Localized epitaxial growth of α-Al_2O_3 thin films on Cr_2O_3 template by sputter deposition at low substrate temperature

P. Jin[a)] and S. Nakao
National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya, 463-8560 Japan

S. X. Wang[b)] and L. M. Wang
Department of Nuclear Engineering and Radiological Science, The University of Michigan, Ann Arbor, Michigan 48109

(Received 14 October 2002; accepted 17 December 2002)

Low-temperature growth of α-Al_2O_3 films by sputtering was studied with x-ray diffraction and high-resolution transmission electron microscopy (HRTEM). Pure α-Al_2O_3 film was formed at 400 °C using Cr_2O_3 as template, whereas amorphous or θ-Al_2O_3 was formed without Cr_2O_3. HRTEM revealed localized epitaxial growth of α-Al_2O_3 on Cr_2O_3 with the relationship $[011]_{Al_2O_3}/[011]_{Cr_2O_3}$, suggesting the importance of Cr_2O_3 as a structural template for the growth of α-Al_2O_3, in addition to other contributions such as good stoichiometry, low sputter pressure, and low deposition rate under optimized deposition conditions. Successful growth of α-Al_2O_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_2O_3 crystal is one of the hardest oxides with a high melting point, superior chemical stability, and good mechanical strength particularly at high temperatures.[1] Thin films of Al_2O_3 have been used as wear resistant and protective coatings.[2] In addition, Al_2O_3 is highly insulating and transparent with convenient refractive index value feasible for microelectronic and optical applications.[3–7] The Al_2O_3 crystal exists in several polymorphs, i.e., the metastable γ, δ, η, θ, κ, and χ, in addition to the thermodynamically stable α-Al_2O_3 which is the most common and most excellent in property.[1,8] However, the conventional formation of α-Al_2O_3 films usually requires a high substrate temperature, e.g., approximately 1000 °C for chemical vapor deposition.[9] High-temperature requirements severely limit the number of usable substrate materials and, therefore, the application range for α-Al_2O_3 thin films. Recent developments in sputter deposition of crystalline Al_2O_3 at a low substrate temperature have been made through an increase in the ionization ratio in ionized sputtering,[9,10] or in combination with a highly enhanced power density in pulsed dc sputtering.[9] 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 α-Al_2O_3. Consequently, they are effective to some extent as can be seen from the most recent result reporting the formation of pure α-Al_2O_3 films at 760 °C by pulsed dc sputtering.[9] On the other hand, the formation of α-Al_2O_3 at room temperature using homoepitaxy with the molecular-beam epitaxy method has been reported,[11,12] 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 α-Al_2O_3 by sputtering using a thin layer of Cr_2O_3, which crystallizes isostructually to α-Al_2O_3 with less than 5% in lattice mismatches, as a structural template. The localized epitaxial growth of α-Al_2O_3 on Cr_2O_3 was demonstrated with high-resolution transmission electron microscopy (HRTEM) characterization.

Thin-film formation was done with a rf magnetron sputtering system.[13] The sputter system was equipped with two ceramic targets (d = 50 mm and 99.99% pure) of Al_2O_3 and Cr_2O_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 2×10^{-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_2O_3 on Cr_2O_3 template were formed by subsequently sputtering the relevant ceramic targets of Cr_2O_3 and Al_2O_3 at a rf power of 150 W without breaking the vacuum. Films of Al_2O_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_2O_3 and Al_2O_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_2O_3/Cr_2O_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_2O_3 template on low-temperature growth of α-Al_2O_3 was demonstrated with the

a)Electronic mail: p-jin@aist.go.jp
b)Present address: Micron Technology, Inc., Boise, ID 83707.

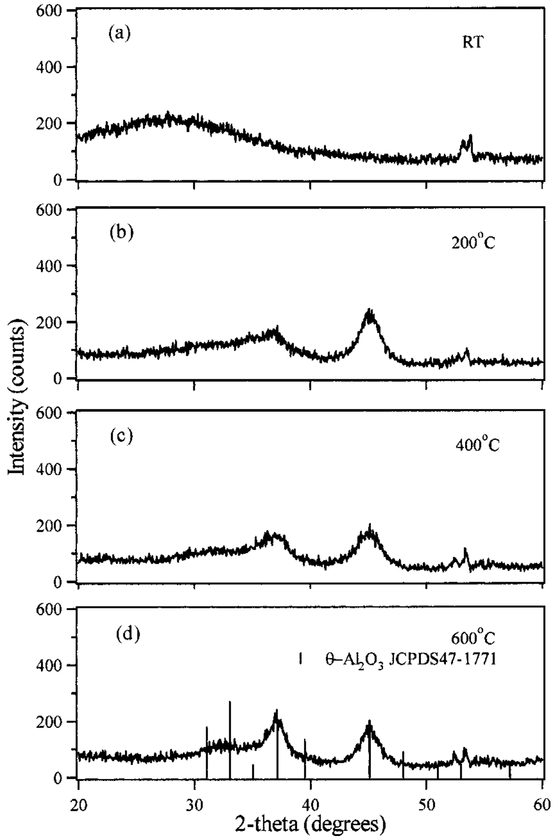

FIG. 1. XRD patterns of Al_2O_3 films (~200 nm in thickness) deposited at various temperatures on Si without template.

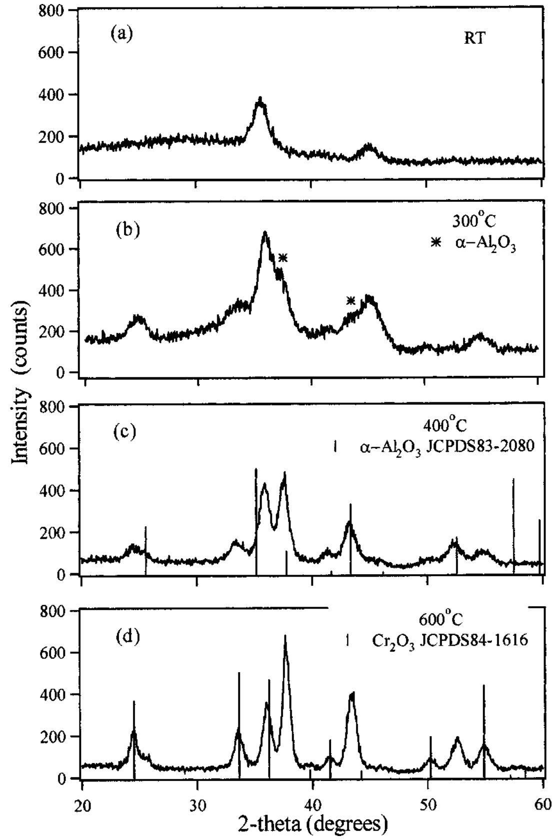

FIG. 2. XRD patterns of Al_2O_3 films (~200 nm in thickness) deposited at various temperatures on Si with ~60 nm Cr_2O_3 as a structural template.

XRD patterns of Al_2O_3 films (~200 nm in thickness) deposited at various temperatures on Si without template (Fig. 1) and with a ~60 nm Cr_2O_3 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-Al_2O_3 formation up to 600 °C, and the broad XRD peaks can most probably attributed to θ-Al_2O_3. On the other hand, the Al_2O_3 films formed on Cr_2O_3 template on Si show dramatically different behavior. The XRD pattern in Fig. 2(a) at room temperature shows broad peaks from the crystalline Cr_2O_3 template, and the peak intensity increases with the increasing substrate temperature. The formation of crystalline Cr_2O_3 at a low temperature suggests the feasibility of Cr_2O_3 as a crystallographic template for α-Al_2O_3 growth. As the result, the growth of α-Al_2O_3 single phase on Cr_2O_3 at 400 °C, which is an extremely low temperature for sputtered α-Al_2O_3 films, was confirmed by the XRD patterns in Figs. 2(c) and 2(d), in which the JCPDS standards for α-Al_2O_3 and Cr_2O_3 are, respectively, displayed for identification. In fact, there is already a trace of α-Al_2O_3 formation evident at around 300 °C by looking carefully at Fig. 2(b), in which the star markers correspond to α-Al_2O_3 (110) at $2\theta = 37.7°$ and (113) at $2\theta = 43.4°$, respectively.

HRTEM study was done on the film deposited at 600 °C (for better crystallinity) with much attention devoted to the α-Al_2O_3/Cr_2O_3 interface. A cross-sectional overview of α-Al_2O_3/Cr_2O_3 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 Cr_2O_3 template layer, and a 185 nm Al_2O_3 top layer. The amorphous oxide on Si diminishes the influence of Si lattice on the growth of Cr_2O_3, suggesting the universality of the template to other substrate materials such as the polycrystalline materials or glass. Both Cr_2O_3 and Al_2O_3 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 Cr_2O_3 template [Fig. 3(b)], the Al_2O_3/Cr_2O_3 interface [Fig. 3(c)], and the Al_2O_3 film [Fig. 3(d)]. Figure 3(b) shows a HRTEM image of the Cr_2O_3 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 Cr_2O_3 $[\bar{1}1\bar{1}]$ from the lattice spacings and the spotlike SAD pattern. The single-crystallinelike structure of the Cr_2O_3 film, at least within localized areas, and the crystallographic similarity to α-Al_2O_3, suggests the great possibility as a template for α-Al_2O_3 growth.

As expected, epitaxial growth of α-Al_2O_3 film on Cr_2O_3 template was observed at the Al_2O_3/Cr_2O_3 interface as

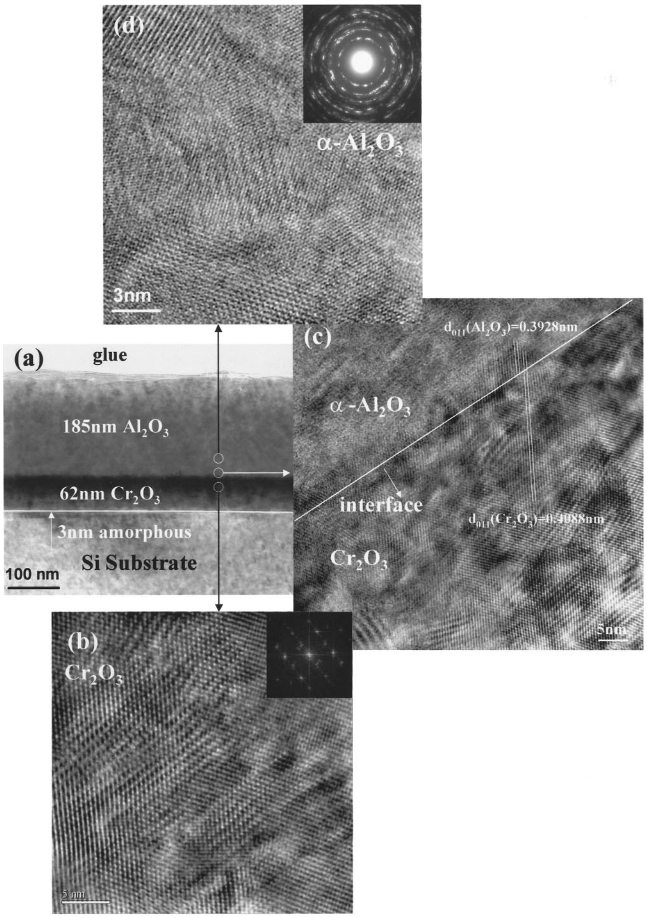

FIG. 3. HRTEM images of the cross-sectional overview of α-Al_2O_3/Cr_2O_3 on Si (a), the Cr_2O_3 template with SAD pattern (b), the α-Al_2O_3/Cr_2O_3 interface (c), and the α-Al_2O_3 top layer with SAD pattern (d). Localized epitaxial growth of α-Al_2O_3 on Cr_2O_3 at the interface with $[011]_{\alpha\text{-}Al_2O_3}//[011]_{Cr_2O_3}$ was identified in (c).

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 α-Al_2O_3 lattice as the extension of crystal structure of Cr_2O_3 grains, as ''localized epitaxial growth'' which contributes greatly to the low-temperature growth of a pure α-Al_2O_3. It was further identified from the image that the localized epitaxy exhibits a growth relationship with $[011]_{\alpha\text{-}Al_2O_3}//[011]_{Cr_2O_3}$, as a reasonable result of the great similarity of the two materials in crystal structure.

Figure 3(d) shows an HRTEM image of the Al_2O_3 top layer with the SAD pattern as an inset. The HRTEM image demonstrates a polycrystalline microstructure. The SAD image exhibits a ring pattern typical of a polycrystalline film, and the pattern was identified as that of α-Al_2O_3. The HRTEM observation confirmed the formation of a well-crystallized polycrystalline α-Al_2O_3 film grown on the Cr_2O_3 template.

The elementary process for sputter deposition can be considered as the phase transformation of sputtered species from vapor to adherent states at the substrate surface, with the process of film formation via crystallite nucleation and growth. There exists a free-energy barrier for nucleation of a film material, which differs from materials or from the polymorphs for Al_2O_3. It was known that the physical vapor deposition of Al_2O_3 films undergoes a phase transformation from amorphous through a γ-, θ- or δ-phase (or their mixture) finally to the thermodynamically stable α-Al_2O_3 which should have the highest free-energy barrier for nucleation and growth.[1] Efforts have recently been made for sputter deposition of α-Al_2O_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.[9,10] 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 α-Al_2O_3. The most recent development reported the formation of α-Al_2O_3 at 760 °C by pulsed dc sputtering.[9] In this study, an approach was made to reduce the energy barrier for α-Al_2O_3 nucleation and growth by providing suitable crystallographic sites using Cr_2O_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 Cr_2O_3 (Eskolaite: $a_0 = 0.495$ nm and $c_0 = 1.360$ nm) is isostructural to α-Al_2O_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 Cr_2O_3 template was very successful for the low-temperature growth of α-Al_2O_3 at 400 °C or even below. The use of structural templates, in combination with optimized conditions such as the guarantee of near stroichiometry under a stable sputter process by use of an Al_2O_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 α-Al_2O_3, might be one of the most effective ways for the low-temperature growth of α-Al_2O_3. Sputter formation of α-Al_2O_3 films at 400 °C or below will undoubtedly expand the application range to even glass substrate materials.

The authors acknowledge the Science and Technology Agency of Japan for financial support, and Professor U. Helmersson and Professor J. M. Schneider for useful discussions. Electron microscopy was conducted at the Electron Microbeam Analysis Laboratory at the University of Michigan.

[1] T. C. Chou, T. G. Nieh, S. D. McAdams, and G. M. Pharr, Scr. Metall. Mater. **25**, 2203 (1991).
[2] C. Deshpandey and L. Holland, Thin Solid Films **96**, 265 (1982).
[3] B. Hirschauer, S. Söderholm, G. Chiaia, and U. O. Karlsson, Thin Solid Films **305**, 243 (1997).
[4] K. K. Shih and D. B. Dove, J. Vac. Sci. Technol. A **12**, 321 (1994).
[5] M. Yoshimoto, T. Maeda, T. Ohnishi, and H. Koinuma, Appl. Phys. Lett. **67**, 2615 (1995).
[6] Q. Y. Zhang, P. S. Wang, W. J. Zhao, and L. Wang, Surf. Coat. Technol. **128**, 121 (2000).
[7] G. Este and W. D. Westwood, J. Vac. Sci. Technol. A **2**, 1238 (1984).
[8] P. Liu and J. Skogsmo, Acta Crystallogr., Sect. B: Struct. Sci. **47**, 425 (1991).
[9] O. Zywistzki and G. Hoetzsch, Surf. Coat. Technol. **86**, 640 (1996).
[10] J. M. Schneider and W. D. Sproul, J. Vac. Sci. Technol. A **15**, 1084 (1997).
[11] T. Maeda, M. Yoshimoto, T. Ohnishi, G. Lee, and H. Koinuma, J. Cryst. Growth **177**, 95 (1997).
[12] D. Ashenford, F. Long, W. Hagston, B. Lunn, and A. Matthews, Surf. Coat. Technol. **116**, 699 (1999).
[13] P. Jin, G. Xu, M. Tazawa, K. Yoshimura, D. Music, J. Alami, and U. Helmersson, J. Vac. Sci. Technol. A **20**, 2134 (2002).