Narrow growth window for stoichiometric, layer-by-layer growth of LaAlO₃ thin films using pulsed laser deposition

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Abstract

We study the structure and surface morphology of the 100 nm homoepitaxial LaAlO₃ films grown by pulsed laser deposition in a broad range of growth parameters. We show that there is a narrow window of growth conditions in which the stoichiometric, bulk-like structure is obtained while maintaining a 2-dimensional (2D) layer-by-layer growth mode. In our system, these optimum growth conditions are 100 mTorr background pressure with laser energy density 1.5–2 J/cm². The sensitivity to growth conditions of the stoichiometry and structure of LaAlO₃ films can have a crucial role in the 2-D electron gas formed at the LaAlO₃/SrTiO₃ interface.

Keywords

A1. Defects; A1. Surface structure; A3. Laser Epitaxy; B1. Oxides; B1. Perovskites; B2. Dielectric materials

1. Introduction

LaAlO₃ (LAO) exhibits a crystal structure and physical properties that make it an appealing material for a broad range of applications. At room temperature, LAO is a rhombohedral perovskite with a pseudocubic lattice parameter of 0.379 nm,¹ a dielectric constant² of 24 and band gap of 5.6 eV.³ Its lattice parameter, high dielectric constant, and low dielectric loss make it a suitable substrate for high-temperature superconductors in microwave devices⁴ and a potential candidate for high-permittivity gate oxides in integrated circuits.⁵ It is also widely used as a substrate and buffer layer^{6,7} in the design of oxide heterostructures with new functionalities.⁸⁻¹⁰

The discovery of the 2-dimensional electron gas (2DEG) between LAO and SrTiO₃ (STO) by Ohtomo and Hwang¹¹ drew much attention to the growth and properties of LAO films during the last decade. Although the origin of the observed interfacial conductivity is still extensively debated, it has been shown that the so-called “polar catastrophe”, an intrinsic electronic reconstruction, plays a significant role.^{12,13} Experimental evidence suggests that defects such as cation non-stoichiometry¹⁴⁻¹⁹ and oxygen vacancies²⁰⁻²⁴ can also contribute to the observed conductivity.

Although LAO films can be grown by various techniques,^{6,25-27} pulsed laser deposition (PLD) is the most common method reported in the literature. In the PLD technique, nonequilibrium conditions in the ablation plume and the high kinetic energy of ablated molecular species²⁸ lead to growth-induced defects that can significantly alter the properties of oxide thin films²⁹. To date, controlling the growth parameters to avoid the formation of defects during the PLD growth remains a major challenge in the thin film community.²⁹⁻³² In the case of LAO films, most previous studies centered on the effect of laser parameters (fluence, spot size) on the film cation stoichiometry.^{15-18,33-35} Oxygen stoichiometry has also been shown to have an impact on the characteristics of LAO^{28,36}. Variations in the oxygen growth pressure have a dramatic effect on the LAO/STO interface properties^{22-24,37} attributed to oxygen vacancies in the STO substrate²² and roughness of the LAO/STO interface³⁸. When used as a high-*K* oxide in complementary metal-oxide semiconductor (CMOS) devices, oxygen vacancies in LAO lead to charge trapping, transient threshold voltage shifts and a degradation of underneath Si substrate³⁹. Until now, only a few studies⁴⁰ have focused on the effect of

oxygen partial pressure on the properties of LAO films. To fully exploit the impact of growth-induced defects on the properties of LAO films, it should be evaluated as an isolated system without the complications arising from substrate/film interactions^{36,41} such as epitaxial strain between the LAO film and the substrate.

To understand the influence of growth conditions on structural properties of LAO films, we have grown homoepitaxial LAO films in a range of background oxygen pressures and laser energy densities and studied the relationship of growth parameters to the structure by x-ray diffraction (XRD) and atomic force microscopy (AFM). We show that only films grown at higher oxygen pressures of 100-300 mTorr, much higher than typically reported in the literature, have lattice parameters identical or close to that of the LAO single crystal substrate. Films grown at oxygen pressures 10^{-2} - 10^{-4} Torr show a 1.3%-2.5% lattice expansion, indicating either cation nonstoichiometry or oxygen deficiency in the films.^{18,36} Moreover, the surface morphology of our films show that, even in the absence of epitaxial strain, the growth mode is highly affected by the growth parameters.⁴² A 2D, layer-by-layer growth mode was achieved in our system at oxygen pressures of up to 100 mTorr and a high laser fluence.

2. Experimental

A total of 15 LAO films were grown on polished, single-crystal (001)_{pc} LAO substrates (Crystec. GmbH, Germany) (We will use pseudocubic notation throughout this paper). All substrates were etched in HCl for 5 minutes followed by an oxygen anneal at 750 °C for 1 hour.⁴³ 100 nm thick LAO films were grown by conventional PLD using a KrF excimer laser ($\lambda = 248$ nm, pulse duration 25 ns) from a single crystal LAO target. The depositions were carried out at laser energy densities of 1, 1.5 and 2 J/cm², and oxygen pressures, between 0.3 and 10^{-4} Torr (the background vacuum is 10^{-6} Torr). Details on the thickness calibration and growth rate are explained elsewhere.³² Deposition was carried out at a substrate temperature of 730 °C, and the samples were cooled down to room temperature after growth in an oxygen pressure of 200 Torr.

The structural properties of the deposited LAO films were analyzed by x-ray diffraction (XRD, Bruker D8 Discover diffractometer using Cu K α radiation). The film texture and epitaxial quality were characterized by θ -2 θ scans and reciprocal space mapping (RSM), from which the out-of-plane and in-plane lattice constants

of the LAO films were evaluated. The surface morphology was determined by atomic force microscopy (AFM, Bruker dimension icon in tapping mode).

3. Results and discussion

Accurate characterization of expansion of the unit cell due to vacancies (either cation or oxygen) can be achieved by studying the lattice parameters of homoepitaxially grown films, as has been done most commonly with STO for which the lattice expansion due to off-stoichiometry is well established.^{29, 44, 45} For homoepitaxial LAO, such an effect has not been studied in detail, however lattice expansion induced by off-stoichiometry has been reported for heteroepitaxial LAO films.¹⁸ Fig. 1(a) shows symmetric ω - 2θ scan around the (002) peak of the substrate for all 15 films in this study. In all three spectra of Panel (i) of Fig. 1(a), corresponding to films grown at 0.3 Torr oxygen and energy densities of 1, 1.5 and 2 J/cm², the film (002) peak is indistinguishable from the substrate peak indicating identical out-of-plane lattice parameter. When the oxygen pressure is reduced to 0.1 Torr (Panel ii in Figure 1(a)), the (002) peak of the films grown at 1.5 and 2 J/cm² fluence exhibit a film peak at a slightly smaller 2θ angle than the substrate, indicating an out-of-plane expansion. As the oxygen pressure is further reduced (Panel iii, iv and v in Figure 1(a)), the peak separation increases, indicating a larger deviation of the film lattice parameters from an ideal single crystal. In certain growth conditions (e.g. 10⁻³ Torr oxygen pressure and energy densities of 1.5 and 2 J/cm²) the film exhibits a double peak that could be explained by the formation of a second phase, or formation of grains with different orientations.

The in-plane lattice spacing of LAO films were evaluated by reciprocal space maps (RSMs) of the (103) reflection of the substrate. Representative RSMs are shown in Figure 1(b) for samples grown at laser energy density of 1 J/cm² and different oxygen pressures, with the substrate shown for comparison. The splitting seen in the substrate (103) peak along the H direction is a result of the twinning of the rhombohedral unit cell that forms upon heating⁴⁶. Although the formation of twins does not have an effect on XRD θ - 2θ scans, it can be seen on the XRD rocking curve scan of the bare substrate (not shown here). In the RSM of Fig. 1(b), the LAO film peaks can be distinguished from the substrate peak by a broadening along L direction or as an

extra film peak at $L < 3$ and $H = 1$. The identical in-plane a lattice parameter to the LAO substrate confirms that all films are coherently strained to the substrate.

For the off-stoichiometric films, we can estimate the bulk pseudocubic LAO (unstrained) lattice parameter c_0 using the Poisson's ratio. To first-order approximation under conditions of biaxial stress, the Poisson ratio can be written as⁴⁷ $\nu = \frac{1}{(1-2\frac{\epsilon_{xx}}{\epsilon_{zz}})}$, where ν is the Poisson's ratio of LAO, and ϵ_{xx} and ϵ_{zz} are in-plane and out-of-plane strain of the LAO films, respectively. We assume $\nu = 0.26$ for LAO⁴⁸ and use the measured a_{film} and c_{film} from the XRD data of Fig. 1. Fig. 2 shows the calculated pseudocubic lattice parameter of the LAO films (i.e. pseudocubic lattice parameter if the films were fully relaxed) as a function of laser energy density for different oxygen pressures. From the graph, it is clear that films grown at an oxygen pressure of 300 mTorr have bulk like lattice parameters regardless of laser energy density. By reducing the growth pressure to 100 mTorr, no c lattice expansion was observed at the lowest energy density (1 J/cm^2), while an expansion of 0.5% was observed at higher energy densities. All films grown at lower pressures of 10^{-2} - 10^{-4} Torr have a c lattice expansion of 1.3%-2.5% that is nearly independent of pressure in this range of energy densities. Fig. 2 shows clearly that, using our PLD configuration, it is impossible to grow a stoichiometric LAO film at a pressure of 10^{-2} Torr and lower.

This conclusion can be interpreted considering the plume kinetics: in the study of Aruta et al., an abrupt decrease in the maximum kinetic energy of the ablated species occurs between an oxygen pressure of 10^{-2} mbar to 10^{-1} mbar;²⁸ above 10^{-1} mbar the molecules' kinetic energies in the plume approach thermalized values, while below they can be several to tens of eV. At the same time, it is known that a high kinetic energy of arriving species can be responsible for intermixing by knock-on, as well as the formation of oxygen vacancies³⁸. Increasing the energy density at fixed pressure also increases the species' kinetic energy, in agreement with the trend at lower pressures in Fig. 2. These considerations suggest that the high kinetic energy of species in plume plasma is responsible for the defects that cause the lattice expansion.

To grow high quality epitaxial films, both growth mode, and surface morphology must be controlled as well. A 2D growth mode, including layer by layer growth mechanism ("Frank-van der Merwe"), can ensure atomically smooth surfaces with root-mean-square roughness $R_q < 1 \text{ nm}$ that are essential for the

construction of sharp interfaces and coherent superlattices. To better evaluate the optimum growth conditions, AFM images were taken to study the growth mode and the surface microstructure of LAO thin films and their evolution with the growth parameters. As shown in Fig. 3(a)-(d), the AFM images show three types of the surface morphology. The first group of the films with R_q less than 0.4 nm (Fig. 3(e)) are atomically flat with monoatomic steps suggesting layer-by-layer growth mode (Fig. 3(b)) in which the final film surface reproduces the starting substrate morphology. Films with R_q of 0.4-1.2 nm are smooth with very fine grains, indicating a pseudo-two-dimensional growth mode (likely layer-plus-island or “Stranski–Krastanov”) (Fig. 3(c)). At low laser energy density of 1 J/cm², the smooth surface transforms into large sized islands (Fig. 3(d)). The morphology of films with the islands and the high surface roughness suggest that, at low laser energy density, depending on pressure, growth occurs in island mode.⁴² The data in Fig. 3 is consistent with the model that a higher kinetic energy of the arriving species on the surface favors higher surface mobility and consequently 2D growth and a smooth surface, with the exception of the data point at 10⁻² Torr and 1.0 J/cm².

Taken together, the data in Figs. 1, 2 and 3 show competition between off-stoichiometry at low growth pressures, solved by increasing pressure to ~10⁻¹ Torr and lowering the energy density, and rough surfaces at low energy density, that is solved by increasing energy density to 1.5–2 J/cm². By combining the condition for obtaining a stoichiometric film and smooth surface, we conclude that the best growth conditions in our chamber are $P = 0.1$ Torr and $E = 1.5\text{--}2$ J/cm².

4. Conclusions

To summarize, by controlling PLD growth parameters we found the optimum condition for the 2D growth of homoepitaxial LAO films with a structure similar to LAO substrate. In our study, oxygen pressure plays a more important role in controlling the structure, while energy density plays a more important role in controlling the growth mode. This results can be important for understanding the mechanism responsible for the conductivity of LAO/STO interface. Our results show that at low growth pressure (<100 mTorr) it is impossible to get bulk like structure in our PLD chamber, while this pressure (100 mTorr) has been shown to be a cut off pressure for obtaining a 2D electron gas²⁸ for which the interface between STO film and LAO

substrate becomes insulating. These results suggest that the deviation from the bulk properties of LAO films may also make a contribution the 2D electron gas observed in these interfaces.

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Figures

Figure 1. (a) XRD θ - 2θ scans for LAO films deposited with 3 different laser energy densities of 1, 1.5 and 2 J/cm² and oxygen pressures of (i) 0.3 Torr, (ii) 0.1 Torr, (iii) 10^{-2} Torr, (iv) 10^{-3} Torr and (v) 10^{-4} Torr. (b) Reciprocal space maps around (103) diffraction peaks for (a) LAO substrate and (b)-(e) 100 nm LAO (001) homoepitaxial thin films grown at laser energy density of 1 J/cm² under different growth oxygen pressures. Peaks at $L=3$ and $H=1$ correspond to the substrate. A red arrow is pointing to the film peak if different from substrate peak. All intensities are in logarithmic scales.

Figure 2. Calculated pseudocubic (relaxed) lattice parameter of LAO films in Fig. 1, setting $a_{film} = c_{film} = c_0$ in Eqn. (2) and fixing $\nu = 0.26$. The strain due to the expanded lattice ranges from 0 to +1.5% (always compressive).

Figure 3. $1\ \mu\text{m} \times 1\ \mu\text{m}$ atomic force microscopy image of the surface of (a) LAO substrate and LAO films grown at laser energy density and Oxygen pressure of (b) 2 J/cm^2 , 100 mTorr, (c) 2 J/cm^2 , 10^{-3} Torr and (d) 1 J/cm^2 , 300 mTorr with R_q of (a) 0.18nm, (b) 0.29nm, (c) 0.97nm and (d) 12.5nm respectively. (e) Surface

root-mean-square roughness (R_q) dependence of the LAO thin films on laser energy density and growth oxygen pressure.