Unbalanced magnetron ion-assisted deposition and property modification of thin films

N. Savvides and B. Window
CSIRO Division of Applied Physics, Sydney, Australia 2070

(Received 17 September 1985; accepted 22 November 1985)

Unbalanced magnetron (UM-gun) sputtering sources with the unique characteristic of a high deposition rate and concomitant high ion flux represent an exciting new development in ion-assisted deposition of thin films. We have used a UM-gun capable of producing ion current densities up to 5 mA cm^{-2} (ion flux 3×10^{16} cm^{-2} s^{-1}) when operated at a power of 500 W to produce a variety of thin films of amorphous and crystalline materials by varying both the bombarding ion energy in the range 2–100 eV and the ion/atom arrival rate ratio in the range 0.4–10. The great flexibility and usefulness of UM-guns is demonstrated with examples which include (a) hard diamondlike *a*-C films prepared under very low ion energy (13–16 eV) bombardment which possess a metastable bonding configuration consisting of a mixture of tetrahedral and trigonal coordination that varies with ion energy, (b) hard and wear-resistant TiN films whose electrical and optical properties change dramatically with ion bombardment, and (c) Ni/Cr alloy films showing ion-induced structural modifications.

I. INTRODUCTION

Ion-assisted deposition of solid films has emerged as a very powerful method of film deposition[1] and there have been a number of recent technological developments in instrumentation and a proliferation of techniques for producing energetic ions for film bombardment and energetic ionized species from which films are condensed.[2–7]

Within the last decade ion–surface and ion–solid interaction studies have established that films condensed under ion bombardment or from energetic ionized species undergo ion-induced modifications in their structure, surface morphology, composition, electronic and optical properties, film stress, adhesion to substrates, etc.[1,4,8–10] Particular investigations[1,6,11] have shown that low energy (10–1000 eV) ion bombardment can lead to interesting and unusual metastable structures.

We have recently developed unbalanced magnetron sputtering sources, UM-guns, with the unique characteristic of providing high deposition rates and concomitant high ion fluxes.[12] We present here the results of measurements of ion flux and condensing atom flux obtained using a UM-gun fitted with a permanent magnet and targets with effective sputtering area of approximately 20 cm^2. Both the energy of impinging ions and the arrival rate ratio of ions to condensing atoms are recognized as important parameters in ion-assisted deposition. The ion current reaching the depositing film is found to be proportional to the discharge current. Operating the UM-gun in the discharge power range to 500 W results in ion current densities up to 5 mA cm^{-2} corresponding to an ion flux of 3×10^{16} cm^{-2} s^{-1}. The deposition rate depends on the target material and the sputtering gas mixture in the same manner as in conventional planar magnetrons while the ion/condensing atom arrival rate ratio varies from about 0.4 to 10. The ions originate from the plasma whose potential with respect to ground is about $+2$ V, and consequently, suitable biasing of the growing film leads to bombardment by ions with energy in the range 2 eV to several hundred eV. Thin films of a variety of amorphous[13–15] and crystalline materials have been deposited in both reactive and nonreactive gas mixtures. We have carried out detailed investigations of the effects of low energy ion bombardment on the properties of a number of thin films of current technological interest and we present representative results to illustrate both the wide applicability of UM-guns and the structural and property modifications that are possible when using these guns to deposit thin films. The results indicate that film structure and properties can be influenced by very low energy ion bombardment.

II. EXPERIMENTAL DETAILS

The UM-gun used in this investigation is similar in construction to conventional planar magnetrons. It differs, however, in one important aspect in that a magnet assembly is used which results in an unbalanced magnetic field configuration. The details of the magnetic field and the motion of charged particles have been presented elsewhere.[12] The most obvious characteristic of a UM-gun discharge is a column of plasma which leaves the magnetic tunnel region and projects normal to the target surface toward the substrate position. A large flux of charged particles (electrons and ions) thus reaches the substrate and by suitable biasing the energy of ions impinging on the growing film can be varied.

Figure 1 shows a schematic arrangement of the sputtering system. The magnet assembly consists of an Alnico V permanent ring magnet fitted with a soft iron center pole. This results in an effective sputtering area of the target of about 20 cm^2. The substrate table is electrically isolated from the vacuum chamber and the fixtures. It is fitted with a cartridge heater and a thermocouple allowing deposition at variable substrate temperature. A metal plate with an aperture masks the table as shown in the figure, and a shutter can be rotated to cover the aperture. The substrate table is placed off-center with respect to the target and can be rotated to allow up to eight individual specimens to be prepared. The chamber fix-

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

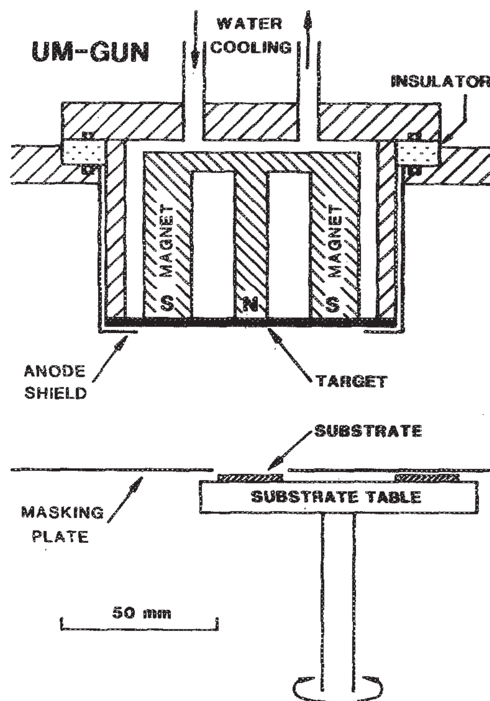

FIG. 1. Schematic diagram of the UM-gun sputtering system used to determine particle fluxes and to deposit films.

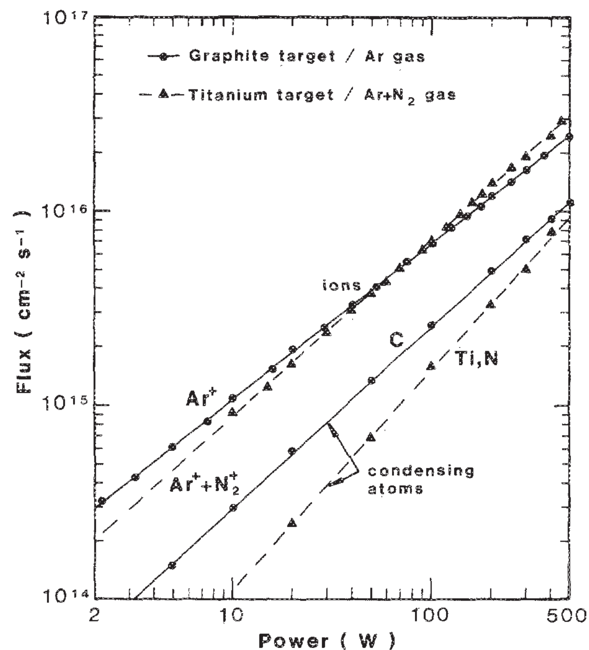

FIG. 2. Flux of ions and condensing atoms vs sputtering power.

tures are normally connected to the vacuum chamber which is at ground (anode) potential. The self-bias potentials of insulating substrates and the table are typically in the range -25 to -10 V with respect to ground.

The plasma potential was determined from the characteristic *V–I* behavior of a Langmuir probe[16] placed in the plasma. Using graphite and titanium targets sputtered in pure argon at a pressure of 1 Pa the plasma potential was found to be $+2.4$ V with respect to ground and it was independent of discharge power. The ion flux was determined from measurements of the ion current density flowing to the negatively biased substrate table through the aperture on the masking plate. A bias of -100 V was found sufficient to cause saturation of the ion current for sputtering power levels up to 500 W. All the measurements indicate that the ion current is proportional to the discharge current. The deposition flux was determined from the deposition rate.

III. RESULTS

The results of measurements of the ion flux and the flux of depositing or condensing atoms as a function of sputtering power are shown in Fig. 2 for graphite and titanium targets. The graphite target was sputtered in pure Ar gas at a pressure of 1 Pa. The ion species are Ar^+ and the condensing species are C atoms forming films of amorphous carbon *a*-C. The titanium target was reactively sputtered in a gas mixture of equal amounts of Ar and N_2 gases at a total pressure of 1 Pa. The principal ion species are Ar^+ and N_2^+.[17] The condensing species are Ti and N atoms forming films of polycrystalline titanium nitride TiN of stoichiometric composition. The deposition rate depends on the sputtering yield of the target material and on the composition of the plasma. It will be seen from the figure that the ion/condensing atom arrival rate ratio (the ratio of ion to atom fluxes) for the two targets is greater than unity. The ratio is highest at the lowest sputtering power level (~ 4 for C and ~ 10 for Ti or N) and it decreases to values of 2–3 at 500 W. Thus varying the sputtering power offers a convenient method of varying both the ion/atom arrival rate ratio and the ion energy (Fig. 3). It is instructive to note that at a power of 500 W, the measured ion flux of $2\text{–}3 \times 10^{16}$ $cm^{-2}\,s^{-1}$ corresponds to an ion current density of 4–5 mA cm^{-2} (1 mA cm^{-2} corresponds to a flux 6.25×10^{15} singly charged ions $cm^{-2}\,s^{-1}$), and that the ion beam is approximately of uniform density over a beam diameter of 5 cm^2. UM-guns, like conventional magnetrons, can be scaled up to larger target areas and, given effective cooling of the target, they can operate in the kW range so that both the ion beam diameter and the ion current density can be increased by several orders of magnitude. Another alternative is to increase the strength of the magnetic field and we have shown[12] using electromagnets that ion current densities up to 9 mA cm^{-2} are easily achieved.

Graphitic or "ordinary" amorphous carbon films are produced by conventional thin film deposition techniques, including ion beam sputtering, conventional magnetron sputtering, and e-beam evaporation. Various investigations have shown that a transition from ordinary amorphous carbon to diamondlike material takes place when the films are subjected during growth to energetic ion bombardment.[6,11,18] We have prepared diamondlike *a*-C films by UM-gun sputtering of a graphite target in Ar gas of 99.999% purity. The films possess outstanding diamondlike properties including extreme hardness, high electrical resistivity, high dielectric strength, optical transparency in the infrared, and an optical band gap up to 0.74 eV.[15,19] It is believed that the diamondlike properties are due to tetrahedral bonding which devel-

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

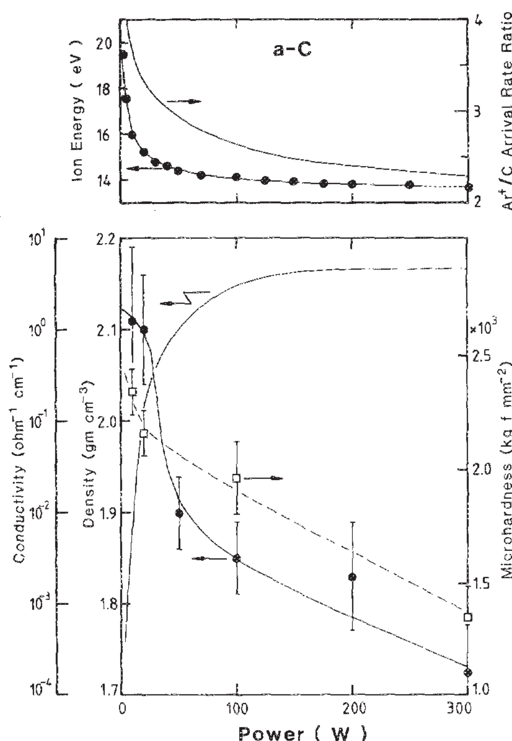

FIG. 3. Preparation conditions for diamondlike *a*-C films and film properties. The data shown in the lower plots were taken from Refs. 15 and 19.

ops from the interaction of ions with the surface or bulk of the material during film growth. We have shown recently[15,18] that diamondlike *a*-C films consist of a metastable mixture of fourfold coordinated and threefold coordinated carbon atoms. The ratio of fourfold to threefold coordinated atoms depends on the degree of ion bombardment and a gradual transition in this metastable mixture can be brought about with the ratio changing from about 3:1 to 1:1 as the sputtering power changes from 5 to 500 W.

Figure 3 shows some of the physical properties of *a*-C films. The films were deposited onto self-biased insulating substrates by sputtering at various power levels. The data at the top of the figure show the ion energy and the Ar^+/C arrival rate ratio (determined using the data of Fig. 2) versus sputtering power. The films that were deposited at low sputtering power (<50 W) possess the best diamondlike properties and have a tetrahedral bonding component of 60%–76%. Scanning electron microscopy has shown that these films have remarkably smooth surfaces and their microstructure is free of columnar growth.[19] These properties correlate with the high ion energy and the high Ar^+/C arrival rate ratio obtained at low sputtering power. As the sputtering power increases both the ion energy and the Ar^+/C arrival rate ratio decreases. The properties and the bonding microstructure of the films change indicating a decrease in the tetrahedral component, so that at power levels $\geqslant 300$ W the films consist of about equal mixtures of fourfold (diamondlike) and threefold (graphitic) coordinated carbon atoms. It is significant that the excellent diamondlike properties of the *a*-C films prepared by UM-gun sputtering are the result of ion bombardment using very low ion energies (13–17 eV) compared to much higher values (500–1000 eV) used previously.[4–7,11] The outstanding properties of diamondlike *a*-C films have made them attractive for many applications including their use as hard protective metallurgical coatings, and as scratch-resistant insulating hermetic barrier coatings on infrared optics, optical memory disks, and optical fibers.

Stoichiometric titanium nitride TiN of the fcc phase (δ-TiN) is a high melting point (2949 °C) refractory nitride and is known for its great hardness and its brilliant golden color. Thin films of TiN with hardness values which lie between those of sapphire and diamond are extensively used as hard and wear-resistant coatings in tribological applications.[20–22] Titanium nitride has a defect structure[23] and deviations from stoichiometry are common. Consequently, the properties of polycrystalline thin films of TiN, including optical and electrical properties, are extremely sensitive to the film microstructure and growth morphology as well as to deviations from stoichiometry. Previous investigations have established that TiN films of stoichiometric composition and possessing exceptional hardness (Vickers microhardness of 2000–3000 kgf mm^{-2}) can be produced at temperatures of 300–600 °C by ion-assisted deposition using ion energies up to 300 eV.[22,24–26]

UM-gun reactive sputtering of a titanium target was used to deposit stoichiometric TiN films, 0.6–2 μm thick, onto glass substrates. During deposition each film was electrically connected to the substrate table which was biased negative in the range 0 to -100 V. A sputtering power of 100 W was used, and thus the ion/atom arrival rate ratio was fixed at 4.6. It is well known that the electrical resistivity of thin films is very sensitive to composition, vacancies, grain size, porosity, intergranular resistance, and film stress. We thus use four-probe measurements of resistivity to assess film quality. Figure 4 shows plots of film resistivity versus bombarding ion energy and the variation in color of films deposited at various temperatures. The results show a dramatic drop of resistivity with increasing ion energy. Films deposited at 500 °C were golden in color and their resistivity reached a minimum of 26.2 ± 0.2 $\mu\Omega$ cm at about 40 eV. This is the lowest room temperature resistivity value obtained so far for a polycrystalline film deposited at 500 °C and it is comparable to a value of 18 ± 0.5 $\mu\Omega$ cm reported recently[27] for an epitaxial single crystal film grown on cleaved MgO at 700 °C. X-ray diffraction and scanning electron microscopy showed that the microstructure and growth habit of crystallites were influenced by the degree of ion bombardment. The films grew with very strong preferential orientation which could be changed by ion bombardment. Film stress was also found to increase with increasing ion energy so that films deposited at temperatures $\leqslant 300$ °C were observed to spall either during deposition or soon after removal from the vacuum. The stress was compressive, and it decreased considerably at higher deposition temperatures reaching a minimum for ion energies of about 40 eV.

The effect of low energy ion bombardment on the evolution of fim microstructure was further investigated by depositing films from a Ni/Cr alloy target. Our interest here was

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

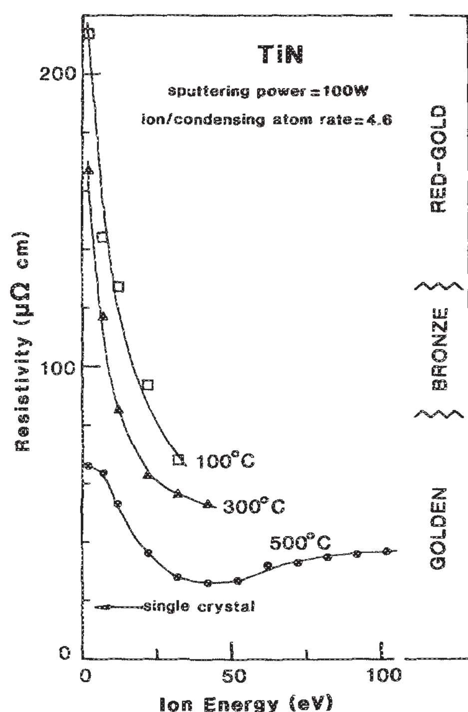

FIG. 4. Stoichiometric TiN films showing the variation of resistivity and color with bombarding ion energy.

to establish suitable preparation conditions for the manufacture of thin film resistors to be used as secondary resistance standards. Thus films of long term stability and a low temperature coefficient of resistance are required. Figure 5 shows SEM micrographs of fracture cross sections and surface morphology of two films deposited at 200 °C onto glass substrates by sputtering the target at a power of 100 W in Ar gas at 1 Pa. The two films shown were deposited at 0 and − 100 V bias and were thus bombarded during growth by ions of energy of about 2 and 102 eV, respectively; the ion/atom arrival rate ratio was approximately 0.4 in both cases. In general, films deposited at low ion energies (<20 eV) showed characteristic porous fibrous columnar growth[28] and although their surface was mirror smooth, scanning electron microscopy showed many surface flaws such as large voids and a porous structure. Increasing the ion energy above 50 eV led to the elimination of the fibrous growth; the films became more dense and large crystals in the form of regular polyhedra appeared which grew from the nucleating surface and reached the top surface of the film. The room temperature resistivity of films prepared at zero bias was approximately 125 $\mu\Omega$ cm and decreased to about 118 $\mu\Omega$ cm for films prepared at − 100 V bias. Using an acid solution, the etching rates for these films were 400 and 20 nm/min, respectively. These results correlate with the observed microstructure and indicate that ion bombardment using energies up to 100 eV and ion/atom arrival rate ratio of 0.4 have led to increased densification due to the elimination of porosity and fibrous growth, and to a reduction in intergranular resistance.

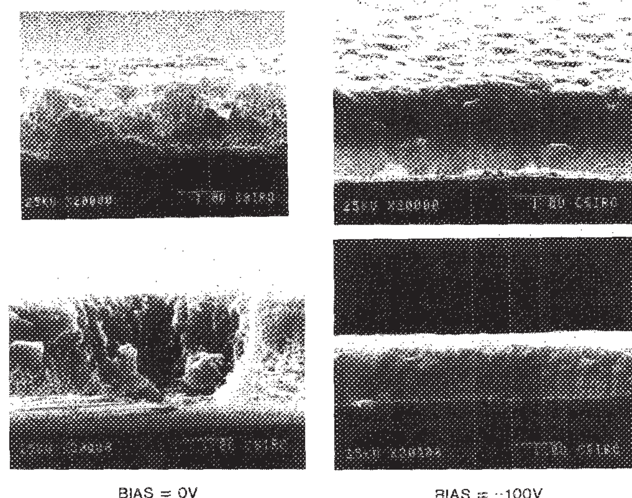

FIG. 5. SEM micrographs showing the effect of ion bombardment on the

IV. CONCLUSION

An unbalanced magnetron sputtering source UM-gun which provides simultaneously high deposition rates and high ion fluxes, has been described. UM-gun ion-assisted sputter deposition was used to investigate the effect of low energy (2–100 eV) ion bombardment on the evolution of film microstructure and to modify the thin film properties of a broad range of materials.

The ion flux and condensing atom flux were determined for several target materials. It was shown that by operating the UM-gun in the power density range 0.1–25 W cm^{-2} the ion flux could be varied between about 1×10^{14} and 3×10^{16} $cm^{-2}\,s^{-1}$ and, depending on the plasma composition and the sputtering yield of the target material, the ion/atom arrival rate ratio could be varied in the range 0.4–10. We note by way of comparison that the latest low energy (100–500 eV) Kaufman broad-beam ion sources[2,17] which are used in dual ion-beam deposition can provide a flux of about 8×10^{15} $cm^{-2}\,s^{-1}$. We conclude that UM-guns are excellent alternatives, especially in industrial scale applications.

ACKNOWLEDGMENT

We would like to thank R. K. Lane for obtaining the SEM micrographs.

[1]O. Auciello and R. Kelly, *Ion Modification of Surfaces* (Elsevier, Amsterdam, 1984).
[2]J. M. E. Harper, J. J. Cuomo, and H. R. Kaufman, J. Vac. Sci. Technol. A **1**, 337 (1983).
[3]H. R. Kaufman, J. J. Cuomo, and J. M. E. Harper, J. Vac. Sci. Technol. **21**, 725 (1981); **21**, 737 (1982).
[4]C. Weissmantel, J. Vac. Sci. Technol. **18**, 179 (1981).
[5]Y. Namba and T. Mori, J. Vac. Sci. Technol. A **3**, 319 (1985).
[6]C. Weissmantel, K. Bewilogua, K. Breuer, D. Dietrich, U. Ebersbach, H.-J. Erler, B. Rau, and G. Reisse, Thin Solid Films **96**, 31 (1982).
[7]T. Miyazawa, S. Misawa, S. Yoshida, and S. Gonda, J. Appl. Phys. **55**, 188 (1984).
[8]R. Kelly, Nucl. Instrum. Methods **182/183**, 351 (1981).
[9]T. Takagi, J. Vac. Sci. Technol. A **2**, 382 (1984).
[10]H. T. G. Hentzell, J. M. E. Harper, and J. J. Cuomo, J. Appl. Phys. **58**, 556 (1985).

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

berg, S. Klose, W. Nowick, and G. Riesse, Thin Solid Films **72**, 19 (1980).
[12]B. Window and N. Savvides, J. Vac. Sci. Technol. A **4**, 196 (1986); J. Vac. Sci. Technol. A (these proceedings).
[13]N. Savvides, J. Appl. Phys. **55**, 4232 (1984).
[14]N. Savvides, D. R. McKenzie, and R. C. McPhedran, Solid State Commun. **48**, 189 (1983).
[15]N. Savvides, J. Appl. Phys. **58**, 518 (1985).
[16]L. Holland and G. Samuel, Vacuum **30**, 267 (1980).
[17]J. M. E. Harper, J. J. Cuomo, and H. T. G. Hentzell, J. Appl. Phys. **58**, 550 (1985).
[18]N. Savvides, J. Appl. Phys. (in press).
[19]N. Savvides and B. Window, J. Vac. Sci. Technol. A **3**, 2386 (1985).
[20]H. E. Hintermann, J. Vac. Sci. Technol. B **2**, 816 (1984).
[21]W. D. Münz, D. Hofmann, and K. Hartig, Thin Solid Films **96**, 79 (1982).
[22]S. Schiller, U. Heisig, G. Beister, K. Steinfelder, J. Strümpfel, C. Korndörfer, and W. Sieber, Thin Solid Films **118**, 255 (1984).
[23]L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, 1971).
[24]H. M. Gabriel and K. H. Kloos, Thin Solid Films **118**, 243 (1984).
[25]Y. Igasaki and H. Mitzuhashi, Thin Solid Films **70**, 17 (1980).
[26]B. Window, F. Sharples, and N. Savvides, J. Vac. Sci. Technol. A **3**, 2368 (1985).
[27]B. O. Johansson, J. -E. Sundgren, and J. E. Green, J. Vac. Sci. Technol. A **3**, 303 (1985).
[28]J. A. Thornton, J. Vac. Sci. Technol. **11**, 666 (1974).

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.