High-quality thin single-crystal $\gamma$-Al$_2$O$_3$ films grown on Si (111)

S. Y. Wu, M. Hong,$^{a}$ A. R. Kortan, J. Kwo,$^{b}$ J. P. Mannaerts, W. C. Lee, and Y. L. Huang
Department of Materials Science and Engineering, National Tsing Hua University, Hsin Chu, Taiwan

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Single-crystal Al$_2$O$_3$ films have been epitaxially grown on Si (111) substrates despite a lattice mismatch of more than 30%. The oxide was electron-beam evaporated from a high-purity sapphire source. The structural and morphological studies carried out by x-ray diffraction, x-ray reflectivity, atomic force microscopy, and transmission electron microscopy, with the initial epitaxial growth observed in situ reflection high-energy electron diffraction show that the oxide films thin as 3.8 nm have the cubic $\gamma$-phase with a very uniform thickness and a high structural perfection. The film surface is very smooth with a roughness of 0.12 nm and the oxide/Si interface is atomically sharp. The $\gamma$-Al$_2$O$_3$ films are well aligned with Si substrate with an orientation relationship of Si(111)//Al$_2$O$_3$(222), Si[220]//Al$_2$O$_3$[440].

Heteroepitaxial growth between insulators and semiconductors is always fascinating in science and important in technology. For example, growth of single-crystal GaN on sapphire$^1$ has been essential for producing blue lasers and light-emitting diodes (LEDs), which may provide a basis for the future lighting industry. Epitaxial growth of insulators on Si is another example, which may find applications in high-k dielectrics for the Si industry.$^2$–$^4$ An urgent technological issue is a subsequent single-crystalline growth of other semiconductors such as GaN (Ref. 5) or GaAs on these single-crystal insulators may integrate high-power microwave devices or lasers with the most advanced Si-based electronic devices.

Single-crystal $\gamma$-Al$_2$O$_3$ films were reported to grow on Si (111) with mixed-sources molecular-beam epitaxy (Al–N$_2$O MBE).$^5$ To obtain higher-quality Al$_2$O$_3$ films, an Al layer thickness was predeposited at room temperature on very thin SiO$_2$ chemically formed on Si surface.$^5$ Then, the substrate temperature was elevated to 800 °C to form an alumina template by the reaction between the predeposited Al and SiO$_2$. A $\gamma$-Al$_2$O$_3$ layer of 4 nm thickness was then grown using the MBE on the template at 800 °C. The claim on obtaining the $\gamma$-Al$_2$O$_3$ films was solely based on the observation and analysis of the reflection high-energy electron diffraction (RHEED) patterns of Al$_2$O$_3$ and Si. For thick Al$_2$O$_3$ films (260 nm in thickness) deposited on Si (111) using Al–N$_2$O MBE, with x-ray diffraction Zborowski et al.$^5$ concluded that their films are polycrystalline and have the cubic structure of $\gamma$-Al$_2$O$_3$ with a lattice constant of $a_0=7.91$ Å. However, the crystallographic information on the thin Al$_2$O$_3$ films using x-ray diffraction and/or transmission electron diffraction has not been given.

The structural quality of single-crystal Al$_2$O$_3$ film grown on Si depends on the initial stage of the growth. It is, therefore, not only interesting but also imperative to probe the Al$_2$O$_3$ films in thin thickness and to give them a definitive crystallographic structure.

In this work, we report the attainment of very high-quality cubic $\gamma$-Al$_2$O$_3$ single crystal films with thickness as thin as 3.8 nm. The crystallographic structure of the thin film was determined using high-resolution x-ray diffraction as well as transmission electron diffraction from the plan- and cross-sectional views. The oxide films have (111) as the normal in parallel with (111) of the Si substrate and the films have [4 4 0] in-plane axis in parallel with [2 2 0] of the Si substrate. The rocking scans at $\gamma$-Al$_2$O$_3$ (222) position of films 3.8 and 11 nm shows a low full width at half maximum (FWHM) of 0.6° and 0.3°, indicative of a single-crystal oxide film. Atomic force microscopy (AFM) and x-ray reflectivity all show a very smooth surface about 0.1–0.2 nm. The oxide/Si interface is also atomically smooth of 0.1–0.2 nm as studied using x-ray reflectivity and cross-sectional transmission electron microscopy (TEM).

In contrast to the previous efforts$^5$–$^7$ using MBE with precursors or gases, a high-purity sapphire (purchased from Maintech, Huntingdon, PA, with a purity of 99.99%) was employed in this work. Electron-beam evaporation was used due to the high melting point of sapphire, and the deposited species (incoming flux) consist of only Al$_2$O$_3$ molecules or clusters. In the latter case, issues such as gas (N$_2$O) etching Si substrate caused serious problems for the epitaxial growth. Si wafers 2 in. in diameter with (111) as the normal to the wafer plane were put into a multichamber MBE/ultrahigh vacuum (UHV) system$^2$, after being cleaned with a Radio Corporation of America (RCA) method and an HF dip. Heating the Si wafers to temperatures above ~550 °C has resulted in a sharp streaky $7\times7$ RHEED pattern with Kikuchi arcs [Fig. 1(a)], indicative of the attainment of a clean surface of Si substrate. The wafers were then transferred under an UHV (hence, any possibility of Si oxidation was eliminated) to an oxide chamber for the Al$_2$O$_3$ deposition. During the oxide deposition, the vacuum in the chamber was maintained in the low 10$^{-9}$ Torr (even with the evaporation of sapphire) and substrate temperatures were maintained at about 700–750 °C. Streaky oxide RHEED patterns along the in-plane axes of [1 1 0] and [1 1 2] [shown in Fig. 1(b)] of Si were observed after growth of oxide 1 nm thick, indicating that a smooth single crystal $\gamma$-Al$_2$O$_3$ film formed on the Si (111) and with in-plane alignment between the oxide film and Si substrate. Single-crystal x-ray measurements were carried out on a four-circle triple-axes diffractometer, using a 12 kW rotating anode Cu K$\alpha$-alpha source. A pair of graphite crystals is used...
to monochromatize and analyze the x-ray beam with a resolution of 0.01 Å⁻¹ along the longitudinal and 0.005 Å⁻¹ along the transverse directions, respectively. We have intentionally chosen this low resolution in order to increase the sensitivity to very thin films. The TEM sample analytical equipment was used for the metal-oxide-semiconductor (MOS) measurements.

A single-crystal x-ray theta-two-theta scan along substrate surface of Si (111) on the oxide film 3.8 nm thick is shown in Fig. 2. Aside from the strong peaks of Si substrate [Si(1/2 1/2 1/2), (111), and (3/2 3/2 3/2)], a broad peak near 40° coincides with the (222) reflection of the cubic gamma phase of Al₂O₃. The broadness of the peak is caused by the thin thickness of the oxide films. In fact, the rocking scan at the γ-Al₂O₃ (222) peak position, as shown in the inset of Fig. 2, exhibits a FWHM of 0.6°. This is a good indication that indeed the film is a single crystal. Our instrument resolution for this mosaic scan is determined from the rocking scan of the nearby Si(3/2 3/2 3/2) peak, which displays a FWHM of 0.14°. This Si peak can only be seen at high sensitivity and is probably caused by a small superlattice ordering of the Si (111) layers.

The relatively strong oscillation at small angle reflectivity on all of our oxide films grown on Si (111) indicates that the film thickness is highly uniform and smooth. Note that the intensity measurement covers eight orders of magnitude, and shows our improved sensitivity to small signals. From the decay of intensity and the periodic oscillation of the collected signal (at small angle region), the oxide thickness and surface roughness were calculated to be about 3.8 nm and 0.13 nm.

The surface morphology of the oxide films was routinely studied by AFM. From the observation of AFM measurement on the film 3.8 nm thick (shown in Fig. 3), the root-mean-square (rms) surface roughness was 0.126 nm, in agreement with the measured value using x-ray reflectivity. Note that the substrate cleaning using the RCA method and the HF dip is, indeed, effective in ensuring a smooth surface and interface. For example, the interface of a sample 7 nm thick was rougher of about 0.9 nm, which is due to the lacking of the substrate cleaning prior to the oxide growth.

The single-crystalline nature of the γ-Al₂O₃ film is further studied by scans along the major zone axes in reciprocal lattice. Figure 4 shows such a scan along the (00L) direction. We find that γ-Al₂O₃ (004) peak lies on the same zone axis with the Si (004) reflection, proving that the film is single crystalline and is aligned with the Si (111).

The FWHM of γ-Al₂O₃ (222) peak position of a thicker film (11 nm) was decreased to 0.3°, which means that the film quality was getting better when the film thickness was increased. These also indicated that the structural imperfections near the substrate interface appear to be confined to this region, and do not propagate into the thick film. The theta-two theta scan (not shown) on this thicker sample has revealed well pronounced γ-Al₂O₃ (222) and γ-Al₂O₃ (111) reflections. A pole figure about Si (111) substrate normal by tilting the Chi angle to bring the γ-Al₂O₃ (044) into the scattering plane and carrying out a full Phi-cone scan was mapped. The peaks are 120° apart. However, the peaks are split into two components at ±3°, while retaining their sharpness. There also exists a very small component of the γ-Al₂O₃ film, which has its in-plane orientation of ±60° rotating with respect to the major portion of the film and has also maintained a three fold in-plane symmetry.

The sample for TEM observations was prepared in two different thinning processes including wet and dry polishing.
FIG. 5. Cross-sectional TEM image and electron diffraction pattern of a 3.8 nm $\gamma$-Al$_2$O$_3$ film, showing a sharp interface and smooth surface (a). The electron diffraction pattern indicates that the film is well aligned with Si substrate. The in-plane electron diffraction pattern of the 3.8 nm $\gamma$-Al$_2$O$_3$ film is shown in (b).

(with and without water) prior to the ion milling. In general, for high-$k$ gate dielectrics deposited on Si, during the thinning, water may be absorbed by the oxide dielectrics, diffuse through the interface and form silicon oxide or silicates. The cross-section TEM on our single-crystal heterostructure of $\gamma$-Al$_2$O$_3$/Si (shown in Fig. 5), nevertheless, shows that no silicon oxide was found at the interface, irrespective of wet or dry polishing. The results strongly indicate that our single-crystal $\gamma$-Al$_2$O$_3$ films were water resisted. The water-resisted characteristics provide advantageous properties for the use of our single crystal $\gamma$-Al$_2$O$_3$ in the high-$k$ gate dielectric applications.

The interface was found to be atomically sharp and smooth, as shown in Fig. 5(a), whose micrograph was taken with the electron beam directing along [112]$_{\text{Si}}$. The electron diffraction pattern also shows the good alignment between oxide film and Si substrate. In the inset of Fig. 5(a), the orientation relation in cross-sectional direction (Si [112]) was found to be Si[112]/$\gamma$-Al$_2$O$_3$(224), Si[1 $\bar{1}$ 1]/$\gamma$-Al$_2$O$_3$(2 2 2). Electron diffraction patterns from the plan-view of the heterostructure [Fig. 5(b)] show Si[111]/$\gamma$-Al$_2$O$_3$(222), Si[220]/$\gamma$-Al$_2$O$_3$(440). The distance of (440) plane of $\gamma$-Al$_2$O$_3$ from electron diffraction pattern [Fig. 5(b)] is 1.3936 Å, which is calculated from the distance ratio of the diffraction spots of Si substrate and $\gamma$-Al$_2$O$_3$ film along the direction of [440]. The distance of (440) plane obtained from the $\gamma$-Al$_2$O$_3$ films 3.8 and 11 nm thick is 1.3912 and 1.401 Å, respectively. The results are consistent with the x-ray diffraction database of 1.3984 Å.

The faint side peaks observed in Fig. 5(b) may be caused by multiple diffraction, commonly observed in TEM. The faint spot on the right of Al$_2$O$_3$ (440) peak results from adding reciprocal lattice points Al$_2$O$_3$ (404) and Si (02 2), while the faint spot on the left results from adding reciprocal lattice points Al$_2$O$_3$ (044) and Si (202). Similarly, all the side peaks can be indexed by the multiple diffraction of electrons in this system. The tangential broadening of the film peaks is consistent with the $\pm 3^\circ$ splitting of the x-ray peaks observed in the pole figure about Si (111). This broadening could be due to slight in-plane misalignment of the film with respect to substrate, in order to accommodate the lattice mismatch.

The cubic $\gamma$-Al$_2$O$_3$ and Si have significantly different atomic structures and lattice constants. The lattice constant of $\gamma$-Al$_2$O$_3$ is 7.91 Å and that of Si is 5.42 Å. Matching the two lattices over a unit-cell dimension will result in a >30% lattice mismatch. It is intriguing that a highly ordered epitaxial growth was obtained in an unusually large mismatch for a heteropitaxial system. It is possible that, over a larger superlattice dimension the film and the substrate may minimize this mismatch. For this system, for example, at 2 times the film lattice constant and three times the substrate lattice constant the mismatch decreases to $\sim 2$–3%.

Electrical measurements show that an electrical leakage current density of $10^{-3}$ A/cm$^2$ at biasing fields of $\sim$1 MV/cm and a breakdown field over 10 MV/cm were obtained for the oxide film 3.8 nm thick. The high leakage currents are caused by the slight imperfection in the thin films as explained above in the cone scans of the x-ray diffraction. For an oxide film 7 nm in thickness, an electrical leakage current density of $10^{-7}$ A/cm$^2$ at $\sim$1 MV/cm and a breakdown field of $6$–$7$ MV/cm were measured. The oxide breakdown field decreases with increase of the oxide thickness, which was also observed in thin gate SiO$_2$/Si MOS structures. The results can be explained using a model of hole generation and trapping.\footnote{10}

We have demonstrated in this work that very thin excellent single-crystal $\gamma$-Al$_2$O$_3$ films have been grown simply by directly depositing A1$_2$O$_3$ on a clean Si (111) substrate without involving any chemical reaction between species containing Al and oxygen on the Si surface, thus avoid any etching issue about Si substrate or contamination between interfaces. Single-crystal GaN has been grown on our high-quality single-crystal $\gamma$-Al$_2$O$_3$ films and the results will be reported in the future.

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