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Molecular content of the deposition flux during reactive Ar/O₂ magnetron sputtering of Al

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The deposition flux obtained during reactive radio frequency magnetron sputtering of an Al target in Ar/O₂ gas mixtures was studied by mass spectrometry. The results show significant amounts of molecular AlO⁺ (up to 10% of the Al⁺ flux) in the ionic flux incident onto the substrate. In the presence of $\sim 10^{-4}$ Pa H₂O additional OH⁺ and AlOH⁺ were detected, amounting to up to about 100% and 30% of the Al⁺ flux, respectively. Since the ions represent a small fraction of the total deposition flux, an estimation of the neutral content was also made. These calculations show that, due to the higher ionization probability of Al, the amount of neutral AlO in the deposition flux is of the order of, or even higher than, the amount of Al. These findings might be of great aid when explaining the alumina thin film growth process. © 2006 American Institute of Physics.

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Alumina (Al₂O₃) thin films are used in a wide variety of applications, ranging from microelectronics to catalysts and wear-resistant coatings. In order to achieve desired properties good control of the deposition conditions is required. This is especially evident in crystalline phase control, which is an important alumina growth issue due to the existence of several metastable crystalline phases. In certain applications, e.g., as catalysts, metastable alumina is desired, while in many (high-temperature) applications the thermodynamically stable α phase is needed. Consequently, phase control of alumina thin films and, in particular, low-temperature growth of α -Al₂O₃ has been studied intensely during the last decade.¹⁻⁵

A thin film is formed through chemical bonding between the species incident onto the substrate. Thus, knowledge of the contents of the deposition flux is of importance in order to understand and control the growth.⁶ Previous works on (nonmagnetron) sputtering of oxide⁷ or oxidized metal⁸ targets (not alumina) show the presence of both atomic and molecular species in the ionic deposition flux. Furthermore, it was shown that the MO^+/M^+ (M =metal) ratio increases as the MO binding energy increases, indicating that a significant amount of AlO molecules should be present in an Al/O magnetron sputtering plasma. Sterling and Westwood⁹ suggested that sputtering of an oxidized Al target is purely molecular, due to the disappearance of Al optical absorption at higher O₂ partial pressures. However, a more recent study by Perry *et al.*¹⁰ shows that the Al optical emission remains even in the oxidized mode, although its intensity decreases dramatically. They also detect AlO optical emission, but make no attempt to quantify the amount of molecules. In this work, the deposition flux originating from an Al target as it is reactively sputtered in an Ar/O₂ mixture has been studied, with the aim to quantify the atomic and molecular contents

in order to aid the understanding of alumina thin film growth.

The experiments were performed in an UHV chamber (base pressure $< 7 \times 10^{-7}$ Pa) equipped with a differentially pumped mass spectrometer (Hiden PSM 003), mounted at a distance of 17 cm from the target with the sampling orifice (\varnothing 0.3 mm) facing the race track of the magnetron. The mass spectrometer was used (with the ionization source turned off) to measure the ionic flux during reactive rf magnetron sputtering of an Al target (\varnothing 50 mm) at a constant power of 80 W. The total Ar+O₂ sputtering pressure was kept constant at 0.33 Pa, while the O₂ partial pressure (measured during sputtering) was varied. The dramatic hysteresis effect (in target bias voltage and O₂ pressure), which is commonly observed as the O₂ flow is raised and lowered to the oxidized target mode and back to the metallic state, was not present, plausibly due to the small target size and the high pumping speed used.^{11,12} In addition to Ar and O₂, deionized H₂O could be introduced into the chamber via a heated leak valve.

Figure 1 shows the measured ionic intensities of the main film-forming species Al, AlO, O, and O₂ as functions of the O₂ partial pressure. In addition to these ions also Ar⁺, Ar²⁺, H⁺, H₂⁺, and small amounts ($< \sim 1\%$ of the Al⁺ signal) of Al₂O⁺, OH⁺, AlOH⁺, and H₂O⁺ were present. As

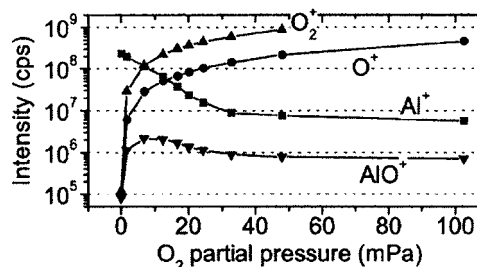


FIG. 1. Measured intensities of the main ionic film-forming species as a function of the O₂ partial pressure at a constant total Ar+O₂ pressure of 0.33 Pa.

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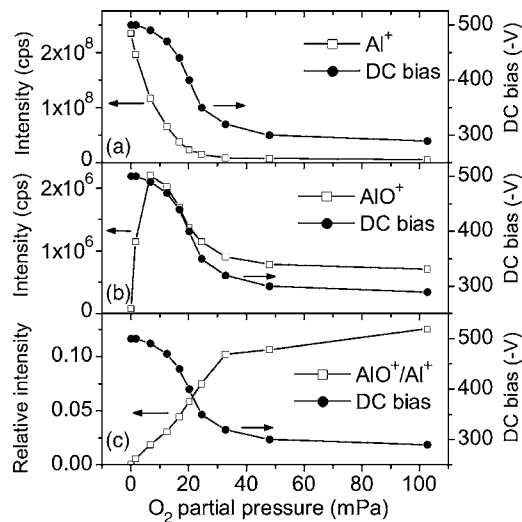


FIG. 2. The (a) Al^+ , (b) AlO^+ , and (c) relative AlO^+/Al^+ intensities compared to the dc bias as functions of the O_2 partial pressure. The total Ar + O_2 pressure was 0.33 Pa.

seen in Fig. 1, the ionic part of the deposition flux contains a significant amount of AlO^+ (up to 10% of the Al^+ flux).¹³ Some more insight into the target oxidation process and the formation of AIO is given by Fig. 2, where the target voltage (self-bias) is compared to the Al^+ and AlO^+ signals and the AlO^+/Al^+ ratio. There are three stages of the commonly accepted target oxidation mechanism.¹⁴ In the first stage, as the O_2 partial pressure increases from 0 to 7 mPa, the Al^+ signal decreases by 50% and the AlO^+ intensity increases, while the voltage is almost constant. The decrease in Al^+ is due to oxygen chemisorption on the target surface leading to sputtering of AIO molecules, while the constant target voltage implies that no oxide compound has yet formed on the target.¹⁴ At 7 mPa, the AlO^+ signal and the bias voltage start to drop, marking the start of the transition from metallic to oxidized mode. This transition is accompanied by a further drop in Al^+ signal (and sputtering rate) of more than one order of magnitude due to both lower sputtering yield and higher secondary electron yield for the oxide.^{14,15} In the third stage, at O_2 partial pressures above 32 mPa, sputtering occurs from a fully oxidized target. Since the probability for gas phase reactions should be very low at these pressures, we believe that the AIO molecules observed originate from the target. This is consistent with Fig. 2(c); if the AIO molecules were formed through gas phase reactions, a linear relation between the AlO^+/Al^+ ratio and the O_2 pressure would be expected. This is not seen; instead, the steep increase in AlO^+/Al^+ intensity in the O_2 pressure range 0–32 mPa demonstrates that AIO is sputtered from the target.

Since the ionic flux is presumably a small fraction of the total deposition flux, an estimation of the neutral content is made in the following sections, using the measurements made on the ions.¹⁶ Ionization in magnetron plasmas mainly occurs through two mechanisms: electron impact and Penning ionization. To deduce the importance of the Penning process in our setup the following experiment was made. The O_2 partial pressure was increased from 0.10 to 0.33 Pa (i.e., a pure O_2 discharge), a range where the sputter rate is known to be approximately constant.^{9,14} The measured Al^+ signal was then found to be constant (not shown). Since the argon was removed and oxygen cannot Penning ionize Al,¹⁷ this

TABLE I. Ionization energies, E_I , of the film-forming species and calculated relative ionization frequencies, ν , at two electron temperatures.

Species	E_I (eV) ^a	ν	
		5 eV	8 eV
Al	5.99	1	1
AlO	9.46	0.065	0.13
O	13.62	0.014	0.032
O_2	12.07	0.020	0.042

^aSee Ref. 27.

implies that the Penning process is not important in our case, as expected due to the low pressure.¹⁸ In the following calculations, we thus assume that the main ionization mechanism is by electron impact.

The probability of electron-impact ionization depends strongly on the electron energy distribution and the ionization cross sections of the plasma species. For rf sputtering of TiO_2 , the electron energies were found¹⁹ to follow the Maxwell-Boltzmann distribution at low energies, but with a depletion at higher energies due to collisions in the plasma. Thus, a Maxwell-Boltzmann electron energy distribution, $f(E)$, should be a reasonable approximation with the remark that concentrations of species with high ionization energy (especially O, O_2) may be underestimated. We use ionization cross sections, $\sigma(E)$, calculated by the Deutsch-Märk^{20,21} (Al, AIO) and binary-encounter-Bethe^{21,22} (O, O_2) models, which have been shown to agree well with experimental values.²¹ Ionization frequencies, ν , relative to Al, are then calculated by the expression²³

$$\nu = \int_{E_I}^{\infty} \sigma(E) \sqrt{E} f(E) dE \bigg/ \int_{E_I^{\text{Al}}}^{\infty} \sigma_{\text{Al}}(E) \sqrt{E} f(E) dE.$$

Table I shows the ionization potentials and calculated relative ionization frequencies of the main film-forming species for two electron temperatures (a typical value for oxide rf magnetron plasmas is ~ 5 eV).^{19,24,25} The probability of ionizing Al is 1–2 orders of magnitude higher than for AIO, O, and O_2 . Consequently, the amounts of neutral AIO, O, and O_2 are much higher relative to Al than in the case of the ions, as seen in Fig. 3. The high AIO/Al ratio is consistent with the findings of Hecq and Hecq⁸ for other metals. They see an increase in molecular fraction with increasing binding energy and for SnO, which has a slightly higher binding energy than

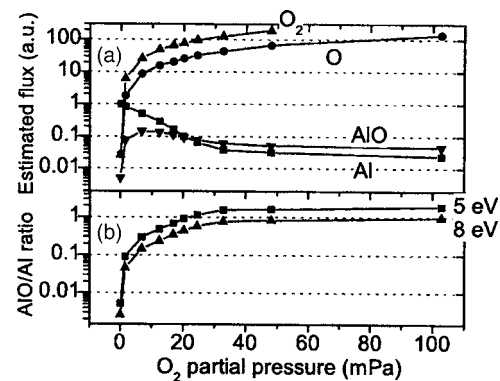


FIG. 3. Estimated neutral fluxes as a function of the O_2 partial pressure. In (a) an electron temperature of 5 eV was used, while (b) shows the AIO/Al ratio also for 8 eV.

AlO, the SnO/Sn ratio is about 2 for a fully oxidized target. It can be noted that these molecular fractions are significantly higher than those observed when sputtering ceramic oxide targets in pure Ar.⁷ This can be explained by preferential sputtering of oxygen, resulting in the development of a metal-rich target surface and, consequently, a lower fraction of sputtered molecules.

Residual gases in the chamber, especially H₂O, are known to affect the properties of alumina thin films.²⁶ These effects are of great importance, since many industrial deposition systems operate under high vacuum conditions with H₂O being one of the main residual gases. To study its effect on the deposition flux, additional measurements were made in a background of $\sim 10^{-4}$ Pa H₂O. The results for Al⁺, AlO⁺, O⁺, and O₂⁺ are similar to the UHV case, but large amounts of OH⁺ and AlOH⁺ are also present (about 100% and 30% of the Al⁺ intensity in the oxidized mode). Cross-section data were not available, but it is likely that these molecules have a lower ionization probability than Al, implying that their relative concentration in neutral form is even higher.

In summary, the ionic deposition flux from an Al target, reactively sputtered in an Ar/O₂ mixture, was measured by mass spectrometry, both at UHV conditions and in a background of H₂O. The results show that up to 10% AlO⁺, relative to Al⁺, is present in the deposition flux and that in a background of $\sim 10^{-4}$ Pa H₂O large amounts of AlOH⁺ and OH⁺ are also present (up to 30% and 100%, respectively, of the Al⁺ signal). Moreover, an estimation of the neutral deposition flux was made, showing that the neutral AlO fraction is of the same order as, or even higher than, the amount of atomic Al. Due to the different reactivity and bonding behavior of atomic and molecular species, these findings are of great importance when understanding the physics behind alumina thin film growth.

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