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Structure of Sc$_2$O$_3$ films epitaxially grown on α-Al$_2$O$_3$ (0001)

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The crystal structure of scandium oxide films epitaxially grown on α-Al$_2$O$_3$ (0001) under an ultrahigh-vacuum is studied by single-crystal x-ray diffraction. The Sc$_2$O$_3$ film grows in bixbyite phase on the basal (0001) surface of the sapphire substrate with its (111) axis aligned parallel to the substrate normal. In-plane orientation of the film, however, exhibits two distinct growth directions that are defined by the two possible surface orientations of the stepped α-Al$_2$O$_3$ substrate. The atomic structure of the high-quality epitaxial film is fully relaxed and the film has unusual thickness uniformity. © 2006 American Institute of Physics. [DOI: 10.1063/1.2163989]

High-κ dielectric oxide films are subjects of intense research, as ever shrinking size of the Si-based electronic devices require new high-performance ultrathin gate oxides with thickness below a nanometer (equivalent thickness of SiO$_2$). When the oxide layer thickness approaches a few atomic layers, the dielectric uniformity may be best supported by epitaxial single-crystalline oxide films. Indeed, this was demonstrated in Gd$_2$O$_3$ films grown on GaAs, which yielded a low interfacial density of states ($D_{it}$) and a very low leakage current density,$^1$ better than many amorphous high-κ dielectrics on Si. For GaN, the semiconductor of choice for blue lasers and high-power electronic devices, thin single-crystal Gd$_2$O$_3$ and Y$_2$O$_3$ films grown epitaxially on GaN give$^2$ a low $D_{it}$. Sc$_2$O$_3$ films grown$^3$ on GaN have also achieved a low $D_{it}$ as well as improved the device performance.$^4$

As the film thickness decreases, substrate starts playing an important role in determining the crystal structure of the film, as we demonstrated in the hexagonal-close-packed (hcp)-phase Gd$_2$O$_3$ film growth on GaN. The hcp phase, normally a high-temperature phase, was stabilized by the epilayer locking to the underlying substrate. In an earlier study, Sc$_2$O$_3$ was conjectured to grow in a cubic crystalline form on GaN, based on a single broad Bragg peak observed in an x-ray diffraction scan.$^3$ In our studies of Sc$_2$O$_3$ grown on GaN using electron-beam (e-beam) evaporation techniques in an ultrahigh vacuum (UHV), we found that Sc$_2$O$_3$ film grows epitaxially in a bixbyite phase on the (0001) surface of the wurzite GaN substrate with its (111) axis aligned parallel to the substrate normal, determined by both in situ reflection high-energy electron diffraction (RHEED) and x-ray diffraction, in single-crystal geometry setup.$^5$

While heteroepitaxial oxide-semiconductor films have been the center of focused research, multilayered heteroepitaxial oxide films have escaped much attention. Multilayered oxide films may provide an extra degree of freedom in many device designs. Here, we report the heteroepitaxial growth of high-quality Sc$_2$O$_3$ films on the (0001) basal plane of sapphire (α-Al$_2$O$_3$) substrate. These findings are remarkable in light of the fact that Sc$_2$O$_3$ and α-Al$_2$O$_3$ atomic structures are significantly different.

Growth of oxide films was carried out in a UHV chamber by e-beam evaporation of a powder packed Sc$_2$O$_3$ target. Sapphire (α-Al$_2$O$_3$) substrates 2 in. in diameter, were heated to over 700 °C in the UHV chamber to clean the surface, and then the substrate temperature was lowered to 600 °C for the oxide film growth. RHEED was used to monitor the film growth. Single-crystal x-ray diffraction measurements were carried out on a triple-axis geometry four-circle goniometer using a 12 kW rotating anode machine and Cu Kα radiation. A focusing graphite monochromator and a flat graphite analyzer crystal provided a resolution of 0.01 Å$^{-1}$ and 0.005 Å$^{-1}$ for the longitudinal and the transverse directions, respectively, which were chosen intentionally low in order to improve the beam intensity. Most importantly, the triple-axis geometry allowed us to map the true reciprocal space by separately resolving two-theta and theta angular measurements.

A reciprocal space scan along the surface normal is shown in Fig. 1, in which narrow peaks of Al$_2$O$_3$ (0003), (0006), and (0009) are observed. The indices refer to the hexagonal unit cell. The broader peaks at 31.400° and 65.387° match well with (222), and (444) peaks of the Sc$_2$O$_3$-bixbyite cubic phase, and suggest a lattice constant of 9.869 Å. A closer look at the Sc$_2$O$_3$ (222) peak reveals an oscillatory behavior of the intensity as shown in the inset (a) of Fig. 1. The period of this oscillation in real space corresponds to a film thickness of 152±2 Å, and the persistence of these oscillations to high orders indicates a highly uniform film thickness. A dynamic diffraction modeling$^6$ with a thickness variation of 2 Å root-mean square as shown in (b) in the inset of Fig. 1, suggests that surface flatness is of the order of few Å. Rounding of the peaks is due to low instrumental...
The inset shows an expanded view of the Sc$_2$O$_3$ (222) peak along the surface normal in (a), and the corresponding curve from a dynamical diffraction model (b).

resolution, and high-order peaks are obscured by the noise floor. In Fig. 2(a), the intensity distribution in two-dimensional reciprocal space confirms the single crystalline nature of the film. The rocking (theta) scans at the Al$_2$O$_3$ (0006), and the Sc$_2$O$_3$ (222) peaks, find widths of 0.21° and 0.29°, respectively, indicating a good crystalline perfection for the thin oxide film.

In order to gain a better understanding of the crystal structure of the film, scans along major zone axes of the substrate (Al$_2$O$_3$) and the bixbyite (Sc$_2$O$_3$) reciprocal space have been carried out. We have found no evidence for diffraction peaks that belonged to other epitaxy-stabilized structures, such as the hexagonal phase (which occurs for the growth of Gd$_2$O$_3$ on GaN) and confirmed that all the observed reflections belonged to the bixbyite structure. Figure 2(b) shows the x-ray intensity distribution in the (H,H,2H,L) plane about Al$_2$O$_3$ (1126) and Sc$_2$O$_3$ (440) peaks. The shape of the oxide film peak is very similar to the substrate peak, indicating that the film does not contain extra defects in addition to that of the substrate.

Phi-angle conical scans about the surface normal (111), for Sc$_2$O$_3$ {440}, and the substrate Al$_2$O$_3$ {0,1,1,2} peaks were taken for comparison. These scans are made by tilting the surface normal chi-angle to bring the particular reflections into the scattering plane and measuring intensity along the phi-angle. Substrate {0,1,1,2} peaks are strong and sharp (0.29° width) and are spaced by 120°, consistent with the R3̅c symmetry. The Sc$_2$O$_3$ {440} peaks are about 3° wide and are spaced by 60°. For this layer of reciprocal space, the rotational symmetry about the {111} axis is three fold with 120° angular spacing. The extra set of peaks is due to a second preferred growth orientation of the film on this substrate surface. This twin growth orientation is also confirmed in other reciprocal space scans. The α-Al$_2$O$_3$ (0001) surface has a pseudo-six-fold symmetry when only the top layer of atoms are considered, as shown in Fig. 3. It may be natural, therefore, to conclude that the {111} growth axis of the cubic bixbyite phase will have two equivalent in-plane orientations or twins, with its C$_3$ symmetry. The six-fold symmetry of the substrate surface, however, gets reduced to three-fold when we consider the second and third layer of atoms under the surface. An adsorbing atom on the surface would clearly feel the presence of atoms few layers down, and would choose sites that maximize the cation-cation separation. Such favorable three-fold sites for the occupation of the adatoms are shown with dark triangles in Fig. 3. In order to explain the
will therefore grow in two distinct in-plane orientations. Films nucleating and growing on terraces separated by steps every minimum-energy surfaces separated by elemental steps are the bulk termination with an aluminum top layer. While faces, where steps cannot be avoided, the Sc$_2$O$_3$ epitaxial structure, and there are two energetically distinct cuts possible, a low surface energy, as expected for this densely packed structure consists of distorted hcp packing of oxygen atoms with cations occupying two-thirds of the available sites. The minimum surface energy of (0001) of 3.7 J/m$^2$ corresponds to the bulk termination with an aluminum top layer. While every (0001) surface is three-fold symmetric, neighboring minimum-energy surfaces separated by elemental steps are rotated by 60$^\circ$ with respect to each other. Figure 3 shows the top view of the two (0001) surfaces separated by a step running along the $\langle 110 \rangle$ direction, as also observed experimentally in MgO growth on $\alpha$-Al$_2$O$_3$ (0001). Over large surfaces, where steps can not be avoided, the Sc$_2$O$_3$ epitaxial films nucleating and growing on terraces separated by steps will therefore grow in two distinct in-plane orientations.

The extreme flatness of the Sc$_2$O$_3$ epitaxial film suggests a low surface energy, as expected for this densely packed (111) surface. Energetics of the surface structure can be constructed through possible cuts of the bulk crystal structure. Bixbyite is a vacancy ordered derivative of the CaF$_2$ structure, and there are two energetically distinct cuts possible, (a) and (b), as shown in Fig. 4. Since a (b) cut cuts through three bonds per anion compared to an (a) cut with one bond per anion, the low energy surface will be oxygen terminated. This was mentioned by Pauling in the original discovery of bixbyites where he referred to the (111) basal cleavage resulting from electrically neutral layers of ions—the double layers of octahedra.

Despite significantly different crystal structures of Sc$_2$O$_3$ and $\alpha$-Al$_2$O$_3$, our measurements suggest a sharp abrupt interface formation. In simple terms, this can be understood by an interface formation that is created by bringing the low-energy surfaces of the film and the bulk, or by placing an oxygen-terminated surface on an aluminum-terminated $\alpha$-Al$_2$O$_3$ (0001) surface. Two structures exhibit matching unit cells at a superlattice distance of $a(\text{Al}_2\text{O}_3)_{\text{inplane}} \times 3 = 14.28$ Å and $a(\text{Sc}_2\text{O}_3)_{\text{inplane}} = 13.96$ Å, with a lattice mismatch of 2.2%, and a fully relaxed epilayer as determined experimentally. At the interface, we expect some atomic rearrangement that is configurationally optimized to both structures. The great dissimilarity between the two layers may be the key to an abrupt interface, and localize misfit defects to the narrow region.

Even with their similar chemistry, it is surprising that the film and the substrate cations with surrounding oxygens do not share the same local symmetry across the interface. Note that there is a 30$^\circ$ rotation between the densely packed planes of the film and the substrate. This must be the key to satisfying the chemical constrains across the interface, while simultaneously satisfying the epitaxial conditions over a superlattice length.

In conclusion, we report high-quality heteroepitaxial film growth of binary oxide Sc$_2$O$_3$ on the $\alpha$-Al$_2$O$_3$ (0001) substrate. The film with 2.2% lattice mismatch is fully relaxed and exhibits remarkable thickness uniformity. Epitaxial lattice matching conditions are met over a superlattice length of three times the lattice constant of the substrate. It is likely that most of the misfit-related defects are confined to a narrow region near the interface, not extending into the film to destroy the crystalline order of the Sc$_2$O$_3$ epitaxial film. The film growth takes place with two distinct, twinned in-plane orientations, characteristic of the stepped $\alpha$-Al$_2$O$_3$ (0001) substrate surface that exhibits 60$^\circ$ rotated three-fold surface symmetries on neighboring terraces separated by steps. The film twinning can be eliminated on short-length scales where a single terrace width matches the ever-shrinking device size.

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