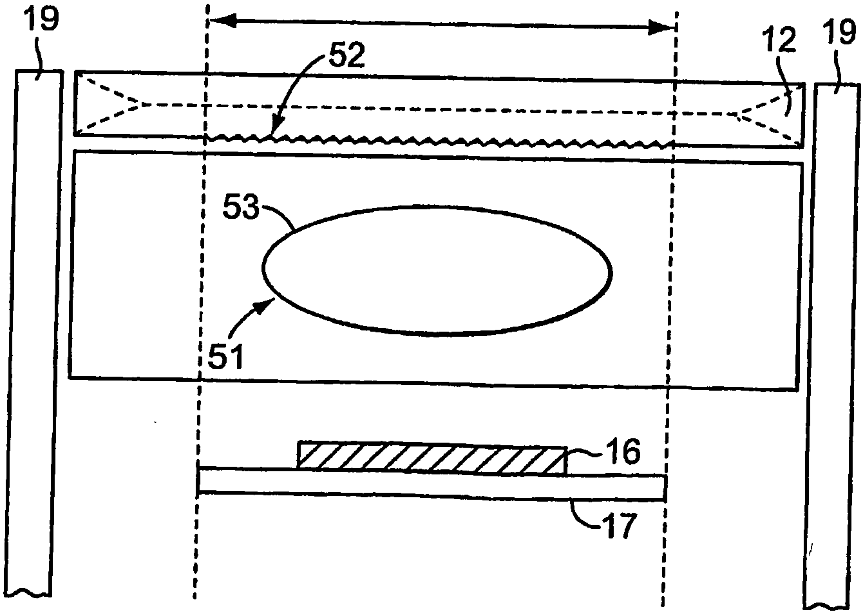

19
52
12
19
53
51
16
17

FIG. 1B

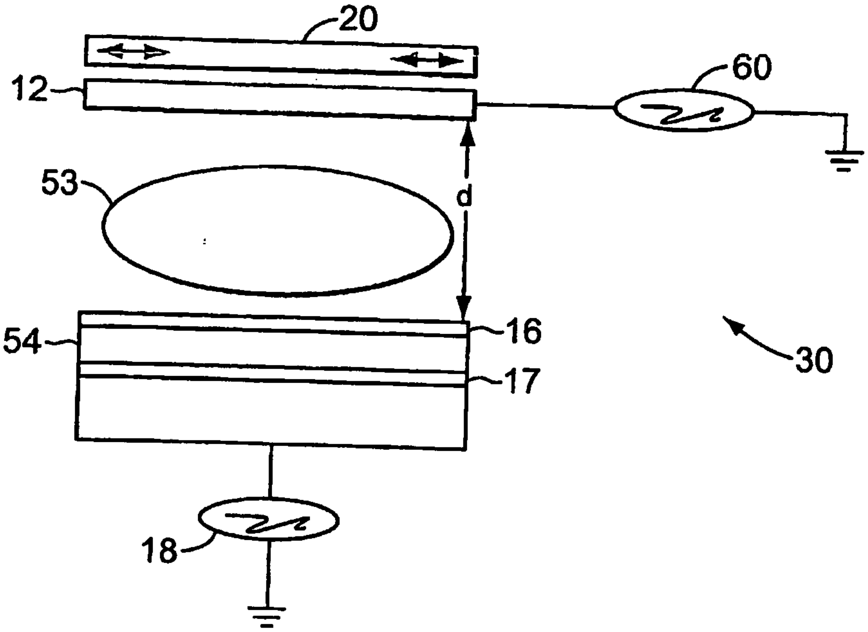


FIG. 1C

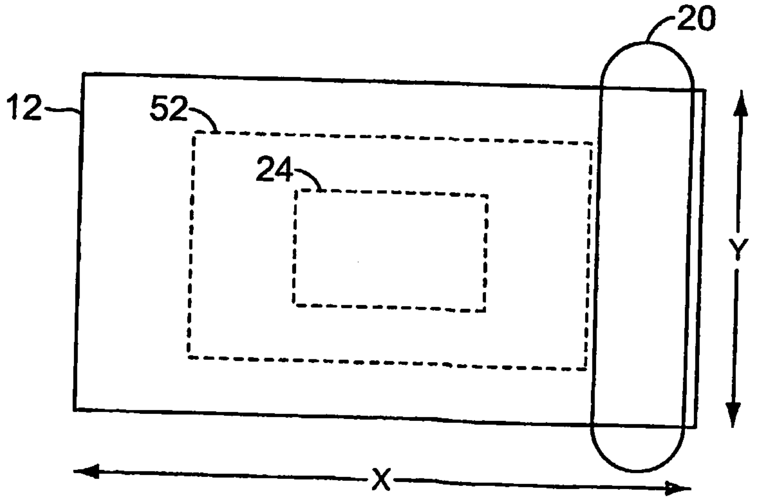


FIG. 2

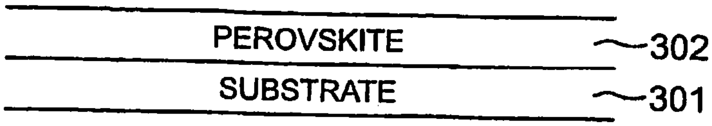


FIG. 3A

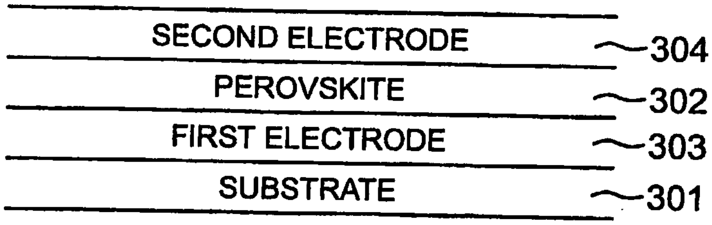


FIG. 3B

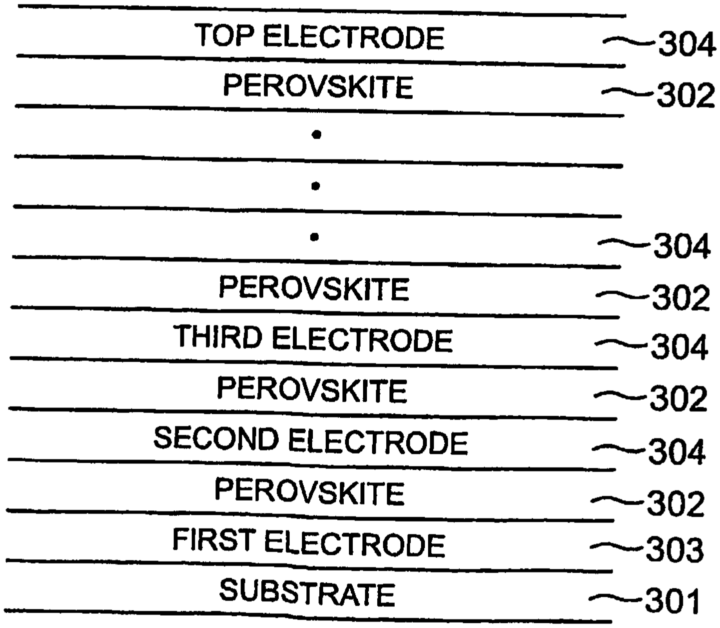


FIG. 6

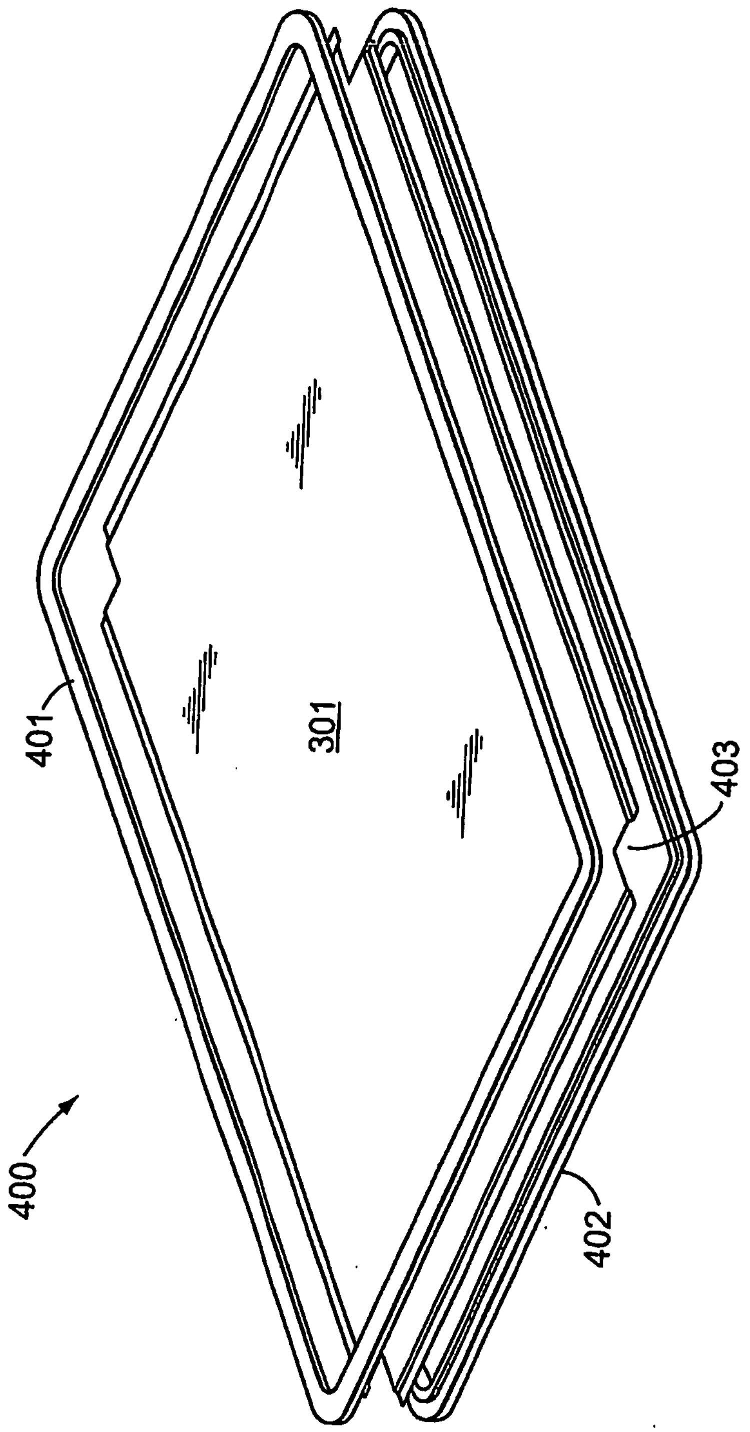


FIG. 4A

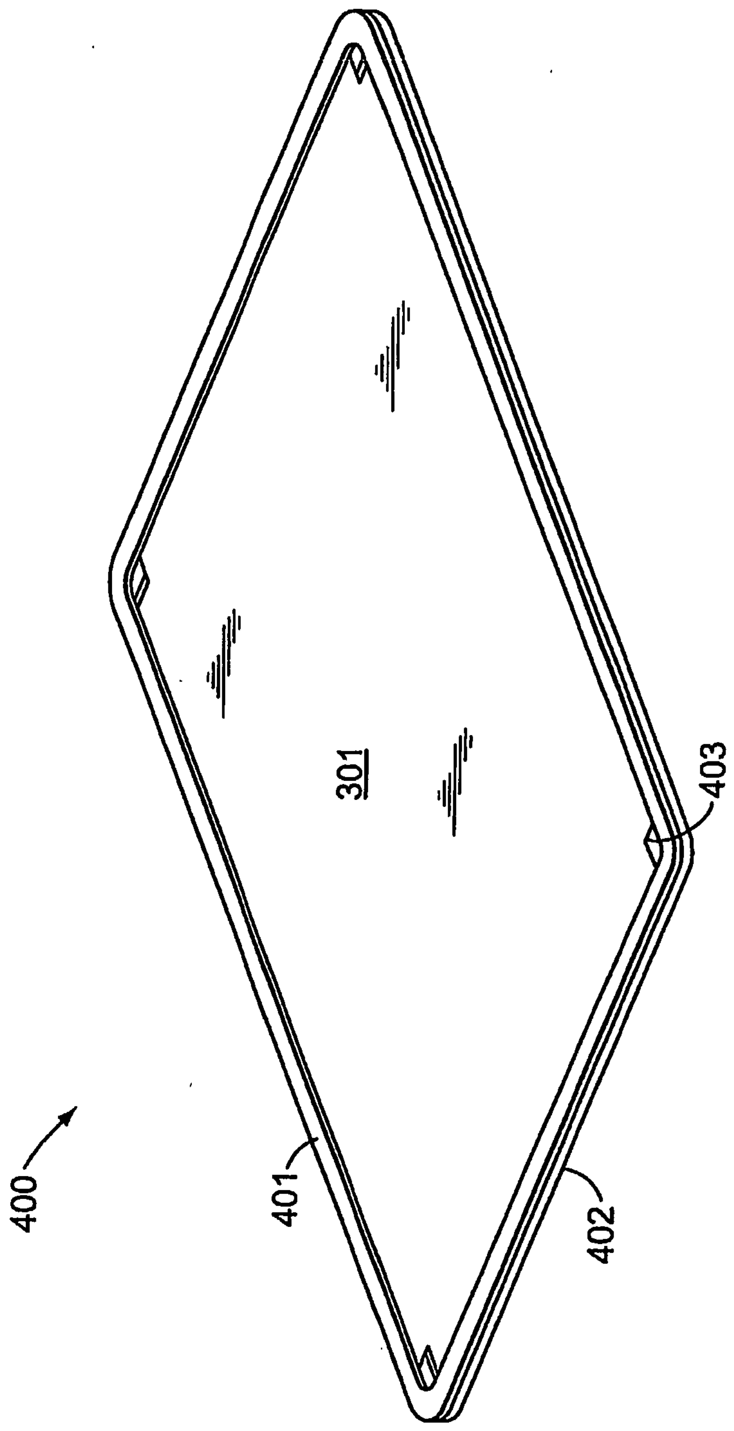


FIG. 4B

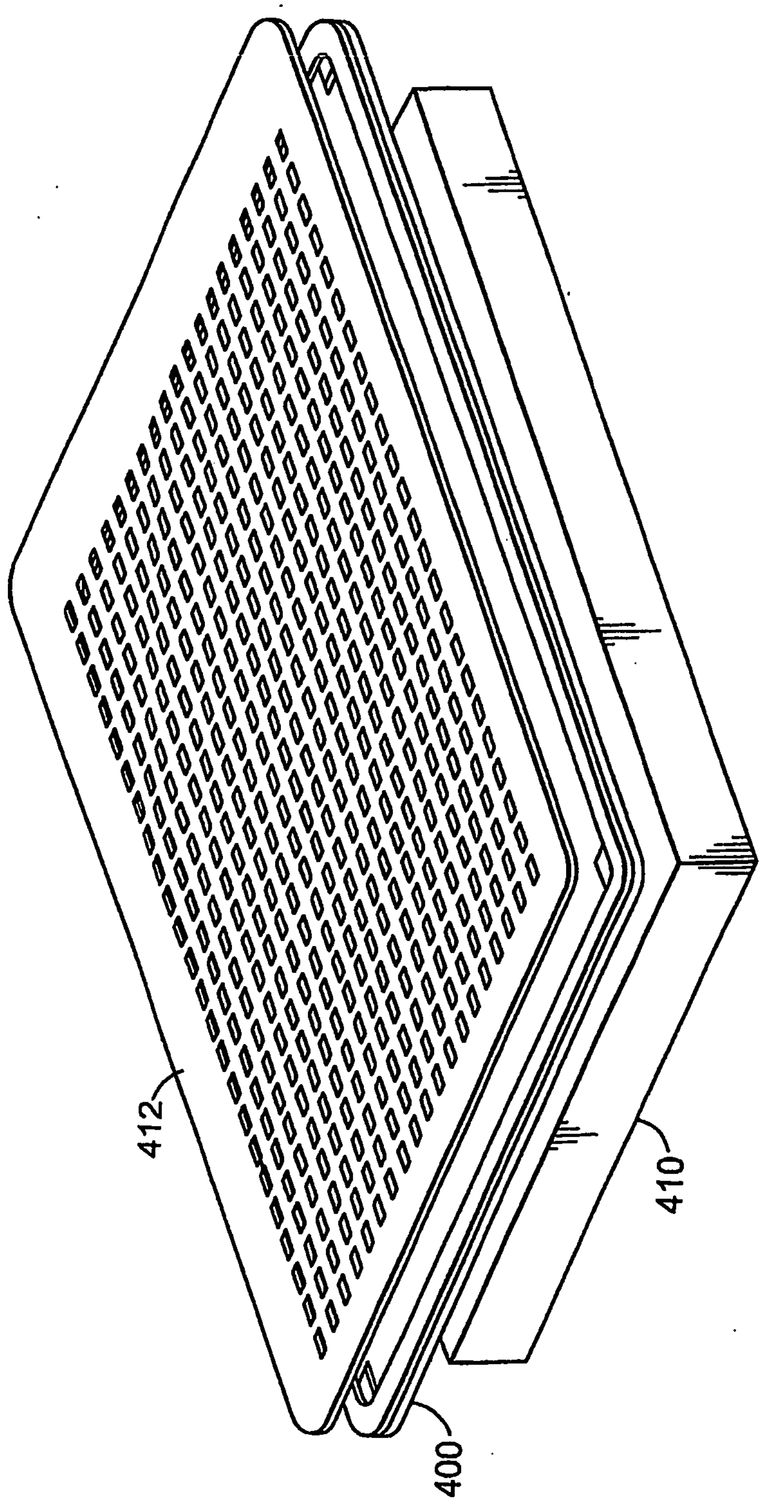


FIG. 4C

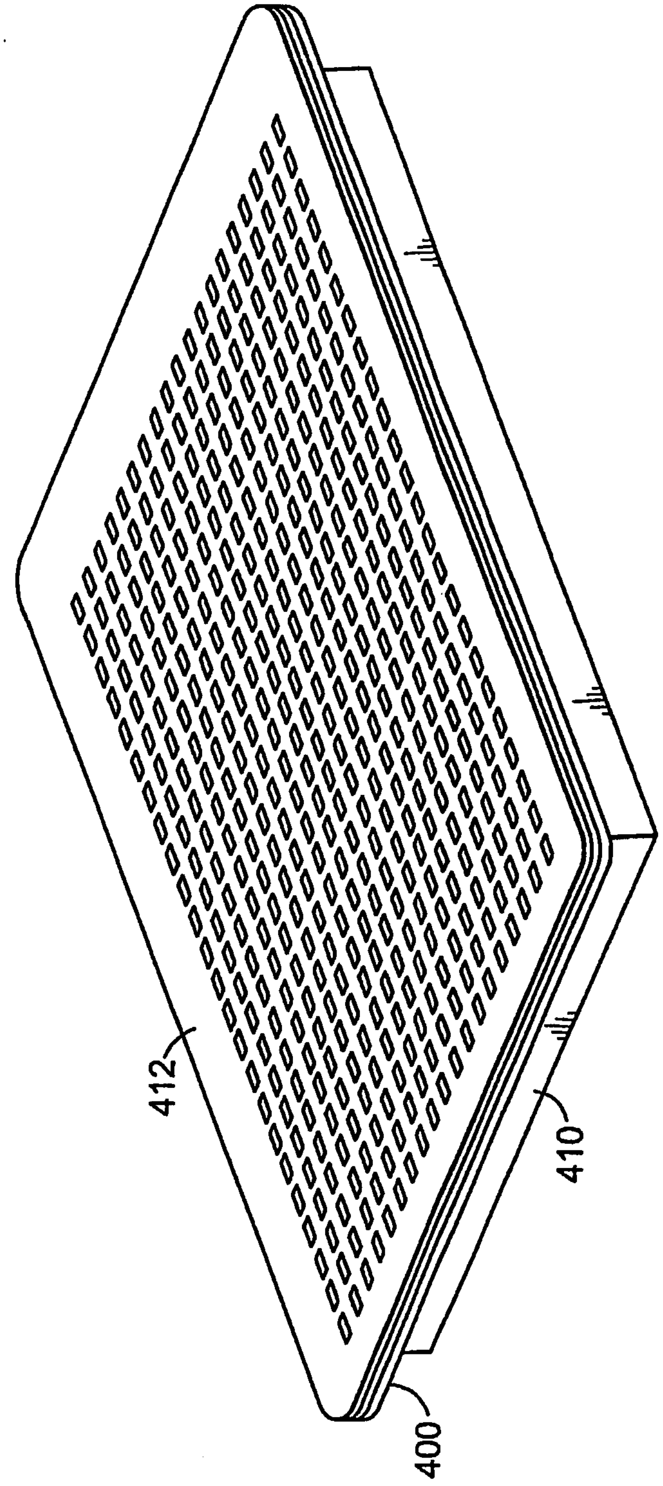


FIG. 4D

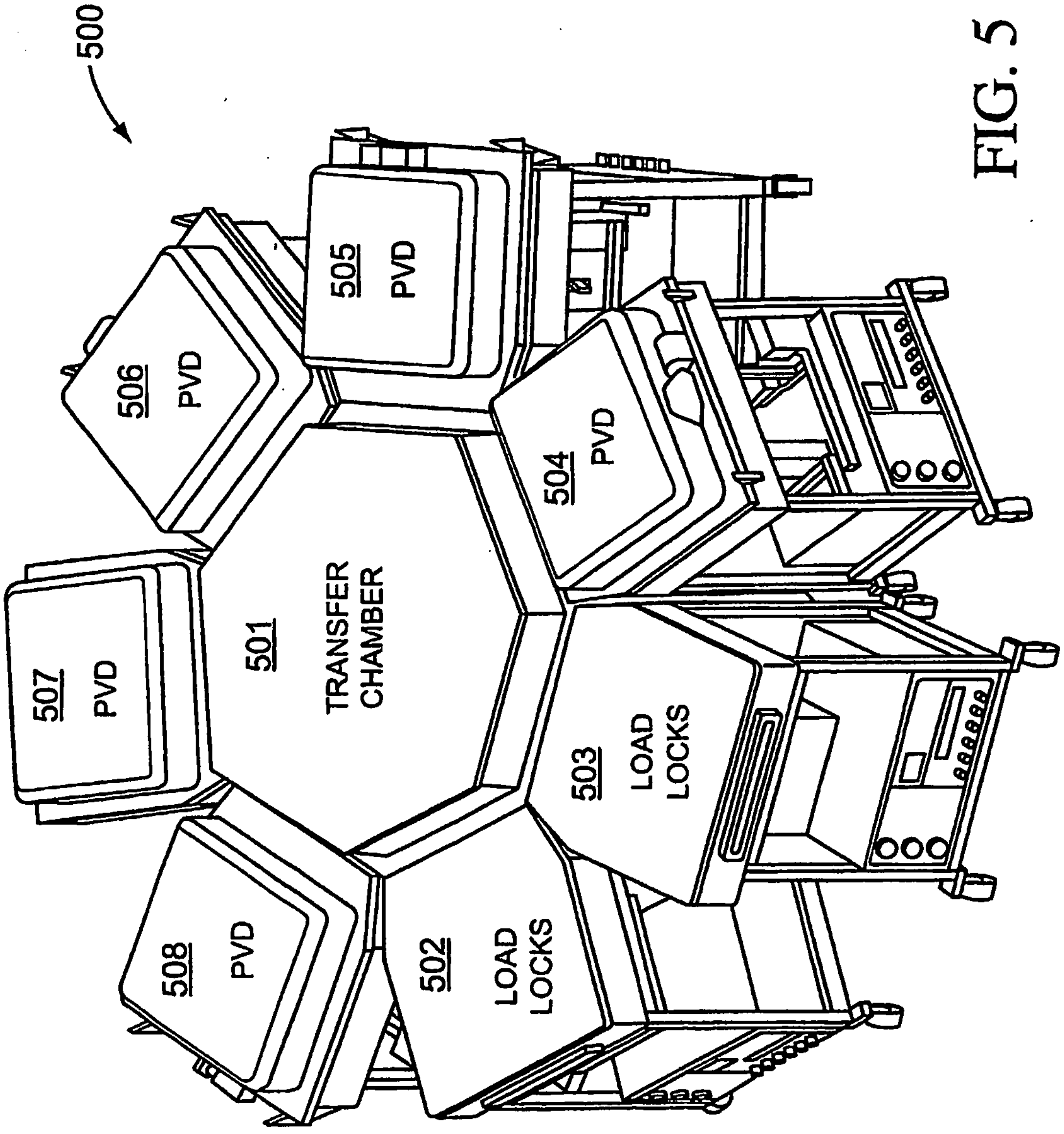

500
501
TRANSFER CHAMBER
502
LOAD LOCKS
503
LOAD LOCKS
504
PVD
505
PVD
506
PVD
507
PVD
508
PVD

FIG. 5

PTO/SB/06 (10-07)
Approved for use through 06/30/2010. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number 10/101 863

## 10/2/07 APPLICATION AS FILED – PART I

RCE

| FOR | NUMBER FILED (Column 1) | NUMBER EXTRA (Column 2) | SMALL ENTITY RATE ($) | SMALL ENTITY FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY FEE ($) |
|---|---|---|---|---|---|---|---|
| BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | |
| SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X = | | OR | X = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X = | | | X = | |
| APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $260 ($130 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | N/A | | | N/A | |
| | | | TOTAL | | | TOTAL | 810. |

paid

* If the difference in column 1 is less than zero, enter "0" in column 2.

## APPLICATION AS AMENDED – PART II

10/2/07

| AMENDMENT A | | CLAIMS REMAINING AFTER AMENDMENT (Column 1) | | HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2) | PRESENT EXTRA (Column 3) | SMALL ENTITY RATE ($) | SMALL ENTITY ADDITIONAL FEE ($) | OR | OTHER THAN SMALL ENTITY RATE ($) | OTHER THAN SMALL ENTITY ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total (37 CFR 1.16(i)) | * 36 | Minus | ** 39 | = — | X = | | OR | X = | |
| | Independent (37 CFR 1.16(h)) | * 3 | Minus | *** 5 | = — | X = | | OR | X = | |
| | Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | N/A | | OR | N/A | |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

| AMENDMENT B | | CLAIMS REMAINING AFTER AMENDMENT (Column 1) | | HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2) | PRESENT EXTRA (Column 3) | RATE ($) | ADDITIONAL FEE ($) | OR | RATE ($) | ADDITIONAL FEE ($) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total (37 CFR 1.16(i)) | * | Minus | ** | = | X = | | OR | X = | |
| | Independent (37 CFR 1.16(h)) | * | Minus | *** | = | X = | | OR | X = | |
| | Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | N/A | | OR | N/A | |
| | | | | | | TOTAL ADD'L FEE | | OR | TOTAL ADD'L FEE | |

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

# EAST Search History

| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
|---|---|---|---|---|---|---|
| L1 | 4 | (pulsed with DC) with target with voltage with positive with negative | US-PGPUB; USPAT | OR | OFF | 2007/11/07 11:48 |
| L2 | 1848876 | @ad>"20020316" or @rlad>"20020316" | US-PGPUB; USPAT | OR | OFF | 2007/11/07 11:48 |
| L3 | 3 | 1 not 2 | US-PGPUB; USPAT | OR | OFF | 2007/11/07 11:48 |

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www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 10655.0016-00 | 6938 |

22852 7590 11/15/2007
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
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901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| **ART UNIT** | **PAPER NUMBER** |
| 2823 | |
| **MAIL DATE** | **DELIVERY MODE** |
| 11/15/2007 | PAPER |

**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

714

| | | |
|---|---|---|
| ***Office Action Summary*** | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 |

***-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --***

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

1)☒ Responsive to communication(s) filed on 02 October 2007.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

4)☒ Claim(s) *2-13,21-24 and 40-60* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *2-13,21-24 and 40-60* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

**Application Papers**

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *10/2/07*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application

6) ☐ Other: _____.

U.S. Patent and Trademark Office
PTOL-326 (Rev. 08-06) **Office Action Summary** Part of Paper No./Mail Date 20071110

## DETAILED ACTION

### *Continued Examination Under 37 CFR 1.114*

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 10/2/07 has been entered.

### *Claim Rejections - 35 USC § 103*

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 10-13, 21, 40-45 and 51-60 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. (6,117,279) in view of Fu et al. (6,306,265), and further in view of Liu et al. (6,086,730) .

With respect to claims 21, 40, 43 and 51, Smolanoff et al. disclose providing pulsed DC power (21) through a filter (22) to a target (16) (Col. 5, lines 50-55); providing RF bias power to a substrate (15) positioned opposite the target (Col. 5, lines 60-65); providing process gas between the target and the substrate (Col. 7, lines 25-28); wherein the filter protects a pulsed DC power supply (21) from the bias power, and wherein a plasma is created by application of the pulsed DC power to the target (Col. 6, lines 8-13); and wherein the film is deposited by exposure of the substrate to the plasma (Col. 6, lines 30-33); using an specific type of filter is a matter of design choice depending on the quality of product needed, and it is obvious that the filter is going to work at certain frequencies. Furthermore, if it is a band rejection, band pass, low-pass, high-pass, or stop band filter, this is a matter of design choice depending on what it is intended or needed for the desired final product or device. It is obvious that the filter is going to work at certain frequencies.

Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface.

Fu et al. disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al. and Fu et al. to enable the conditioning step of Smolanoff et al. to be performed according to the teachings of Fu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed conditioning step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

The combination of Smolanoff et al. and Fu et al. does not clearly disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages.

Liu et al. disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages (Col. 8, lines 1-5 and Figs. 4B-4C).

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al. and Liu et al. to enable the pulsed DC power application step of the combination to be performed according to the teachings of Liu et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable methods of performing the disclosed pulsed DC power application step of the combination and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claims 8 and 52, Smolanoff et al. disclose wherein the process gas includes a mixture of oxygen and argon (Col. 7, lines 21-27).

With respect to claim 10, Smolanoff et al. disclose wherein the process gas further includes nitrogen (Col. 7, lines 25-26).

With respect to claim 11, Smolanoff et al. disclose wherein providing pulsed DC power to a target includes providing pulsed DC power to a target which has an area larger than that of the substrate (See fig. 1).

With respect to claims 12, 49 and 55, Smolanoff et al. disclose further including uniformly sweeping the target with a magnetic field (Col. 6, lines 1-7).

With respect to claims 13 and 50, Smolanoff et al. disclose wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction (Col. 6, lines 1-6).

With respect to claims 56-60, One of ordinary skill in the art would have been led to the recited time pulse, bias power and frequency to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of time pulse, bias power and frequency, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233

(CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed time pulse, bias power and frequency or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen time pulse, bias power and frequency or upon another variable recited in a claim, the Applicant must show that the chosen time pulse, bias power and frequency are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 2-4, 6 and 22-24 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. and Liu et al. as applied to claims 10-13, 21, 40-45 and 51-60 above, and further in view of the following comments.

With respect to claims 2-4, 6 and 22-24, 41, 42, 44-48, One of ordinary skill in the art would have been led to the recited temperature, DC power, gas flow, time pulse and bias power to routine experimentation to achieve a desire layer thickness, device dimension, device associated characteristics and device density on the finished wafer in view of the range of values disclosed.

In addition, the selection of temperature, DC power, gas flow, time pulse and bias power, its obvious because it is a matter of determining optimum process conditions by routine experimentation with a limited number of species of result effective variables. These claims are prima facie obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. In re Woodruff, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also In re Huang, 40 USPQ2d 1685, 1688 (Fed. Cir. 1996)(claimed ranges or a result effective variable, which do not overlap the prior art ranges, are unpatentable unless they produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art). See also In re Boesch, 205 USPQ 215 (CCPA) (discovery of optimum value of result effective variable in known process is ordinarily within skill or art) and In re Aller, 105 USPQ 233 (CCPA 1995) (selection of optimum ranges within prior art general conditions is obvious).

Note that the specification contains no disclosure of either the critical nature of the claimed temperature, DC power, gas flow, time pulse and bias power or any unexpected results arising therefrom. Where patentability is said to be based upon particular chosen temperature, DC power, gas flow, time pulse and bias power or upon another variable recited in a claim, the Applicant must show that the chosen temperature, DC power, gas flow, time pulse and bias power are critical. *In re Woodruf*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Cir. 1990).

Claims 7 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over Smolanoff et al. in view of Fu et al. and Liu et al. as applied to claims 10-13, 21, 40-45 and 51-60 above, and further in view of Le et al. (2003/0077914).

The combination of Smolanoff et al. and Fu et al. does not disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization.

With respect to claim 7, Le et al. disclose wherein the film is an upper cladding layer of a waveguide structure and the bias power is optimized to provide planarization Page 5, Paragraph [0075].

It would have been within the scope of one of ordinary skill in the art to combine the teachings of Smolanoff et al., Fu et al., Liu et al. and Le et al. to enable the film material of Smolanoff et al. to be the same according to the teachings of Le et al. because one of ordinary skill in the art would have been motivated to look to alternative suitable film materials for the disclosed film formation step of Smolanoff et al. and art recognized suitability for an intended purpose has been recognized to be motivation to combine. See MPEP 2144.07.

With respect to claim 9, Le et al. disclose wherein the oxygen flow is adjusted to adjust the index of refraction of the film (Page 5, Paragraph [0076]).

## *Response to Arguments*

Applicant's arguments, filed 10/2/07, with respect to the rejection(s) of claim(s) 21, 43 and 51 under 35 USC 103 have been fully considered and are persuasive. Therefore, the rejection has been withdrawn. However, upon further consideration, a new ground(s) of rejection is made in view of Liu et al.

## *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Michelle Estrada whose telephone number is 571-272-1858. The examiner can normally be reached on Monday through Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Matthew Smith can be reached on 571-272-1907. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 571-272-2800.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Michelle Estrada
Primary Examiner
Art Unit 2823

ME
November 13, 2007

OIPE
OCT 0 2 2007

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

## INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| | | | |
|---|---|---|---|
| Sheet | 1 | of | 1 |

| Complete If Known | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 10655.0016-00 |

### FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[1] Number[2] Kind Code[3] (*if known*) | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[4] |
|---|---|---|---|---|---|---|
| ME | | WO 2007/027535 A2 | 03-08-2007 | Symmorphix, Inc. | | |

### NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| ME | | Office Action dated September 22, 2006, from Korean Patent Office in Application No. 10-2005-7016055 (Attorney Docket No. 9140.0030-00202). | Yes |
| | | Office Action mailed May 21, 2007, in U.S. Application No. 10/291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Final Office Action mailed April 13, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Amendment filed August 9, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Final Office Action mailed September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Final Office Action mailed September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Notice of Non-Compliant Amendment mailed April 12, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Response to Notice of Non-Compliant Amendment filed April 23, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Final Office Action mailed July 24, 2007 in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Response to Office Action filed July 9, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Corrected Notice of Allowance mailed June 7, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| | | Supplemental Notice of Allowance mailed July 5, 2007, in U.S. Application No. 11/228,805 (Attorney Docket No. 9140.0030-01). | |
| | | Second Supplemental Preliminary Amendment filed May 31, 2007, in U.S. Application No. 11/297,057 (Attorney Docket No. 9140.0042-00). | |
| ME | | PCT International Preliminary Report on Patentability mailed June 21, 2007, in PCT Application No. PCT/US2005/044781 (Attorney Docket No. 9140.0042-304). | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 11/7/07 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EM 100825487 US**

| | | |
|---|---|---|
| ***Notice of References Cited*** | Application/Control No.<br>10/101,863 | Applicant(s)/Patent Under Reexamination<br>ZHANG ET AL. |
| | Examiner<br>Michelle Estrada | Art Unit<br>2823 \| Page 1 of 1 |

**U.S. PATENT DOCUMENTS**

| * | | Document Number<br>Country Code-Number-Kind Code | Date<br>MM-YYYY | Name | Classification |
|---|---|---|---|---|---|
| * | A | US-6,086,730 | 07-2000 | Liu et al. | 204/192.16 |
| * | B | US-5,584,974 | 12-1996 | Sellers, Jeff C. | 204/192.13 |
| | C | US- | | | |
| | D | US- | | | |
| | E | US- | | | |
| | F | US- | | | |
| | G | US- | | | |
| | H | US- | | | |
| | I | US- | | | |
| | J | US- | | | |
| | K | US- | | | |
| | L | US- | | | |
| | M | US- | | | |

**FOREIGN PATENT DOCUMENTS**

| * | | Document Number<br>Country Code-Number-Kind Code | Date<br>MM-YYYY | Country | Name | Classification |
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**NON-PATENT DOCUMENTS**

| * | | Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages) |
|---|---|---|
| | U | |
| | V | |
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| | X | |

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

U.S. Patent and Trademark Office
PTO-892 (Rev. 01-2001) **Notice of References Cited** Part of Paper No. 20071110

| **Index of Claims** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
|---|---|---|
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | **Rejected** | - | **Cancelled** | N | **Non-Elected** | A | **Appeal** |
| = | **Allowed** | ÷ | **Restricted** | I | **Interference** | O | **Objected** |

☐ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

| CLAIM | | DATE | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 | 11/11/2007 | | | | | | | |
| | 1 | - | - | | | | | | | |
| | 2 | ✓ | ✓ | | | | | | | |
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| | 5 | ✓ | ✓ | | | | | | | |
| | 6 | ✓ | ✓ | | | | | | | |
| | 7 | ✓ | ✓ | | | | | | | |
| | 8 | ✓ | ✓ | | | | | | | |
| | 9 | ✓ | ✓ | | | | | | | |
| | 10 | ✓ | ✓ | | | | | | | |
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| | 23 | ✓ | ✓ | | | | | | | |
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| ***Index of Claims*** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | **Rejected** | | - | **Cancelled** | | N | **Non-Elected** | | A | **Appeal** |
| = | **Allowed** | | ÷ | **Restricted** | | I | **Interference** | | O | **Objected** |

☐ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

| **CLAIM** | | **DATE** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 | 11/11/2007 | | | | | | | |
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| | 43 | ✓ | ✓ | | | | | | | |
| | 44 | ✓ | ✓ | | | | | | | |
| | 45 | ✓ | ✓ | | | | | | | |
| | 46 | ✓ | ✓ | | | | | | | |
| | 47 | ✓ | ✓ | | | | | | | |
| | 48 | ✓ | ✓ | | | | | | | |
| | 49 | ✓ | ✓ | | | | | | | |
| | 50 | ✓ | ✓ | | | | | | | |
| | 51 | ✓ | ✓ | | | | | | | |
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| | 55 | ✓ | ✓ | | | | | | | |
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| | 58 | ✓ | ✓ | | | | | | | |
| | 59 | ✓ | ✓ | | | | | | | |
| | 60 | ✓ | ✓ | | | | | | | |

| ***Search Notes*** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
|---|---|---|
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

## SEARCHED

| Class | Subclass | Date | Examiner |
|---|---|---|---|
| | | | |

## SEARCH NOTES

| Search Notes | Date | Examiner |
|---|---|---|
| See East search attached | 10/2/07 | ME |

## INTERFERENCE SEARCH

| Class | Subclass | Date | Examiner |
|---|---|---|---|
| | | | |

11-29-07

2823

OIPE IAP21
NOV 27 2007
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
Hongmei ZHANG et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
) Confirmation No.: 6938
For: BIASED PULSE DC REACTIVE )
SPUTTERING OF OXIDE FILMS )

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(c)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(c), Applicants bring to the attention of the Examiner the documents on the attached listing. This Supplemental Information Disclosure Statement is being filed after the events recited in Section 1.97(b) but, to the undersigned's knowledge, before the mailing date of either a Final action, Quayle action, or a Notice of Allowance. Under the provisions of 37 C.F.R. § 1.97(c), this Supplemental Information Disclosure Statement includes a certification as specified by Section 1.97(e).

Based on reasonable inquiry, no document listed in this Supplemental Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Supplemental Information Disclosure Statement was known to any individual designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Supplemental Information Disclosure Statement.

Copies of the listed non-patent literature documents are attached. A copy of the U.S. patent is not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to Deposit Account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: November 27, 2007

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

**EXPRESS MAIL LABEL NO.
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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 1 |
|---|---|---|---|

| ***Complete if Known*** | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | Michelle ESTRADA |
| *Attorney Docket Number* | 10655.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US-7,262,131 | 08-28-2007 | Narasimhan et al. | |
| | | US- | | | |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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## NONPATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Amendment/RCE filed October 31, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Amendment/RCE filed October 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Office Action dated November 15, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Final Office Action dated October 10, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| | | Amendment/RCE filed October 31, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |

| | | | |
|---|---|---|---|
| Examiner Signature | | Date Considered | |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

EXPRESS MAIL LABEL NO.
EM 074696455 US

- A22,852
Customer No. 550 0 -0
Attorney Docket No. 106 . 0 16 0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )
)
Hongmei ZHANG et al. ) Group Art Unit: 2823
)
Application No.: 10/101,863 ) Examiner: ESTRADA, Michelle
)
Filed: March 16, 2002 )
)
For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS ) Confirmation No.: 6938

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## AMENDMENT AND RESPONSE TO OFFICE ACTION

In reply to the Office Action mailed November 15, 2007, please amend the above-identified application as follows:

**Amendments to the Claims** are reflected in the listing of claims in this paper beginning on page 2.

**Remarks/Arguments** follow the amendment sections of this paper beginning on page 8 -

**AMENDMENTS TO THE CLAIMS:**

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Canceled).

2. (Previously presented): The method of Claim 21, further including holding the temperature of the substrate substantially constant.

3. (Previously presented): The method of Claim 21, wherein applying pulsed DC power through the filter includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 μs.

4. (Previously presented): The method of Claim 21, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

5. (Canceled).

6. (Previously presented): The method of claim 4, wherein the RF bias power is zero.

7. (Previously presented): The method of Claim 21, wherein the RF bias power is optimized to provide planarization.

8. (Previously presented): The method of Claim 21, wherein a process gas of the process gas flow includes a mixture of Oxygen and Argon.

9. (Previously presented): The method of Claim 8, wherein the mixture is adjusted to adjust the index of refraction of the film.

10. (Previously presented): The method of Claim 8, wherein the mixture further includes nitrogen.

11. (Previously presented): The method of Claim 21, wherein applying pulsed DC power to the target includes adjusting pulsed DC power to a target which has an area larger than that of the substrate.

12. (Previously presented): The method of Claim 21, further including uniformly sweeping the target with a magnetic field.

13. (Previously presented): The method of Claim 12, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

14-20. (Canceled).

21. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

conditioning a target;

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow; and

applying pulsed DC power to the target such that a ~~target~~ voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film; and

narrow band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target, wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poisonous mode to prepare the surface.

22. (Previously presented ): The method of Claim 21, wherein setting the process gas flow includes adjusting constituents in order to adjust the index of refraction of the film.

23. (Previously presented): The method of Claim 21, wherein applying pulsed DC power includes setting the frequency in order to adjust the index of refraction of the film.

24. (Previously presented): The method of Claim 21, further including adjusting a temperature of the substrate in order to adjust the index of refraction of the film.

25-40. (Canceled).

41. (Previously presented): The method of claim 21, wherein a bandwidth of the narrow band rejection filter is about 100 kHz.

42. (Previously presented): The method of claim 21, wherein the frequency of the RF bias is about 2 MHz.

43. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

preparing the substrate;

adjusting an RF bias power to the substrate;

setting a process gas flow;

applying pulsed DC power to a target such that a ~~target~~ voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate; and

narrow band rejection filtering the DC power at a frequency of the bias power before applying the DC power to the target.

44. (Previously presented): The method of claim 43, wherein band rejection filtering the DC power includes utilizing a band rejection filter with a bandwidth of less than about 100 kHz.

45. (Previously presented): The method of claim 43, wherein the frequency of the RF bias is about 2 MHz.

46. (Previously presented): The method of Claim 43, wherein applying pulsed DC power includes supplying up to about 10 kW of power at a frequency of between about 40 kHz and about 350 kHz and a reverse time pulse between about 1.3 and 5 µs.

47. (Previously presented): The method of Claim 43, further including holding the temperature of the substrate substantially constant.

48. (Previously presented): The method of Claim 43, wherein adjusting an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

49. (Previously presented): The method of Claim 43, further including uniformly sweeping the target with a magnetic field.

50. (Previously presented): The method of Claim 49, wherein uniformly sweeping the target with a magnetic field includes sweeping a magnet in one direction across the target where the magnet extends beyond the target in the opposite direction.

51. (Currently amended): A method of depositing an insulating oxide film on a substrate, comprising:

providing a process gas between the substrate and a target;

applying an RF bias power to the substrate;

applying pulsed DC power to the target such that a ~~target~~ voltage on the target oscillates between positive and negative voltages; and

narrow band rejection filtering the pulsed DC power at a frequency of the bias power before applying pulsed DC power to the target,

wherein the oxide film is deposited on the substrate.

52. (Previously presented): The method of claim 51, wherein the process gas includes one or more gasses chosen from the group consisting of Ar, $N_2$, $O_2$, $C_2F_6$, $CO_2$, CO, $NH_3$, NO, and halide containing gasses.

53. (Previously presented): The method of claim 51, wherein the target is a metallic target.

54. (Previously presented): The method of claim 51, wherein the target is an intermetllic target.

55. (Previously presented). The method of claim 51, further including sweeping the target with a magnetic field.

56. (Previously presented): The method of claim 51, wherein the pulsed DC power is supplied with a reverse time pulse between about 1.3 and 5 μs.

57. (Previously presented): The method of Claim 51, wherein applying an RF bias power to the substrate includes supplying up to 1000 W of RF power to the substrate.

58. (Previously presented) The method of claims 21, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

59. (Previously presented) The method of claim 43, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

60. (Previously presented) The method of claim 51, wherein applying pulsed DC power includes supplying pulsed DC power at a pulse frequency of between about 40 kHz and about 350 kHz.

## REMARKS

Claims 2-13, 21-24, and 40-60 are pending in the above-identified application. The Examiner has rejected claims 2-13, 21-24, and 40-60. In this application, claims 21, 43, and 51 are amended as discussed during an interview with the Examiner on December 11, 2007. Claim 40 is canceled.

### Examiner's Interview

Applicant thanks the Examiner for meeting with us on December 11, 2007 (the "Interview"). In attendance at the Interview were Examiner Michelle Estrada, Inventor R. Ernest Demaray, and Applicant's representative Gary J. Edwards. During the interview, all of the claims were discussed as well as the art that has been cited against the claims. Agreement with respect to the claims was reached. In this Amendment, the claims have been amended as discussed during the interview. The Examiner indicated in the Interview Summary that the proposed language for the claims "would overcome the rejection on record."

The substance of the discussion with the Examiner with respect to the claims and the art is provided below.

### Claim Rejections Under 35 U.S.C. § 103(a)

#### Claims 10-13, 21, 40-45, and 51-60

Claims 10-13, 21, 40-45, and 51-60 were rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,117,279 to Smolanoff et al. ("Smolanoff") in view of U.S. Patent No. 6,306,265 to Fu et al. ("Fu"), and in further view of U.S. Patent No. 6,086,730 to Liu et al. ("Liu"). Claims 21, 43, and 51 are independent claims. As discussed during the Interview, Smolanoff, Fu, and Liu, either separately or in combination, do not teach or suggest "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

Further, both Smolanoff and Liu teach away from aspects of the claimed invention. As a result, there is no reason to combine Smolanoff or Liu with any other art in order to find claims 21, 43, or 51 obvious under 35 U.S.C. § 103 (a).

*I. Smolanoff does not teach, and in fact teaches away from, "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages."*

As discussed during the Interview, Smolanoff teaches away from a system where the target voltage becomes positive, as is recited in each of claims 21, 43, and 51. Smolanoff teaches a directed ion metal vapor source for deposition of conductive films. Although Smolanoff states that the DC source can be a pulsed DC source, Smolanoff also states that "[p]ower from the steady or **pulsed DC power supply 21** and/or RF generator 24 **produces a negative potential on the target 16.**" (Smolanoff, col. 5, line 66, -col. 6, line 1) (emphasis added). In every disclosure of target voltage, Smolanoff teaches that the target voltage must be negative. (*See, e.g.* col. 5, lines 39-44 ("[t]he magnet structure 20 preferably includes magnets that produce a closed magnetic tunnel over the surface of the target 16 that traps electrons given off into the chamber 12 by the cathode assembly 17 when the cathode assembly 17 is **electrically energized to a negative potential** as is familiar to one skilled in the art"); col. 6, lines 9-12 ("[t]his main plasma in the region 23 becomes a source of positive ions of gas that are accelerated toward, and collide against, **the negatively charged surface of the target 16**, thereby ejecting particles of coating material from the target 16") (emphasis added)).

Smolanoff never teaches that the target can be positive and, in accordance with the teachings of Smolanoff, the target voltage must always be negative. <u>Therefore, Smolanoff teaches away from "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in each of claims 21, 43, and 51.</u> Smolanoff, then, also teaches away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

In addition, the Examiner indicated, with regard to the filter, that "if it is a band rejection, band pass, low-pass, high-pass, or stop band filter, this is a matter of design choice depending on what it is intended or needed for the desired final product or device." and then opined that "[i]t is obvious that the filter is going to work at certain frequencies." However, as explained during the Interview, that is not the case. The filter allows the combination of pulsed-DC power to the target (where the target voltage is oscillated between positive and negative voltages) and an RF bias on the substrate. A filter that blocks too many of the constituent frequencies of the pulsed DC waveform results in the target voltage not attaining a positive voltage. A filter that does not block the RF bias voltage can result in failure of the DC power supply. Smolanoff does not teach the "narrow band rejection filtering" recited in each of claims 21, 43, and 51.

### *II. Liu does not teach, and in fact teaches away from, the combination of pulsed DC voltage (where a voltage on the target oscillates between positive and negative voltages) and applying RF bias to the substrate.*

The Examiner stated that "[t]he combination of Smolanoff et al. and Fu et al. does not clearly disclose applying pulsed DC power to the target such that a target voltage oscillates between positive and negative voltages." (Office Action, page 4). The Examiner then relies on Liu to teach this aspect of claims 21, 43, and 51. As discussed above, Smolanoff teaches away from applying voltage to the target that causes the target voltage to become positive. Therefore, there is no reason to combine Smolanoff with Liu as suggested. Further, as discussed below, Liu also teaches away from combining a pulsed DC voltage to the target where the target voltage becomes positive and any bias voltage applied to the substrate except for a DC voltage applied to a conducting substrate.

Liu teaches deposition of conductive, diamond-like carbon thin films by sputtering with a pulsed-DC process. (*See, e.g.,* Liu, Abstract). Liu teaches that the carbon film is deposited by "a special type of pulsed DC power supply," (Liu, col. 6, lines 21-26), where the pulse characteristics provide "a positive potential to the target, by as much as, e.g. 300 volts positive," (Liu, col. 6, lines 44-45), and then "a negative potential to the target," (Liu, col. 6, line 50).

However, Liu teaches away from applying any bias to the substrate that is not a DC bias, and then only if the substrate is a conducting substrate. As taught in Liu,

> In addition to the pulsed DC sputtering with above mentioned characteristics, the substrate can also be biased in order to enhance the ta-C:H characteristics of the carbon film. **Although this can only be done with conductive substrates**, the effect is pronounced and useful. Nominally, the substrate is biased negative to the ground . . . .

(Liu, col. 6, line 66, to col. 7, line 3). Liu further teaches only DC bias voltages. (*See*, Liu, col. 7, lines 2-11).

Therefore, Liu does not teach the combination of pulsed DC where a voltage on the target oscillates between positive and negative voltages and applying an RF bias to the substrate, and in fact teaches away from such a combination especially as it applies to insulating films. As a result, Liu can not teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

There would be no reason to combine Smolanoff and Liu as suggested by the Examiner because each of these references teaches away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

### *III. Fu does not teach or suggest the claimed invention, and further Fu does not teach the elements for which it is being cited.*

The Examiner stated that "Smolanoff et al. do not clearly disclose wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface." (Office Action' page 3). Fu is relied upon to disclose "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and sputtering with the target in a poisonous mode to prepare the surface (Col. 19, lines 35-40)." (Office Action, page 3).

As discussed above, there is no reason to combine either of Smolanoff and Liu with Fu because both Smolanoff and Liu teach away from the combination of pulsed-DC voltage to the target where the voltage on the target oscillates between positive and negative voltages and an RF bias applied to the substrate, as is recited in claims 21, 43, and 51. Additionally, Fu does not teach the elements for which it is relied or itself teach the combination of pulsed-DC power and RF bias recited in the claims.

Fu teaches high density, magnetic field enhanced ionized metal vapor deposition of conducting films. (*See* Fu, abstract). Fu, however, teaches utilization of a DC power supply (Fu, col. 1, lines 30-32) in combination with an RF bias applied to the substrate (Fu, col. 2, lines 36-

41). Therefore, Fu fails to teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21; "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to a target such that a voltage on the target oscillates between positive and negative voltages and an oxide film is deposited on the substrate," as is recited in claim 43; or "applying an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages," as is recited in claim 51.

Fu does teach operation in the poison mode and operation in the metallic mode as applied to TiN deposition, but does not teach "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poison mode to prepare the surface," as is recited in claim 21. As stated by Fu,

> Reactive sputtering to produce TiN is known to operate in two modes, metallic mode and poison mode. Metallic mode produces a high-density, gold-colored film on the wafer. Poison mode, which is often associated with a high nitrogen flow, produces a purple/brown film which advantageously has low stress. However, the poison-mode film has many grain boundaries, and film defects severely reduce chip yield. Furthermore, the deposition rate in poison mode is typically only one-quarter of the rate in metallic mode. It is generally believed that in poison mode the nitrogen reacts with the target to form a TiN surface on the Ti target while in metallic mode the target surface remains clean and TiN forms only the wafer.

(Fu, col. 19, lines 28-30). Fu teaches operation in either metallic mode or poison mode, and does not teach "wherein conditioning the target includes sputtering with the target in a metallic mode to remove the surface of the target and then sputtering with the target in poisonous mode to prepare the surface," as is recited in claim 21. Independent claims 43 and 51 do not include this limitation.

*IV. Summary*

As discussed above, claims 21, 43, and 51 are allowable over the combination of Smolanoff, Fu, and Liu. Claims 10-13, 41-42, and 58 depend from claim 21 and are therefore allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 21. Claim 40 has been canceled. Claims 44-45 and 59 depend from claim 43 and are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 43. Claims 52-57 and 60 depend from claim 51 and are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 51.

<u>Claims 2-4, 6, and 22-24</u>

Claims 2-4, 6, and 22-24 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Fu and Liu, as applied to claims 10-13, 21, 40-45, and 51-60.

Claims 2-4, 6, and 22-24 depend from claim 21. As discussed above, claim 21 is allowable over the combination of Smolanoff, Fu, and Liu. Therefore, claims 2-4, 6, and 22-24 are allowable over the combination of Smolanoff, Fu, and Liu for at least the same reasons as is claim 21.

Claims 7-9

Claims 7 and 9 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Smolanoff in view of Fu and Liu, as applied to claims 10-13, 21, 40-45, and 51-60, and in further view of U.S. Patent Publication No. 2003/0077914 to Le et al. ("Le").

Claims 7 and 9 depend from claim 21. As discussed above, claim 21 is allowable over the combination of Smolanoff, Fu, and Liu. Le does not cure the defects in the teachings of Smolanoff, Fu, and Liu. Further, there is no reason to combine Smolanoff and Liu with any other art in order to find claim 21 obvious because both Smolanoff and Liu teach away from "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21.

Le teaches deposition of an anti-reflective coating by pulsing a DC source with no bias applied to the substrate. As taught in Le,

> The pulsed DC power source 22 applies a pulsed DC (direct current) voltage to the target 14. The pulsed DC voltage may be oscillated between negative and positive states. In one version, the pulsed DC voltage is pulsed between "on" and "off" states . . . .

(Le, par. 0071). As further stated, "[t]he pulsed DC voltage alleviates this problem by maintaining "on" and "off" states during each pulse cycle." (Le, par. 0072). Therefore, Le does not teach that the target voltage goes positive, and only teaches that the DC voltage is pulsed. Further, there is no teaching of a bias applied to the substrate. Therefore, Le does not teach "adjusting an RF bias power to the substrate" in combination with "applying pulsed DC power to the target such that a voltage on the target oscillates between positive and negative voltages to create a plasma and deposit the oxide film" as is recited in claim 21.

Further, Le was apparently presented to teach "wherein the RF bias power is optimized to provide planarization," as is recited in claim 7. However, Le does not teach RF bias or planarization of a cladding layer.

Therefore, claims 7 and 9 are allowable over the cited art for at least the same reasons as is claim 21.

## Conclusion

In view of the foregoing amendments, which are discussed during the Interview, and the remarks, which provides the substance of the discussion during the Interview, Applicant respectfully requests the timely allowance of the pending claims, which the Examiner indicated would be allowable after the amendments provided herein. If the Examiner has any questions or concerns regarding this Amendment or these Remarks, the Examiner is invited to call Applicant's representative.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 18, 2007

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

# Electronic Acknowledgement Receipt

| | |
|---|---|
| **EFS ID:** | 2610189 |
| **Application Number:** | 10101863 |
| **International Application Number:** | |
| **Confirmation Number:** | 6938 |
| **Title of Invention:** | Biased pulse DC reactive sputtering of oxide films |
| **First Named Inventor/Applicant Name:** | Hongmei Zhang |
| **Customer Number:** | 22852 |
| **Filer:** | Gary James Edwards/Annie Wong |
| **Filer Authorized By:** | Gary James Edwards |
| **Attorney Docket Number:** | 10655.0016-00 |
| **Receipt Date:** | 18-DEC-2007 |
| **Filing Date:** | 16-MAR-2002 |
| **Time Stamp:** | 19:10:11 |
| **Application Type:** | Utility under 35 USC 111(a) |

## Payment information:

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| Submitted with Payment | no |

## File Listing:

| Document Number | Document Description | File Name | File Size(Bytes) /Message Digest | Multi Part /.zip | Pages (if appl.) |
|---|---|---|---|---|---|
| 1 | Amendment - After Non-Final Rejection | Amendment_Response_to_OA_10655-0016-00.pdf | 237230<br>5b7b12a167c6082e1fe7acb03285f0060eea8dbe | no | 17 |

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# PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

| Application or Docket Number | Filing Date | |
|---|---|---|
| 10/101,863 | 03/16/2002 | ☐ To be Mailed |

## APPLICATION AS FILED – PART I

| | (Column 1) | (Column 2) | SMALL ENTITY ☒ | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|
| FOR | NUMBER FILED | NUMBER EXTRA | RATE ($) | FEE ($) | | RATE ($) | FEE ($) |
| ☐ BASIC FEE (37 CFR 1.16(a), (b), or (c)) | N/A | N/A | N/A | | | N/A | |
| ☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m)) | N/A | N/A | N/A | | | N/A | |
| ☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q)) | N/A | N/A | N/A | | | N/A | |
| TOTAL CLAIMS (37 CFR 1.16(i)) | minus 20 = | * | X $ = | | OR | X $ = | |
| INDEPENDENT CLAIMS (37 CFR 1.16(h)) | minus 3 = | * | X $ = | | | X $ = | |
| ☐ APPLICATION SIZE FEE (37 CFR 1.16(s)) | If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s). | | | | | | |
| ☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j)) | | | | | | | |
| | | | TOTAL | | | TOTAL | |

* If the difference in column 1 is less than zero, enter “0” in column 2.

## APPLICATION AS AMENDED – PART II

| | | (Column 1) | | (Column 2) | (Column 3) | SMALL ENTITY | | OR | OTHER THAN SMALL ENTITY | |
|---|---|---|---|---|---|---|---|---|---|---|
| AMENDMENT | **12/18/2007** | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
| | Total (37 CFR 1.16(i)) | * 35 | Minus | ** 39 | = 0 | X $25 = | 0 | OR | X $ = | |
| | Independent (37 CFR 1.16(h)) | * 3 | Minus | ***5 | = 0 | X $105 = | 0 | OR | X $ = | |
| | ☐ Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | ☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | | | OR | | |
| | | | | | | TOTAL ADD’L FEE | **0** | OR | TOTAL ADD’L FEE | |

| | | (Column 1) | | (Column 2) | (Column 3) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| AMENDMENT | | CLAIMS REMAINING AFTER AMENDMENT | | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE ($) | ADDITIONAL FEE ($) | | RATE ($) | ADDITIONAL FEE ($) |
| | Total (37 CFR 1.16(i)) | * | Minus | ** | = | X $ = | | OR | X $ = | |
| | Independent (37 CFR 1.16(h)) | * | Minus | *** | = | X $ = | | OR | X $ = | |
| | ☐ Application Size Fee (37 CFR 1.16(s)) | | | | | | | | | |
| | ☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) | | | | | | | OR | | |
| | | | | | | TOTAL ADD’L FEE | | OR | TOTAL ADD’L FEE | |

* If the entry in column 1 is less than the entry in column 2, write “0” in column 3.
** If the “Highest Number Previously Paid For” IN THIS SPACE is less than 20, enter “20”.
*** If the “Highest Number Previously Paid For” IN THIS SPACE is less than 3, enter “3”.
The “Highest Number Previously Paid For” (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
eugenia v. hardy

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

# EAST Search History

| | | | | | | |
|---|---|---|---|---|---|---|
| S66 | 105 | (n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench)) | US-PGPUB; USPAT | OR | OFF | 2004/02/17 14:39 |
| S67 | 100 | ((n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench))) not (@ad>"20020511" or @rlad>"20020511") | US-PGPUB; USPAT | OR | OFF | 2004/02/17 14:39 |
| S68 | 97 | (((n-well and p-well) and ((STI or isolation) and (epitaxial$3 with trench))) not (@ad>"20020511" or @rlad>"20020511")) not (438/429. ccls. not (@ad>"20020511" or @rlad>"20020511")) | US-PGPUB; USPAT | OR | OFF | 2004/02/17 14:39 |
| S69 | 1236723 | @ad>"20020511" or @rlad>"20020511" | US-PGPUB; USPAT | OR | OFF | 2006/09/05 09:32 |
| S70 | 121 | band with (rejection or stop or low or narrow) with filter with frequency with bias | US-PGPUB; USPAT | OR | OFF | 2006/09/05 09:33 |
| S71 | 93 | S70 not S69 | US-PGPUB; USPAT | OR | OFF | 2006/09/05 09:33 |
| S72 | 1 | ("7262131").PN. | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:13 |
| S73 | 2456 | (438/769,770,771,787,788).CCLS. | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:17 |
| S74 | 1939945 | @ad>"20020316" or @rlad>"20020316" | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:17 |
| S75 | 1498 | S73 not S74 | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:18 |
| S78 | 3342 | (204/192.12,192.15).CCLS. | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:18 |
| S79 | 316 | (427/533).CCLS. | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:19 |
| S80 | 1190 | (257/E21.273,E21.278,E21.462).CCLS. | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:26 |
| S81 | 550 | S80 not S74 | US-PGPUB; USPAT | OR | OFF | 2008/01/17 12:26 |

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FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
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901 NEW YORK AVENUE, NW
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| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| ART UNIT | PAPER NUMBER |
| 2823 | |

DATE MAILED: 01/25/2008

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 10655.0016-00 | 6938 |

TITLE OF INVENTION: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

| APPLN. TYPE | SMALL ENTITY | ISSUE FEE DUE | PUBLICATION FEE DUE | PREV. PAID ISSUE FEE | TOTAL FEE(S) DUE | DATE DUE |
|---|---|---|---|---|---|---|
| nonprovisional | YES | $720 | $300 | $0 | $1020 | 04/25/2008 |

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**THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.**

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| B. If the status above is to be removed, check box 5b on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and twice the amount of the ISSUE FEE shown above, or | B. If applicant claimed SMALL ENTITY status before, or is now claiming SMALL ENTITY status, check box 5a on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and 1/2 the ISSUE FEE shown above. |

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

**IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.**

PTOL-85 (Rev. 08/07) Approved for use through 08/31/2010.

# PART B - FEE(S) TRANSMITTAL

**Complete and send this form, together with applicable fee(s), to: Mail**

**Mail Stop ISSUE FEE**
**Commissioner for Patents**
**P.O. Box 1450**
**Alexandria, Virginia 22313-1450**

**or Fax (571)-273-2885**

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

**Certificate of Mailing or Transmission**

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 10655.0016-00 | 6938 |

TITLE OF INVENTION: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

| APPLN. TYPE | SMALL ENTITY | ISSUE FEE DUE | PUBLICATION FEE DUE | PREV. PAID ISSUE FEE | TOTAL FEE(S) DUE | DATE DUE |
|---|---|---|---|---|---|---|
| nonprovisional | YES | $720 | $300 | $0 | $1020 | 04/25/2008 |

| EXAMINER | ART UNIT | CLASS-SUBCLASS |
|---|---|---|
| ESTRADA, MICHELLE | 2823 | 438-788000 |

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) the names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 ____________________
2 ____________________
3 ____________________

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:

☐ Issue Fee
☐ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies ____________

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**

☐ A check is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number __________ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)

☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27.
☐ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature ____________________ Date ____________________

Typed or printed name ____________________ Registration No. ____________________

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PTOL-85 (Rev. 08/07) Approved for use through 08/31/2010. OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 10655.0016-00 | 6938 |

22852 7590 01/25/2008

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| **ART UNIT** | **PAPER NUMBER** |
| 2823 | |

DATE MAILED: 01/25/2008

## Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)

(application filed on or after May 29, 2000)

The Patent Term Adjustment to date is 0 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 0 day(s).

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

PTOL-85 (Rev. 08/07) Approved for use through 08/31/2010.

8

| | | | |
|---|---|---|---|
| **Notice of Allowability** | **Application No.**<br>10/101,863 | **Applicant(s)**<br>ZHANG ET AL. | |
| | **Examiner**<br>Michelle Estrada | **Art Unit**<br>2823 | |

***-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--***

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *12/18/07*.

2. ☒ The allowed claim(s) is/are *2-4,6-13,21-24 and 41-60*.

3. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
   a) ☐ All b) ☐ Some* c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
**THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.**

4. ☐ A SUBSTITUTE OATH OR DECLARATION must be submitted. Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL PATENT APPLICATION (PTO-152) which gives reason(s) why the oath or declaration is deficient.

5. ☐ CORRECTED DRAWINGS ( as "replacement sheets") must be submitted.
   (a) ☐ including changes required by the Notice of Draftsperson's Patent Drawing Review ( PTO-948) attached
   1) ☐ hereto or 2) ☐ to Paper No./Mail Date _____.
   (b) ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   **Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).**

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

**Attachment(s)**

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Notice of Draftperson's Patent Drawing Review (PTO-948)
3. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 11/27/07
4. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
5. ☐ Notice of Informal Patent Application
6. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
7. ☐ Examiner's Amendment/Comment
8. ☐ Examiner's Statement of Reasons for Allowance
9. ☐ Other _____.

MICHELLE ESTRADA
PRIMARY EXAMINER

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| | | | |
|---|---|---|---|
| Sheet | 1 | of | 1 |

| Complete if Known | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | Michelle ESTRADA |
| *Attorney Docket Number* | 10655.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| ME | | US-7,262,131 | 08-28-2007 | Narasimhan et al. | |
| | | US- | | | |
| | | US- | | | |
| | | US- | | | |
| | | US- | | | |
| | | US- | | | |
| | | US- | | | |
| | | US- | | | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

## NONPATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| ME | | Amendment/RCE filed October 31, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| | | Amendment/RCE filed October 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Office Action dated November 15, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
| | | Final Office Action dated October 10, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |
| ME | | Amendment/RCE filed October 31, 2007, in U.S. Application No. 10/650,461 (Attorney Docket No. 9140.0025-00). | |

| | | | |
|---|---|---|---|
| Examiner Signature | Michelle Estrada | Date Considered | 1/17/08 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

**EXPRESS MAIL LABEL NO.**
**EM 074696455 US**

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UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

Bib Data Sheet

CONFIRMATION NO. 6938

| | | | | |
|---|---|---|---|---|
| SERIAL NUMBER<br>10/101,863 | FILING DATE<br>03/16/2002<br>RULE | CLASS<br>438 | GROUP ART UNIT<br>2823 | ATTORNEY DOCKET NO.<br>M-12245 US |

APPLICANTS

Hongmei Zhang, San Jose, CA;

Mukundan Narasimhan, San Jose, CA;
Ravi B. Mullapudi, San Jose, CA;Richard E. Demaray, Portola Valley, CA;

** CONTINUING DATA *************************
none

** FOREIGN APPLICATIONS ********************
none

IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** SMALL ENTITY **
** 05/17/2002

| | | | | |
|---|---|---|---|---|
| Foreign Priority claimed ☐ yes ☑ no<br>35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance<br>Verified and Acknowledged Examiner's Signature Initials | STATE OR COUNTRY<br>CA | SHEETS DRAWING<br>27 | TOTAL CLAIMS<br>~~39~~ 19 | INDEPENDENT CLAIMS<br>~~3~~ 2 |

ADDRESS
22852
FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON , DC
20001-4413

TITLE
Biased pulse DC reactive sputtering of oxide films

| | | |
|---|---|---|
| FILING FEE<br>RECEIVED | FEES: Authority has been given in Paper<br>No. _________ to charge/credit DEPOSIT ACCOUNT<br>No. _________ for following: | ☐ All Fees<br>☐ 1.16 Fees ( Filing )<br>☐ 1.17 Fees ( Processing Ext. of time ) |

| | | |
|---|---|---|
| ***Index of Claims*** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | **Rejected** | | - | **Cancelled** | | N | **Non-Elected** | | A | **Appeal** |
| = | **Allowed** | | ÷ | **Restricted** | | I | **Interference** | | O | **Objected** |

☐ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

| **CLAIM** | | **DATE** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 | 11/11/2007 | 01/17/2008 | | | | | | |
| | 1 | - | - | | | | | | | |
| 2 | 2 | ✓ | ✓ | = | | | | | | |
| 3 | 3 | ✓ | ✓ | = | | | | | | |
| 4 | 4 | ✓ | ✓ | = | | | | | | |
| | 5 | ✓ | ✓ | - | | | | | | |
| 5 | 6 | ✓ | ✓ | = | | | | | | |
| 6 | 7 | ✓ | ✓ | = | | | | | | |
| 7 | 8 | ✓ | ✓ | = | | | | | | |
| 8 | 9 | ✓ | ✓ | = | | | | | | |
| 9 | 10 | ✓ | ✓ | = | | | | | | |
| 10 | 11 | ✓ | ✓ | = | | | | | | |
| 11 | 12 | ✓ | ✓ | = | | | | | | |
| 12 | 13 | ✓ | ✓ | = | | | | | | |
| | 14 | - | - | - | | | | | | |
| | 15 | - | - | - | | | | | | |
| | 16 | - | - | - | | | | | | |
| | 17 | - | - | - | | | | | | |
| | 18 | - | - | - | | | | | | |
| | 19 | - | - | - | | | | | | |
| | 20 | - | - | - | | | | | | |
| 1 | 21 | ✓ | ✓ | = | | | | | | |
| 13 | 22 | ✓ | ✓ | = | | | | | | |
| 14 | 23 | ✓ | ✓ | = | | | | | | |
| 15 | 24 | ✓ | ✓ | = | | | | | | |
| | 25 | - | - | - | | | | | | |
| | 26 | - | - | - | | | | | | |
| | 27 | - | - | - | | | | | | |
| | 28 | - | - | - | | | | | | |
| | 29 | - | - | - | | | | | | |
| | 30 | - | - | - | | | | | | |
| | 31 | - | - | - | | | | | | |
| | 32 | - | - | - | | | | | | |
| | 33 | - | - | - | | | | | | |
| | 34 | - | - | - | | | | | | |
| | 35 | - | - | - | | | | | | |
| | 36 | - | - | - | | | | | | |

U.S. Patent and Trademark Office

Part of Paper No. : 20080117

| | | |
|---|---|---|
| *Index of Claims* | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ✓ | Rejected | - | Cancelled | N | Non-Elected | A | Appeal |
| = | Allowed | ÷ | Restricted | I | Interference | O | Objected |

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

| CLAIM | | DATE | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Final | Original | 04/30/2007 | 11/11/2007 | 01/17/2008 | | | | | | |
| | 37 | - | - | - | | | | | | |
| | 38 | - | - | - | | | | | | |
| | 39 | - | - | - | | | | | | |
| | 40 | ✓ | ✓ | - | | | | | | |
| 16 | 41 | ✓ | ✓ | = | | | | | | |
| 17 | 42 | ✓ | ✓ | = | | | | | | |
| 18 | 43 | ✓ | ✓ | = | | | | | | |
| 19 | 44 | ✓ | ✓ | = | | | | | | |
| 20 | 45 | ✓ | ✓ | = | | | | | | |
| 21 | 46 | ✓ | ✓ | = | | | | | | |
| 22 | 47 | ✓ | ✓ | = | | | | | | |
| 23 | 48 | ✓ | ✓ | = | | | | | | |
| 24 | 49 | ✓ | ✓ | = | | | | | | |
| 25 | 50 | ✓ | ✓ | = | | | | | | |
| 26 | 51 | ✓ | ✓ | = | | | | | | |
| 27 | 52 | ✓ | ✓ | = | | | | | | |
| 28 | 53 | ✓ | ✓ | = | | | | | | |
| 29 | 54 | ✓ | ✓ | = | | | | | | |
| 30 | 55 | ✓ | ✓ | = | | | | | | |
| 31 | 56 | ✓ | ✓ | = | | | | | | |
| 32 | 57 | ✓ | ✓ | = | | | | | | |
| 33 | 58 | ✓ | ✓ | = | | | | | | |
| 34 | 59 | ✓ | ✓ | = | | | | | | |
| 35 | 60 | ✓ | ✓ | = | | | | | | |

| ***Issue Classification*** | **Application/Control No.**<br>10101863 | **Applicant(s)/Patent Under Reexamination**<br>ZHANG ET AL. |
|---|---|---|
| | **Examiner**<br>Estrada, Michelle | **Art Unit**<br>2823 |

## ORIGINAL

| CLASS | SUBCLASS |
|---|---|
| 438 | 778 |

## CROSS REFERENCE(S)

| CLASS | SUBCLASS (ONE SUBCLASS PER BLOCK) | | | | |
|---|---|---|---|---|---|
| 438 | 787 | 788 | | | |
| 427 | 533 | | | | |
| 204 | 192.12 | 192.15 | | | |

## INTERNATIONAL CLASSIFICATION

| CLAIMED | | | | | NON-CLAIMED |
|---|---|---|---|---|---|
| H | 0 | 1 | L | 21 / 31 (2006.01.01) | |
| H | 0 | 1 | L | 21 / 469 (2006.01.01) | |

| | | |
|---|---|---|
| NONE<br>(Assistant Examiner) (Date) | Michelle Estrada<br>MICHELLE ESTRADA<br>PRIMARY EXAMINER | **Total Claims Allowed:**<br>35 |
| J. Stephens 1-24-08<br>(Legal Instruments Examiner) (Date) | Estrada, Michelle 1/17/08<br>(Primary Examiner) (Date) | O.G. Print Claim(s): 1<br>O.G. Print Figure: 1A |

U.S. Patent and Trademark Office

Part of Paper No. 20080117

| Search Notes | Application/Control No.<br>10101863 | Applicant(s)/Patent Under Reexamination<br>ZHANG ET AL. |
|---|---|---|
| | Examiner<br>Estrada, Michelle | Art Unit<br>2823 |

## SEARCHED

| Class | Subclass | Date | Examiner |
|---|---|---|---|
| Updated as before | | 1/17/08 | ME |
| 257 | E21.273,E21.278,E21.462 | 1/17/08 | Me |

## SEARCH NOTES

| Search Notes | Date | Examiner |
|---|---|---|
| See East search attached | 10/2/07 | ME |
| Inspected parent for pertinent prior art | 1/17/08 | ME |

## INTERFERENCE SEARCH

| Class | Subclass | Date | Examiner |
|---|---|---|---|
| PG Pub text search | | 1/17/08 | ME |

OIPE
FEB 1 3 2008
PATENT & TRADEMARK OFFICE

IDS Form PTO/SB/08: Substitute for form 1449A/PTO

# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 1 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | Hongmei ZHANG |
| *Art Unit* | 2823 |
| *Examiner Name* | Michelle ESTRADA |
| *Attorney Docket Number* | 10655.0016-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
|---|---|---|---|---|---|
| | | US- | | | |

**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
|---|---|---|---|---|---|---|
| | | | | | | |

## NONPATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
| | | Response to Office Action dated November 21, 2007, in U.S. Appl. No. 10/291,179 (Attorney Docket No. 9140.0001-00). | |
| | | Response to Office Action dated December 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Final Office Action dated January 29, 2008, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| | | Office Action dated January 25, 2008, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
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| Examiner Signature | | Date Considered | |
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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 1 | of | 1 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/650,461 |
| *Filing Date* | August 27, 2003 |
| *First Named Inventor* | DAWES, David |
| *Art Unit* | 2883 |
| *Examiner Name* | DUPUIS, Derek L. |
| *Attorney Docket Number* | 10655.0025-00 |

## U.S. PATENTS AND PUBLISHED U.S. PATENT APPLICATIONS

| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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## NON PATENT LITERATURE DOCUMENTS

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
|---|---|---|---|
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| /DLD/ | | Office Action dated September 5, 2007, in U.S. Application No. 09/903,081 (Attorney Docket No. 9140.0014-00). | |
| /DLD/ | | Final Office Action dated September 7, 2007, in U.S. Application No. 11/100,856 (Attorney Docket No. 9140.0015-01). | |
| /DLD/ | | Response to Final Office Action filed October 2, 2007, in U.S. Application No. 10/101,863 (Attorney Docket No. 9140.0016-00). | |
| /DLD/ | | Final Office Action dated July 24, 2007, in U.S. Application No. 10/954,182 (Attorney Docket No. 9140.0016-01). | |
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| Examiner Signature | /Derek Dupuis/ | Date Considered | 11/12/2007 |
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FEB 1 3 2008
PATENT & TRADEMARK OFFICE

PATENT
Customer No. 22,852
Attorney Docket No. 10655.0016-00

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ZHANG, Hongmei et al.

Application No.: 10/101,863

Filed: March 16, 2002

For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS

Group Art Unit: 2823

Examiner: ESTRADA, Michelle

Confirmation No.: 6938

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(d)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(d), Applicants brings to the attention of the Examiner the documents on the attached listing. This Supplemental Information Disclosure Statement is being filed after a Notice of Allowance but before payment of the issue fee and the Commissioner is authorized to charge the fee of $180.00 to Deposit Account No. 06-0916, as specified under § 1.17(p) and a statement as specified under § 1.97(e).

Based on reasonable inquiry, no document listed in this Supplemental Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Supplemental Information Disclosure Statement was known to any individual designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Supplemental Information Disclosure Statement.

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01 FC:1806 180.00 DA

Copies of the listed non-patent literature documents are attached. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and Applicants determine that the cited documents do not constitute "prior art" under United States law, Applicants reserve the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any additional fee due in connection with the filing of this Statement, please charge the fee to Deposit Account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 13, 2008

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008
(650) 849-6622

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| APPLICATION NO. | FILING DATE | FIRST NAMED INVENTOR | ATTORNEY DOCKET NO. | CONFIRMATION NO. |
|---|---|---|---|---|
| 10/101,863 | 03/16/2002 | Hongmei Zhang | 10655.0016-00 | 6938 |

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FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| ESTRADA, MICHELLE | |
| **ART UNIT** | **PAPER NUMBER** |
| 2823 | |
| **MAIL DATE** | **DELIVERY MODE** |
| 03/03/2008 | PAPER |

**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

PTOL-90A (Rev. 04/07)

**UNITED STATES DEPARTMENT OF COMMERCE**
**U.S. Patent and Trademark Office**
Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450

| APPLICATION NO./ CONTROL NO. | FILING DATE | FIRST NAMED INVENTOR / PATENT IN REEXAMINATION | ATTORNEY DOCKET NO. |
|---|---|---|---|
| 10101863 | 3/16/02 | ZHANG ET AL. | 10655.0016-00 |

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER
LLP
901 NEW YORK AVENUE, NW
WASHINGTON, DC 20001-4413

| EXAMINER | |
|---|---|
| Michelle Estrada | |
| ART UNIT | PAPER |
| 2823 | 20080221 |

**DATE MAILED:**

**Please find below and/or attached an Office communication concerning this application or proceeding.**

**Commissioner for Patents**

Attached are the IDS filed 7/28/05 and 7/13/06 that have been considered.

/Michelle Estrada/
Primary Examiner, Art Unit 2823

PTO-90C (Rev.04-03)

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PATENT
Customer No. 22,852
Attorney Docket No. 9140.0016-00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | |
| ZHANG, Hongmei et al. | Group Art Unit: 2823 |
| Application No.: 10/101,863 | Examiner: ESTRADA, Michelle |
| Filed: March 16, 2002 | |
| For: BIASED PULSE DC REACTIVE SPUTTERING OF OXIDE FILMS | Confirmation No.: 6938 |

**MAIL STOP AMENDMENT**
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

## SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. § 1.97(b)

Pursuant to 37 C.F.R. §§ 1.56 and 1.97(b), applicants bring to the attention of the Examiner the documents on the attached listing. This Information Disclosure Statement is being filed before the mailing date of a first Office Action after the filing of a Request for Continued Examination in the above-referenced application. Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

Based on reasonable inquiry, no document listed in this Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and no document listed in this Information Disclosure Statement was known to any individual designated in 37 C.F.R. § 1.56(c) more than three months prior to the filing date of this Information Disclosure Statement.

Copies of the listed foreign patents and non-patent literature documents are attached. Copies of the U.S. patents and patent publications are not enclosed.

Applicants respectfully request that the Examiner consider the listed documents and indicate that they were considered by making appropriate notations on the attached form.

This submission does not represent that a search has been made or that no better art exists and does not constitute an admission that each or all of the listed documents are material or constitute "prior art." If the Examiner applies any of the documents as prior art against any claims in the application and applicants determine that the cited documents do not constitute "prior art" under United States law, applicant reserves the right to present to the office the relevant facts and law regarding the appropriate status of such documents.

Applicants further reserve the right to take appropriate action to establish the patentability of the disclosed invention over the listed documents, should one or more of the documents be applied against the claims of the present application.

If there is any fee due in connection with the filing of this Statement, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: July 28, 2005

By: Gary J. Edwards
Gary J. Edwards
Reg. No. 41,008

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| Sheet | 1 | of | 9 |

| ***Complete if Known*** | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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| Examiner Initials* | Cite No.[1] | Document Number<br>Number-Kind Code[2] *(if known)* | Issue or Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear |
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|---|---|---|---|
| Examiner Signature | /Michelle Estrada/ | Date Considered | 02/21/2008 |

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO<br>**INFORMATION DISCLOSURE STATEMENT BY APPLICANT**<br>*(Use as many sheets as necessary)* | | ***Complete if Known*** | |
| | | *Application Number* | 10/101,863 |
| | | *Filing Date* | March 16, 2002 |
| | | *First Named Inventor* | ZHANG, Hongmei |
| | | *Art Unit* | 2823 |
| | | *Examiner Name* | ESTRADA, Michelle |
| Sheet 2 | of 9 | *Attorney Docket Number* | 9140.0016-00 |

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|---|---|---|---|
| Examiner Signature | /Michelle Estrada/ | Date Considered | 02/21/2008 |

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# INFORMATION DISCLOSURE STATEMENT BY APPLICANT

*(Use as many sheets as necessary)*

| Sheet | 3 | of | 9 |
|---|---|---|---|

| *Complete if Known* | |
|---|---|
| *Application Number* | 10/101,863 |
| *Filing Date* | March 16, 2002 |
| *First Named Inventor* | ZHANG, Hongmei |
| *Art Unit* | 2823 |
| *Examiner Name* | ESTRADA, Michelle |
| *Attorney Docket Number* | 9140.0016-00 |

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**Note: Submission of copies of U.S. Patents and published U.S. Patent Applications is not required.**

## FOREIGN PATENT DOCUMENTS

| Examiner Initials* | Cite No.[1] | Foreign Patent Document<br>Country Code[3] Number[4] Kind Code[5] *(if known)* | Publication Date MM-DD-YYYY | Name of Patentee or Applicant of Cited Document | Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear | Translation[6] |
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| | | | | | | |

| Examiner Signature | /Michelle Estrada/ | Date Considered | 02/21/2008 |
|---|---|---|---|

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| IDS Form PTO/SB/08: Substitute for form 1449A/PTO | | | | **Complete if Known** | |
| | | | | *Application Number* | 10/101,863 |
| **INFORMATION DISCLOSURE STATEMENT BY APPLICANT** | | | | *Filing Date* | March 16, 2002 |
| | | | | *First Named Inventor* | ZHANG, Hongmei |
| | | | | *Art Unit* | 2823 |
| *(Use as many sheets as necessary)* | | | | *Examiner Name* | ESTRADA, Michelle |
| Sheet | 4 | of | 9 | *Attorney Docket Number* | 9140.0016-00 |

**NON PATENT LITERATURE DOCUMENTS**

| Examiner Initials* | Cite No.[1] | Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published. | Translation[6] |
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| | | | |
|---|---|---|---|
| Examiner Signature | /Michelle Estrada/ | Date Considered | 02/21/2008 |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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