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Cationic Disorder and Phase Segregation in $\text{LaAlO}_3/\text{SrTiO}_3$ Heterointerfaces Evidenced by Medium-Energy Ion Spectroscopy

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Medium-energy ion spectroscopy (MEIS) has been used to study the depth profile and deduce the distribution of possible cationic substitutions in $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) heterointerfaces. Analysis of La and Sr peaks in aligned and random MEIS spectra indicates that the surface layers of LAO on an STO substrate are not homogeneous and stoichiometric if the film thickness is less than 4 unit cell layers. This is possibly caused by a redistribution of La and Sr at the interface. Kelvin probe force microscopy reveals an inhomogeneous distribution of the surface potential in a 4 unit cell LAO film, indicating micrometer-sized regions of different compositions. Our findings provide a novel view on the microstructural origin of the electrically conductive interfaces.

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An unexpected electronic configuration at the interface of an epitaxially grown thin LaAlO_3 (LAO) film and a TiO_2 -terminated (001) SrTiO_3 (STO) substrate has attracted a lot of attention [1]. Several possible mechanisms explaining the formation of a quasi-two-dimensional electron gas (q2DEG) at the interface between the two insulating, perovskite-type multicomponent oxides are lively discussed, and a consensus has not yet been reached. A polar discontinuity [2], a formation of a high density of oxygen vacancies in the STO substrate [3,4] and/or interdiffusion of La into the substrate [5], may contribute to the high in-plane conductance of the LAO/STO interface. The electronic reconstruction model was supported by the observation of a critical thickness between 3 and 4 unit cells (uc) where a transition from an insulating into a conducting state occurs [6]. Another important feature of the LAO/STO interface is the dependence of its electrical properties on oxygen pressure during deposition of the LAO film. An increase of the oxygen pressure results in decreased conductivity and even insulating behavior [7,8]. These observations are difficult to explain altogether assuming electronic or ionic models separately.

Nucleation processes and structural changes during the initial growth of the LAO on STO are sparsely documented. Deficiency (abundance) of oxygen atoms, as well as any of the other components (La and/or Al) adsorbed at the surface of the STO substrate, may markedly affect the nucleation rate, growth mode, strain, and stoichiometry of the LAO film [9]. To clarify processes during the initial stage of the LAO layer formation, we used medium-energy ion spectroscopy, MEIS, which provides monolayer resolution [10]. We present data for LAO/STO heterostructures grown at an oxygen partial pressure which

promotes a high mobility q2DEG at the interface. We show that La atoms distribute inhomogeneously with La-rich and -poor areas at the surface of the LAO film up to 4 uc thickness. A presence of micrometer-size regions of differing composition is also indicated by scanning Kelvin probe force microscopy (KPFM). Our results provide new evidence that cationic defects contribute decisively to the high conductivity of the interface and suggest a new percolative model to explain the insulator-to-metal transition between 3 and 4 uc thick LAO film.

LAO films with thicknesses of 1, 2, 3, 4, 6, and 8 uc were grown by pulsed laser ablation (KrF, $\lambda = 248$ nm, $\tau = 30$ ns) on TiO_2 terminated (001)STO substrates [11]. The nominal thickness d was determined *in situ* from intensity oscillations of reflection high-energy electron diffraction (RHEED). The film properties depended upon process conditions which have been described earlier [12]. Substrate temperature was kept at 800 °C during the deposition, and oxygen pressure at 10^{-4} mbar. Laser energy density at the target surface was 1.5 J/cm^2 within a spot of $1 \times 2 \text{ mm}^2$. An additional *in situ* oxidation was done for all samples in 500 mbar oxygen at 600 °C for 2 hours. All samples with LAO thicknesses above 4 uc prepared at these conditions are conductive and show typical electrical resistivity values of $5 \times 10^4 \text{ } \Omega/\square$ and charge carrier concentration of $2 \times 10^{13} \text{ cm}^{-2}$ at room temperature. Samples with $d \leq 3$ uc showed no detectable electrical conductance.

The MEIS system is equipped with a monochromatic source of He^+ ions bombarding the surface of the sample placed in a UHV chamber [13]. An attractive feature of the MEIS technique, as compared with Rutherford backscattering, is the high depth resolution of film composition achieved by the electrostatic analyzer with high-energy

resolution ($\Delta E/E = 0.005$). The ion beam has also relative energy spread of less than 10^{-4} , and the angular energy divergence at the sample surface is less than 0.05° . The depth resolution of MEIS in case of He^+ ions ($E = 100$ keV) scattering at an angle of 120° in the LAO film is about 5 \AA , i.e., about one monolayer of the LAO film. The MEIS spectra were obtained using 96 keV He^+ ions in two configurations: (a) in aligned (or channeling) orientation, where the He^+ ion beam was parallel to $[001]$ LAO, and (b) in random orientation, where the angle between the He^+ ion beam and (001) LAO was 8° . The ion beam spot area at the surface of the LAO/STO is about 1 mm^2 .

A basis of backscattering spectra simulation method is given in Ref. [14]. We have developed an algorithm based on a “retrograde method” suggested in Ref. [15]. Details of our calculations are described in Ref. [16].

Atomic force microscopy (AFM) in tapping mode and KPFM were used to study morphology of the surface and distribution of surface potential, respectively. KPFM maps contact potential difference between the probe and surface which mainly depends on the work functions of the two materials, i.e., reflects composition of the surface [17].

We first verified that He^+ ion bombardment did not result in a modification of the LAO surface. The dose was small (10^{13} cm^{-2}) during measurements, and the intensity of the aligned MEIS signal did not change over very long exposure times, up to several hours. Furthermore, no difference in surface morphology was found by AFM after and before the MEIS experiments. In addition, electrical characterization of the 4 uc thick LAO sample did not show any change in the interface resistance due to He^+ ion irradiation.

Aligned MEIS spectra of LAO/STO heterostructures with different thicknesses of LAO film are shown in Fig. 1. Two peaks of interest at about 88 and 84 keV are seen, which are caused by backscattering on La and Sr atoms, respectively. The intensity of the La peak increases with d and saturates above 4 uc , while the Sr peak decreases and disappears at $d > 4 \text{ uc}$.

Random MEIS spectra for samples with different LAO thicknesses are plotted in Fig. 2. Note that the scale units for the yield in Figs. 1 and 2 are the same. The La peak broadens and shifts towards lower energy as the LAO thickness increases. The increase of the LAO thickness on the top of STO leads to the corresponding shift of the Sr edge towards lower energy due to inelastic energy losses of backscattered ions.

A subset of aligned and random spectra for the case of a 1 uc thick LAO film is presented in Fig. 3. It is clearly visible that the intensity of the La peak in the aligned spectrum is lower compared to the random orientation. In the aligned orientation, the signal originates from ions backscattered from the very top surface atoms. In the random case, the ions may backscatter from atoms deeper into the film and the substrate. For the case of a stoichiometric 1 uc thick LAO film, both random and aligned La

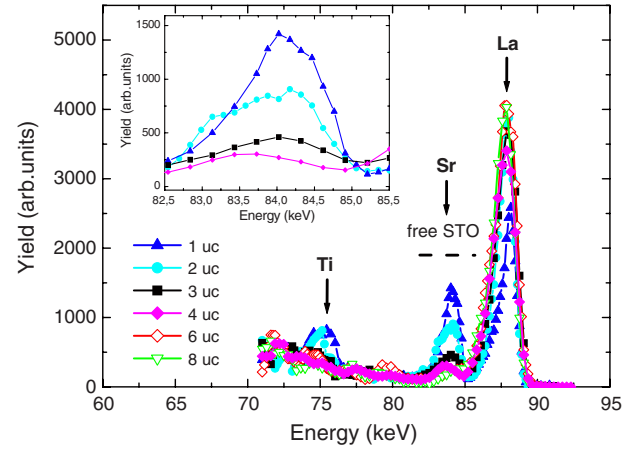


FIG. 1 (color online). Energy spectra of 96 keV He^+ ions, backscattered from LAO/STO heterostructures, measured in the aligned regime with the ion beam direction coinciding with $[001]$ LAO. The height of the Sr surface peak for an STO single crystal is depicted by the horizontal dashed line. The inset shows a close-up of the Sr peak in the aligned spectra for LAO thicknesses up to 4 uc .

peaks should be the same. One possible reason for the difference is an islandlike structure and discontinuity of the LAO film. Formation of such islands, however, is not consistent with RHEED oscillations during film growth nor confirmed by AFM measurements. Another possibility is a partial diffusion of the La atoms into the STO substrate which can lead to the observed broadening of the peak in the random spectrum. One can also see the Sr peak in the aligned spectra (inset in Fig. 1) for d up to 4 uc . Since the peak is observed for the same energy of 84.6 keV for the films with d between 1 and 3 uc LAO, one may conclude that there is a diffusion of Sr into the very thin LAO film.

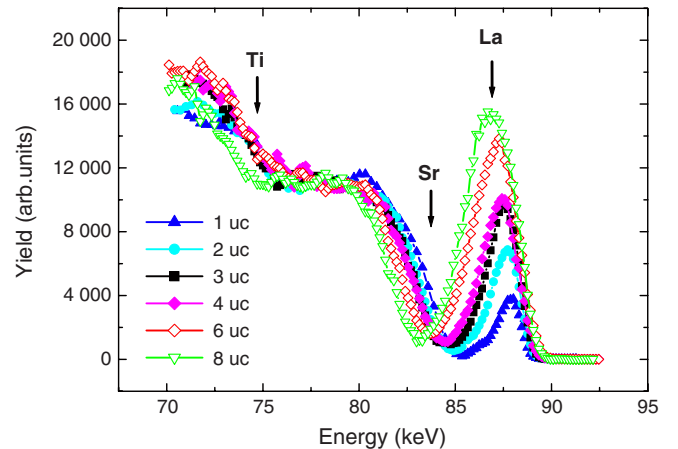


FIG. 2 (color online). Energy spectra of 96 keV He^+ ions, backscattered from LAO/STO heterostructures, measured in the random regime where the angle between the He^+ ion beam and $[001]$ LAO is higher than 8° .

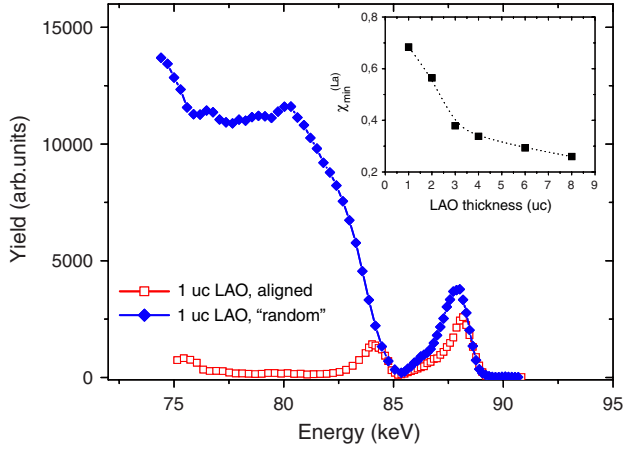


FIG. 3 (color online). A subset of aligned and random spectra obtained for the 1 uc thick LAO film. The inset shows thickness dependence of the ratio between maximum yields of the La peak in aligned and random spectra.

A dependence of the ratio between the maximum La peak yields in aligned and random spectra, χ_{\min}^{La} , on LAO thickness is shown in inset of Fig. 3. There is quite a rapid decrease in χ_{\min}^{La} as d increases, especially between 1–4 uc. For films thicker than 4 uc, the ratio still decreases, but not as rapidly and almost linearly. The faster decrease from 1 to 4 uc can be explained by an increasing stoichiometry of the LAO film and the slower dependence by the proportional increase of the thickness.

This suggests an intermixing scenario, where La atoms reside inside the STO. In order to further see if this intermixing scenario is supported, numerical modeling was done for a 1 uc thick LAO, where the top layer is deficient with La, which, instead, has diffused into the substrate. We normalized simulated spectrum using part of the experimental spectrum which is fully determined by backscattering from the substrate. This allowed us to exclude a dependence of the simulation results on the parameters of the experimental setup. An example is given in Fig. 4 for 1 uc LAO with 50% of La in the film and next three layers of STO containing 25, 15, and 10% La, respectively. A reasonably good agreement with the experimental random data is obtained for such a crude model.

Surface morphology and electrical potential images of the LAO films with different thicknesses are shown in Fig. 5. For the 2 uc thick film [Fig. 5(b)], the KPFM image indicates presence of islands which vary in size between 100–1000 nm. These islands are not related to the surface morphology [Fig. 5(a)]. For thicker films, KPFM images are qualitatively different with more homogeneous distribution of surface potential [Figs. 5(c) and 5(d)]. Since the measured contact potential between the probe and surface is most probably related to the variations in composition of the surface layer, one can suggest a transition from non-stoichiometric (2 uc) to almost stoichiometric (4 uc) and

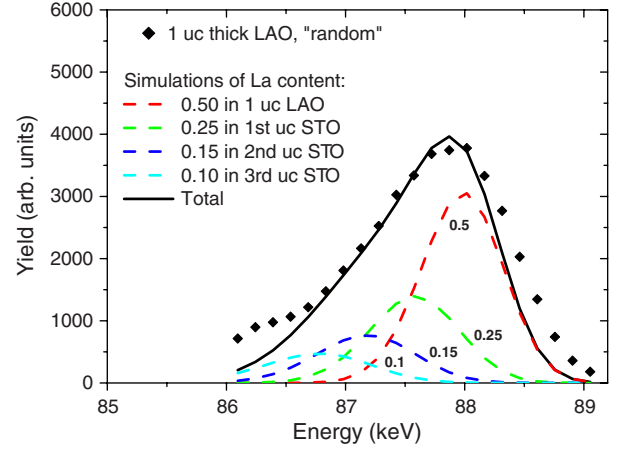


FIG. 4 (color online). Modeling of random spectra for a 1 uc thick LAO film. Experimental data are shown by solid diamonds. Calculations are performed for the 50% of La in the LAO film and the rest of La in the 3 topmost layers of the STO substrate.

finally to completely stoichiometric (6 uc) top layers of the LAO films.

Hence, according to these data, it appears that the LAO film is not uniform, and there is an intermixing of La and Sr near the interface at least for LAO films up to 4 uc thick. We note that intermixing between La and Sr in very thin LAO films has been observed in our high-resolution transmission electron microscopy studies (HRTEM), to be reported separately. The intermixing was also recently reported by HRTEM in [18].

Our results suggest that La stoichiometric and deficient regions are formed in the beginning of the LAO growth.

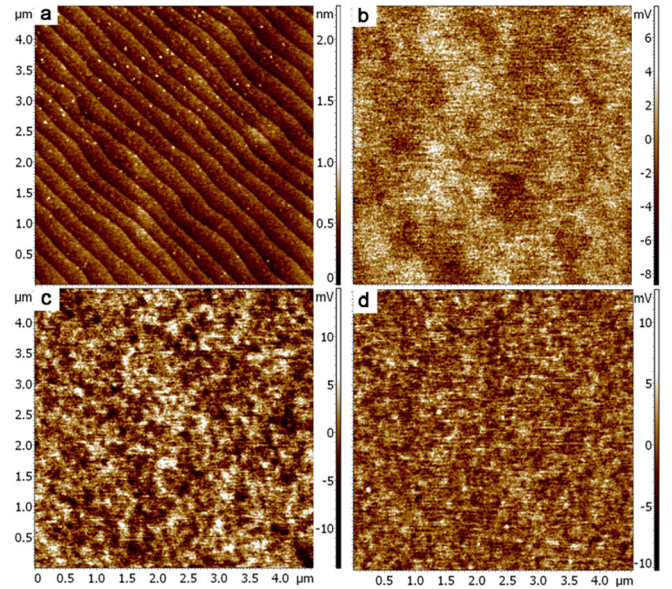


FIG. 5 (color online). (a) AFM and (b) KPFM images of 2 uc thick LAO film. (c) and (d) are KPFM images of 4 and 6 uc thick films, correspondingly. The size of all images is 4.5 by 4.5 μm .

The coverage by the stoichiometric phase increases with thickness and reaches full coverage above 4 uc layers. The phase separation may be caused by a combination of cationic intermixing and modification of structure and composition of the (100) STO surface. Segregation and desorption of Sr from a TiO₂ terminated (100) STO surface may occur already at 600 °C under oxidation conditions [19]. This leads to a TiO₂-rich surface with a (2 × 1) reconstruction [20]. In the beginning of the LAO film growth, La ions may be incorporated into the top TiO₂ overlay or fill Sr vacancies in the STO since La³⁺ and Sr²⁺ ions have very similar ionic radii, 1.12 and 1.06 Å, correspondingly [21]. It has also been shown that a La-doped STO surface is more stable [19]. Therefore, La-doped areas in STO may provide stable nucleation sites and promote a formation of stoichiometric LAO film. We note that the presence of a La-doped layer at the interface between LAO and STO is in agreement with recent surface x-ray studies [5].

This interpretation may provide a first microstructural explanation for a critical thickness between 3 and 4 uc LAO. The coverage by stoichiometric LAO increases when the film is thicker than 4 uc. This may result in formation of conductive areas, either due to a La doping in the STO substrate, or due to other mechanisms like polar catastrophe or oxygen vacancies. The conductive areas may grow and give percolation conductivity above a critical thickness of 4 uc layers.

Summarizing, MEIS and KPFM studies suggest intermixing of La and Sr at the LAO/STO interface that also leads to formation of La-poor regions in the films with thicknesses below 4 uc. The intermixing is also shown in recent HRTEM measurements. Increase of the thickness leads to more homogeneous distribution of La atoms at the surface of LAO which approaches stoichiometry above 4 uc. Our results suggest a percolative model which, in addition to previously discussed polar catastrophe, may explain the insulator-to-metal transition between 3 and 4 uc thick LAO on STO.

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