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Epitaxial polymorphism of La$_2$O$_3$ on Si(111) studied by in situ x-ray diffraction

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The phase formation of La$_2$O$_3$ epitaxial films during growth on Si(111) is investigated by synchrotron-based in situ grazing incidence x-ray diffraction and high resolution transmission electron microscopy. We find that first a 2–4 nm thick cubic bixbyite La$_2$O$_3$ layer grows at the interface to Si(111) substrate, followed by a hexagonal La$_2$O$_3$ film. Hence, to keep a cubic on cubic heteroepitaxy and to achieve high quality epitaxial nanostructures or multi-layers, the thickness of the interfacial La$_2$O$_3$ layer has to be restricted to 2 nm. The larger formation energy of the cubic phase can only partially be compensated by the biaxial strain in the epitaxial film based on density functional perturbation theory. Hence, the stabilization of the cubic phase is not due to bulk strain but could be related to a lower surface or interface free energy, or to kinetic effects.

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A continuous downscaling of functional logic elements demands an ongoing size reduction of relevant device components, particularly, of gate dielectrics in complementary metal-oxide-semiconductor (CMOS) technology. The search for a replacement for the widely used gate dielectric SiO$_2$ and the currently used HfO$_2$ by a reliable alternative is still in progress. Various high-$\kappa$ dielectrics have been considered in the past years. A promising candidate is the binary rare-earth oxide (REO) La$_2$O$_3$ with a dielectric constant $\kappa$ of 30, larger than that of HfO$_2$, a band gap of 6 eV, and an advantageous conduction band offset to silicon of 2.3 eV. Even thin La$_2$O$_3$ films have, compared to HfO$_2$ and Al$_2$O$_3$, a lower gate leakage current density. But there are material properties resulting in serious disadvantages of REOs for the integration into silicon technology. La$_2$O$_3$ is hygroscopic and tends to form a hydroxide, La(OH)$_3$, in a humid environment. As a direct consequence, uncapped La$_2$O$_3$ films are not chemically stable. Moreover, they are prone to the formation of carbonates in carbon containing environments.

Very recently, the use of La$_2$O$_3$ in multi-layer gate dielectrics has been suggested. La$_2$O$_3$ can also serve as an oxide buffer layer for integration of non-silicon-based semiconductors on silicon and GaAs (Ref. 9) substrates. The crystal structure of La$_2$O$_3$ is important for these applications. Two crystalline phases of La$_2$O$_3$ have been reported, namely, a hexagonal and a cubic (bixbyite type) one, showing its polymorphic character with direct effect on the electrical properties. According to the thermodynamic phase diagram, the crystal structure of La$_2$O$_3$ is hexagonal above 550°C (space group $P$3$m$1, no. 164, lattice constants at room temperature $a = 3.95$ Å and $c = 6.15$ Å), whereas below 550°C, a cubic bixbyite phase is (meta)stable (space group Ia$_3$, no. 206, lattice constant $a = 11.35$ Å). Our recent calculations reveal a lower formation energy of 120 meV per formula unit for the hexagonal phase compared to the cubic one indicating that the cubic phase is not thermodynamically stable. However, both crystal phases can be grown heteroepitaxially on Si(111) despite the in-plane lattice mismatch of 4.3% for cubic and 2.7% for hexagonal phase, respectively. Additionally, the cubic phase is lattice matched to GaAs and enables GaAs based MOS structures.

This Letter focuses on molecular beam epitaxy (MBE) of the binary REO La$_2$O$_3$ on Si(111). It is investigated in situ during growth by synchrotron-based high-resolution x-ray diffraction under grazing incidence (GID). We especially concentrate on the initial growth which reveals an unexpected phase sequence. We trace it to effects arising from the surface and the interface. The results provide further insights into the growth dynamics of La$_2$O$_3$ as interfacer oxide layer for nano-fabrication and for multi-layers constructed of La$_2$O$_3$ and Lu$_2$O$_3$, two REOs with symmetric lattice mismatch to silicon of about +4.3% and −4.3%, respectively.

The experiments were performed in a dedicated MBE chamber on a (4 + 2)-circle diffractometer located at the beamline U125/2-KMC at the synchrotron BESSY II (Helmholtz Center for Materials and Energy, Berlin). A photon energy of $E = 12$ keV was selected by a double crystal Si(111) monochromator. The beam had dimensions of $300 \times 500 \mu$m$^2$ and an energy resolution $\Delta E / E$ of about 10$^{-4}$. An incidence angle of 0.3°, slightly above the critical angle for total external reflection, was selected to probe the entire film, the substrate and, in particular, the interface between the La$_2$O$_3$ film and the Si substrate. In our experiment, the crystal growth is monitored in situ. It provides detailed information on the growth kinetics in contrast to a retrospective analysis of the final as-grown state after cooling-down, without direct access to nucleation or subsequent processes taking place during growth and post-growth treatments.

The standby pressure in the growth chamber is in the order of $10^{-10}$ mbar. Ultra-high vacuum (UHV) conditions prevent the parasitic formation of carbonates and La(OH)$_3$. Previously, we have demonstrated the sublimation of REOs by MBE using advanced high-temperature effusion cells.

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(TUBO, Createc GmbH).\textsuperscript{20–22} \(\text{La}_2\text{O}_3\) was grown by subliming \(\text{La}_2\text{O}_3\)-source material at \(T_{\text{La}_2\text{O}_3} = 1650\,^\circ\text{C}\) onto the \(\text{Si}(111)\) substrate, heated to \(T_{\text{sub}} = 700\,^\circ\text{C}\), resulting in a growth rate of 1.44 Å/min. The growth rate was determined by dividing the final film thickness (measured by x-ray reflectivity) by the total growth time. All nominal thickness values are calculated as a product of growth rate and time. We used Boron-doped (resistivity = 10–20 Ω cm) substrates, which were covered by 100 nm thermal SiO\(_2\). The oxide was removed by a single 5 min 5% hydrogen fluoride (HF) dip.\textsuperscript{23} After removing the oxide, the substrate was transferred into the growth chamber for a final annealing step at \(T_{\text{sub}} = 750\,^\circ\text{C}\) for another 30 min to establish a flat \(\text{Si}(111)\) surface with a \((7 \times 7)\) reconstruction, confirmed by reflection high-energy electron diffraction (RHEED) (not shown). Two growth experiments were performed, one without and another one with supplying molecular oxygen (\(\text{O}_2\)), at a partial pressure of \(2 \times 10^{-7}\) mbar. The supplied \(\text{O}_2\) serves to compensate for the oxygen deficiency of the source vapor and to prevent the associated formation of interface silicides.\textsuperscript{22}

Fig. 1 visualizes a two-dimensional out-of-plane section in reciprocal space and illustrates the regions that we have probed by GID. Two regions of interest are extended perpendicular to each other and highlighted by rectangles in Fig. 1(a). Corresponding scans in reciprocal space allow to study, respectively, in- and out-of-plane strain components during the interface formation and crystal growth. Crystal truncation rods (CTRs) run along the surface normal and probe out-of-plane strain. We have chosen the non-symmetric \((1\overline{1}L)\) CTR, where contributions from the hexagonal and cubic phases are well separated. To monitor the in-plane relaxation, we follow \textit{in situ} the \(\text{Si}[112]\) direction parallel to the sample surface. In presentation of the GID results below, we use the hexagonal coordinate system based on the \(\text{Si}(111)\) surface.\textsuperscript{24,25} The Miller indices in this coordinate system are denoted by a subscript “SURF.”

![Cross section of the reciprocal space](Image)

FIG. 1. (a) Cross section of the reciprocal space perpendicular to the [110] view direction. Low order reflections from different phases are marked by color dots. Two regions of interest, \((1\overline{1}L)\) CTR and \((1\overline{1}L)-\text{CTR}\) during growth without \(\text{O}_2\) supply. The diffraction pattern reveals an initial nucleation of cubic \(\text{La}_2\text{O}_3\) domains, which manifest themselves by the cubic bixbyite \(\text{La}_2\text{O}_3\{404\}\) reflection, followed by the formation of the silicide \(\text{LaSi}_2\), giving rise to a \(\text{LaSi}_2\{105\}\) reflection. The thickness of the cubic layer is estimated to about 1.5 nm, as obtained by Scherrer formula from the full width at half maximum (FWHM) of Gaussian fits to the corresponding Bragg reflection along the \((1\overline{1}L)\) CTR.

![GID intensity distributions](Image)

FIG. 2. GID intensity distributions along the \((1\overline{1}L)-\text{CTR}\) during growth without \(\text{O}_2\) supply. The diffraction pattern reveals an initial nucleation of cubic \(\text{La}_2\text{O}_3\) domains, which manifest themselves by the cubic bixbyite \(\text{La}_2\text{O}_3\{404\}\) reflection, followed by the formation of the silicide \(\text{LaSi}_2\), giving rise to a \(\text{LaSi}_2\{105\}\) reflection. The thickness of the cubic layer is estimated to about 1.5 nm, as obtained by Scherrer formula from the full width at half maximum (FWHM) of Gaussian fits to the corresponding Bragg reflection along the \((1\overline{1}L)\) CTR.

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![GID intensity distributions](Image)

FIG. 2. GID intensity distributions along the \((1\overline{1}L)-\text{CTR}\) during deposition of \(\text{La}_2\text{O}_3\) without (a) and with (b) additional \(\text{O}_2\) supply. The diffraction pattern serves as a direct fingerprint of the phase formation. An initial cubic \(\text{La}_2\text{O}_3\) phase appeared in both cases. After that \(\text{LaSi}_2\) formed in the absence of \(\text{O}_2\) (a) whereas a hexagonal \(\text{La}_2\text{O}_3\) phase formed (b) when additional \(\text{O}_2\) was supplied.
to the substrate. To gain more information on the delayed nucleation of the hexagonal and the relaxation of the cubic phase, we have studied the evolution of the in-plane lattice parameter by in situ GID at the same growth conditions, see Fig. 4 bottom. The coinciding positions of the sharp substrate and broad layer diffraction peaks (at $H = 3$ rlu) indicates an initially pseudomorphic growth. The cubic phase begins to relax when the nominal thickness exceeds 2 nm. The relaxation is observed by a linear shift of the cubic La$_2$O$_3$(448) reflection up to a thickness of 6 nm, as is shown by the dotted line. The peak shifts away from the substrate position $H = 3.00$ rlu to about 2.87 rlu, which corresponds to the lateral mismatch of 4.3%.

Fig. 4 top shows the intensity distribution at the end of the growth. Both cubic and hexagonal phases are relaxed. Since the peak of cubic phase moves away from the substrate CTR, the probed intensity of La$_2$O$_3$(404) reflection in Fig. 2(b) decreases. An extended reciprocal space map measured at the end of the growth around the (11L) CTR is shown in Fig. 1(b). The La$_2$O$_3$(404) reflection is shifted by 4.3% towards smaller q-values, i.e., to larger lattice constants. The lattice mismatch for the hexagonal phase at the end of the growth is 2.4%.

To discuss the unexpected initial formation of the thermodynamically meta-stable cubic La$_2$O$_3$ phase on Si(111), we consider a possible epitaxial constraint that stabilizes the energetically unfavorable cubic La$_2$O$_3$ phase on Si(111) surface during growth up to a critical thickness. Taking into account the larger in-plane lattice mismatch of the cubic (4.3%) compared to the hexagonal (2.4%) phase with respect to silicon, it is conceivable that this observation is related to different elastic properties of both phases. Therefore, we calculated all relevant components of Hooke’s tensor by density functional perturbation theory. For the hexagonal phase, we obtained: $C_{11} = 232$, $C_{12} = 140$, $C_{13} = 94$, $C_{33} = 139$, $C_{14} = 28$, $C_{44} = 70$, and $C_{66} = 46$ GPa and for the cubic one:
For a better comparison, the cubic tensor was transformed into a hexagonal tensor obtaining the relevant values \( C_{11} = 188, C_{12} = 97, C_{13} = 94, \) and \( C_{33} = 191 \) GPa. These values indicate a slightly stiffer hexagonal lattice compared to its cubic counterpart. The accumulated elastic energy for biaxial strain of the pseudomorphic layer, \( E = d^2(C_{11} + C_{12} - 2C_{13}/C_{33})V_0 \), is smaller for the cubic phase under identical strain. Here, \( V_0 \) is the volume of the unit cell and \( d \) is the relative in-plane lattice mismatch to Si(111). Nevertheless, within the observed range of strains (up to 4.3\%) the elastic energy difference does not overcome the calculated difference in formation energy of 120 meV per formula unit of unstrained \( \text{La}_2\text{O}_3 \) in favor of the hexagonal phase. Therefore, bulk strain does not stabilize the cubic phase during MBE. An alternative stabilization of the cubic phase could be related to a lower surface energy (as, for example, shown for \( \text{ZrO}_2 \) (Ref. 27)), interface energy or a kinetic stabilization on Si(111).

Another issue is the atomic structure of the interface between cubic and hexagonal phases. The oxygen distributions between each \( \text{La} \)-layers in both phases differs, namely, 24 oxygen atoms are between each \( \text{La}_2\text{O}_3(222)_{\text{cub}} \) net planes and alternating 16 or 32 oxygen atoms are between subsequent \( \text{La}_2\text{O}_3(0004)_{\text{hex}} \) net planes per in-plane unit cell. This discrepancy leads to an oxygen deficiency or excess of four oxygen atoms per unit cell depending on what \( \text{La}_2\text{O}_3\) interface has formed on the \( \text{La}_2\text{O}_3_{\text{cub}} \) surface. The different in-plane lattice constants make the growth of hexagonal on cubic \( \text{La}_2\text{O}_3 \) unfavorable, too. An interesting coincidence is that the hexagonal layer starts to grow at about 2 nm when the cubic film begins to relax, see Figs. 3 and 4. In this case the locally reduced lattice mismatch between both phases could favor the hexagonal growth. The rough interface between both phases revealed by HRTEM indicates a non-uniform lattice relaxation. This growth scenario may either promote an oxygen excess or deficiency enabling the observed cubic/hexagonal interface.

In summary, we have monitored by \textit{in situ} GID the stabilization of the meta-stable cubic phase for thin layers of \( \text{La}_2\text{O}_3 \) on Si(111) during MBE. To achieve a high quality epitaxial multi-layer (cubic on cubic) a maximum layer thickness of 2 nm is needed for the first \( \text{La}_2\text{O}_3 \) layer on Si(111) or within the considered multi-layer stack. Up to this thickness, \( \text{La}_2\text{O}_3 \) grows pseudomorphically on Si(111) in its cubic bixbyite phase. At larger thicknesses, the thermodynamically stable hexagonal phase of \( \text{La}_2\text{O}_3 \) grows on top of a cubic film. The initially formed cubic phase is not stabilized by bulk strain. Instead, surface or interface energy, or kinetic effects could play a decisive role in this stabilization on Si(111).

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\[ C^{(c)}_{11} = 179, C^{(c)}_{12} = 100, C^{(c)}_{33} = 49 \] GPa.