Atomic-scale investigations of perovskite oxide heteroepitaxy

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We have developed a low-temperature, high-magnetic-field scanning tunneling microscope combined with pulsed laser deposition. This system enables us to study atomic-scale growth of oxide thin films. In this paper, we investigated growth-mode-controlled epitaxial SrTiO\textsubscript{3} (STO) and LaAlO\textsubscript{3} films on STO(001) single-crystal substrates. A \((\sqrt{13} \times \sqrt{13})\)-R33.7° STO(001) substrate, prepared in oxygen atmosphere, is atomically resolved and plays a crucial role in elucidating the initial growth process. Atomic-scale microscopic approach performed in this study opens up a way to novel functionalities in oxide thin films and heterostructures.

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1. Introduction

Transition-metal oxides represent a very important class of materials owing to their diverse functional properties. The distinctive and exceptional properties of metal oxides are the manifestations of their inherent chemical and physical complexities, originating due to the interplay of their charge, spin, lattice, and orbital degrees of freedom. Lately, the inhomogeneities of the electronic states at the atomic-scale have been strongly correlated to the remarkable properties of the materials.

In particular, the heterointerfaces of such oxides have attracted considerable interest because of its potential contribution to the origin of intriguing properties, such as conductivity, magnetism, and superconductivity, observed at the interface between LaAlO\textsubscript{3} (LAO) and SrTiO\textsubscript{3} (STO). Although intense studies have been conducted to clarify the origin of these properties, a comprehensive picture of the physics and chemistry underlying this phenomenon has not been established yet. This necessitates further insights on the microscopic growth behavior of oxide thin films, in order to gain a better understanding of the phenomena occurring in complex oxide thin films and heterostructures. To this end, scanning tunneling microscopy/spectroscopy (STM/STS), combined with pulsed laser deposition (PLD) for the growth of oxide films, will enable us to examine the growth of oxide thin films on an atomic-scale, with higher resolution below 1 meV.

Herein, we report the investigation of the growth of STO and LAO epitaxial films, on atomically ordered reconstructed STO substrate. Atomically resolved STM imaging of oxide thin films with a unit cell (UC) reveals unexpected initial growth behaviors. Firstly, we have compared the homoepitaxial STO films surface prepared by both step-flow and layer-by-layer growth modes. Subsequently, we have discussed the initial growth behavior of LAO on these two substrates, namely, reconstructed and unreconstructed STO substrates. The microscopic and spectroscopic investigations performed in this study is expected to provide deeper insights on the growth of functional oxide films, and suggest possible guiding principles for creating novel functionalities in oxide heterostructures.

2. Experimental

In this study, the oxide films were deposited on two different types of substrates. The main substrate used in this study is a reconstructed STO \((\sqrt{13} \times \sqrt{13})\)-R33.7° surface, hereafter called as the reconstructed surface. In the typical process, buffered-HF (BH)-etched Nb-doped STO(001) (Nb: 0.1 at.%) substrates were first annealed at 500°C for 2 h, in order to degas the substrate. Following that, the degassed substrate was annealed at 850°C for 0.5 h, in oxygen partial pressure \((P_{O_2})\) of \(1 \times 10^{-5}\) Torr. During the annealing process, the sample temperature was raised to 1000°C, in order to straighten the steps and terraces. Detailed explanation of the experimental procedure has been published earlier in the literature. The other substrate, hereafter mentioned as unreconstructed STO surface, was prepared by the conventional protocol adopted for the preparation of substrates. Prior to the deposition of oxide film, the BHF-etched substrate was kept maintained at a temperature of 1000°C and \(P_{O_2}\) of \(1 \times 10^{-6}\) Torr for 0.5 h. Both the STO substrates used in this study are Nb-doped, in order to ensure necessary conductivity for STM observations at low temperature. The samples were heated via direct current resistive heating, and the presence of wide terraces with straight step-edges of the height of UC was confirmed by using STM.

Subsequently, undoped STO and LAO thin films were grown on the prepared substrates by using PLD. A KrF excimer laser of wavelength 248 nm was employed for the ablation of single-crystal STO and LAO targets, with the laser fluence of 1.2 and 0.41 J/cm\(^2\), respectively at the target surfaces. In the PLD process, the STO and LAO films were grown at a temperature of 700–1100°C, under \(P_{O_2}\) of \(1 \times 10^{-6}\) and \(1 \times 10^{-5}\) Torr, respectively. Growth of the films was monitored in situ by reflection high-energy electron diffraction (RHEED). Details on the PLD conditions adopted for the deposition have been reported elsewhere. After deposition, the samples were cooled down to room temperature and then immediately transferred to the STM chamber without exposing the sample surface to air ambient.

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The STM/STS measurements were conducted at 5 and 78 K with W and Pt-Ir tips. All STM images were obtained in a constant current mode.

3. Results and discussions

Figure 1 illustrates the schematic diagram of the STM-PLD system used in this study. The system consists of three chambers, namely, a PLD chamber, an STM tip preparation chamber, and a low-temperature STM with a superconducting vector magnet. This system enables us to perform in situ STM measurements immediately after the deposition of oxide thin films, without exposing the samples to air ambient. Moreover, the use of two vibration isolation systems, namely, active and passive damper, facilitates high-resolution spectroscopic imaging. In other terms, the tunneling spectra are collected from all the imaging sites. Details of this STM-PLD system have been published elsewhere.13,14)

Using this system, we deposited STO homoepitaxial films in two different growth modes, namely, step-flow and layer-by-layer growth and the resulting surface structures have been compared. Figure 2(a) shows the RHEED oscillations of (00) specular beam intensity, where we could observe the oscillatory behavior between exponential recovery and the initial intensity. This characteristic is typical of a step-flow growth. The STM image (100 nm x 100 nm) of the thin film deposited on conventional STO substrates at 1100°C and P_O2 of 1 x 10^-6 Torr (100-UCs STO film), shown in Fig. 2(b), indicates straight steps with wide terraces. It could be noticed that the surface is completely covered with one-dimensional (1D) nanostructures of width ~1 nm. This nanostructure is known as the (6 x 2) reconstruction, which is composed of TiO_x, although nearly stoichiometric STO films were deposited by PLD.12)

In contrast, the surface structure of the STO films grown in layer-by-layer mode was found to be different from that prepared in step-flow growth mode. In this study, two undoped STO thin films with 10-UCs and 10.5-UCs were grown in layer-by-layer mode. As can be seen from the pattern shown in Fig. 2(c), both the films show sinusoidal-like RHEED oscillations, clearly indicating the signature of layer-by-layer growth. The deposition process was stopped, when the reflection intensities reached maximum (10-UCs) and minimum (10.5-UCs). The former [top in Fig. 2(c)] is expected to show a relatively smooth surface than the latter [bottom in Fig. 2(c)], since the oscillation maximum can be interpreted as to completely cover the plane of STO crystals. Besides, only negligible differences could be observed in the final RHEED patterns shown in Figs. 2(d) and 2(e), except for the reflected specular beam intensities. However, STM imaging shows distinct differences between these two films.

Figures 2(f) and 2(g) show the representative wide-area STM images (150 nm x 150 nm) of 10-UCs and 10.5-UCs STO film surfaces, respectively. Sparse isolated holes and islands with a constant height of the UC (0.4 nm) could be clearly observed on the terraces in the 10-UCs film [Fig. 2(f)]. In contrast, meandering step edges and holey terraces were observed in 10.5-UCs...
STO film [Fig. 2(g)], as if a number of STO islands deposited on the terraces are connected with each other to form larger domains. The observed differences in STM images are quite consistent with the interpretation of RHEED intensity oscillations, shown in Fig. 2(c). Notably, the magnified STM images of 10-UCs and 10.5-UCs STO films were indistinguishable [insets of Figs. 2(f) and 2(g)], both indicating a $(2 \times 2)$ surface reconstruction, as confirmed by the fast Fourier transformed pattern.11) These results reveal that the growth of surface atomic structures strongly depends on the growth modes, implying that the surface properties can be tuned by adept control of the growth conditions. Moreover, the results suggest a potential route for the fabrication of oxide nanostructures on various surfaces, including conductive wire and magnetic nanostructures.

Further studies were conducted to investigate the surface of the STO substrate. Here, the conventional STO crystal surface, referred to as the unreconstructed STO in this paper, is not considered suitable for understanding the atomic initial growth of oxide, especially below 1-UC. Figure 3(a) shows the typical STM image $(15 \text{ nm} \times 15 \text{ nm})$ of conventional STO surface, which is a BHF-etched STO substrate annealed at $1000^\circ \text{C}$ for $0.5 \text{ h}$. To our surprise, a closer view of the terraces indicates a disordered surface, besides the presence of steps and terrace surfaces [Fig. 3(a) inset]. This clearly indicates that the surface of the conventional STO substrate is not atomically flat, rather, has defects or adsorbates on the terraces. Intriguingly, this surface displayed sharp $(1 \times 1)$ diffraction patterns in both the RHEED and low energy electron diffraction (LEED) patterns shown in Figs. 3(b) and 3(c), respectively. The bright $(1 \times 1)$ spots could have possibly resulted from the contribution of bulk STO, present underneath the topmost surfaces.

Furthermore, we investigated the atomic structure of the LAO film deposited on the unreconstructed surface. Even after the 1-UC growth of LAO [Fig. 3(f)], we could not observe any periodic atomic arrangement [Fig. 3(d)], although the RHEED analysis showed $(1 \times 1)$ pattern [Fig. 3(e)]. This result indicates that the unreconstructed STO substrate surface is not suitable for conducting initial growth study with atomic resolution.

Therefore, further studies were performed on the genuinely prepared atomically flat STO surface, which is the $(\sqrt{13} \times \sqrt{13})$-R33.7$^\circ$ reconstructed STO surface, in order to unveil the initial growth stages of oxide films.9,13,15,16) Among the several different reconstructions made to the STO surfaces, the reconstructed surface analyzed in this study is stable under typical thin film growth conditions, for example, room temperature to $-800^\circ \text{C}$ in air or vacuum.17) Thus, this reconstructed substrate surface can serve as an ideal platform for the growth of oxide films.

The STM image $(10 \text{ nm} \times 10 \text{ nm})$ of the reconstructed substrate surface shown in Fig. 4(a) indicates periodic dark squares, apparently indicating an ordered arrangement of atoms. Experimental and theoretical results suggest that this surface structure is composed of an additional TiO$_x$ adlayer, formed on a bulk-like termination of the TiO$_x$ plane.16) The RHEED and LEED patterns of reconstructed surface shown in Figs. 4(b) and 4(c), respectively, demonstrate very sharp diffraction patterns, indicating an atomically flat STO surface, consistent with previous reports.13) The flatness of this reconstructed surface was found to exceed that of the unreconstructed STO surface. In order to demonstrate the importance of using atomically flat substrate, we deposited LAO film on the reconstructed STO substrate surface, analyzed the atomistic initial growth, and compared it with that of the reconstructed STO surface [Fig. 3(d)]. The STM images of 0.2-UC LAO shown in Figs. 4(d) and 4(e) indicates the growth of island structures on the reconstructed STO. Here, the circular-shaped islands correspond to the LAO islands, while the surrounding area corresponds to the reconstructed STO surface. Intriguingly, we could observe $(\sqrt{13} \times \sqrt{13})$-R33.7$^\circ$ structure on the LAO island surface in Fig. 4(e). Here, the emphasis is on the
fact that the periodic structure on the LAO surface structures. This microscopic picture suggested in this study can be considered to be applicable, in general, to understand the growth process of oxide films on the conventional reconstructed STO substrates, because such surfaces are known to be Ti-rich. 19) Such complexities at the early stage of LAO/STO heteroepitaxy provide significant insights for deeper understanding of perovskite heteroepitaxy.

4. Conclusions

In summary, we have developed a low-temperature, high-magnetic field STM-PLD system that can enable atomic-scale investigations of oxide thin films. Using this system, we have successfully demonstrated precise control of growth modes and revealed the importance of STO (√13 × √13)-R33.7° reconstructed surface in determining the initial thin film growth modes and surface structures. The use of reconstructed substrate enabled us to directly visualize the initial growth behavior of LAO film. Based on our observations, we would like to emphasize that atomic-scale viewpoints should be taken into account for gaining comprehensive understanding of a rich variety of phenomena observed in complex oxide heterostructures. We believe that the inferences obtained in this study would open up a dimension for realizing the novel functionalities observed in various oxide thin films and their future utilization in devices.

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