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Structure of Sc_2O_3 films epitaxially grown on α-Al_2O_3 (0001)

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The crystal structure of scandium oxide films epitaxially grown on α-Al_2O_3 (0001) under an ultrahigh-vacuum is studied by single-crystal x-ray diffraction. The Sc_2O_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_2O_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_2O_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-k dielectrics on Si. For GaN, the semiconductor of choice for blue lasers and high-power electronic devices, thin single-crystal Gd_2O_3 and Y_2O_3 films grown epitaxially on GaN give[2] a low D_{it}. Sc_2O_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_2O_3 film growth on GaN. The hcp phase, normally a high-temperature phase, was stabilized by the epitaxial locking to the underlying substrate. In an earlier study, Sc_2O_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_2O_3 grown on GaN using electron-beam (e-beam) evaporation techniques in an ultrahigh vacuum (UHV), we found that Sc_2O_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_2O_3 films on the (0001) basal plane of sapphire (α-Al_2O_3) substrate. These findings are remarkable in light of the fact that Sc_2O_3 and α-Al_2O_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_2O_3 target. Sapphire (Al_2O_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 ganiometer using a 12 kW rotating anode machine and Cu $K\alpha$ 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_2O_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_2O_3-bixbyite cubic phase, and suggest a lattice constant of 9.869 Å. A closer look at the Sc_2O_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

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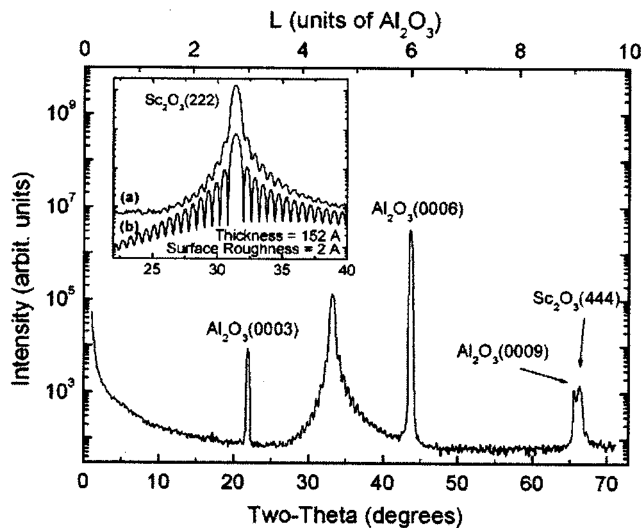

FIG. 1. Single crystal x-ray scans along the surface normal reveal α-Al_2O_3 substrate and the (222), and (444) peaks of the Sc_2O_3-bixbyite cubic phase. The inset shows an expanded view of the Sc_2O_3 (222) peak along the surface normal in (a), and the corresponding curve from a dynamical diffraction 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_2O_3 (0006), and the Sc_2O_3 (222) peaks, find widths of 0.21° and 0.29°, respectively, indicating a good crystalline perfection for the thin oxide film.

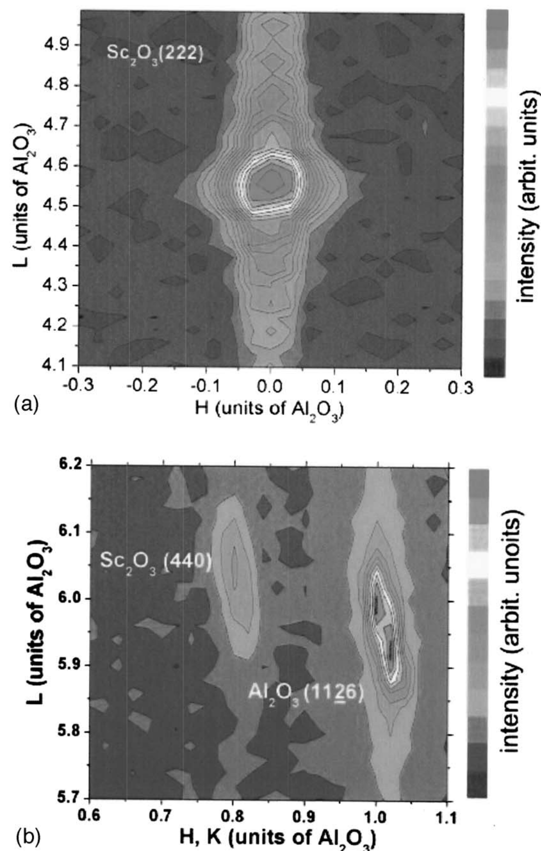

FIG. 2. An area scan about the Sc_2O_3 (222) peak (a), in single crystal geometry is shown in the $(H,0,\bar{H},L)$ plane. Single-crystal x-ray diffraction measurements in the reciprocal space are shown in the plane of the Al_2O_3 lattice $(H,H,\bar{2}H,L)$, about the Al_2O_3 $(11\bar{2}6)$ and Sc_2O_3 (440) peaks in (b). [The splitting of the Al_2O_3 peak in (b) is an artifact of the two-dimensional scans.]

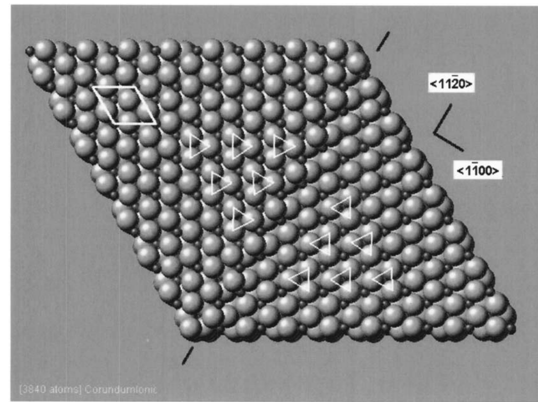

FIG. 3. The low-energy Al-terminated (0001) basal plane of α-Al_2O_3 with a step running along the $\langle 11\bar{2}0\rangle$ direction is shown. Unit cell is indicated by white lines, Al atoms by small dark circles and symmetry-equivalent adatom sites are marked by dark triangles. Elemental steps on this surface give rise to a 60° rotation of adatom site symmetry on the neighboring terraces.

In order to gain a better understanding of the crystal structure of the film, scans along major zone axes of the substrate (Al_2O_3) and the bixbyite (Sc_2O_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_2O_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 $(H,H,\bar{2}H,L)$ plane about Al_2O_3 $(11\bar{2}6)$ and Sc_2O_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 $\langle 111\rangle$, for Sc_2O_3 {440}, and the substrate $Al_2O_3\{0,1,\bar{1},2\}$ 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 $\{0,1,\bar{1},2\}$ peaks are strong and sharp (0.29° width) and are spaced by 120°, consistent with the $R\bar{3}c$ symmetry. The Sc_2O_3 {440} peaks are about 3° wide and are spaced by 60°. For this layer of reciprocal space, the rotational symmetry about the $\langle 111\rangle$ 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_2O_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 $\langle 111\rangle$ 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

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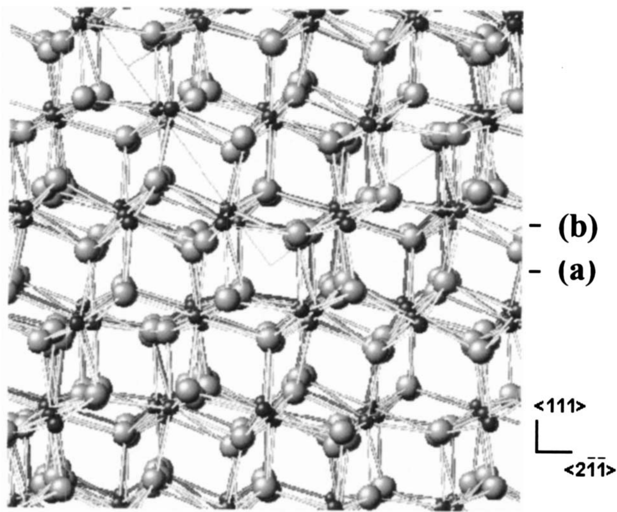

FIG. 4. Side view of the bixbyite Sc_2O_3 crystal structure, in the $\langle 111 \rangle$, $\langle 2\bar{1}\bar{1} \rangle$ plane. The structure consists of bilayers of oxygen separating scandium atoms. Two distinct cuts possible through the structure are shown in (a) and (b).

twinned growth, we must consider film growth on stepped surfaces.

The α-Al_2O_3 (0001) is one of most intensively studied surfaces because of its technological importance. Bulk 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.[7] While every (0001) surface is three-fold symmetric, neighboring minimum-energy surfaces separated by elemental steps are rotated by 60° with respect to each other.[7] Figure 3 shows the top view of the two (0001) surfaces separated by a step running along the $\langle 11\bar{2}0 \rangle$ direction, as also observed experimentally in MgO growth on α-Al_2O_3 (0001).[8] Over large surfaces, where steps can not be avoided, the Sc_2O_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_2O_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[9] 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_2O_3 and α-Al_2O_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 α-Al_2O_3 (0001) surface. Two structures exhibit matching unit cells at a superlattice distance of $a(Al_2O_3)_{inplane} \times 3 = 14.28$ Å and $a(Sc_2O_3)_{inplane} = 13.96$ 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° 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_2O_3 on the α-Al_2O_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_2O_3 epitaxial film. The film growth takes place with two distinct, twinned in-plane orientations, characteristic of the stepped α-Al_2O_3 (0001) substrate surface that exhibits 60° 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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