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Influence of residual water on magnetron sputter deposited crystalline Al_2O_3 thin films

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ABSTRACT

The effects of residual water on the phase formation, composition, and microstructure evolution of magnetron sputter deposited crystalline alumina thin films have been investigated. To mimic different vacuum conditions, depositions have been carried out with varying partial pressures of H_2O . Films have been grown both with and without chromia nucleation layers. It is shown that films deposited onto chromia nucleation layers at relatively low temperatures (500 °C) consists of crystalline α -alumina if deposited at a low enough total pressure under ultra high vacuum (UHV) conditions. However, as water was introduced a gradual increase of the γ phase content in the film with increasing film thickness was observed. At the same time, the microstructure changed drastically from a dense columnar structure to a structure with small, equiaxed grains. Based on mass spectrometry measurements and previous *ab initio* calculations, we suggest that either bombardment of energetic negative (or later neutralized) species being accelerated over the target sheath voltage, adsorbed hydrogen on growth surfaces, or a combination of these effects, is responsible for the change in structure. For films containing the metastable γ phase under UHV conditions, no influence of residual water on the phase content was observed. The amounts of hydrogen incorporated into the

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films, as determined by elastic recoil detection analysis, were shown to be low. Overall, the results demonstrate that residual water present during film growth drastically affects film properties, also in cases where the hydrogen incorporation is found to be low.

Keywords: Sputtering; Aluminium oxide; Water; Phase formation.

1. INTRODUCTION

Alumina, Al_2O_3 , thin films are used in a wide range of applications including microelectronics and catalysis, as well as diffusion barrier, thermal barrier, and wear-resistant coatings [1]. It exists in several different crystallographic polymorphs with different properties [2]. In catalysis, metastable phases such as γ -alumina are used due to their high specific surface areas, whereas the thermodynamically stable α phase is desirable in wear-resistant coatings, owing to its excellent mechanical properties, and chemical and thermal stability. In industrial applications, α -alumina is commonly deposited using chemical vapor deposition techniques at high temperatures (usually around 1000 °C) [3]. The elevated substrate temperatures limit the choice of substrate materials and might also, e.g., induce thermal cracks in the coatings, due to different thermal expansion coefficients of film and substrate [4]. Consequently, much work has recently been devoted to finding ways of depositing crystalline alumina coatings at lower temperatures. In this endeavor, several authors have turned to physical vapor deposition (PVD) techniques. For example, Schneider *et al.* deposited metastable κ - and θ -alumina at temperatures < 450 °C by ionized magnetron sputtering, but did not observe the α phase [5], Zywitzki *et al.* utilized pulsed dual magnetron sputtering to synthesize α -alumina at 760 °C [6], and several authors have demonstrated growth of films containing α -alumina by reactive arc evaporation at temperatures around 600-700 °C [7,8]. In most of the low-temperature growth studies, fairly high substrate bias values have been used and an increased supply of energy to the growth surface through bombardment of energetic particles has been attributed as the reason for the decreased formation temperature of the α phase. However, nucleation control using chromia (Cr_2O_3) nucleation layers [9] has been utilized to deposit the α phase from a ceramic

Al_2O_3 target at temperatures as low as 280 °C [10], indicating that the nucleation stage of growth is a key to controlling the phase formation. It has been suggested that this could be due to surface energy stabilization of metastable phases at the initial stages of growth [10]. Recently, this method was demonstrated to also work for reactive sputtering [11]. It was, however, shown that a combination of nucleation control and bombardment of energetic oxygen is needed [11,12]. The exact role of the energetic bombardment in the α phase formation is yet to be elucidated, but possible explanations include creation of lattice distortions (strains), facilitation of diffusion processes, and removal of impurities (e.g. hydrogen) on the growth surfaces. The above examples demonstrate that PVD based growth of alumina have been studied intensely in the past. However, the mechanisms behind the formation of different phases and microstructures are poorly understood and there is a need to systematically investigate how different factors affect phase formation, microstructure evolution, and composition of physically vapor deposited alumina.

Previous studies of magnetron sputter deposited amorphous alumina thin films have demonstrated the importance of residual water for the resulting film properties. For example, correlations between hydrogen incorporation and elastic modulus have been shown [13]. The hydrogen incorporation in arc evaporated and magnetron sputtered films has been suggested to mainly occur through aluminum oxide hydroxide formation in the film and at the cathode [14]. In ref. 11, some investigations were presented concerning the influence of residual water on the phase formation of crystalline alumina, with x-ray diffraction results showing essentially no effects on the phase content for water partial pressures up to 1×10^{-4} Pa. In this work, these studies are

extended to include investigations of phase formation, microstructure, as well as plasma and film composition for water partial pressures up to 1 mPa.

2. EXPERIMENTAL DETAILS

Depositions were carried out in an ultra high vacuum (UHV) system with a base pressure $< 3 \times 10^{-6}$ Pa, using rf magnetron sputtering of an Al_2O_3 target at a constant rf power of 80 W. (From hereon, background pressures $< 3 \times 10^{-6}$ Pa are referred to as UHV conditions.) Ar (99.9997% purity) was used as sputtering gas, and Si(001) wafers with the natural SiO_x layer kept intact were used as substrates. The substrates were ultrasonically cleaned in acetone and 2-isopropanol, and dried in pure N_2 before they were inserted into the vacuum chamber. During the depositions, the substrates were electrically floating. Due to the geometry of the deposition system used, the Al_2O_3 target ($\varnothing$ 50 mm, 99.99% purity) was mounted at a 45° off-axis position, with a target-to-substrate distance of 9 cm. Prior to some of the alumina depositions, a chromia nucleation layer was grown *in situ* using a Cr_2O_3 target ($\varnothing$ 50 mm, 99.8% purity) mounted with the same geometry as the alumina target. All Al_2O_3 depositions were carried out at a substrate temperature of 500 °C, while the Cr_2O_3 layers were grown at 300 °C. The final film thickness was determined using a surface profilometer (Dektak 3030). Since water is often the most common residual gas under poorer (high) vacuum conditions, different background pressures were mimicked by introducing deionized water into the chamber through a leak valve. The H_2O content in the chamber was monitored during depositions using a differentially pumped residual gas analyzer (RGA) (Spectra Vision 1000-P). The RGA signal intensity was separately calibrated against the system pressure gauges. Note that all depositions of chromia nucleation layers were carried out at UHV conditions.

The phase content and microstructure of the films were determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD measurements were done in a Philips MRD diffractometer, operated with Cu K α radiation, in a parallel beam configuration. A grazing incidence XRD (GIXRD) setup was used with a fixed incidence angle of 4° relative to the sample surface. The TEM analysis was carried out in a FEI Technai G² TF20 UT field emission gun transmission electron microscope operated at 200 kV. Samples for cross sectional TEM (XTEM) analyses were first mechanically thinned and polished, and thereafter ion milled to electron transparent thickness. A final polishing step using low-energy ions was performed in order to remove the damaged surface layer caused by the preceding step.

The film composition was determined using elastic recoil detection analysis (ERDA), utilizing 35 MeV Cl⁷⁺ ion irradiation at an incidence angle of 15° with respect to the sample surface. Al and O was detected in a Bragg ionization chamber at a scattering angle of 31.1°, while the H content was measured using a Si detector with an 18 μ m Al range foil.

The ion content of the deposition flux was measured using a differentially pumped energy-resolved mass spectrometer (Hiden PSM 003). These measurements were performed separately, with the mass spectrometer mounted close to the substrate position during the film depositions (with the probe facing in the direction normal to the substrate surface). The front plate of the mass spectrometer was electrically floating, and the distance between the front plate and the target was ~15 cm. The sampling orifice in the front plate had a diameter of 0.3 mm. To deduce the total ion flux of

different species, energy scans performed for different mass-to-charge ratios were integrated. During magnetron sputtering of oxides, negative ions might form at the target and be accelerated to high energies over the target sheath voltage [15] Since the mass spectrometer used is limited to measure energies below 100 eV, a lower rf power (resulting in a target voltage of below 100 V) was applied during measurements on negative ions. Moreover, the measurements on negative ions were carried out with the Al_2O_3 target mounted in an on-axis position, due to the relatively low acceptance angle of the instrument and the directionality of the energetic species.

3. RESULTS

Table 1 summarizes deposition conditions, film thicknesses, and compositions as obtained by ERDA for the six different samples discussed. The deposition time was 8 h for all films. Consequently, the large changes in film thickness for different conditions were caused solely by the corresponding changes in deposition rate. All films are seen

Table 1. Deposition conditions, film thicknesses, and compositions for the studied samples. Samples III and IV were grown without chromia nucleation layers.

Sample	H ₂ O partial pressure (Pa)	Sputtering pressure (Pa)	Cr ₂ O ₃ layer thickness (nm)	Al ₂ O ₃ film thickness (nm)	Al content (at.%)	O content (at.%)	H content (at.%)
I	UHV	0.33	30	500	40.4	59.4	0.2
II	1×10^{-3}	0.33	30	100	37.5	61.8	0.7
III	UHV	0.33	-	450	41.1	58.6	0.3
IV	1×10^{-3}	0.33	-	100	37.6	61.7	0.7
V	UHV	2	30	700	41.0	58.6	0.4
VI	1×10^{-3}	2	30	250	40.7	59.0	0.3

to have very low H content, although a slightly increased H signal at the higher H₂O partial pressures was measured for the films deposited at a total pressure of 0.33 Pa. It is possible to distinguish a trend where a higher H incorporation is accompanied by an increased O content, even though the differences are small and, consequently, can be

expected to be within the measurement errors. During the depositions with ~ 1 mPa, a slightly lower negative target voltage was obtained as compared to UHV conditions, indicating changes in the target and/or discharge conditions also at these relatively low water partial pressures.

Figure 1. Grazing incidence x-ray diffractograms for samples I and II, grown onto chromia nucleation layers at 0.33 Pa total pressure. The solid, dashed, and dotted vertical lines show the expected peak positions for α - Al_2O_3 [17], Cr_2O_3 [18], and γ - Al_2O_3 [16], respectively.

The film grown onto a chromia nucleation layer at 0.33 Pa total pressure under UHV conditions (sample I) consists predominantly of the α phase, as seen from the grazing incidence x-ray diffractograms shown in Fig. 1. All peaks from sample I can be ascribed to either α -alumina or the chromia nucleation layer. Note that since chromia and α -alumina are isostructural, they exhibit the same peaks in XRD, although shifted due to the difference in lattice constant. The chromia layers are thin in all cases (see Table 1), causing low intensity of these peaks. Due to the reduced film thickness of sample II, the diffracted intensity is very low, complicating the interpretation of this diffractogram. However, the peak at 43.3° is unique to the α phase, and, hence, proves the presence of this phase. The peaks at $\sim 46^\circ$ and $\sim 39^\circ$ indicate that the film also contains γ -alumina [16]. Thus, the introduction of 1 mPa H_2O caused a change from a pure α -alumina film to a film containing a mixture of the α and γ phases. As the total pressure was increased to 2 Pa (samples V and VI), or if the films were deposited directly onto the oxidized Si substrates (samples III and IV), only the metastable γ phase was formed, as seen from

the diffractograms shown in Fig. 2. In these cases, no correlation between residual water and the phase formation was found in the XRD investigations. Observe that the peak intensities for different films in general are not comparable, due to the variations in film thickness.

Figure 2. Grazing incidence x-ray diffractograms for samples III-VI. The solid vertical lines show the expected peak positions for $\gamma\text{-Al}_2\text{O}_3$ [16].

Cross sectional transmission electron micrographs of the films containing α -alumina show large changes in microstructure for the two different water partial pressures. In Fig. 3, overview bright field and dark field images of sample I, grown at UHV conditions, are shown, revealing a dense, but defected, columnar microstructure. The selected area electron diffraction (SAED) inset in Fig. 3 confirms that the film contains α -alumina. Figure 4 shows a high resolution image of the chromia/alumina interface, where the continuing crystalline growth of the columnar alumina grains on top of the chromia layer can be seen, as expected from the local epitaxy between chromia and alumina grains observed in previous studies [10]. Conversely, sample II, which was grown at a H_2O partial pressure of ~ 1 mPa, exhibits a less dense microstructure consisting of small, equiaxed grains, as seen from Fig. 5. SAED of this sample reveals a transition in phase composition with increasing film thickness as deduced from Fig. 6. In the diffraction pattern taken at an area (of diameter ~ 150 nm) containing the whole

alumina layer, most of the diffraction rings can be attributed to the α phase as indicated in Fig. 6(a), while the remaining diffraction maxima fit well with available data for γ -alumina (not shown). Consequently, it is concluded that the film contains an α and γ phase mixture. However, if the SAED only includes the topmost part of the alumina layer, the phase content is dominated by γ -alumina as shown in Fig. 6(b). Hence, the film seems to gradually change towards a more γ -alumina rich phase composition, and, despite the relatively low H content of sample II, a pronounced effect on the microstructure as well as on the alumina phase formation was observed. The smaller, seemingly randomly oriented, grains give rise to a more ring shaped SAED pattern, as opposed to the points in the diffractogram for the columnar film.

Figure 3. Bright field (a) and dark field (b) cross sectional transmission electron micrographs of sample I, revealing a columnar microstructure. The inset shows a selected area electron diffraction pattern from the alumina layer, with expected diffraction rings for α - Al_2O_3 [17].

Figure 4. Cross sectional high resolution transmission electron micrograph of sample I, showing the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ interface.

Mass spectrometry measurements were carried out in order to gain further insight into the origin of the altered structure and deposition rate. Fig. 7 shows a comparison between the composition of the ion flux at UHV conditions and at a H_2O partial pressure of ~ 1 mPa, during sputtering at a total pressure of 0.33 Pa. A clear change in the deposition flux is seen, with a decreased amount of Al^+ ions and a dramatic increase in the AlOH^+ signal. Note, however, that the decrease in Al^+ signal does not account for

the full reduction in deposition rate in the low pressure case. A similar trend is observed at a total pressure of 2 Pa, as shown in Fig. 8. The flux of neutral species expected from the ion measurements are not directly comparable for the two total pressures, due to the change in the ionized fraction expected with different pressures caused by, e.g., the possible onset of Penning ionization processes [19].

Figure 5. Cross sectional bright field transmission electron micrograph of sample II, revealing a structure consisting of small, equiaxed grains.

Figure 6. Selected area electron diffraction patterns from the alumina layer of sample II. Diffraction pattern (a) is from a region close to the Cr_2O_3 interface extending throughout the film thickness, while pattern (b) only includes the top part of the film. The expected diffraction rings for α -alumina [17] (a) and γ -alumina [16] (b) are shown.

Figure 7. Mass spectrometer intensity in logarithmic scale for positive ions of different Al containing species at UHV conditions and with 1 mPa H_2O . The Ar pressure was 0.33 Pa.

Negative ions have previously been shown to affect film properties during oxide sputtering, causing, e.g., film resputtering, stresses, and composition changes [20,21,22], and could consequently be important also in the present case. Fig. 9 shows the occurrence of different negatively ionized species in the deposition flux as a

function of water partial pressure, measured at a total pressure of 0.33 Pa. (Note that the conditions were slightly different during the negative ion measurements as explained in section 2. Hence, the exact pressures are not directly transferable to the situation during the depositions.) A pronounced increase in the negative ion bombardment with higher water partial pressures can be observed. The increase is particularly accentuated for the OH^- signal, while the increase in the O_2^- and H_2O^- fluxes is moderate. Ion energy distributions for the negative species show a relatively broad peak at an energy corresponding to ion acceleration over the target sheath voltage, with a tail extending to lower energies (not shown).

Figure 8. Mass spectrometer intensity in logarithmic scale for positive ions of different Al containing species at UHV conditions and with 1 mPa H₂O. The Ar pressure was 2 Pa.

4. DISCUSSION

The results for the films grown under UHV conditions agree well with what can be expected from previous studies [9,10,11]. Hence, α -alumina formed when the Al_2O_3 depositions were carried out onto chromia nucleation layers at low enough total pressure, so that energetic bombardment from species originating from the target is

allowed [11,12]. This bombardment is impeded at higher total pressure, inhibiting the α phase growth onto chromia nucleation layers during deposition by reactive sputtering of Al in Ar/O₂ [11]. Here, we show that this is also the case when depositing from ceramic Al₂O₃ targets, as seen when comparing the films deposited at 0.33 and 2 Pa total pressure onto chromia (samples I and V). Hence, energy supplied from energetic neutral or negatively ionized species which has proved to be essential in the reactive case [11,12], can be concluded to be a necessary condition for low-temperature α -alumina growth onto Cr₂O₃ also in the non-reactive case. The columnar structure and column widths of the α -alumina film are in agreement with previous investigations [10].

Figure 9. Mass spectrometer intensity for different negative ions as a function of water partial pressure, measured at a total pressure of 0.33 Pa. The H₂O partial pressures were measured with the differentially pumped RGA. The lowest value on the horizontal scale corresponds to UHV conditions and the largest number to a H₂O partial pressure of $\sim 5 \times 10^{-4}$ Pa, as separately calibrated against the system pressure gauges.

Residual water at a pressure of 1 mPa H₂O clearly inhibited the continued columnar α -alumina growth and caused a transition to a small-grained, equiaxed, structure. This transition was accompanied by a gradual increase of γ -alumina content with increasing film thickness, as deduced from the XRD, XTEM, and SAED investigations. We

identify two possible reasons for this change in microstructure and phase composition as water was introduced; (i) adsorbed H on growth surfaces causing grain renucleation, or (ii) renucleation and defect generation caused by energetic bombardment originating from negative ions formed at, or in the vicinity of, the target. As renucleation occurs, the formation of γ -alumina is favored if no template effect is achieved from the underlying layer, as shown for the results of the samples grown directly onto Si/SiO_x. The first argument is supported by recent first principles calculations of α -Al₂O₃ (0001) surfaces clearly showing that Al adsorption corresponding to the bulk crystal stacking sequence becomes unstable, or considerably weaker, on a completely hydrogenated surface [23]. Hence, this effect could give rise to renucleation, prohibit epitaxial effects between underlying and newly forming grains, and result in a consequent transition to γ -alumina growth and a small-grained microstructure. The second argument is supported by the fact that a pronounced increase in the amount of negative ions originating from the target was observed as water was introduced (see Fig. 9). It is well known that ion bombardment in the energy range of a few hundreds of eV (i.e., corresponding to the typical target voltage during deposition) can cause renucleation, e.g., through defect generation, and a corresponding disruption of columnar growth [24]. Hence, this must be considered as another possible cause of the altered film structure. However, it is not clear how this would affect the phase formation, since we have shown that a moderate energetic bombardment is a necessary condition for the formation of the α phase [11,12]. Thus, if the increased bombardment is also responsible for the phase change, this would imply that there exists a window for the energetic bombardment in which α -alumina formation is promoted. Hence, if this is the case, a too low bombardment would result in γ phase formation as discussed above, an intermediate bombardment would promote α -alumina growth, whereas a too extensive energetic bombardment would lead

to renucleation and possibly a consequent formation of γ phase. Separating the influence of adsorbed H on growth surfaces and the increased bombardment on the α -alumina growth is difficult, and we find it possible that both discussed mechanisms are active during growth in our case. In ref. 11, essentially no effects on the phase composition were observed by XRD as $\sim 10^{-4}$ Pa of water was introduced during deposition of α -alumina onto chromia nucleation layers using reactive sputtering of Al in Ar/O₂. Considering the large effects observed with 1 mPa of water in this study, this suggests that a critical limit of the water background pressure seems to exist in the 10^{-4} - 10^{-3} Pa pressure regime, below which α -alumina growth still is possible. This critical pressure plausibly depends on other deposition parameters. For example, in an industrial deposition system the deposition rate can be significantly higher than in the case studied here. It is reasonable to assume that the critical water background pressure would also be higher, since the molecular impingement rate onto a surface is proportional to pressure.

In cases where γ -alumina was formed under UHV conditions, no effect on the phase content of the film was detected as the water partial pressure was increased. This is in line with the study of the effects of residual water on amorphous films made by Schneider *et al.* [13]. In their study, the film grown at the highest water partial pressure contained crystalline γ -alumina (as shown by SAED), while films deposited at lower water partial pressures were amorphous under otherwise identical growth conditions. Hence, this suggests that residual water might actually promote γ -alumina formation as compared to the amorphous phase.

That the increase in energetic bombardment as water is introduced is appreciable can be confirmed by more closely investigating the reduction in deposition rate, and comparing it to the observed changes in the ion flux to the substrate. For the films deposited at 2 Pa total pressure, where the effects of negative ion bombardment from the target are small due to the short mean free path, the reduction in deposition rate as water was introduced was 64 %, as seen from Table 1. This scales well with the reduction in Al^+ signal for the mass spectrometry measurements presented in Fig. 8, which was found to be 61 %. Hence, the reduction in deposition rate at this pressure is caused by a corresponding decrease in deposition flux [25]. At 0.33 Pa, however, the reduction in deposition rate was found to be significantly larger than the reduction in Al^+ signal; 78-80 % compared to 56 % (see Table 1 and Fig. 7). If the AlOH species are considered to contribute to the film formation in the calculation, the reduction in the incoming deposition flux becomes smaller and, consequently, the difference between incoming flux and resulting deposition rate even larger. This indicates that the deposition rate was further reduced through film resputtering effects occurring due to the increased energetic bombardment in the low pressure case. Similar effects on the deposition rate, being induced by energetic oxygen, have been observed in previous work studying magnetron sputter deposition of oxides [20,22].

Regarding the composition of the alumina layers, the H content is surprisingly low in all cases (see Table 1). The highest values (0.7 %) were observed for the films grown with 1 mPa H_2O at 0.33 Pa total pressure, while no increase in the amount of incorporated hydrogen compared to UHV conditions was observed at 2 Pa total pressure. The H incorporation through adsorption on growth surfaces might in the present case be suppressed by the fairly high deposition temperature. Moreover, at lower pressures it

might be further suppressed by energetic bombardment, as recently shown for amorphous alumina growth [26]. One can also note that the increase in H concentration in the films is accompanied by an increased O content. This might indicate that the H incorporation occurs through hydroxide formation as previously suggested [14]. However, the reported changes are very small and this result could also be influenced by other effects. Concerning hydroxide formation, it can further be noted that the large amounts of OH-containing species in the deposition flux is a strong indication that hydroxide-like compounds are also formed on the target surface, corroborating suggestions made in previous work [14].

5. CONCLUSIONS

Crystalline alumina thin films have been grown under varying partial pressures of water. Films deposited under UHV conditions at low total pressure (0.33 Pa) onto chromia nucleation layers exhibited a columnar structure with α -alumina being the only detectable alumina phase. However, as water to a partial pressure of 1 mPa was introduced, the columnar growth was interrupted and a more porous microstructure consisting of small, equiaxed grains was formed. This microstructure change was accompanied by a change in the phase composition of the films, where the γ -alumina content was found to increase with increasing film thickness. This change in film properties can be explained by one of, or a combination of, at least two effects; (i) H adsorbing on growth surfaces, causing renucleation of grains with limited epitaxial relationship with the underlying grains, and (ii) renucleation due to an increased energetic bombardment caused by target surface reactions. Films deposited at higher total pressures, or without chromia nucleation layers, were found to be essentially phase pure γ -alumina regardless of the water partial pressure. In all studied cases, the H

content was found to be low (< 1 at. %) and varied only slightly with the water partial pressure.

This study provides important insights into the influence of impurities on low temperature α -alumina growth. Moreover, it is shown that effects of residual gases during sputter deposition of oxides can be considerable, also in cases where the impurity incorporation into the films is found to be low.

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