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The deposition of aluminium oxide coatings by reactive unbalanced magnetron sputtering

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Abstract

The problems associated with the reactive d.c. sputtering of highly insulating materials, such as alumina, are well documented. Deposition rates are low and an insulating layer can build up on the surface of the target, causing arcing. Arc events prevent stable operation and can result in droplets of material being ejected from the target. Such droplets can cause defects in the growing film. However, studies have shown that the formation of arcs can be significantly reduced if the magnetron discharge is pulsed at a frequency in the 10–200 kHz range. In this investigation, AlO_x (where $0.7 \leq x \leq 1.5$) coatings were deposited by reactive unbalanced magnetron sputtering using either a d.c. power supply in series with a fixed 20 kHz pulse unit, or a variable frequency supply with a maximum frequency of 33 kHz (for comparison purposes, coatings were also deposited by reactive d.c. sputtering, without pulsing the discharge). Deposition parameters were varied systematically to produce a range of coating compositions and properties. The resulting coatings ranged from extremely dense, stoichiometric Al_2O_3 films, with Knoop microhardness values >2500 kg mm^{-2}, to very soft (<100 kg mm^{-2}) columnar, sub-stoichiometric films. Deposition rates varied from 4 to 20 μm h^{-1}. Some initial results of wear tests carried out on these coatings are also reported. The pulsed power supplies were found to be very stable in operation, with very few arc events being observed.

Keywords: Reactive unbalanced magnetron sputtering; Aluiminium oxide coatings; Pulsed magnetron sputtering process

1. Introduction

The technique of closed-field unbalanced magnetron sputtering (CFUBMS) has become established as a versatile, commercially viable method of depositing high quality metal, alloy and multi-layer coatings onto complex components [1]. It has also successfully been used to deposit a wide range of ceramic coatings, including titanium nitride, alloy nitrides and diamond-like carbon, by reactive sputtering from metallic targets [2–4]. CFUBMS is generally considered to be a high rate deposition process. Metallic coatings can be deposited at rates in the microns per minute range [5]. However, when operating in the reactive sputtering mode, deposition rates are relatively low, and can be in the microns per hour range [2].

Arc discharges at the target are another problem that can occur during reactive sputtering, particularly during the deposition of highly insulating materials, such as alumina. As the coating process proceeds, areas of the targets away from the main racetrack become covered with reaction products, as do the target earth shields. This can lead to arc discharges on the target. Droplets of material can be ejected from the target and cause defects in the coating. Also, the damaged area on the target can become a source of further arc discharges. This results in an increasing frequency of arcing, which prevents stable operation. The reactive sputtering process is controlled by a feedback loop. Instabilities caused by arcing can cause fluctuations in the coating parameters which, in turn, can effect the stoichiometry of the resulting film [6].

These problems limit some of the applications of the CFUBMS system. Low deposition rates are commercially unattractive. The presence of defects in films can be unacceptable in many optical and microelectronic applications, and can effect the performance of a film as a corrosion, or thermal barrier. Also, variations in stoichiometry can give rise to anisotropic film properties.

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R.f. sputtering is generally considered too slow and complex a process for large scale commercial applications [7,8].

However, the pulsed magnetron sputtering process (PMS) offers the potential to overcome the problems encountered when operating in the reactive sputtering mode with the CFUBMS system. Initial studies have indicated that pulsing the magnetron discharge at medium frequencies (10–200 kHz), when depositing highly insulating materials, can significantly reduce the formation of arcs and, consequently reduce the number of defects in the resulting film [6–11]. For example, Schiller [9,10] found that during the reactive sputtering of Al_2O_3, raising the pulse rate from 10 to 50 kHz reduced the defect density of the coating by several orders of magnitude. Furthermore, deposition rates of 4–5 nm s^{-1} were achieved, which compares with less that 1 nm s^{-1} for RF sputtering of Al_2O_3. This rate amounted to about 60% of the rate achieved by Schiller for the non-reactive sputtering of pure aluminium. Pulsing was also found to stabilise the discharge. This allowed Frach [7] to deposit virtually defect-free Al_2O_3 coatings up to 50 μm thick.

If a single magnetron discharge is pulsed, then the system is described as unipolar pulsed sputtering. In this situation, the pulse-on time is limited so that the charging of the insulating layers does reach the point where breakdown and, therefore, arcing occurs. The discharge is dissipated during the pulse-off time through the plasma. If two magnetrons are connected to the same pulse supply then the configuration is described as bipolar pulsed sputtering. Each magnetron source then alternately acts as an anode and a cathode of a discharge. The periodic pole changing promotes discharge of the insulating layers, hence preventing arcing.

The high rate deposition of defect-free ceramic coatings onto complex components would be a commercially attractive process. In view of this, the PMS process is being increasingly studied. This paper, therefore, reports on work carried out at Salford University to investigate the deposition of alumina coatings in a closed-field unbalanced magnetron system, utilising the PMS process.

2. Experimental

Alumina coatings were deposited by reactive magnetron sputtering in a Teer Coatings UDP 450 rig. The rig is equipped with two 300 × 100 mm vertically opposed unbalanced magnetrons installed in a closed-field configuration. The aluminium sputter targets were 99.5% pure and were also obtained from Teer Coatings. Coatings were deposited onto silicon wafers, polished aluminium SEM pin stubs and ground stainless steel coupons.

The reactive sputtering process was controlled using spectral line monitoring [12–14]. The optical emission monitor (OEM) was tuned to the 396 nm line in the aluminium emission spectrum. The target current was ramped up and pure Al films were deposited for 2 min. The OEM signal at this point was taken as the "100%" metal signal. The reactive gas was then allowed into the chamber until the OEM signal fell to a pre-determined proportion of the initial 100% metal signal. The value of the "turn-down" signal was maintained by the feedback loop throughout the remainder of the deposition run. After each reactive deposition, the targets were sputter cleaned until the OEM signal returned to its initial value.

The coatings were deposited using, either a d.c. power supply in series with a fixed 20 kHz pulse unit, or a supply with a variable frequency in the range 0.05 Hz to 33 kHz (for comparison purposes, coatings were also deposited by reactive d.c. sputtering, without pulsing the discharge). The 20 kHz unit was an Advanced Energy SPARC-LE unit, which was connected in series with the existing Advanced Energy MDX magnetron driver [8]. The magnitude of the positive pulse is fixed at about 10% of the magnitude of the negative pulse. The variable frequency supply was a Magtron unit [15]. This unit is more sophisticated than the SPARC-LE. It can be used in unipolar or bipolar mode and the pulse-on and pulse-off times can be varied independently. Only the unipolar configuration was used in this investigation.

All the coatings were deposited at a substrate-to-target separation of 110 mm and a pressure of 1.25 mTorr. Target current, substrate bias and OEM turn-down signal were varied. The run conditions are summarised in Table 1. The coatings deposited on silicon wafers were fractured to allow the coating structure to be examined in the SEM. Thickness measurements were taken from SEM micrographs of the fracture sections. Knoop microhardness measurements were also made of these coatings. Measurements were taken at three appropriate loads. The results were then extrapolated to zero load to remove any influence of the substrate material on the apparent hardness of the coatings. The composition of the coatings, deposited on polished pin stubs, was determined using a JEOL JXA-50A microanalyser, equipped with WDAX. The accuracy of this machine, as quoted by the manufacturer, is between 1 and 5 at.%.

Pin-on-disc wear tests were carried out on selected specimens, deposited onto ground stainless steel coupons. The "pin" was a 6.35 mm diameter hardened steel ball. The normal load was 3 N; the sliding speed 4.4 m min^{-1}; and the sliding distance 61.6 m. Profilometry tests and SEM examination were carried out on the specimens after testing. Some initial results are presented.

3. Results

The deposition rates, microhardnesses and compositions of the coatings are listed in Table 1. As expected,

Table 1
Run conditions and properties of aluminium oxide coatings depositedby d.c. and pulsed magnetron sputtering

Run no.	Target current (A)	Substrate bias (V)	Turn down signal (%)	Thickness (μm)	Dep. rate (μm min^{-1})	Hk (kg mm^{-2})	Al/O (at.%)	Power supply
1	6	−50 rf	60	13.9	0.52	90	51/49	d.c. only
2	6	−50 rf	50	7.7	0.28	210	51/49	d.c. only
3	6	−50 rf	50	5.3	0.19	320	58/42	d.c.+SPARC-LE
4	6	−30 rf	30	3.1	0.11	2650	45/55	d.c.+SPARC-LE
5	6	−30 rf	30	2.0	0.07	1240	44/56	d.c.+SPARC-LE
6	6	−100 rf	15	3.3	0.07	1180	37/63	d.c.+SPARC-LE
7	8	−50 rf	15	3.8	0.07	2480	41/59	d.c.+SPARC-LE
8	6	self-bias (−19)	25	40.0	0.31	270	54/46	Magtron 15.4 kHz
9	6	−50 dc	20	13.0	0.13	1940	42/58	d.c.+SPARC-LE
10	6	−50 dc	20	10.0	0.18	1710	43/57	Magtron (15.4 kHz)
11	3	−100 dc	15	4.9	0.06	1020	41/59	Magtron (15.4 kHz)
12	3	−50 dc	20	8.1	0.07	1510	40/60	Magtron (25 kHz)
13	3	−30 dc	15	5.0	0.06	2010	37/63	Magtron (25 kHz)

the d.c. reactive sputtering of aluminium oxide coatings proved extremely difficult. Arcing took place from the target throughout the runs, and the process was highly unstable, even at turn-down signals of 60% of the pure metal signal, i.e., relatively low levels of target poisoning. The structure of one of these coatings (run no. 1) is shown in Fig. 1. As can be seen, the coating has a granular, porous structure. Reference to Table 1 indicates a sub-stoichiometric composition and very low microhardness.

By contrast, when operating with the SPARC-LE units the process was very stable, with few arc events at the target. This was found to be the case, even at turn-down signals of 15%, i.e., sputtering from a heavily poisoned target. Figs. 2 and 3 show SEM micrographs of the fracture sections of coatings 7 and 9, respectively. Both coatings are fully dense with no discernible structural aspects on the fracture surface. Also, both coatings remained well adhered to the substrate after fracture. The composition of these coatings is very close to

Fig. 1. SEM micrograph of fracture section of aluminium oxide coating number 1, deposited by d.c. magnetron sputtering onto silicon wafer.

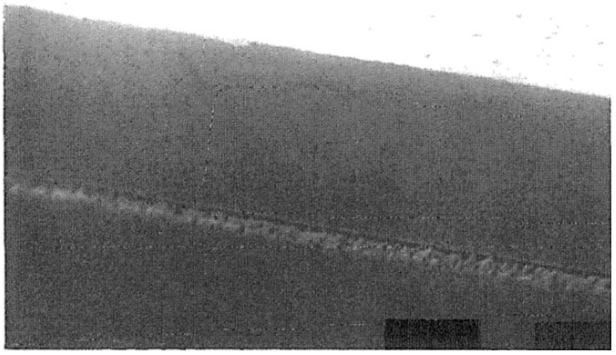

Fig. 2. SEM micrograph of fracture section of aluminium oxide coating number 7, deposited by d.c. magnetron sputtering with SPARC-LE pulse unit attachment. The substrate is a silicon wafer.

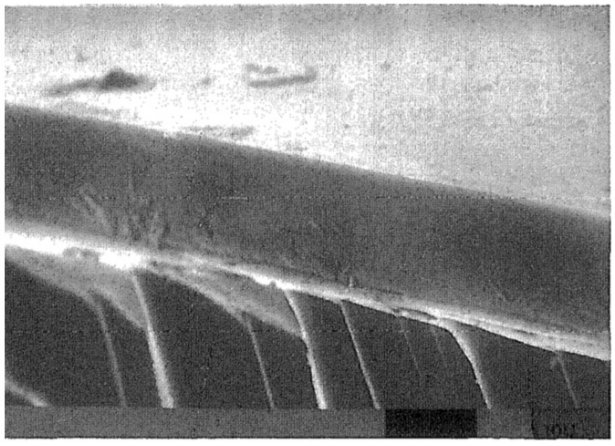

Fig. 3. SEM micrograph of fracture section of aluminium oxide coating number 9, deposited by d.c. magnetron sputtering with SPARC-LE pulse unit attachment. The substrate is a silicon wafer.

stoichiometric Al_2O_3. Both have high microhardness values (2480 and 1940 kg mm^{-2}, respectively). However, the deposition rate for run 9 was nearly twice that of run 7, despite the fact that the target current was lower. This, presumably, reflects the greater degree of target poisoning (i.e., the lower OEM signal) during run 7.

It proved difficult to optimize the performance of the Magtron unit. When operating at a target current of 6 A and a pulse frequency of 15.4 kHz, arcing occurred at the target throughout the run, with the frequency of arcs increasing with run time. The supply operated most successfully when delivering a target current of 3 A, at a frequency of 20 kHz with identical pulse-on and pulse-off times. Fig. 4 shows an SEM micrograph of the fracture section of coating 13, deposited using the Magtron supply. Again, the coating has a fully dense structure and good coating-to-substrate adhesion. The microhardness, deposition rate and composition of this coating are very similar to coating 7, deposited using the SPARC-LE unit. However, coating 7 was deposited at a target current of 8 A, whereas, coating 13 was deposited at a target current of 3 A. The similarity in deposition rates, despite the significant difference in target powers between these two coatings cannot be explained at this stage, particularly as both coatings were deposited at the same turn-down signal.

Pin-on-disc tests were carried out on a number of selected specimens, as described earlier. The results of these tests are listed in Table 2. Profilometry measurements were made of the wear tracks for coatings 7, 8 and 13 and, from this, wear volumes were calculated. Fig. 5 shows a SEM micrograph of the surface of coating 8, showing part of the wear track. The wear track for coating 9 was within the original surface roughness and, therefore, a wear volume could not be calculated for this specimen. A section of the wear track on the surface of coating 9 is shown in Fig. 6. For coating 12, material transfer occurred from the steel ball to the coating surface. SEM examination of the wear track showed that only transferred material was present, and no wear of the coating was observed. Figs. 7 and 8 are SEM micrographs of the wear track region for coating 12, in which transferred material can clearly be seen. Fig. 7 also demonstrates how closely the topography of the coating surface matches the topography of the substrate.

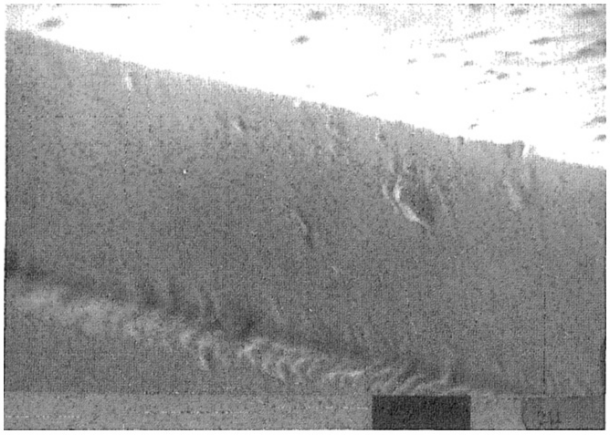

Fig. 4. SEM micrograph of fracture section of aluminium oxide coating number 13, deposited by pulsed magnetron sputtering onto silicon wafer.

Table 2
Results of pin-on-disc tests on selected aluminium oxide coatings deposited on stainless steel coupons

	Coating number				
	7	8	9	12	13
Frictional force (N)	0.25	0.1	0.26	0.2	0.26
Steady state coef. of friction (μs)	0.83	0.33	0.87	0.63	0.87
Wear volume (mm^3)	1.02E-3	0.11	–	–	1.23E-3

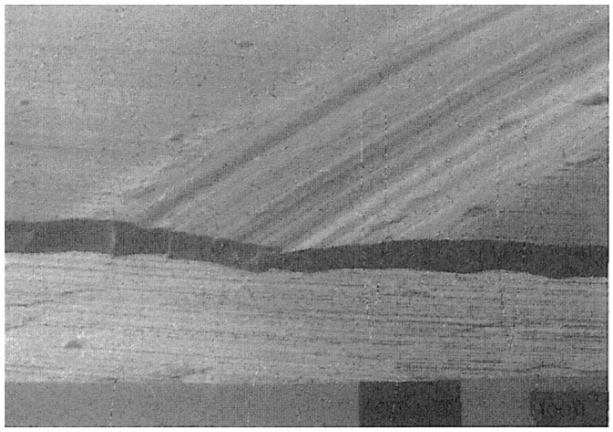

Fig. 5. SEM micrograph of surface of aluminium oxide coating number 8, showing part of pin-on-disc wear track.

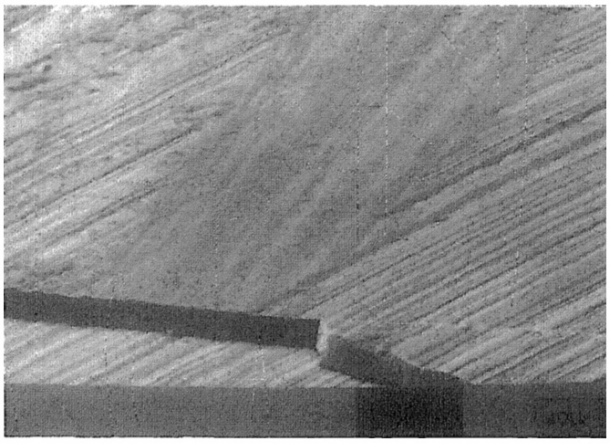

Fig. 6. SEM micrograph of surface of aluminium oxide coating number 9, showing part of pin-on-disc wear track.

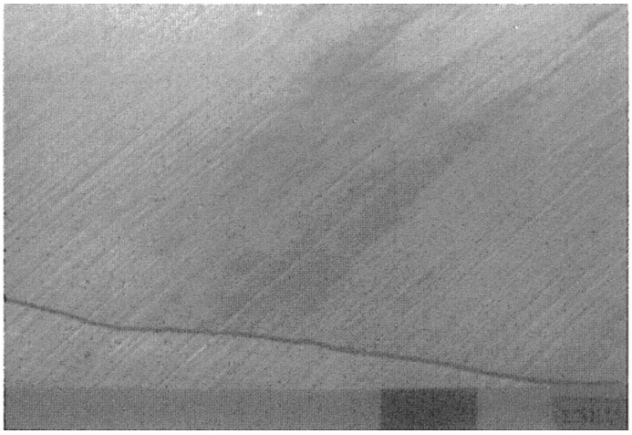

Fig. 7. SEM micrograph of surface of aluminium oxide coating number 12, showing part of pin-on-disc wear track and topographical detail.

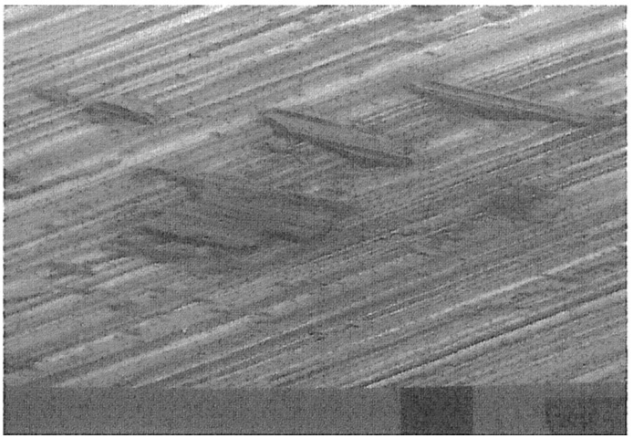

Fig. 8. SEM micrograph of wear track region of aluminium oxide coating number 12, showing transferred material from steel ball.

Grinding marks on the substrate are perfectly reproduced through a coating thickness of (in this case) 8 μm.

Based on these results described above, the coatings were ranked in the following order of increasing wear resistance; run 8, run 13, run 7, run 9 and run 12. As mentioned earlier, these are preliminary results. The tribological properties of these coatings will be investigated in more detail in the future.

4. Discussion

This investigation has demonstrated that fully dense, stoichiometric alumina coatings can be deposited at relatively high rates by closed-field unbalanced magnetron sputtering, provided the magnetron discharge is pulsed. Extremely dense coatings with high microhardness values were deposited at rates of up to 0.13 μm min^{-1}. This rate is equivalent to 47.5 and 39.4%, respectively, of the rates obtained for the deposition of pure aluminium films using the SPARC-LE attachment and for d.c. sputtering alone under otherwise identical conditions.

Both of the pulse units investigated were stable in operation (once optimized), with very few arcs being observed at the target. Both allowed control over the reactive sputtering process to be established. Thus, the composition of the coating and, therefore, its properties, could be controlled.

5. Conclusions

This investigation has demonstrated that fully dense coatings of alumina can be deposited in a CFUBMS system at rates of about 40% of that obtained for the d.c. sputtering of aluminium. The pulsed magnetron sputtering process is a major development in the reactive sputtering field. The prevention of arcs at the target provides stability to the reactive sputtering process. This, in turn, permits the coating composition and properties to be controlled. The ability to deposit defect-free oxide coatings at high rates offers the potential to improve the performance and extend the range of applications of these coatings.

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