Interface formation and defect structures in epitaxial La$_2$Zr$_2$O$_7$ thin films on (111) Si

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We have studied the growth of epitaxial La$_2$Zr$_2$O$_7$ thin films on (111) Si. Although the interface structure can be strongly affected by the Si oxidation during the deposition process, epitaxial growth of La$_2$Zr$_2$O$_7$ was obtained. A detailed study by means of transmission electron microscopy reveals two types of structures (pyrochlore and fluorite) with the same average chemical composition but strong differences in reactivity and interface formation. The structural complexity of the ordered pyrochlore structure seems to prevent excess oxygen diffusion and interfacial SiO$_2$ formation.


In recent years, there has been considerable interest in the growth of epitaxial oxides on Si. In particular, the need for materials with a high dielectric constant (high $k$) as a replacement for SiO$_2$ in complementary metal–oxide–semiconductor technology has driven this research. Pioneered by the Oak Ridge National Laboratory, the epitaxy of SrTiO$_3$ on Si (Ref. 1) has led to significant progress in this field and made the integration of perovskite materials in device structures very promising.$^{2–4}$ At low temperatures of 300–400 °C, the growth process is well controlled,$^5$ but chemical and structural issues in device integration remain unresolved. Considerable effort has also been devoted to binary oxides, including for example lanthanum-, yttrium-, and ceriumoxide.$^6–8$ The main obstacles to the integration of these materials remain to be (i) the thermodynamical instability against Si, (ii) oxygen diffusion and the formation of amorphous SiO$_2$, and (iii) a high oxide defect density, resulting in poor electrical performance.

The metal oxides La$_2$O$_3$ and ZrO$_2$ have been considered to be thermally stable in contact with Si,$^9$ both systems reveal a positive free energy for silicide formation at 1000 K.$^{10}$ Hence, intuitively, the same should apply to the solid-solution system La$_2$Zr$_2$O$_7$ (LZO). Furthermore, LZO, with a dielectric constant of $\approx 20$,$^{11}$ has a cubic pyrochlore structure with a lattice parameter of $a = 10.786$ Å that leads to a mismatch of 0.68% with Si ($2a_{Si} = 10.86$ Å). The similarity between the pyrochlore and the face-centered-cubic diamond (Si) structure also suggests a good structural compatibility because all the lattice vectors present in Si can be found in LZO as well. Recently, we have reported the epitaxial growth of LZO on (111) Si.$^{11}$ Here, we now systematically analyze the growth process, the structure, and the stability of the complex oxide/Si interface. The initial growth is determined by a competition between the oxygen diffusion (with SiO$_2$ formation) and the establishment of long-range crystalline order. Two different phases of LZO are observed, which favor either one or the other process.

LZO films were grown in a molecular-beam epitaxy chamber designed for oxide epitaxy. Standard Radio Corporation of America cleaning recipes were used, followed by a 30 s HF dip, prior to loading. Lanthanum and zirconium were evaporated from metal sources using electron-beam guns, under a molecular or atomic oxygen pressure generated by an Oxford Applied Research (Witney, U.K.) HD25 source. Films were grown at 550–650 °C under pressure in the range of $5 \times 10^{-10}$ to $1 \times 10^{-5}$ Torr. Structural characterization was carried out during growth using reflection high-energy electron diffraction (RHEED) and ex situ using a Siemens D8 x-ray diffractometer (XRD). The transmission electron microscopy (TEM) sample preparation involved grinding and Ar$^+$-ion milling—with flat angle and low-energy guns (Technoorg-Linda Co., Budapest, Hungary)—to electron transparency. For TEM studies, JEOL2010 and CM300FEG microscopes were used for conventional and high-resolution mode operating at 200 and 300 kV, respectively. Both microscopes were equipped with an energy-dispersive x-ray detector, and the latter also with a Gatan Image Filter (GIF 6000,Gatan, Inc., Pleasanton, CA) for chemical analysis.

Figures 1(a)–1(c) show RHEED patterns obtained from the Si substrate, after deposition of the first unit cell, and at the end of the growth (12 nm). Surprisingly, first an amorphous interlayer forms, but the epitaxial structure is quickly recovered. This is confirmed by a $\Theta$–2$\Theta$ XRD scan (Fig. 2). Film peaks at $2\Theta = 28.68$ and 59.38, corresponding to the

![FIG. 1. RHEED pattern taken (a) before growth, (b) after deposition of the first LZO unit cell, and (c) at the end of the growth process.](image-url)
Precipitates. Substrate and films are clearly separated by an single crystalline without indications of phase separation or sample. In agreement with the XRD results, the LZO film is confirmed to be SiO\textsubscript{2}~orientations of LZO on the angle of 54.74° and the supplementary angle of 125.26° between the film and the substrate is as follows: [1 1 0]\textsubscript{LZO}, [1 1 0]\textsubscript{Si}, and (1 1 1)\textsubscript{LZO}(1 1 1)\textsubscript{Si}.

Figure 3(a) shows an overview TEM micrograph of the sample. In agreement with the XRD results, the LZO film is single crystalline without indications of phase separation or precipitates. Substrate and films are clearly separated by an amorphous interface layer (up to 2 nm thick) that was confirmed to be SiO\textsubscript{2} by electron-energy loss spectroscopy. However, in several areas (about 10% of the interface), the amorphous layer was almost absent, as can be seen in Fig. 3(b), and lattice fringes are observed that connect the substrate and the film (inset of Fig. 3). This intriguing result suggests a local variation in LZO that provides an epitaxial phase that is stable against Si without interfacial oxidation.

A detailed structural analysis revealed A/B twinning, where the B orientation is a twin related to the matrix A by a 180° rotation across the surface (1 1 1) normal. The A/B twinning relationship has been observed in many epitaxial oxides grown on (1 1 1)Si (e.g., Y\textsubscript{2}O\textsubscript{3}, Ref. 12, and (La\textsubscript{y}Y\textsubscript{1−y})\textsubscript{2}O\textsubscript{3}, Ref. 13). The twinning is caused by the two equivalent (1 1 1) orientations of LZO on the (1 1 1) Si surface, with the inclined angle of 54.74° and the supplementary angle of 125.26° between the (1 1 1) and (0 0 1) planes. In this twin configuration, the low-energy twin plane is the (1 1 1)\textsubscript{LZO} plane because coincidence-lattice sites are only found there. Indeed, the twin boundaries are mainly parallel to the interface, whereas other orientations lead to a poorly defined habit plane with defects and disorder between domains.

Besides twin structures, two different phases of LZO have been observed. As shown in Fig. 4(a), one phase, which covers most of the film, yields a fast Fourier transform (FFT) image with pronounced (2 2 2) and (0 4 0) spots, corresponding to an interplanar spacing of 3.1 and 2.7 Å, respectively. The second phase [Fig. 4(b)], which corresponds to the epitaxial phase that is stable against Si, reveals faint superreflections at (1 1 1) locations, indicating a double periodicity with a spacing of 6.2 Å. The diffraction pattern calculated based on the LZO pyrochlore structure [Fig. 4(d)] indeed confirms the faint superreflections observed in Fig. 4(b). Nevertheless, the phase shown in Fig. 4(a) is definitely not pyrochlore. From simulated diffraction images, the structure was determined to correspond to a fluorite-type LZO structure [Fig. 4(c)].

Pyrochlore is derived from the fluorite structure (e.g., ZrO\textsubscript{2}) with one-eighth of the anions absent and two cation sites; the cations at the La and Zr sites and the oxygen vacancies can be ordered (pyrochlore) or disordered (fluorite). The phase diagram of the La\textsubscript{2}O\textsubscript{3}−ZrO\textsubscript{2} solid solution shows a well-defined pyrochlore structure for the composition La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. At our growth temperature, its nonstoichiometric range is about 5%. For most pyrochlore compositions, the defect fluorite structure has been obtained, e.g., by thermal treatment, chemical substitution, or ion irradiation. Ion-irradiation experiments in zirconate pyrochlores demonstrated that the irradiation-damage resistance is related to the order–disorder transformation from pyrochlore to fluorite.

In LZO, Kido et al. observed a temperature dependence of the bulk crystal structure: Below 900 °C, the fluorite type of LZO, with a pseudo-cubic lattice constant of 5.4 Å, is stable. At higher temperatures, a pyrochlore-like structure with a cubic lattice constant of 4.6 Å is observed. This transformation is triggered by the ordering of defects in the fluorite lattice, leading to a phase separation into a fluorite-like matrix and a pyrochlore-like phase, which results in a volume expansion. The transformation is reversible upon cooling, indicating a metastable nature of the pyrochlore phase.

Figure 4(b) shows simulated diffraction images assuming an LZO disordered fluorite structure and an ordered pyrochlore structure, respectively. Line scans taken parallel to the row, indicated by two white arrows in (b), are inserted as (e) and (f); the faint superreflections are indicated by two dark arrows.
was obtained, whereas above 1000 °C, the pyrochlore type stabilized. Hence, our low growth temperature (650 °C) explains the preponderance of the fluorite structure in our films. As the growth temperature was increased, a larger fraction of the pyrochlore phase was observed.

For thin films, the growth temperature controls the order–disorder transformation. In general, the growth temperature must be kept as low as possible for the oxide epitaxy on Si because (i) oxygen diffusion can induce and thicken an amorphous SiO$_2$ interfacial layer, and (ii) metal diffusion can induce silicide formation. On the other hand, the formation of the stable La$_2$Zr$_2$O$_7$ pyrochlore phase requires a certain degree of cation diffusion to obtain the ordered stacking sequence required. Along the (111) orientation, this sequence corresponds to varying the Zr:La ratio as follows: (Zr$_3$:La$_1$)/(Zr$_3$:La$_1$)/(Zr$_1$:La$_3$)/(Zr$_3$:La$_1$)/. Hence, the deposition of the first Zr and La monolayers initially leads to disorder, i.e., disappearance of RHEED intensity, which requires sufficient intermixing before the ordered lattice appears. A better approach to growing pyrochlores at lower temperatures would be to apply the above-mentioned stacking sequence.

Comparing different samples, we have observed that films with a higher fluorite fraction yield a thicker amorphous interfacial SiO$_2$ layer than those with a higher pyrochlore fraction and grown at slightly higher temperature. These observations strongly suggest that the pyrochlore phase is more stable against oxygen diffusion. Related pyrochlores [Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$] studied for their fast oxygen ion conductivity revealed an increase in ionic conductivity with a larger cation antisite disorder (substitution of Zr for Ti). As demonstrated, oxygen is the predominant migrating species, and vacancies and cation disorder promote its migration. These results corroborate our conclusion that cation ordering in the pyrochlore phase provides a barrier against oxygen diffusion and favors a clean epitaxial interface between LZO and Si.

In conclusion, we have shown that LZO thin films can be grown epitaxially on (111) Si substrates. Depending on the growth temperature, the disordered fluorite and the ordered pyrochlore structure can be stabilized. Both phases have been found to be stable against Si, whereas high oxygen migration in the disordered fluorite phase led to the formation of an amorphous SiO$_2$ interfacial layer. With the high-temperature pyrochlore phase, the amorphous interface is significantly reduced. These results are promising for epitaxial growth of crystalline LZO without any SiO$_2$ formation.

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