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Phase control of Al$_2$O$_3$ thin films grown at low temperatures

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Low-temperature growth (500°C) of α-Al$_2$O$_3$ thin films by reactive magnetron sputtering was achieved for the first time. The films were grown onto Cr$_2$O$_3$ nucleation layers and the effects of the total and O$_2$ partial pressures were investigated. At 0.33 Pa total pressure and ≥16 mPa O$_2$ partial pressure α-Al$_2$O$_3$ films formed, while at lower O$_2$ pressure or higher total pressure (0.67 Pa), only γ phase was detected in the films (which were all stoichiometric). Based on these results we suggest that α phase formation was promoted by a high energetic bombardment of the growth surface.

Alumina (Al_2O_3) thin films are widely used as, e.g., wear-resistant or diffusion barrier coatings. In such high-temperature applications the hard and thermally stable α phase is usually desired. However, synthesis of this phase is not straight-forward. The existence of several metastable phases complicates growth of α-Al_2O_3, especially when low temperature growth is required (to limit the thermal load of the substrate). Consequently, many low-temperature growth studies, aimed at forming the α phase, have been made during the last decade. Notably, α-Al_2O_3 films were achieved at 760 °C by pulsed DC reactive magnetron sputtering,[1] at 580 °C using plasma assisted chemical vapor deposition,[2] and at 280 °C by non-reactive RF magnetron sputtering from an Al_2O_3 target using chromia (Cr_2O_3) nucleation layers.[3, 4] In this article, the method of a chromia "template" is applied to reactive magnetron sputtering, with the aim to understand and control alumina growth at low temperatures. To this end the crystalline structure and chemical composition of the grown films were studied as functions of O_2 partial pressure and Ar+O_2 total pressure. Moreover, in order to study the effect of water, which is known to be important in alumina growth,[5] films were deposited both at ultra high vacuum (UHV) and in a background of ~10^{-4} Pa H_2O.

The depositions were made in a UHV chamber (base pressure: <7×10^{-7} Pa) by reactive Ar/O_2 RF magnetron sputtering of an on-axis Al target (Ø 50 mm) at a constant RF power of 80 W. The target-to-substrate distance was 11 cm and the substrates used were Si wafers, ultrasonically cleaned in acetone and isopropanol, but with the natural oxide not removed. Before each AlO_x deposition, a thin (~30 nm) chromia nucleation layer was deposited from a 45° off-axis Cr_2O_3 target in 0.33 Pa pure Ar at a substrate temperature of 300 °C.[3] All AlO_x depositions were subsequently made onto electrically floating substrates at a temperature of 500 °C, while the total

Ar+O_2 and the partial O_2 pressures could be varied (the O_2 pressure was measured during sputtering by a differentially pumped mass spectrometer). For the experiments with water vapor, deionized water was introduced into the chamber via a heated leak valve. The crystalline phases of the deposited films were identified by grazing incidence x-ray diffraction (GIXRD) at an incident angle of 4°. Elastic recoil detection analysis (ERDA), by a 35 MeV Cl^{7+} ion beam incident at an angle of 15° with respect to the sample surface, was used to measure the chemical composition. The H content was measured using a Si detector with an 18 μm Al range foil, while the Al and O recoils were detected in a Bragg ionization chamber at a scattering angle of 31.1°. The error in the measured Al and O compositions is approximately ± 2 at.%.

Figure 1 shows the deposition rate and target self-bias voltage as a function of the O_2 partial pressure at a constant total pressure of 0.33 Pa. The change in target voltage from -500 to -300 V, as the O_2 partial pressure increases from 7 to 32 mPa, reflects the shift from metallic to oxidized target state.[6] The oxidization is also accompanied by a drop in deposition rate by more than an order of magnitude, due to the decrease in sputter yield and increase in secondary electron yield.[7, 8] Interestingly, at 7 mPa O_2 the deposition rate had already decreased by more than 50%, while the target voltage was almost unaffected. The latter indicates that an oxide compound had not yet formed, i.e., the target was still in the metallic state, whereas the reduction in rate is believed to be due to oxygen chemisorption on the target surface, occurring prior to the formation of an oxide compound.[7, 9] The commonly observed hysteresis behavior in the O_2 partial pressure and target voltage, when increasing and decreasing the O_2 flow, was not seen. A qualitative estimation, using the Berg model for reactive sputtering,[10] showed that this was due to the combination of small target area and high pumping speed (~400 l/s).
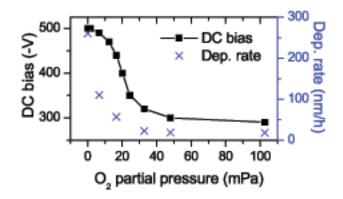
Figure 1. The target (self-bias) voltage and the deposition rate as functions of the O_2 partial pressure. The total pressure was 0.33 Pa.

Figure 2 shows GIXRD results for five AlO_x films grown at 0.33 Pa total pressure at different O_2 partial pressures (deposition rates can be found in Table I). The films exhibit a phase change as the O_2 partial pressure increases from 7 to 16 mPa (corresponding to deposition rates of about 40% and 20% of the rate in pure Ar). At 7 mPa solely peaks corresponding to γ-Al_2O_3 are seen, while at O_2 pressures of 16 mPa or higher the diffractograms show only α-Al_2O_3 peaks. (Note that the peaks at 33.6° and 54.9° are ascribed to the chromia layer[11] and that the peak intensities from different films cannot be directly compared due to differences in film thickness.) Figure 3 shows diffractograms from films grown at a total pressure of 0.67 Pa. At this higher pressure only γ phase was detected in the films, irrespective of the O_2 partial pressure. The three O_2 partial pressures (16, 24, and 32 mPa) correspond to deposition rates of about 35%, 20%, and 15%, respectively, of the rate in pure Ar (absolute rates are found in Table I). The ERDA measurements showed that all films were close to the ideal stoichiometry, as shown in Table I, which excludes variations in composition as a possible reason for the observed phase changes.

The phase changes might instead be explained by an increased bombardment of the growth surface by energetic particles, increasing the mobility at the surface. For example, in recent arc
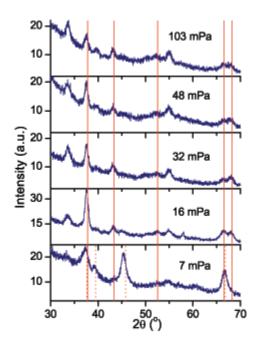
Figure 2. Grazing incidence x-ray diffractograms of five AlO$_x$ films grown at different O$_2$ partial pressures. All films were deposited at a total pressure of 0.33 Pa and a substrate temperature of 500 °C onto chromia nucleation layers. The vertical lines correspond to peak positions of α-Al$_2$O$_3$ (solid lines) and γ-Al$_2$O$_3$ (dotted).[11]
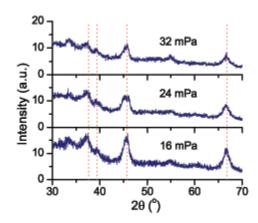

Figure 3. Grazing incidence x-ray diffractograms of AlO$_x$ films grown at different O$_2$ partial pressure at a total pressure of 0.67 Pa and a substrate temperature of 500 °C onto chromia nucleation layers. The dotted lines correspond to γ-Al$_2$O$_3$ peaks.[11]

Table I. Deposition rate and film compositions as functions of total and O$_2$ partial pressure.

Total pressure (Pa)			0.33				0.67	
O$_2$ pressure (mPa)	7	16	32	48	103	16	24	32
Dep. rate (nm/h)	110	57	23	19	18	93	57	39
Al (at. %)	39.1	41.0	39.2	39.5	39.7	39.6	38.7	38.9
O (at. %)	60.9	59.0	60.8	60.5	60.3	60.4	61.3	61.1

evaporation experiments the use of a high substrate bias has been found to promote growth of α-Al$_2$O$_3$.[12, 13] In our case we do not apply any bias, but instead the phase change from γ to α is achieved by the combination of low total pressure and high enough O$_2$ partial pressure. The low total pressure implies that a larger part of the energetic particles originating from the target will retain their initial energy. A rough estimation using atomic radii yields mean free paths in Ar of 16 and 8 cm, for O, and 5 and 2.5 cm, for Al, at 0.33 and 0.67 Pa, respectively. At a target-to-substrate distance of 11 cm, this corresponds to probabilities for reaching the substrate without any collisions of 50 % and 25 %, respectively, for O and 6 % and 0.4 % for Al. Thus, a significantly higher fraction of energetic particles, e.g., sputtered neutrals or energetic oxygen,[14] will bombard the substrate at 0.33 Pa. The energetic oxygen particles originate from the oxidized parts of the target surface as negative ions and are accelerated to high energies over the target sheath voltage (in our case 300-500 V), as shown by Tominaga *et al.*[15] for reactive sputtering of Zn. This has been observed also for other oxides and shown to cause resputtering of the films during deposition.[16] As the O$_2$ partial pressure increases, the target oxidizes and the amount of energetic oxygen increases strongly.[15] Hence, if the amount of bombardment is high enough, this could explain the observed phase changes from γ- to α-Al$_2$O$_3$.

In high vacuum deposition systems significantly higher amounts (compared to UHV conditions) of residual gases are present during the film growth. This background gas mostly consists of water, which is known to affect the formation and properties of alumina thin films.[5] In order to study its effect on low-temperature growth of α-Al_2O_3, films were deposited in a (high vacuum) background of ~10^{-4} Pa H_2O at a total pressure of 0.33 Pa, substrate temperature of 500 °C, and O_2 partial pressures of 16 and 103 mPa. The GIXRD results from these films (not shown) are very similar to the UHV case above and demonstrate that the films consist of α-Al_2O_3. Furthermore, the stoichiometry was close to ideal also for these films and no H (≤ 0.1 at. %) was detected by ERDA. Hence, under the conditions studied here, the presence of water does not seem to disturb the growth of the α phase.

In summary, we have studied alumina thin films grown by reactive magnetron sputtering at low temperatures (500 °C), both at UHV and in a background of ~10^{-4} Pa H_2O. All films were stoichiometric (with no incorporated H) and crystalline in the metastable γ or stable α phases. The formation of the α phase occurred only at a low total pressure (0.33 Pa), suggesting that it was promoted by a high energetic bombardment of the growth surface. Plausible sources of this bombardment, in our case, are sputtered neutrals and energetic oxygen originating from the target surface. Overall, these studies show that low-temperature growth of α-Al_2O_3 is possible by reactive sputtering and that the phase content of the films can be controlled by controlling the kinetic energy of the depositing species. These findings will aid further developments in the field of alumina growth control.

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