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Synthesis of α -Al₂O₃ thin films using reactive high power impulse magnetron sputtering

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Short title: Synthesis of Al₂O₃ thin films using high power impulse magnetron sputtering

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Abstract

α -alumina coatings have been deposited directly onto cemented carbide and Mo substrates at a temperature as low as 650 °C using reactive high power impulse magnetron sputtering (HiPIMS) of Al in an Ar/O₂ gas mixture. The coatings consisted of plate-like crystallites, as revealed by scanning electron microscopy. α phase growth was retained over the studied range of substrate bias voltages (from floating potential up to -100 V), with films exhibiting a slightly denser microstructure at higher bias voltages. X-ray diffraction indicated that the α -alumina grains had a preferred orientation of (0001)-planes perpendicular to the substrate surface. Films deposited at 575 °C were found to consist of γ -alumina, whereas films grown at 500 °C or lower were x-ray amorphous.

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Alumina (Al_2O_3) in thin film form is commonly used for, *e.g.*, wear-protective layers on cutting tools. In such applications, crystalline alumina, in particular the thermodynamically stable α phase, is desired in order to assure a good mechanical, thermal, and chemical stability [1]. Industrially, α -alumina coatings are commonly deposited using chemical vapour deposition at elevated substrate temperatures (~ 1000 °C) [1]. The high temperatures, of course, put limitations on the substrate materials that are possible to use and might in addition cause unwanted effects such as chemical reactions between the coating and substrate materials [2], or cracks in the coatings arising due to different thermal expansion of substrate and film [3]. Consequently, many researchers have investigated the possibilities of depositing α -alumina at lower substrate temperatures using physical vapour deposition (PVD) techniques such as arc evaporation [4,5] and reactive sputtering [6]. Using PVD methods, growth of films with strongly dominating α phase content has been achieved at temperatures down to around 600 °C [4,5]. However, α -alumina formation at the lowest temperatures only took place when high substrate bias voltages, typically of a few hundred volts, were applied during the arc evaporation [4,5]. Growth of the α phase at lower temperatures than this have only been possible by manipulating the substrate surface in order to promote α -alumina nucleation [7,8,9], *e.g.* by predepositing a Cr_2O_3 nucleation layer. (Cr_2O_3 is isostructural with $\alpha\text{-Al}_2\text{O}_3$ and therefore facilitates growth of this phase [10].) Hence, there is still a need to find an effective method for low-temperature deposition of α -alumina. In this work, the viability of using the newly developed ionized PVD technique high power impulse magnetron sputtering (HiPIMS) for producing alumina coatings at low to moderate temperatures has been explored.

In HiPIMS, high power pulses are applied to a conventional sputtering magnetron at a low duty cycle [11]. This results in a highly ionized deposition flux with an inherently broad energy distribution, while the average power and target heating are kept at moderate levels [11]. The interest in the technique has increased immensely lately, owing to the many possibilities of tailoring and improving coating properties arising as a consequence of the energetic and ionized deposition flux. Reactive HiPIMS deposition of both nitrides [12] and oxides [13,14,15] has been shown feasible. Recently, it was shown for reactive sputtering of Al in Ar/O₂ mixtures that the use of HiPIMS can lead to improved process properties, such as reduced or eliminated hysteresis effects and higher deposition rates due to suppressed target poisoning [16]. In the present study, the properties of alumina films deposited under such conditions have been investigated.

Depositions were carried out in an ultra-high-vacuum chamber evacuated to a base pressure $< 3 \times 10^{-5}$ Pa. Sputtering was performed from an on-axis planar circular magnetron (diameter 50 mm) equipped with a 3 mm thick Al target (99.999 % purity). Cemented carbide consisting of WC with 10 wt.% Co was used as substrate material, together with pieces of sheet Mo for reference. The substrates were placed at a target-to-substrate distance of 11 cm. Deposition temperatures in the range of 400 – 650 °C were studied at both floating substrate potential (not measured) as well as with applied bias voltages, U_b , of -40 and -100 V. Biasing of the dielectric films was achieved by applying radio frequency power using an RFX-600 power supply (Advanced Energy). The DC bias of the substrates was monitored during depositions using a digital oscilloscope and only minute fluctuations were observed during the HiPIMS pulsing cycle. However, it is still possible that short fluctuations of the surface potential

during the pulse remained undetected. The total pressure during depositions was kept at 0.8 Pa, with an O₂ (99.9995 % purity) to Ar (99.9997 % purity) gas flow ratio of ~ 2 % resulting in a stable deposition process for stoichiometric alumina at a reasonably high deposition rate [16]. Power was supplied to the magnetron using a SPIK 1000A pulsing unit (Melec) fed by a constant voltage from an MDX Pinnacle DC supply (Advanced Energy). The pulsing unit used produces approximately square voltage pulses with a specified length and repetition frequency. In this study, a pulse length of 35 μs and a repetition frequency of 1 kHz were used. The voltage and current were monitored using a digital oscilloscope and the magnitude of the discharge voltage during pulses was adjusted so that the average power was kept constant at 110 W. This resulted in typical values for the peak voltage and peak current of about 650 V and 12 A, respectively.

The phase content of the grown films was analyzed by θ - 2θ x-ray diffraction (XRD) scans using a Philips PW1820 Bragg-Brentano diffractometer equipped with a Cu K_α x-ray source. Figure 1(a) and (b) show diffractograms obtained for films deposited at 650 °C and floating substrate potential onto cemented carbide and Mo substrates, respectively. It is evident that both films predominantly consist of α -alumina. All other peaks can be attributed to the substrate materials and no evidence for other crystalline alumina phases can be found. The formation of α -alumina on both the cemented carbide and Mo substrates indicates that the low-temperature growth of the α phase in the present case is not due to favourable nucleation conditions, but rather caused by inherent properties of the HiPIMS deposition process. When directly comparing the α -alumina peak intensities with powder diffraction data, no strongly dominating preferred orientation is evident. However, a trend can be seen from Fig. 2,

where the texture factors for the different diffraction peaks obtained from the film deposited onto cemented carbide have been plotted as a function of the angle between the diffracting plane and the (0001)-plane. (Texture factors were obtained by comparing normalized measured integrated peak intensities, corrected for the variation in absorption factor with diffraction angle, with expected ones from powder diffraction data [17,18].) The higher texture factors for planes forming an angle close to 90° with the (0001)-plane, as compared to planes with lower angle to the (0001)-plane, suggest a preferred orientation of the (0001)-planes (c-planes) perpendicular to the substrate surface (*i.e.*, an in-plane orientation of the c-axis). A similar in-plane orientation of the c-axis was observed for films deposited by arc evaporation at temperatures around 600°C by Yamada-Takamura *et al.* using infrared spectroscopy [4]. For the film deposited onto Mo, this trend was also present although less pronounced (not shown).

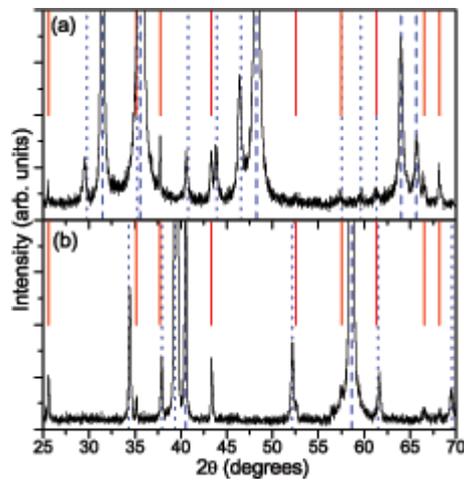


Fig. 1: (Colour online) X-ray diffractograms of films deposited at 650°C and floating substrate potential onto cemented carbide (a) and Mo (b). Expected peak positions for α -alumina [18] (solid, red, lines) as well as the cemented carbide (WC (dashed, blue, lines) and Co_3W (dotted, blue, lines) phases [19]) and Mo (bcc-Mo (dashed) and α - Mo_2C impurity phase (dotted) [20]) substrates are indicated in (a) and (b).

α -alumina growth was retained as the substrate bias voltage was varied, with only slight variations in the preferred crystallite orientation, as seen from Fig. 3 displaying

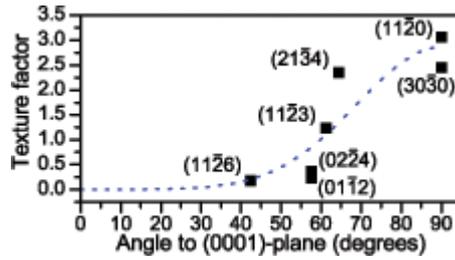


Fig. 2: (Colour online) Texture coefficients for the film deposited onto cemented carbide at 650 °C and floating potential [cf. Fig. 1(a)] plotted as a function of the angle between the diffracting plane and the (0001)-plane. The dotted line shows a fitted Gaussian distribution and serves as a guide for the eye only.

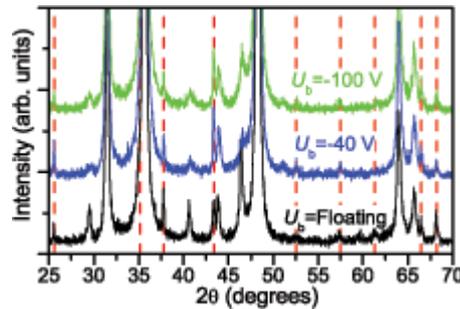


Fig. 3: (Colour online) X-ray diffractograms of films deposited at 650 °C at varying substrate bias voltages, U_b , onto cemented carbide. Expected peak positions for α -alumina [18] are indicated.

x-ray diffractograms for films grown onto cemented carbide at different U_b values; floating potential, -40 and -100 V. This indicates a robust process for α -alumina growth at this substrate temperature, suggesting that film properties such as microstructure and stress can be tailored by varying the applied bias without compromising the α phase content of the films. However, the differences in film properties observed in the present study were fairly small as discussed below. The tendency of a preferred in-plane orientation of the c-axis was seen also for the films deposited with applied substrate bias, although less pronounced (not shown). XRD of films deposited at 575 °C or lower yielded low intensity from the film. In order to improve the relative film intensity, these films were also studied using grazing incidence XRD in a parallel beam Philips MRD diffractometer, operated with Cu K_α

radiation and a fixed incidence angle $\omega = 4^\circ$. The resulting diffractograms are shown in Fig. 4. The film deposited at 575 °C contains γ -alumina, as most easily identified by the peak at $2\theta \approx 67^\circ$, while the films deposited at 500 and 400 °C are essentially x-ray amorphous. Note, however, that γ -alumina, due to the inherent properties of this phase [28], often forms a very small-grained structure and that the existence of nanocrystalline γ -alumina in the two latter samples therefore cannot be excluded without further investigations using, *e.g.*, transmission electron microscopy.

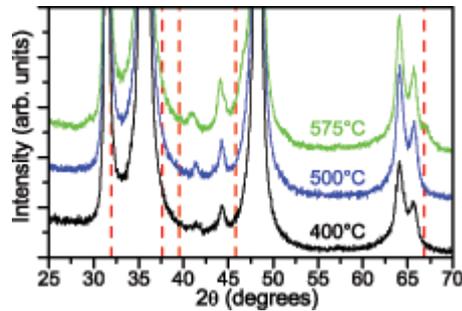


Fig. 4: (Colour online) Grazing incidence x-ray diffractograms of films deposited at 400, 500, and 575 °C at a substrate bias voltage $U_b = -40$ V onto cemented carbide. Expected peak positions for γ -alumina [21] are indicated.

The microstructure of the coatings was studied using scanning electron microscopy (SEM) in a Hitachi S4300 FEG SEM. Fracture sections of coatings for SEM analysis were prepared by first cutting a slit in the carbide up to a point just below the coated surface, and then mechanically compressing the slit so as to produce a tensile crack in the coating. Micrographs of films deposited onto cemented carbide at 650 °C with different bias values, as well as of the film deposited at 575 °C, are shown in Fig. 5. All α -alumina films exhibit a structure consisting of slightly wedge-shaped platelets standing up from the surface. Based on this observation, and the preferential orientation of c-planes perpendicular to the surface described above, we propose the plates to be terminated by (0001)-surfaces oriented perpendicular to the substrate. This suggests that the (0001)-surfaces grow considerably slower than other surfaces,

resulting in plates terminated by these surfaces and an orientation of the c-axis perpendicular to the growth direction as growth of these surfaces is outrivalled. This could be due to the fact that the (0001)-surface is a low-energy surface [22]. However, since the energy difference between this surface and other common surfaces is moderate [22], it is likely that the growth is also affected by other effects, such as impurities. For example, it has been shown that adsorbed H, which in the present case could originate from the residual gas in the deposition chamber, strongly inhibits continued α -Al₂O₃ growth on (0001)-surfaces [23]. A similar plate-like microstructure of α -alumina was observed by Kohara *et al.* [9] for sputter deposited films grown onto oxidized CrN layers (forming a Cr₂O₃ nucleation layer) at a temperature of 750 °C. The tendency of forming plates could in their case be suppressed by applying a bias voltage of -300 V [9]. However, this also resulted in concurrent formation of γ -alumina as a minority phase in the film [9]. In our case, the growth mode is similar as U_b is increased up to -100 V. However, films grown with bias appear to have wider platelets and a somewhat denser microstructure, with smaller grains appearing between the platelets. This is plausibly caused by increased adatom mobility, resulting in wider grains, in combination with bombardment-induced renucleation events leading to the formation of the smaller grains. A clear distinction in microstructure can be made between the α -alumina films and the γ -alumina film shown in Figs. 5(c) and (f). No platelets are formed in the γ -alumina case, and the film surface is smoother.

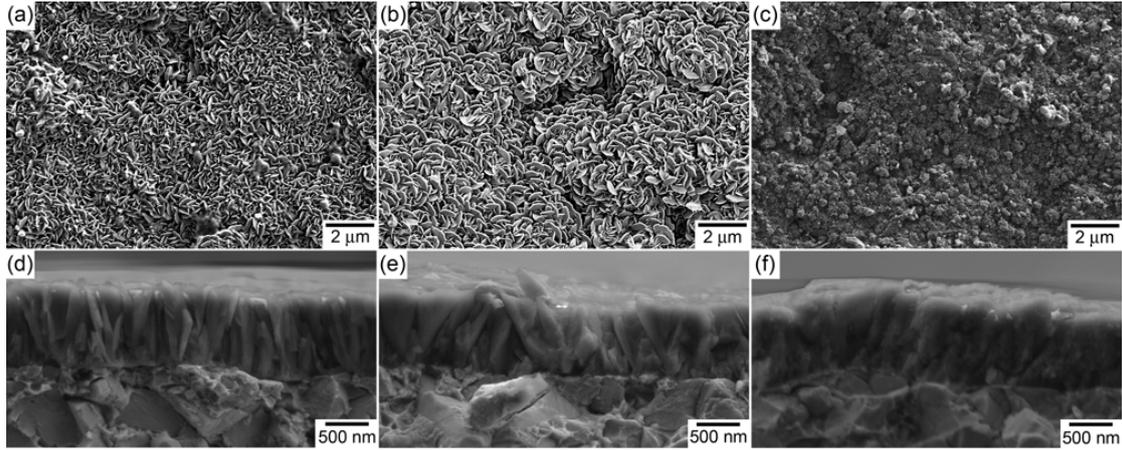


Fig. 5: Top-view [(a)-(c)] and cross-sectional [(d)-(f)] scanning electron micrographs of the α -alumina films deposited at 650 °C at floating substrate bias potential [(a) and (d)] and with an applied bias voltage, U_b , of -100 V [(b) and (e)], as well as of the γ -alumina film deposited at 575 °C with $U_b=-40$ V [(c) and (f)].

Compared to previous reports of alumina growth using conventional reactive sputtering, 650 °C is a very low deposition temperature considering that no substrate bias voltage or nucleation layer was applied in the present case, and is more similar to the lowest temperatures obtainable by arc evaporation under favourable conditions. Still, the inherent energy of the depositing species in the HiPIMS discharge is typically < 100 eV with only around 50 % of the ions having an energy > 20 eV [24], and does consequently not compensate for the absence of a high substrate bias or reach the same energies as in typical arc evaporation experiments [25]. Hence, the key for achieving low-temperature α -alumina growth seems not to be just a high energetic bombardment, but rather bombardment within a suitable energy window. The same argument can be made based on other studies, where a too high substrate bias has been observed to cause a transition from α - back to γ -alumina growth [9]. The role of the energetic bombardment in low-temperature alumina growth is not known and is plausibly manifold. Possible suggestions include removal of impurities [26,27] promotion of diffusion processes [28], and stress and defect generation [28].

For example, it has been shown that residual water in the deposition chamber might compromise the α phase content of magnetron sputter deposited films [26] and that ion bombardment during growth can substantially reduce the H incorporation into the films [27]. Overall, the complete picture is not clear and in order to optimize deposition processes further, more investigations elucidating how different mechanisms affect low-temperature alumina growth are needed.

In conclusion, reactive HiPIMS has been used to deposit alumina thin films on cemented carbide and Mo substrates. α -alumina formed readily on both substrates at a temperature of 650 °C, both at floating substrate potential and with applied bias voltages of up to -100 V. The α -alumina films exhibited a preferred in-plane orientation of the c-axis and a plate-like microstructure, as deduced from XRD and SEM. This tendency was strongest for the film deposited at floating potential onto cemented carbide and less pronounced for the coatings deposited onto Mo and with applied substrate bias. Films deposited with bias were found to be slightly denser with wider platelets. Coatings deposited at 575 °C consisted of γ -alumina, whereas films grown at 500 °C or lower were x-ray amorphous. The synthesis route for α -Al₂O₃ coatings at moderate substrate temperatures demonstrated here may lead to improved performance of alumina coatings in existing applications through the suppression of unwanted temperature-effects, such as thermal cracks, in the films. In addition, it might open the possibility of utilizing α -alumina in novel applications, *e.g.*, involving heat-sensitive substrates.

Acknowledgements

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