Growth of La$_2$Ti$_2$O$_7$ and LaTiO$_3$ thin films using pulsed laser deposition

S. Havelia, K.R. Balasubramaniam, S. Spurgeon, F. Cormack, P.A. Salvador*

Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA

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Abstract

The influence of substrate temperature, oxygen activity of the ambient gas, and substrate type on the growth morphology, phase selection, and epitaxy of thin films in the LaTiO$_x$ (x≈3.0 or 3.5) family were investigated. The films were deposited using pulsed laser deposition (PLD) from a La$_2$Ti$_2$O$_7$ target and were characterized using X-ray diffraction. In oxygen atmospheres, coupled with high deposition temperatures and use of (1 1 0)-oriented SrTiO$_3$ substrates, the growth of epitaxial films of (1 1 0)-layered perovskite La$_2$Ti$_2$O$_7$ is observed. However, under similar deposition conditions, on SrTiO$_3$(1 0 0) substrates, no crystalline peaks were observed even at the higher temperatures. The reduction of Ti$^{4+}$ to Ti$^{3+}$ was achieved by the use of nitrogen atmospheres. This resulted in the formation of the cubic perovskite LaTiO$_3$, on SrTiO$_3$(1 1 0), SrTiO$_3$(1 0 0), and LaAlO$_3$(1 0 0) substrates.

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1. Introduction

Layered perovskites having the general formula A$_2$B$_2$O$_7$ have attracted great interest for their ferroelectric [1–4] and photocatalytic properties [5–8]. These compounds are the n=4 members of the homologous series of compounds having a general formula A$_n$B$_n$O$_{3n+2}$, 1≤n≤∞, based on the number of perovskite unit-cells in each layer [9–12]. With respect to the parent perovskite (n=∞), the structure has an extra layer of O$_2$ inserted after every four (n=4) distorted perovskite units, as described by Brandon and Megaw [9], A$_2$Ti$_2$O$_7$ [10], A$_2$Nb$_2$O$_7$ [11], and A$_2$Ta$_2$O$_7$ [12] with A = RE or AE (RE = rare-earth, AE = alkaline-earth) are some of the compounds that belong to this family.

The RE$_2$Ti$_2$O$_7$ compound with RE = La crystallizes in a monoclinic form of the (1 1 0)-layered perovskite structure in the bulk [10]. La$_2$Ti$_2$O$_7$ has been the most commonly studied compound in the RE$_2$Ti$_2$O$_7$ family of materials, owing to the fact that it forms easily when synthesized using normal ceramic preparation methods [13–18], and it exhibits a high Curie temperature (≈1500°C) [1,2]. Most film studies have focused on polycrystalline forms; epitaxial films of La$_2$Ti$_2$O$_7$ have also been synthesized on SrTiO$_3$ (1 1 0) substrates using molecular beam epitaxy (MBE) [19]. However, there are no reports on the epitaxial growth of La$_2$Ti$_2$O$_7$ films using pulsed laser deposition (PLD). Owing to the large instantaneous supersaturation present during PLD, one expects very different kinetics during PLD growth when compared with MBE growth, which may have a significant impact on the growth of materials that have large unit cells (such as La$_2$Ti$_2$O$_7$).

The literature on the growth of LaTiO$_3$ is very sparse; only a few reports on the synthesis of bulk [20,21] or thin film [22–25] LaTiO$_3$ exist. Thin film studies have focused largely on the synthesis of La$_{1-x}$Sr$_x$TiO$_3$ [23–25], where 0<x<0.5. Recently, Shibuya et al. [26] have synthesized LaTiO$_3$/SrTiO$_3$ superlattice structures under very low oxygen pressures of 10$^{-6}$ Torr O$_2$ using PLD. In most of these reports, a low overall pressure is used to yield a low oxygen activity, which causes the reduction of the titanium that is required to form LaTiO$_3$ in the perovskite structure. To control the oxygen activity at such low pressures, a much lower chamber base pressure is required, leading to the necessity of ultra-high vacuum equipment. Moreover, the overall pressure used in PLD affects both the thermodynamics (oxygen activity both in the plasma and between pulses for the growing film) and kinetics (type of
species and their kinetic energy on arrival) significantly and in a manner that is difficult to predict [27].

We are interested in understanding the phase competition in the RETiO$_3$ system ($3 \leq x \leq 3.5$) during PLD growth of thin films at total pressures more typical to oxide film growth by PLD: in the range of $10^{-2}$–$10^{-4}$ Torr. In this report, we focused on the growth of LaTiO$_3$ on SrTiO$_3$(1 1 0) and SrTiO$_3$(1 1 0) substrates in both molecular oxygen (high oxygen activity) and molecular nitrogen (low oxygen activity) ambients, allowing us to vary the chamber oxygen activity without altering other ablation characteristics.

The principal observation of this study is that the phase selection in the La$_2$TiO$_4$ material system can be dictated by changing the oxygen activity of the ambient gas, without changing absolute pressure. In O$_2$ environments, films grow in the bulk-stable (1 1 0)-layered perovskite phase (La$_2$Ti$_2$O$_7$). Owing to the large unit cell, other factors strongly affect the crystalline quality of the deposited film, such as substrate orientation, substrate temperature, and absolute pressure. In contrast, carrying out the deposition in a N$_2$ atmosphere (while all else was held constant) results in the reduction of Ti$^{4+}$ accompanied by the formation of perovskite LaTiO$_3$ thin films. Since the LaTiO$_3$ unit cell is small and dense, substrate temperature and absolute pressure play a less significant role in crystal quality.

2. Experimental procedure

The La$_2$Ti$_2$O$_7$ target was synthesized using standard solid-state ceramic synthesis methods [13]. The precursor compounds, which were La$_2$O$_3$ (99.999%) and TiO$_2$ (99.995%), were weighed in the correct proportions and mixed together. The materials were first wet ground in ethanol and then were dry ground; both grindings were for 20 min using an alumina mortar and pestle. The ground powders were pressed into pellets using a uniaxial press. The pellets were annealed at three different temperatures of 700–900 °C, then at 1200 °C, and finally at 1400 °C. The first two annealing steps were for 12 h each and the final step was for 24 h. Between each annealing step, the pellets were re-ground and re-pressed as described above. The sintered pellet was characterized using a Rigaku X-ray diffractometer; it was verified to be polycrystalline (1 1 0)-layered perovskite La$_2$Ti$_2$O$_7$. The La$_2$Ti$_2$O$_7$ pellet was then used as the target in the film deposition process.

Films were deposited on single crystal substrates, (1 0 0)- and (1 1 0)-oriented SrTiO$_3$ and (1 0 0)-LaAlO$_3$ (using pseudocubic indices), obtained from a commercial vendor (Crystal GmbH, Berlin, Germany). Prior to deposition, the substrates were cleaned, etched, and annealed as follows. All substrates were first ultrasonically cleaned in acetone and ethanol (each for 5 min). The substrates were etched in a 3:1 HCl:HNO$\text{}_3$ mixture for 4 min and rinsed using deionized water [28]. All samples were then mounted to the PLD heater-plate using silver paste. This was followed by a thermal anneal in the PLD chamber at 800 °C in 100 mTorr O$_2$ for 1 h.

PLD was carried out in a commercial deposition system (Neocera®, Maryland, USA) using a KrF excimer laser operating at a wavelength of 248 nm. The laser was pulsed at a rate of 3 Hz with an energy density of $\approx 2$ J/cm$^2$ and a spot size of 8 mm$^2$ at the target surface. The chamber was pumped down to a base pressure of $\approx 10^{-6}$ Torr at room temperature before heating was commenced. The heater was maintained at different temperatures, in the range of 700–900 °C, and the target to substrate distance was fixed at $\approx 60$ mm. During deposition, the dynamic pressure was maintained between 1 and 100 mTorr by throttling the turbomolecular pump to 40% of its rotation speed while the process gas (O$_2$ or N$_2$) was bled into the chamber through a leak valve. The films were grown for 60 min and were $\approx 100$ nm thick as determined by X-ray reflectivity. All films were cooled down to room temperature under a static pressure of 200 Torr of the process gas. To explore the effect of background oxidizing species, some depositions were carried out using a titanium sublimation pump to decrease the background pressure to $4 \times 10^{-7}$ Torr at room temperature and to $7.5 \times 10^{-6}$ Torr at 900 °C, before depositing as described above.

The crystalline nature (phase, crystalline quality, and epitaxial relationship) of the films was characterized using both a Rigaku and a Philip’s X’Pert X-ray diffractometers equipped with Cu K$\alpha$ radiation; normal $\theta–2\theta$ scans were carried out on the former, while $\omega$ and $\phi$ scans were carried out on the latter.

3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns for La$_2$Ti$_2$O$_7$ films deposited at three different temperatures of $T =$ (a) 700, (b) 800, and (c) 900 °C on SrTiO$_3$ (1 1 0)
La$_2$Ti$_2$O$_7$ are observed. Such a relationship between film X-ray peaks corresponding to the (0 0 1) orientation of La$_2$Ti$_2$O$_7$ is expected, because the planes share the geometric arrangement of the perovskite (1 1 0)-planes. However, this is observed only at higher temperatures, because considerable diffusion is required both parallel to and normal to the substrate surface in order for the layers to align properly. In general, diffusion normal to the substrate requires substantial thermal energy. Therefore, higher temperatures lead to better c-axis alignment of the La$_2$Ti$_2$O$_7$ films. At lower temperatures where diffusion is limited, the c-axis cannot order properly out-of-plane and therefore results in X-ray amorphous films.

Fig. 2 shows the X-ray diffraction pattern of La$_2$Ti$_2$O$_7$ films deposited at 900 °C in a background oxygen pressure of 50 mTorr on (a) SrTiO$_3$(1 1 0) and (b) SrTiO$_3$(1 0 0). On SrTiO$_3$(1 1 0) substrates (Fig. 2(a)), the film is (0 0 1)-oriented, has good crystallinity, and is epitaxial (as shown below) with the substrate. However, on SrTiO$_3$(1 0 0) substrates, X-ray amorphous films are produced even at these high temperatures, Fig. 2(b). This contrasting growth of epitaxial, high quality, crystalline La$_2$Ti$_2$O$_7$ on SrTiO$_3$(1 1 0) compared with growth of X-ray amorphous La$_2$Ti$_2$O$_7$ on SrTiO$_3$ (1 0 0) can be attributed to the geometric similarity/dissimilarity between the La$_2$Ti$_2$O$_7$ (0 0 1)/(h k l) planes and the (1 1 0)/(1 0 0) planes of SrTiO$_3$. The layered perovskite does not have any geometrically similar plane to the (1 0 0) plane of SrTiO$_3$ (although it does have some geometrically similar directions) and thus the crystallization of La$_2$Ti$_2$O$_7$ thin films on SrTiO$_3$(1 0 0) substrates is frustrated. As a consequence, X-ray amorphous (i.e., nanocrystalline or amorphous) films are obtained. On the other hand, high-quality crystalline peaks are obtained when the substrate favors a specific film orientation (such as La$_2$Ti$_2$O$_7$(0 0 1) on SrTiO$_3$(1 1 0)) and when the kinetics are sufficient to promote that growth (temperatures sufficient to fully order the complex layered perovskite).

Fig. 3 shows the φ-scans registered from the {2 0 4} reflections (indexed using the P2$_1$1 crystal symmetry of the bulk material) of the La$_2$Ti$_2$O$_7$ (1 1 0)-layered perovskite and from the {1 1 1} reflections of the SrTiO$_3$(1 1 0) substrate (ψ = 34.94°, 2θ = 39.99°). Two {2 0 4} peaks are observed in the scan (registered with ψ = 43.28°, 2θ = 33.49°), which indicates that the epitaxial film is twinned. The epitaxial relationship between the film and the substrate is given by \( {0 0 1}_{\text{La}_2\text{Ti}_2\text{O}_7} // \{1 1 1\}_{\text{SrTiO}_3} \) and \( \{0 1 0\}_{\text{La}_2\text{Ti}_2\text{O}_7} // \{1 1 0\}_{\text{SrTiO}_3} \). The inset of Fig. 3 shows the \( \theta–2\theta \) scan registered at ψ = 43.28°, φ = 90.57° for La$_2$Ti$_2$O$_7$. The presence of only \( \{0 2 0\}_{\phi} \) reflections further confirms the high-quality epitaxy of the films. The presence of \( \{3 0 6\} \) reflections confirms that the structure is monoclinic and isostructural to bulk La$_2$Ti$_2$O$_7$ (as opposed to adopting an orthorhombic form isostructural to Sr$_2$Nb$_2$O$_7$).

The lattice parameters for La$_2$Ti$_2$O$_7$ were refined in a monoclinic lattice using the Unit Cell program [31]. Six different families of out-of-plane film peaks \( \{0 2 4\}, \{2 0 4\}, \{0 2 6\}, \{0 1 1\}, \{2 1 1\}, \text{and} \{2 1 0\} \) with reflections in the range \( \theta = 10–90° \) were used to refine the lattice parameters. While we assumed the films to be completely relaxed, the lattice parameters we determined include any homogeneous strain present in the system. The unit cell parameters

![Fig. 2. XRD patterns of La$_2$Ti$_2$O$_7$ thin films grown at $p_{O_2}$ = 50 mTorr and 900 °C on (a) SrTiO$_3$(1 1 0) and (b) SrTiO$_3$(1 0 0) substrates.](image-url)

![Fig. 3. Azimuthal φ-scans of the {2 0 4} reflection from the La$_2$Ti$_2$O$_7$ film (upper graph) and the (1 1 1) reflection from the substrate (lower graph). The film was deposited on SrTiO$_3$(1 1 0) at 900 °C and 50 mTorr $O_2$. The inset shows the $\theta–2\theta$ XRD pattern of the {2 0 4} reflections from the film.](image-url)
are given in Table 1, along with several values previously reported in the literature for La$_2$Ti$_2$O$_7$, made using various techniques; our film values are in good agreement with the previously reported values, which indicates that the films are largely or completely relaxed.

In order to facilitate the reduction of the Ti$^{4+}$ cation, one needs to be in reducing conditions. Shibuya et al. [26] have realized the growth of extremely thin films of LaTiO$_3$ (in a superlattice structure with SrTiO$_3$) under very low oxygen pressures. Our hypothesis is that nitrogen atmospheres of $\approx 10^{-3}$–$10^{-4}$ Torr are sufficiently reducing to lead to the formation of an epitaxial LaTiO$_3$ perovskite phase rather than the formation of La$_2$Ti$_2$O$_7$. In other words, since the partial pressure of oxygen in nitrogen gas is $\approx 10^{-6}$–$10^{-5}$ Torr, the activity of oxygen in our chamber can be approximated between $\approx 10^{-9}$ and $10^{-6}$ Torr (ignoring contributions from the chamber walls). This activity range is similar to the absolute oxygen activity used for the growth of LaTiO$_3$ in O$_2$ ambients.

Fig. 4 shows the XRD patterns for films deposited on (a) SrTiO$_3$(1 0 0) and (b) SrTiO$_3$(1 1 0) from the La$_2$Ti$_2$O$_7$ oxide target for 1 h in a background pressure of 50 mTorr N$_2$ and at $T_s = 900$ °C. Note that these conditions are identical to the conditions used above for La$_2$Ti$_2$O$_7$ growth, with the exception that nitrogen has replaced oxygen as the process gas. However, in these conditions, the Ti$^{4+}$ is reduced and the films form as the LaTiO$_3$ perovskite in an epitaxial fashion on both substrates. In Fig. 4(a), peaks corresponding to a (1 0 0)-oriented perovskite film are observed. The lattice parameter of LaTiO$_3$ is very close to that of SrTiO$_3$, so in order to see the peak distinctly, the $2\theta$ space around the (2 0 0) peak has been shown in the inset. From the $2\theta$ positions of these peaks, the $d$-spacing of the (1 1 1) planes is 2.279 Å. Combined with the out-of-plane lattice parameter of 3.957 Å, this gives an in-plane lattice parameter of 3.942 Å. The in-plane lattice parameter is smaller than the out-of-plane perovskite lattice parameter, i.e., the films are slightly tetragonally distorted. These results are

![Log Intensity vs 2 Theta for LaTiO3 thin films grown in 50 mTorr N2 at 900°C](image)

**Table 1**

| Lattice parameters of the (1 1 0)-layered perovskite La$_2$Ti$_2$O$_7$ obtained in this study after refinement using Unit Cell program [31] |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| La$_2$Ti$_2$O$_7$ | This work | High pressure [17] | Sol–gel [18] | MBE [19] |
| a | 7.804 | 7.80 | 7.814 | 7.812 |
| b | 5.538 | 5.54 | 5.547 | 5.544 |
| c | 13.01 | 13.01 | 13.019 | 13.01 |
| $\beta$ | 98.48 | 98.37 | 98.43 | 98.66 |

Lattice parameters for La$_2$Ti$_2$O$_7$ made using various synthesis techniques collected from the literature are given in columns 3-5 [17–19].
consistent with the film adopting a distorted perovskite phase, which might be expected for a partially relaxed film experiencing an in-plane compressive stress (the SrTiO$_3$ substrate has a smaller lattice parameter—3.905 Å—than those the film). It should be noted that both the out-of-plane (3.957 Å) and in-plane (3.942 Å) lattice parameters of these films are larger than the reported values for bulk LaTiO$_3$ (3.928 Å [20]). The larger lattice parameter of our films could be attributed to various different possibilities. Planar defects like stacking faults are known to occur in LaTiO$_3$ films deposited under low oxygen pressures [22]. Background oxygen, or other oxidizing species desorbing from the chamber walls, could also have affected the crystalline quality of the reduced phases.

To explore this possibility, a set of films were grown in which the background chamber pressure was decreased by approximately an order of magnitude by using a titanium sublimation pump, such that the chamber pressure at 900 °C was $7.5 \times 10^{-6}$ Torr. Atomic force microscopy experiments (not shown) indicated that such conditions severely degraded the surfaces of the SrTiO$_3$ substrates, but that LaAlO$_3$(0 0 1) surfaces were stable in these aggressively reducing conditions. Fig. 6 shows the XRD patterns for films deposited on LaAlO$_3$(0 0 1) substrates using (a) the standard background pressure and (b) the reduced background pressure; both were deposited from the La$_2$Ti$_2$O$_7$ oxide target for 1 h in a background pressure of 50 mTorr N$_2$ and at $T_s = 900$ °C.

4. Conclusions

The choice of the ambient gas plays the major structure-directing role in the phase selection between La$_2$Ti$_2$O$_7$ and LaTiO$_3$ during thin film growth using PLD. Deposition from a La$_2$Ti$_2$O$_7$ target in oxygen atmospheres resulted in the formation of an epitaxial La$_2$Ti$_2$O$_7$ thin film on perovskite SrTiO$_3$(1 1 0) substrates. High substrate temperatures are needed to obtain high-quality crystalline films of the layered perovskite, whose epitaxial relationship is $(0 0 1)_{\text{La}_2\text{Ti}_2\text{O}_7} \parallel (1 1 0)_{\text{SrTiO}_3}$; $(0 1 0)_{\text{La}_2\text{Ti}_2\text{O}_7} \parallel (1 1 0)_{\text{SrTiO}_3}$. The lattice parameters measured on the film were similar to the expected bulk parameters. Deposition from the same target in nitrogen atmospheres resulted in the formation of LaTiO$_3$ perovskite on SrTiO$_3$(1 1 0), SrTiO$_3$(1 0 0), and LaAlO$_3$(1 0 0) substrates.
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