Localized epitaxial growth of $\alpha$-Al$_2$O$_3$ thin films on Cr$_2$O$_3$ template by sputter deposition at low substrate temperature

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Low-temperature growth of $\alpha$-Al$_2$O$_3$ films by sputtering was studied with x-ray diffraction and high-resolution transmission electron microscopy (HRTEM). Pure $\alpha$-Al$_2$O$_3$ film was formed at 400 °C using Cr$_2$O$_3$ as template, whereas amorphous or $\theta$-Al$_2$O$_3$ was formed without Cr$_2$O$_3$. HRTEM revealed localized epitaxial growth of $\alpha$-Al$_2$O$_3$ on Cr$_2$O$_3$ with the relationship $[011]_{\text{Al}_2\text{O}_3}/[011]_{\text{Cr}_2\text{O}_3}$, suggesting the importance of Cr$_2$O$_3$ as a structural template for the growth of $\alpha$-Al$_2$O$_3$, in addition to other contributions such as good stoichiometry, low sputter pressure, and low deposition rate under optimized deposition conditions. Successful growth of $\alpha$-Al$_2$O$_3$ by sputtering at 400 °C or below makes the film widely applicable to even glass substrates. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544442]

The Al$_2$O$_3$ crystal is one of the hardest oxides with a high melting point, superior chemical stability, and good mechanical strength particularly at high temperatures. Thin films of Al$_2$O$_3$ have been used as wear resistant and protective coatings. In addition, Al$_2$O$_3$ is highly insulating and transparent with convenient refractive index value feasible for microelectronic and optical applications. The Al$_2$O$_3$ crystal exists in several polymorphs, i.e., the metastable $\gamma$, $\delta$, $\eta$, $\theta$, $\kappa$, and $\chi$, in addition to the thermodynamically stable $\alpha$-Al$_2$O$_3$ which is the most common and most excellent in property. However, the conventional formation of $\alpha$-Al$_2$O$_3$ films usually requires a high substrate temperature, e.g., approximately 1000 °C for chemical vapor deposition. High-temperature requirements severely limit the number of usable substrate materials and, therefore, the application range for $\alpha$-Al$_2$O$_3$ thin films. Recent developments in sputter deposition of crystalline Al$_2$O$_3$ at a low substrate temperature have been made through an increase in the ionization ratio in ionized sputtering, or in combination with a highly enhanced power density in pulsed dc sputtering. Such methods have concentrated mainly in increasing the energy and activity of the sputtered species to overcome the energy barrier required for the formation of $\alpha$-Al$_2$O$_3$. Con sequently, they are effective to some extent as can be seen from the most recent result reporting the formation of pure $\alpha$-Al$_2$O$_3$ films at 760 °C by pulsed dc sputtering. On the other hand, the formation of $\alpha$-Al$_2$O$_3$ at room temperature using homoepitaxy with the molecular-beam epitaxy method has been reported, strongly suggesting the importance of the substrate crystal structure itself in addition to an optimized deposition condition.

In this letter, we report an approach to low-temperature growth of $\alpha$-Al$_2$O$_3$ by sputtering using a thin layer of Cr$_2$O$_3$, which crystallizes isostructurally to $\alpha$-Al$_2$O$_3$ with less than 5% in lattice mismatches, as a structural template. The localized epitaxial growth of $\alpha$-Al$_2$O$_3$ on Cr$_2$O$_3$ was demonstrated with high-resolution transmission electron microscopy (HRTEM) characterization.

Thin-film formation was done with a rf magnetron sputtering system. The sputter system was equipped with two ceramic targets ($d = 50$ mm and 99.99% pure) of Al$_2$O$_3$ and Cr$_2$O$_3$ positioned at 30° inclination to the substrate center with a target-to-substrate distance of 150 mm. The Si (100) substrates without the removal of natural oxide were clamped on a rotatable Inconel plate with temperature control by lamp heating from the back side. The precise substrate temperature reading was calibrated using another thermocouple directly attached to a dummy Si sheet. The deposition system was evacuated to a background pressure of $2 \times 10^{-6}$ Pa, and pure Ar (99.9995%) gas was introduced near the target surface at a flow rate of 5.5 sccm providing a total pressure of 0.1 Pa. Thin films of Al$_2$O$_3$ on Cr$_2$O$_3$ template were formed by subsequently sputtering the relevant ceramic targets of Cr$_2$O$_3$ and Al$_2$O$_3$ at a rf power of 150 W without breaking the vacuum. Films of Al$_2$O$_3$ were also deposited directly on bare Si under the same condition for comparison. The described conditions resulted in deposition rates, independent of substrate temperature, of 0.6 and 1.0 nm/min for Cr$_2$O$_3$ and Al$_2$O$_3$, respectively.

The crystal structure was studied using thin-film x-ray diffraction (XRD) with a Rigaku XRD system using Cu $K\alpha$ at 40 kV and 25 mA at a fixed incident angle of 2° with sample rotation. The microstructure of the deposited films, particularly that at the Al$_2$O$_3$/Cr$_2$O$_3$ interface, was studied with cross-sectional HRTEM. Preparation of transmission electron microscopy specimens was done conventionally by mechanical polishing using wedge techniques followed by 3.5 keV Ar ion milling. The HRTEM images were made on a JEOL 4000EX electron microscope operated at 400 keV.

The significant effect of the Cr$_2$O$_3$ template on low-temperature growth of $\alpha$-Al$_2$O$_3$ was demonstrated with the
XRD patterns of Al₂O₃ films (~200 nm in thickness) deposited at various temperatures on Si without template (Fig. 1) and with a ~60 nm Cr₂O₃ template (Fig. 2). In Fig. 1, the film on bare Si exhibits an amorphous feature at room temperature, and shows a few broad peaks at elevated temperatures, suggesting the formation of certain crystalline phases. However, there is no trace of α-Al₂O₃ formation up to 600 °C, and the broad XRD peaks can most probably attributed to υ-Al₂O₃. On the other hand, the Al₂O₃ films formed on Cr₂O₃ template on Si show dramatically different behavior. The XRD pattern in Fig. 2 at room temperature shows broad peaks from the crystalline Cr₂O₃ template, and the peak intensity increases with the increasing substrate temperature. The formation of crystalline Cr₂O₃ at a low temperature suggests the feasibility of Cr₂O₃ as a crystallographic template for α-Al₂O₃ growth. As the result, the growth of α-Al₂O₃ single phase on Cr₂O₃ at 400 °C, which is an extremely low temperature for sputtered α-Al₂O₃ films, was confirmed by the XRD patterns in Figs. 2(c) and 2(d), in which the JCPDS standards for α-Al₂O₃ and Cr₂O₃ are, respectively, displayed for identification.

HRTEM study was done on the film deposited at 600 °C for better crystallinity with much attention devoted to the α-Al₂O₃/Cr₂O₃ interface. A cross-sectional overview of α-Al₂O₃/Cr₂O₃ on Si is shown with the bright-field TEM image in Fig. 3(a). The image in Fig. 3(a) demonstrates distinctly in sequence the Si substrate with a 3 nm amorphous oxide layer, a 62 nm Cr₂O₃ template layer, and a 185 nm Al₂O₃ top layer. The amorphous oxide on Si diminishes the influence of Si lattice on the growth of Cr₂O₃, suggesting the universality of the template to other substrate materials such as the polycrystalline materials or glass. Both Cr₂O₃ and Al₂O₃ exhibit a dense structure with quite a flat and sharp interface in between. It is noticed that no significant columnar structure, which is usually observed for most of the sputtered films, is seen due presumably to the very low sputter pressure (0.1 Pa). Low sputter pressure results in a small number of particle collisions, by which much of the initial energy from the sputtered particles is maintained to bombard the growing film surface, leading to the destruction of columnar growth.

Detailed observations were done on several areas indicated in Fig. 3(a), i.e., the Cr₂O₃ template [Fig. 3(b)], the Al₂O₃/Cr₂O₃ interface [Fig. 3(c)], and the Al₂O₃ film [Fig. 3(d)]. Figure 3(b) shows a HRTEM image of the Cr₂O₃ template with the selected area electron diffraction (SAD) pattern as an inset. The HRTEM image demonstrates a well defined crystal lattice, and the imaged area exhibits a strong preferred orientation which can be identified as Cr₂O₃ [1 1 1] from the lattice spacings and the spotlike SAD pattern. The single-crystallinelike structure of the Cr₂O₃ film, at least within localized areas, and the crystallographic similarity to α-Al₂O₃, suggests the great possibility as a template for α-Al₂O₃ growth.
shown in Fig. 3(c). The relevant lattice spacings were calculated and identified in Fig. 3(c). We express such growth, i.e., the preferential growth of $\alpha$-$\text{Al}_2\text{O}_3$ lattice as the extension of crystal structure of $\text{Cr}_2\text{O}_3$ grains, as “localized epitaxial growth” which contributes greatly to the low-temperature growth. There exists a free-energy barrier for nucleation of a film material, which differs from materials or from the poly-morphs for $\text{Al}_2\text{O}_3$. It was known that the physical vapor deposition of $\text{Al}_2\text{O}_3$ films undergoes a phase transformation from amorphous through a $\gamma$, $\theta$ or $\delta$ phase (or their mixture) finally to the thermodynamically stable $\alpha$-$\text{Al}_2\text{O}_3$ which should have the highest free-energy barrier for nucleation and growth. Efforts have recently been made for sputter deposition of $\alpha$-$\text{Al}_2\text{O}_3$ at a low temperature by increasing the ionization ratio of sputtered species or in combination with a highly enhanced power density in pulsed dc sputtering. In other words, much attention has been paid mainly to increasing the energy and activation of the sputtered species to overcome the energy barrier required for the formation of $\alpha$-$\text{Al}_2\text{O}_3$. The most recent development reported the formation of $\alpha$-$\text{Al}_2\text{O}_3$ at 760°C by pulsed dc sputtering. In this study, an approach was made to reduce the energy barrier for $\alpha$-$\text{Al}_2\text{O}_3$ nucleation and growth by providing suitable crystallographic sites using $\text{Cr}_2\text{O}_3$ as a structural template, similarly to homoepitaxy, in contrast to the reported methods by increasing only the energy and activation of the sputtered species. The $\text{Cr}_2\text{O}_3$ (Eskolite: $a_0 = 0.495$ nm and $c_0 = 1.360$ nm) is isostructural to $\alpha$-$\text{Al}_2\text{O}_3$ ($a_0 = 0.476$ nm and $c_0 = 1.299$ nm) with lattice mismatches of 4.0% and 4.7% for the a and c axes, respectively. As a result, the use of the $\text{Cr}_2\text{O}_3$ template was very successful for the low-temperature growth of $\alpha$-$\text{Al}_2\text{O}_3$ at 400°C or even below. The use of structural templates, in combination with optimized conditions such as the guarantee of near stoichiometry under a stable sputter process by use of an $\text{Al}_2\text{O}_3$ ceramic target, a low sputter pressure (0.1 Pa) to produce high energy species, and a low deposition rate resulting in sufficient surface diffusion distances for adatoms (or molecules) to allow the formation of $\alpha$-$\text{Al}_2\text{O}_3$, might be one of the most effective ways for the low-temperature growth of $\alpha$-$\text{Al}_2\text{O}_3$. Sputter formation of $\alpha$-$\text{Al}_2\text{O}_3$ films at 400°C or below will undoubtedly expand the application range to even glass substrate materials.

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