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Structure and properties of Cr_2O_3 coatings deposited using DCMS, PDCMS, and DOMS

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ABSTRACT

The crystallinity of oxide phases strongly affects the properties of oxide coatings. In general, a well-crystallized oxide coating is desired because it usually results in improved mechanical and chemical properties. This paper presents a comparative study of the chromium oxide (Cr_2O_3) coatings deposited by deep oscillation magnetron sputtering (DOMS), mid-frequency pulsed dc magnetron sputtering (PDCMS) and continuous dc magnetron sputtering (DCMS) without applying external substrate heating. The DOMS-Cr_2O_3 coating deposition showed a peak substrate current density of 65 mA cm^{-2} and a substrate saturation temperature of 250 °C, while the DCMS process exhibited a mean substrate current density of 1.29 mA cm^{-2} and the lowest substrate saturation temperature of 212 °C. The sputtering techniques strongly affected the crystallinity of the Cr_2O_3 coatings. The DCMS-Cr_2O_3 coating exhibited an amorphous like structure. The PDCMS-Cr_2O_3 coating contained a mixture of amorphous and crystalline α-Cr_2O_3 phases. In contrast, the DOMS-Cr_2O_3 coating showed a strong crystallinity with a (110) preferential orientation. The improved crystallinity of the DOMS-Cr_2O_3 coating is attributed to the enhanced ion flux bombardment and a higher substrate saturation temperature, which is correlated to the energetic electron bombardment observed from the oscillatory substrate current. With the improved crystallinity, the DOMS-Cr_2O_3 coatings exhibited significantly improved mechanical properties (a hardness of 35 GPa) and wear resistance (a dry coefficient of friction of 0.37 and a wear rate of 5.7×10^{-7} mm^3 N^{-1} m^{-1}) as compared to the coatings deposited using DCMS and PDCMS.

1. Introduction

Chromium oxide forms a wide range of oxide phases, e.g. CrO, CrO_2, Cr_2O_3, Cr_3O_4, etc. Among these phases, alpha Cr_2O_3 (α-Cr_2O_3) is the most stable form, which has a corundum structure (a = 4.96 Å, c = 13.59 Å, c/a = 2.74) similar to alpha Al_2O_3. The α-Cr_2O_3 coatings exhibit high hardness, good wear resistance, good thermal and chemical stability, and interesting electrical and optical properties. It is a potential candidate for many applications in wear and corrosion protection [1,2], sand dusting protection [3], electronics [4], and optics [5]. Different techniques have been used to synthesize Cr_2O_3 coatings, including magnetron sputtering [6,7], thermal spray [8–10], chemical vapor depositions [11], and evaporation [5]. Among these techniques, magnetron sputtered Cr_2O_3 coatings exhibited good adhesion, uniformity, and dense structure.

The properties of the Cr_2O_3 coatings are strongly tied to the crystallinity of oxide phases. In general, a well-crystallized oxide phase is desired as it usually results in improved mechanical and chemical properties. However, it is a challenge for conventional dc magnetron sputtering (DCMS) to deposit oxide coatings with a well-defined crystallinity at a low processing temperature without applying external substrate heating. To obtain a completely crystallized Cr_2O_3 coating for improved properties, the substrate temperature normally needs to reach 300 °C and above [2,4,6,12]. If the substrate temperature is low, amorphous or partially crystallized Cr_2O_3 coatings were usually obtained [13].

Besides thermal energy, kinetic energy of the species arriving at the growing film also affects the structure of oxide coatings. Ion bombardment increases the density and changes the grain size of the coatings. In addition, an increase in the ion bombardment has been correlated to the amorphous to crystalline phase transformation and thus to the improved mechanical and chemical properties of the coatings [14]. The feasibility of producing well crystallized oxide coatings at a lower processing temperature (without applying external substrate heating) is practically important as it greatly broadens the selection range of substrate materials, improves coating quality, and reduces production costs.

Using energetic ions is an effective way to increase ion bombardment, e.g. using higher bias voltages or a high energy ion source. However, high ion energies may also introduce high residual stresses and defect densities in the coatings, which are detrimental to the adhesion and toughness

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of the coatings. Recent studies have shown that by keeping the ion energies low (e.g. 20–40 eV), while increasing the number of low energy ions, namely ion flux, is an effective way to enhance the ion bombardment and also to avoid introducing excessive residual stresses and defects in the coatings [15].

Since many oxides are insulating in nature, another challenge for reactive magnetron sputtering deposition of oxide coatings is the generation of an arc free deposition process [16,17]. When an arc occurs, droplets are ejected from the target surface. Some droplets can be trapped in the growing coatings and degrade the quality of the coatings. Today arcing can be prevented by using either bipolar pulsed DC magnetron sputtering (PDCMS) or AC power sources [16]. In addition to the significant arc reduction as compared to DCMS, the PDCMS plasma also showed higher ion energies (up to hundreds of eV) and ion fluxes, which provide enhanced ion bombardment on the coatings [18,19]. And the enhanced ion bombardment has been usefully used to modify the structure and properties of the coatings [19,20].

With the development of the high power impulse magnetron sputtering (HiPIMS) technique [21,22], it is possible to generate a highly ionized plasma by applying a pulsed high peak target power on the target. The peak substrate current density measured in a HiPIMS plasma can be hundreds of mA cm^{-2} [23], which provides conditions that favor a high surface mobility of the condensing species. Efforts have been made for the deposition of oxide coatings using the HiPIMS technique, e.g. ZrO_x [24], AlO_x [25,26], TiO_x [27,28], SiO_2/Ta_2O_5 [29], VO_2 [30]. However, it is still a challenge for HiPIMS to generate an arc free and stable high power discharge for reactive sputtering oxide films. The arcing problem is related to the fact that a much higher peak target current (power) is applied on the target and generally no positive reversal voltage was used between high power pulses in HiPIMS.

Recently, it was found that when the HiPIMS pulse was created in an oscillatory voltage pulse form, virtually arc free high power pulse depositions for some insulating coatings can be achieved under certain deposition/pulsing conditions [31]. This form of HiPIMS is named as deep oscillation magnetron sputtering (DOMS) [32–34], which is a modification of the early modulated pulsed power magnetron sputtering (MPPMS) technique [15]. Similar to the MPPMS technique, DOMS also generates long modulation pulses (e.g. up to 3 ms). However, the long pulse contains a packet of deep oscillation pulses. By varying the oscillation pulse on and off times, the peak target voltage and current can be manipulated, which played a critical role in determining the structure and properties of the coatings [32–34].

From a practical point of view, the new DOMS technique offers virtually arc-free deposition conditions for reactive sputtering of many insulating films (e.g. AlN, Al_2O_3, Si_3N_4, SiO_2, etc.) under optimized pulsing and deposition conditions. The high power pulsed plasma combined with controlled ion energies (e.g. via bias voltage control) may be usefully utilized to change the reactivity of the deposition species and allow them to overcome the energy barrier for crystallization by the enhanced ion bombardment. This advantage, in turn, provides potential of producing dense crystalline oxide coatings without using high substrate temperatures or post-deposition annealing.

In this study, Cr_2O_3 coatings were deposited by DCMS, middle frequency PDCMS and DOMS without applying external substrate heating. The substrate current density and the substrate saturation temperature (T_{sub}) were measured and correlated to the microstructure and properties of the Cr_2O_3 coatings deposited by the three sputtering techniques.

2. Experimental details

The depositions were carried out in a closed field unbalanced magnetron sputtering (CFUBMS) system equipped with two unbalanced magnetrons. Detailed descriptions of the deposition system can be found in ref [15]. Silicon (100) wafers and AISI304 stainless steel flat coupons (2.5 cm × 2.5 cm) were used as the substrates. The substrates were mounted on a flat substrate holder (80 cm^2) which was facing

Table 1
Deposition parameters for the Cr_2O_3 coating depositions using DCMS, PDCMS and DOMS.

	P_a [kW]	V_p [V]	I_p [A]	f [Hz]	Long pulse duty cycle [%]	dc Bias [V]	Oscillation pulse on time [µs]	Oscillation pulse off time [µs]	Oscillation pulse frequency [kHz]	Oscillation pulse duty cycle [%]	Pressure [Pa]	O_2:Ar ratio	Mean I_{sub} [mA cm^{-2}]	Peak I_{sub} [mA cm^{-2}]	Deposition rate [nm·min^{-1}]	Substrate temperature [°C]
DCMS	1.5	420	3.58	–	–	−60	–	–	–	–	0.27	40:60	1.29	–	33	212
PDCMS	1.5	385	3.91	100,000	90%	−60	–	–	–	–	0.27	40:60	3.89	–	30	230
DOMS	1.5	1000	63	235	47%	−60	4	34	26.3	10.5%	0.27	40:60	–	65	25	250