Recent advances in magnetron sputtering

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Abstract

The paper will outline the historical development of sputtering techniques up to the recent development of closed-field unbalanced magnetron sputtering (CFUBMS). Examples will then be given of the use of CFUBMS to develop advanced coatings for industrial applications, including corrosion resistant coatings for aerospace, hard ceramic coatings for wear resistance, and coatings with novel thermal and chemical properties. Finally, current development in the technology and in understanding of the principles of the process will be described. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The basic sputtering process, in which materials are evaporated from the solid state by bombarding their surfaces with energetic ions, has been known and used for many years [1]. Although many materials have been successfully deposited by this process, it is limited by low deposition rates, low ionisation efficiency in the plasma, and high substrate heating effects. These limitations have been overcome by the introduction of magnetron sputtering and, more recently, unbalanced magnetron sputtering.

The main difference between conventional and unbalanced magnetrons is in the degree to which the plasma is confined. In a conventional magnetron the plasma is strongly confined to the target region, with a region of dense plasma extending about 60 mm in front of the target. During film growth, substrates positioned inside this region are subjected to ion bombardment, which can strongly modify the structure and properties of the resulting film. Substrates positioned outside this region of high plasma density experience insufficient ion bombardment to modify the microstructure of the growing film, and it is, therefore, difficult to produce fully dense, high quality coatings on large, complex components using conventional magnetrons. This problem has been overcome by the development of the unbalanced magnetron, and its incorporation into multiple-magnetron systems. These developments are outlined in Sections 2 and 3, and the development of a structure zone model for such systems is described in Section 4.

A second limitation of sputtering techniques has been, until very recently, the inability to deposit, at commercially useful rates, dense, defect-free coatings of highly insulating coatings such as oxides. This disadvantage has recently been overcome by the development of the technique of pulsed, or mid-frequency sputtering, which is described in Section 5.

2. Unbalanced magnetrons

The concept of the unbalanced magnetron was first developed by Window and Savvides who investigated the effect of varying the magnetic configuration of an otherwise conventional magnetron [2–4]. By strengthening the outer ring of magnets, some electrons in the plasma were no longer confined to the target region, but were able to follow the magnetic field lines and flow out towards the substrate. As a result, ion bombardment at the substrate was increased with a consequent improvement in coating structure.

The use of unbalanced magnetron configurations allows high ion currents to be transported to the substrate so that coatings of excellent quality can be deposited. However, it is still difficult to deposit uniform coatings onto complex components using a single magnetron source. Therefore, in order to exploit this technol-

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ogy commercially, a number of multiple-magnetron systems have been introduced. If two unbalanced magnetrons are installed opposed to each other, they can be configured with opposite magnets of the same polarity (mirrored), or with opposite magnets of opposite polarity (closed-field). The use of the closed-field system has led to great improvements in the structure and properties of sputtered coatings [5]. This process is now referred to as closed-field unbalanced magnetron sputtering (CFUBMS).

3. Closed-field unbalanced magnetron sputtering

In the closed-field configuration, the magnetic field lines between the magnetrons form a closed trap for electrons in the plasma. Few electrons are therefore lost to the chamber walls and a dense plasma is maintained in the substrate region, leading to high levels of ion bombardment of the growing film. The magnetic fields in a conventional magnetron, an unbalanced magnetron and a dual-magnetron closed-field system are compared schematically in Fig. 1.

Various magnetron arrangements have been developed to suit specific applications, and some of them are shown schematically in Fig. 2. These systems have been used successfully to deposit a range of high quality novel materials, and materials with novel properties.

In addition to pure metal and alloy films, CFUBMS systems have been successfully used to deposit a wide range of reactively sputtered coatings onto various components. The reactive sputtering process can be controlled by plasma emission monitoring [6] or by partial pressure control of the reactive gas [7], both processes offering control of the coating composition and properties.

Single element nitrides, most commonly titanium nitride, are straightforward to produce. However, the multiple-magnetron CFUBMS systems are ideally suited to the deposition of alloy nitrides, as each of the magnetron targets can, in principle, be of a different material, and, by sputtering the targets at different rates, any desired alloy composition can be attained.

Use of the CFUBMS system also allows coatings with graded properties to be produced. Thus, both the coating/substrate interface and the coating surface properties can be optimised, so that very high performance coatings can be produced with excellent coating-to-substrate adhesion.

Very recently, the introduction of grading of the coatings to form multilayer-structured coatings using the CFUBMS technique has led to great improvement in adhesion of the DLC coatings to the substrate; this has made the successful practical application of such coatings possible [8].

Although the conventional closed-field arrangement is with the two unbalanced magnetrons facing each other, as in Fig. 2(a), this is not the only useful arrangement. Novel, highly supersaturated alloys and amorphous alloys have been deposited using two co-planar magnetrons of opposite polarity, as shown on Fig. 2(b). In addition to pure metal and alloy films, CFUBMS systems have been successfully used to deposit a wide range of reactively sputtered coatings onto various components. Many alloy systems have been studied using this technique, and a particularly successful application has been the deposition of highly corrosion resistant aluminium.
Fig. 3. SEM micrograph of the fracture section of a typical Al/Mg alloy film.

4. The development of a structure zone model for CFUBMS coatings

For many years, the relationship between process parameters and coating properties has been displayed on structure zone models (SZMs). Several such models have been developed to describe the structure of coatings deposited by various sputtering processes [10–13]. In all cases, homologous temperature is used to describe the thermally induced mobility of coating atoms. A second variable attempts to describe the influence of the simultaneous bombardment of the coating by energetic particles. Parameters which have been used for this second axis include coating pressure [10,13], substrate bias voltage [11], and a combined energy parameter, described as the average energy per depositing atom [12]. However, none of the current models is adequate to describe the CFUBMS process, and the authors have therefore recently carried out a study aimed at developing a SZM for this process. The study is described in detail elsewhere [14], and is summarised here.

The system selected for characterisation was a Teer Coatings Ltd UDP 450 rig, which is equipped with two 300 mm × 100 mm vertically opposed unbalanced magnetrons installed in the closed-field arrangement. Aluminium, zirconium and tungsten coatings were deposited by CFUBMS, under systematically varied conditions, and characterised in terms of their structures and properties. These metals were chosen for their wide range of physical properties — particularly melting temperature — and their different crystal structures. For each metal, experimental arrays were developed using the Taguchi method [15], the deposition variables being target current, substrate bias voltage, coating pressure and substrate-to-target separation. The ratios of the fluxes of ions and condensing atoms at the substrate
were estimated from ion current density and deposition rate measurements. The structures of the Al, Zr and W coatings were distinct from each other, but, within each metal group, there were only modest variations in structure from one coating to another.

Aluminium coatings were deposited at homologous temperatures, $T/T_m$, over the range 0.43 to 0.68. All had fully dense, highly ductile structures, which “necked-down” completely on fracture. SEM and TEM investigations showed that they all had zone 3-type structures, in accordance with the Thornton classifications [6].

The zirconium and tungsten coatings were deposited at homologous temperatures over the ranges 0.22 to 0.28 and 0.13 to 0.17, respectively, and all had dense columnar structures. Fig. 4 shows a through-thickness TEM micrograph of a tungsten coating deposited at $T/T_m=0.13$. Large (100–200 nm) polygonal grain-like regions are clearly visible, and are similar in size to the width of the columns. It is postulated that the grain-like regions are actually sections through these columns. Thus, the structure appears to consist of a series of columns, separated by regions of high dislocation density. Again, in accordance with the Thornton classifications, the Zr and W coatings were considered to have zone 2-type structures.

The formation of zone 2 structures at $T/T_m$ as low as 0.13 and zone 3 structures at $T/T_m$ as low as 0.43 are major departures from the Thornton structure zone model, and other models relating to sputtered coatings [10,11]. This is illustrated in Fig. 5, which compares, in terms of homologous temperature, the positions of the zonal boundaries for other published zone models, with those observed in this study. It is clear the CFUBMS process has promoted the formation of “high temperature” structures at relatively low homologous temperatures, and suppressed the formation of “low temperature” zone 1 and zone T structures.

Fig. 4. Through-thickness TEM micrograph of a tungsten coating deposited at $T/T_m=0.13$. Additional experiments were carried out to investigate the influence of deposition parameters on deposition rate and substrate ion current density. Both were found to be directly proportional to target current, but to decrease with increasing substrate-to-target separation. Over the ranges tested (−30 to −70 V and 0.5 to 3 mTorr), bias and pressure had no significant influence on deposition rate.

A typical comparison of the variation in ion current density and deposition rate with substrate-to-target separation is shown in Fig. 6(a). Deposition rate falls more rapidly with increasing separation than does substrate ion current, because the CFUBMS maintains a dense plasma in the substrate region. The ion-to-atom ratio at the substrate increases with increasing separation, as shown in Fig. 6(b).

These results mean that the ion-to-atom ratio can be varied only over a limited range, the only variable which significantly affects this ratio being the substrate-to-target separation. To increase the ratio for given conditions, it is necessary to increase separation, which in turn means accepting lower deposition rates. However, the fact that the ion-to-atom ratio remains virtually constant with increasing target current [14], means that the deposition rate can still be maximised at each set of conditions. Unlike in other ion plating processes, the ion-to-atom ratio does not decrease with increasing deposition rate, and this can be an important practical consideration in commercial coating processes.

Magnetrons, in which the degree of unbalancing can be varied *in situ*, are now becoming available and will allow far greater control over the ion-to-atom ratio at the substrate, compared to the “fixed” configuration magnetrons used in this study.

Based on these results, a structure zone model has been developed, in which the structures of coatings deposited by CFUBMS are described in terms of three
parameters, namely homologous temperature, ion-to-atom ratio and bias voltage (to represent ion energy). Attempts have been made to describe coating structure in terms of a single energy parameter based on the average energy per deposited atom [16] but such a parameter is of limited applicability [17,18]. Ion energy and the incident ion-to-atom ratio must be considered separately when modelling the effects of concurrent ion bombardment on coating microstructure [19,20].

To allow three parameters to be accommodated, the conventional schematic representation of structure is dispensed with, as it is assumed to be well known. The new three-dimensional SZM is shown as Fig. 7, with the zone 2/zone 3 boundary approximated as a spherical surface. A second boundary is shown inside the zone 2 region. This represents the lower levels of each of the variables used, and marks the lower limits of normal operating; it is not the zone 1/zone 2 boundary, which could not be identified, as only coatings with zone 2 and zone 3-type structures were produced. The CFUBMS system inherently developed conditions which suppressed the formation of porous columnar zone 1-type structures.

Clearly, a number of assumptions were made in the development of this model. In particular, there are sources of error in the estimation of ion-to-atom ratio, and the plasma potential is assumed to be constant. However, the development of the model is on-going, and it is felt that it will, ultimately, accurately reflect the parameters which determine coating structure in the CFUBMS system.

5. Pulsed magnetron sputtering

Despite its many successful applications, there are still a number of problems associated with reactive sputtering, in particular, a reduced deposition rate and arc-induced coating defects. CFUBMS is generally considered to be a high rate deposition process, with metallic coatings being deposited at rates of the order of microns per minute. However, when operating in the reactive sputtering mode, deposition rates are usually relatively low, and can be only of the order of microns per hour. Arc discharges also occur during reactive sputtering of highly insulating materials, such as alumina. These can lead to the ejection of droplets of material from the target which cause defects in the growing film. The damaged area on the target becomes a source of further arc discharges, which cause an increasing frequency of arcing, and prevent stable operation. However, a new development, the pulsed magnetron sputtering process (PMS) largely overcomes these problems. Initial studies have shown that pulsing the magnetron discharge at medium frequencies (10–200 kHz), when depositing highly insulating materials, can stabilise the discharge, almost eliminating arcing and the formation of defects in the film [21]. Furthermore, deposition rates during
pulsed reactive sputtering approach those obtained for the non-reactive sputtering of pure metal films [7].

A magnetron discharge can be pulsed in either unipolar, or bipolar mode. In both cases the pulse-on time is limited so that the charging of the insulating layers does not reach the point where arcing occurs and the discharge is dissipated through the plasma during the pulse-off time. In the unipolar mode the target voltage varies between ground and the normal negative operating voltage. In the bipolar mode the target voltage is actually reversed and becomes positive during the pulse-off period. Due to the much higher mobility of electrons in the plasma than ions, it is often only necessary to reverse the target voltage to between 10 and 20% of the negative operating voltage to fully dissipate the discharge. Alternatively, two magnetrons can be connected to the same pulse supply. In this case, the target voltage is fully reversed and each magnetron source then acts alternately as the anode and cathode of the discharge. The periodic pole changing promotes a self-cleaning effect at the targets, which allows stable long-term deposition of highly insulating materials to take place.

The target voltage waveforms for each mode of operation are summarised in Fig. 8.

The authors have used the PMS process to investigate the reactive sputtering of alumina films [22]. A fixed 20 kHz Advanced Energy SPARC-LE pulse unit was connected in series with a standard DC magnetron driver. In the SPARC-LE unit used, the target voltage was reversed during the pulse-off period to about 10% of the normal operating voltage. For comparison purposes, coatings were also deposited by DC reactive sputtering without pulsing the discharge.

As expected, the DC reactive sputtering of alumina films proved extremely difficult. Arcing took place throughout the deposition and the process was highly unstable. By contrast, when operating in the PMS mode with the SPARC-LE unit the process was very stable, with very few arc events observed at the target. Fig. 9 compares the structures of the coatings produced by the two processes. The DC coating has a granular, porous structure, while the PMS coating is extremely dense with no discernible structure and no visible defects. Also EPMA showed that the DC coating was sub-stoichiometric while the PMS coating was stoichiometric. Furthermore, the PMS Al₂O₃ coating was deposited at a rate approaching 50% of the deposition rate achieved for pure aluminium under similar operating conditions.

6. Conclusions

The closed-field unbalanced magnetron sputtering technique has now been developed to the point where it can be routinely used to deposit high quality coatings of a very wide range of materials. Metals, alloys, ceramics, multi-layers and functionally-graded materials can
Fig. 9. SEM micrographs of fracture sections of aluminium oxide coatings deposited by (a) DC reactive sputtering, and (b) pulsed reactive sputtering.

all be deposited with excellent structures and properties. Detailed studies of the CFUBMS process have led to the development of a novel structure zone model relating coating structures to deposition parameters. Despite the successes of the CFUBMS system, until recently the deposition of highly insulating materials was problematic. However, the development of pulsed magnetron sputtering has overcome many of the problems associated with the deposition of these materials. The PMS process is a major development in the reactive sputtering field. The high rate deposition of defect-free ceramic coatings onto complex components is now achievable through the use of this technique, in conjunction with the CFUBMS process.

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