

α -Cr₂O₃ template-texture effect on α -Al₂O₃ thin-film growth

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ABSTRACT

We employ textured α -Cr₂O₃ thin films as templates for growth of α -Al₂O₃ by reactive inductively coupled plasma magnetron sputtering. The texture of the template has a strong influence on the nucleation and growth of α -Al₂O₃. Extended growth of α -Al₂O₃ at a substrate temperature of 450 °C is obtained using a predominantly [10 $\bar{1}$ 4]-textured α -Cr₂O₃ template layer, while only limited α -Al₂O₃ nucleation is seen on a [0001]-textured α -Cr₂O₃ template.

Alumina, Al_2O_3 , is widely used since it exists in several polymorphs with very different properties. Metastable phases like γ -alumina are used in catalysis applications due to their high surface area.¹ The thermodynamically stable α phase is chemically inert with excellent mechanical properties, and is widespread in wear-resistant coating applications. In industry, α -alumina is typically deposited at substrate temperatures of ~ 1000 °C using chemical vapor deposition.^{2,3} Such high temperatures limit the choice of substrate, a fact that has led researchers to apply physical vapor deposition (PVD) to grow crystalline alumina at reduced temperatures. In conventional PVD, the depositing species are mainly neutrals; energetic bombardment is provided by sputtering-gas ions. Ionized PVD (I-PVD) techniques⁴ have a highly ionized deposition flux, offering control of the energy and the directionality of the depositing species by applied electric and magnetic fields. This approach has yielded low-temperature-deposited alumina films with higher crystallinity than for conventional PVD. However, below 700 °C the films typically comprise θ -, κ -, and/or γ -alumina rather than α .^{5,6} The nucleation of α - Al_2O_3 can be promoted by a crystallographic template such as α - Cr_2O_3 ,^{7,8} which is isostructural with α - Al_2O_3 and relatively easy to deposit at low temperature.⁹

Here, we demonstrate that the texture of the template influences the nucleation and growth of α - Al_2O_3 deposited by the I-PVD technique inductively coupled plasma magnetron sputtering (ICP-MS). Extended growth of α - Al_2O_3 at a substrate temperature of 450 °C is obtained using a predominantly $[10\bar{1}4]$ -textured α - Cr_2O_3 template, while only limited α - Al_2O_3 nucleation is seen on a $[0001]$ -textured α - Cr_2O_3 template.

Al_2O_3 and Cr_2O_3 thin films were deposited by reactive ICP-MS from elemental Al and Cr targets in a high-vacuum (base pressure $\leq 10^{-5}$ Pa) setup described elsewhere.¹⁰ The substrates were Si(001) ($15 \times 15 \text{ mm}^2$) with native oxide; bias was applied through an rf power supply. Cr_2O_3 template layers with predominant $[10\bar{1}4]$ and $[0001]$ textures¹¹ were deposited to a thickness of ~ 250 nm. Al_2O_3 was deposited to a thickness of ~ 350 nm (or $\sim 1.4 \mu\text{m}$ for samples used for nanoindentation¹²) at a working pressure of 0.80 Pa with partial pressures of Ar and O_2 (99.99990%) of 0.70 and 0.10 Pa, respectively. The rf coil power was 150 W, the substrate bias was -50 V (dc), and the substrate temperature was 450°C . Within the measurement accuracy, Rutherford backscattering spectroscopy showed that all films were stoichiometric Al_2O_3 and Cr_2O_3 . X-ray diffraction (XRD) measurements in θ - 2θ and grazing incidence (GI) geometry (10° incidence) were performed in a Bruker D8 diffractometer ($\text{CuK}\alpha$). XRD pole figures were acquired in the tilt-angle (χ) range $0 - 80^\circ$ and the azimuth-angle (φ) range $0 - 360^\circ$ with χ and φ steps of 2.5° . Scanning electron microscopy (SEM) was performed in a FEI NOVA 600 SEM with accelerating voltage 5 kV and working distance 5 mm. Transmission electron microscopy (TEM) was performed in a JEOL JEM 3000F TEM (300 kV).

Figures 1(a) and 1(b) show θ - 2θ X-ray diffractograms of (a) a $[10\bar{1}4]$ -textured α - Cr_2O_3 template and (b) Al_2O_3 deposited onto the template in (a). The θ - 2θ scans exhibit strong $10\bar{1}4$ peaks from α - Cr_2O_3 and α - Al_2O_3 , small $11\bar{2}6$ peaks and two barely visible peaks indicating other orientations or phases. GI-XRD (not shown) of this Al_2O_3 film showed mainly α - Al_2O_3 . However, small peaks from γ - Al_2O_3 could be detected; thus,

some γ phase is present and indicated in Fig 1(b). The inset in Fig. 1 shows a pole-figure plot of the α - Al_2O_3 $10\bar{1}4$ peak, essentially identical to the pole figure (not shown) of the α - Cr_2O_3 $10\bar{1}4$ peak for the pure Cr_2O_3 film in Fig. 1(a). These results prove that the α - Al_2O_3 layer follows the fiber texture of the template, i.e., for both α - Al_2O_3 and α - Cr_2O_3 , $[10\bar{1}4]$ is the predominant out-of-plane orientation, while the in-plane orientation is random. Figure 1(c) shows a θ - 2θ X-ray diffractogram of Al_2O_3 deposited onto a $[0001]$ -textured α - Cr_2O_3 template. Here, only a minor 0006 α - Al_2O_3 peak is present, and distinct peaks from γ - Al_2O_3 are observed. Thus, for Al_2O_3 films deposited *under otherwise identical conditions* onto α - Cr_2O_3 templates, the $[10\bar{1}4]$ -textured template promotes α - Al_2O_3 nucleation to a much higher extent than the $[0001]$ -textured template does.

Fig 2(a) shows a cross-section SEM image of α - Al_2O_3 deposited onto a $[10\bar{1}4]$ -textured α - Cr_2O_3 template (cf. Fig 1(b)). Fig 2(b) shows a cross-section TEM image of the same sample. The template exhibits a columnar structure. At the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ interface, it can be seen in both SEM and TEM that the columnar structure of the α - Cr_2O_3 continues into the Al_2O_3 layer. In agreement with XRD, electron diffraction (not shown) demonstrated that the template layer consisted of α - Cr_2O_3 and that the alumina layer was mainly α - with presence of some γ - and amorphous alumina. Figure 3(a) shows a representative high-resolution TEM image of the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ interface region, showing two adjacent α - Cr_2O_3 grains in the template (the regions (b) and (c) marked in Fig. 3(a) are shown magnified in Figs. 3(b) and 3(c), respectively). The observed lattice-plane

spacing d in the left grain corresponds to $\{10\bar{1}2\}$ planes ($d = 3.52 \text{ \AA}$ for $\alpha\text{-Al}_2\text{O}_3$ and 3.68 \AA for $\alpha\text{-Cr}_2\text{O}_3$), which likely means that, as expected from XRD, a plane of the $\{10\bar{1}4\}$ family is parallel to the surface (the angle between $(10\bar{1}4)$ and $(0\bar{1}12)$ is $\sim 81^\circ$). The lattice planes in the $\alpha\text{-Cr}_2\text{O}_3$ template continue in the $\alpha\text{-Al}_2\text{O}_3$ layer; this $\alpha\text{-Al}_2\text{O}_3$ grain was observed to continue throughout the film. The growth mode for the individual grain is a relaxed (local) heteroepitaxial growth as evidenced by XRD (Fig 1(b)). Relaxation occurs by the introduction of misfit dislocations at the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ interface; as shown in Fig. 3(c). On the other hand, for the $\alpha\text{-Cr}_2\text{O}_3$ grain on the right in Fig. 3(a), the lattice planes in the template terminate at a $[0001]$ -oriented facet at the interface,¹³ followed by amorphous (as verified by electron diffraction) Al_2O_3 .

The presence of $\gamma\text{-Al}_2\text{O}_3$ in the samples deposited onto $[0001]$ -oriented templates is evident (Fig. 1(c)); however, some $\gamma\text{-Al}_2\text{O}_3$ was detected also in $[10\bar{1}4]$ -textured samples where Al_2O_3 was mainly in α form. In the latter case, $[10\bar{1}4]$ is the dominant *but not the only* orientation. This fact further supports the interpretation that Al_2O_3 nucleates in α form on $(10\bar{1}4)$ Cr_2O_3 planes but not on, e.g., (0001) surfaces. The formation of amorphous Al_2O_3 enables renucleation of $\gamma\text{-Al}_2\text{O}_3$, since the deposition conditions then correspond to growth onto effectively amorphous substrates. Under these conditions, Al_2O_3 is predominantly amorphous but with small ($\sim 5 \text{ nm}$) γ grains, as shown in our previous work.¹⁰

Our results seemingly contradict theoretical studies, where density functional theory (DFT) calculations have suggested that the most suitable α -Cr₂O₃ surfaces for promoting α -Al₂O₃ growth should be the low-energy surfaces {0001}, {10 $\bar{1}$ 2}, and {11 $\bar{2}$ 0},^{14,15,16} This explanation is unlikely here since our findings demonstrate that α -Al₂O₃ readily nucleates and grows onto a [10 $\bar{1}$ 4]-textured template (not a low-energy surface) but only to a minor extent onto [0001]-textured template. However, these DFT studies assume *pure* surfaces. A more plausible explanation for the texture effect we observe is differences in impurity adsorption on different surfaces. Hydrogen (e.g., from residual water vapor) is known to affect the growth of alumina¹⁷ and DFT calculations of hydrogen adsorption onto the Al₂O₃(0001) surface¹⁸ have demonstrated that hydrogen impedes adsorption of Al into its bulk positions. Further, homoepitaxial growth of α -Al₂O₃ has been demonstrated by low-temperature molecular beam epitaxy onto *clean* α -Al₂O₃(0001), (10 $\bar{1}$ 2), and (11 $\bar{2}$ 0) surfaces.¹⁹

Based on our results and the literature discussed above, we propose that the reason for the influence of the template texture on the nucleation and growth of α -Al₂O₃ is differences in adsorption of impurities – probably especially hydrogen – onto different surfaces. To test this hypothesis, theoretical studies investigating impurity adsorption on a range of different alumina and chromia surfaces and experimental studies with growth onto single-crystal substrates are required.

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- ¹⁰ M. Sridharan, M. Sillassen, J. Bøttiger, J. Chevallier, and H. Birkedal *Surf. Coat. Technol.* **202**, 920 (2007).
- ¹¹ The parameters for the template layers were 100 W rf coil power, -50 V dc bias, and 30° (off-normal) angle between target and substrate for the [1014]-textured template; no rf coil power, floating potential, and substrate directly facing the target (0° angle) for the [0006]-textured template. The chamber was vented between Cr₂O₃ and Al₂O₃ depositions.
- ¹² Nanoindentation was done using a TriboIndenter (Hysitron Inc) with a Berkovich tip. 100 indents in the load range 1 – 10 mN were made for each sample; the hardness, H , and reduced elastic modulus, E_r , were determined according to the Oliver-Pharr procedure. The H and E_r values were determined to $H = 25 \pm 3$

GPa, $E_r = 230 \pm 20$ GPa for the $[10\bar{1}4]$ -textured Al_2O_3 and $H = 24 \pm 3$ GPa, $E_r = 230 \pm 20$ GPa for Al_2O_3 deposited onto a $[0001]$ -textured template. In comparison, the values for a 1.2- μm thick $[10\bar{1}4]$ -textured α - Cr_2O_3 , deposited with the same parameters as the one in Fig. 1(a), were $H = 29 \pm 3$ GPa and $E_r = 250 \pm 20$ GPa.

¹³ The plane spacing of $d = 2.67$ Å marked in Fig. 3(b) corresponds to $(10\bar{1}4)$ planes of α - Cr_2O_3 . The angle between these $(10\bar{1}4)$ planes and the facet is 38° , which corresponds to the angle between $(10\bar{1}4)$ and (0001) planes.

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FIGURE CAPTIONS

FIG. 1. θ - 2θ X-ray diffractograms of (a) a $[10\bar{1}4]$ -textured α - Cr_2O_3 template, (b) Al_2O_3 deposited onto the template in (a), and (c) Al_2O_3 deposited onto a $[0001]$ -textured α - Cr_2O_3 template. Inset: pole figure of the $10\bar{1}4$ peak for the sample in (b).

FIG. 2. (a) Cross-section SEM image of α - Al_2O_3 deposited onto a $[10\bar{1}4]$ -textured α - Cr_2O_3 template (cf. Fig 1(b)). (b) Cross-section TEM image of the same sample.

FIG. 3. (a) HRTEM image of the α - Cr_2O_3 / Al_2O_3 interface region. (b) and (c) Magnifications of the areas marked in (a). Misfit dislocation indicated by T symbol in (c).