Structural coupling across the LaAlO$_3$/SrTiO$_3$ interface: High-resolution x-ray diffraction study


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Here, we demonstrate a structural interaction between LaAlO$_3$ thin films and SrTiO$_3$ substrates using high-resolution x-ray diffraction. X-ray diffraction profiles reveal the presence of periodic lattice distortions in the LaAlO$_3$ thin films, whose in-plane periodicity is determined by the miscut angle and miscut direction of the substrate. We show that the structural distortions in LaAlO$_3$ thin films induce similar distortions in the SrTiO$_3$ substrate.

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I. INTRODUCTION

Heteroepitaxy is a powerful method to enhance and control the properties of functional perovskite materials. The physical ground state is closely related to the local symmetry of the perovskites. By controlling the oxygen octahedra rotations, physical deposition offers the possibility to tune the electronic properties of perovskite thin films, as observed for LaNiO$_3$ thin films. Moreover, at an interface between two perovskites with different symmetry, a structural coupling across the interface is possible. For example, the interfacial coupling of oxygen octahedral rotations in PbTiO$_3$/SrTiO$_3$ superlattices can stabilize improper ferroelectricity, allowing for the coexistence of magnetism and a strong magneto-electric coupling. Recently the two-dimensional electron gas (2DEG) at the LaAlO$_3$/SrTiO$_3$ interface has attracted large attention, resulting in the observation of magnetic effects and superconductivity at the interface, and possible device applications have been demonstrated. There is a symmetry difference between the SrTiO$_3$ and LaAlO$_3$, opening for the possibility of structural coupling across the interface. The crystal structure of LaAlO$_3$ is rhombohedral at room temperature, however, commonly described as pseudocubic with a lattice constant of 3.79 Å and a lattice angle of 90.087°, which is due to the rotations of the oxygen octahedral (the subscripts pc and c will be used to differentiate between the pseudocubic and cubic symmetry). Epitaxial LaAlO$_3$ below the critical thickness of 3.8 nm has been reported to be fully commensurate with the cubic SrTiO$_3$ substrate, and the LaAlO$_3$ lattice adjusts its in-plane lattice parameter to the in-plane lattice parameter of SrTiO$_3$, which is 3.905 Å. Transmission electron microscopy has revealed that the rotation of the oxygen octahedra in LaAlO$_3$ couple to the oxygen octahedra in SrTiO$_3$ and induce oxygen octahedra rotations in the three SrTiO$_3$ unit cells adjacent to the interface.

However, a complete understanding of the conductance of this interface and the influence of defects, such as oxygen vacancies and intermixing, is still lacking. Recent experiments revealed that the interface conductance decreased with increased LaAlO$_3$ layer thickness and that the electronic mobility decreased toward the interface. Furthermore, anisotropic electrical transport dependent on the step and terrace structure of the substrate has been observed. An effect of the lower symmetry of LaAlO$_3$ with respect to SrTiO$_3$ is the possibility of ferroelastic domain formation that can affect the transport properties of the interface. For example, in La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films the formation of periodic in-plane lattice modulations disturb the conductance of such films.

II. EXPERIMENTAL

LaAlO$_3$ thin films were grown on TiO$_2$-terminated (001) SrTiO$_3$ substrates by pulsed laser deposition using a single crystalline LaAlO$_3$ target at a distance of 4.5 cm from the substrate. For the deposition, a KrF excimer laser ($\lambda=248$ nm), with a repetition rate of 1 Hz and a fluency of $\sim2$ J/cm$^2$, a substrate temperature of 650–750 °C, and an oxygen ambient of 0.01–0.03 mbar was used. Prior to deposition, the substrates were annealed in oxygen for one hour at 950 °C. After the deposition, the samples were cooled at a rate of 15 °C/min in a 0.1-bar oxygen ambient. In situ reflection high-energy electron diffraction (RHEED) was consistent with layer-by-layer growth, and atomic force microscopy (AFM) showed that all the samples had a clear step and terrace structure. The crystalline quality was investigated with four circle XRD (D8, Bruker) equipped with a temperature dome (Anton Paar, DHS 900). The thin films used in this study were grown in thicknesses ranging from 8 to 19 nm in order to allow for large signal-to-noise ratio in the XRD studies. Fits of the Scherrer equation to the thickness fringes in $\theta$-2$\theta$ scans.
confirmed the film thicknesses, as inferred from the RHEED analysis. From the (002)$_{pc}$ reflection, a typical out-of-plane lattice parameter of 3.78 Å was obtained. The typical full width at half maximum of the rocking curves for the (001)$_{pc}$ reflection of the films was $\sim 0.03^\circ$, compared to a value of $\sim 0.02^\circ$ for the substrates. Reciprocal space maps around SrTiO$_3$ (103)$_{pc}$ reflection were made in order to ascertain the in-plane lattice constant. All films were close to coherent and only showed a slightly relaxed in-plane lattice constant, as shown in Fig. 1(a) and in agreement with Qiao et al. We attribute the absence of a critical thickness for strain relaxation due to lattice mismatch to domain formation.

III. RESULTS AND DISCUSSION

A. Structural modulation in LaAlO$_3$

High-resolution reciprocal space maps were recorded around the LaAlO$_3$ (001)$_{pc}$ reflection in order to study the crystal structure of the LaAlO$_3$ films in detail. Diffuse scattering satellite peaks can be seen in these reciprocal space maps, Fig. 1(b), displaying a set of representative data for a 19-nm-thick LaAlO$_3$ film. Linear $q_x$ scans around the (001)$_{pc}$ and (002)$_{pc}$ reflections, Fig. 1(c), show that the satellite peaks have a constant separation from the Bragg reflection in reciprocal space, which indicates that the satellite peaks derive from a periodic change of the crystal structure and not from twinning. Another possible cause for the observed satellite peaks are misfit dislocations. An estimated of the periodicity of misfit dislocations was determined using $a_{lat}/a_{sto} - a_{lat}$, where $a$ is the in-plane lattice constant. For the sample in Fig. 1(c), which has an in-plane lattice constant of 3.90 ± 0.02 Å, an average periodicity of 300 nm was estimated for misfit dislocations. Since, the real space periodicity of the structural modulation is inversely proportional to the satellite to Bragg peak separation, $\Delta q_z$, it equals 166 nm for the sample in Fig. 1(b) and is thus in disagreement with the estimated periodicity for misfit dislocations. No correlation between the observed relaxations and the in-plane periodicities was observed in this study. Furthermore, a decrease in the satellite intensity and a constant $\Delta q_z$ were observed upon further relaxation upon high-temperature annealing. Therefore, it is concluded that misfit dislocations do not explain the observed structural modulation.

The reciprocal space maps for the LaAlO$_3$ (001)$_{pc}$ reflection, as shown in Fig. 1(b), also revealed that the position of the satellite peaks was centered at a lower $q_z$ value than the main Bragg reflection. The positions of the satellite peaks and the Bragg reflection were determined by fits using the Scherrer equation. The separation in $q_z$ between the satellite peaks and the Bragg reflection was determined at $\Delta q_z = (4 \pm 1) \times 10^{-4}$ Å$^{-1}$ for the film in Fig. 1(b). It was found that $\Delta q_z$ increases with the in-plane lattice constant, hence the degree of epitaxial coherency as shown in Fig. 1(d). Hence, the data reveal no dependence on the film thickness. Furthermore, the position of the diffuse scattering surrounding the satellite peaks was also centered at a lower $q_z$ value than the main Bragg reflection. The lower $q_z$ values for the positions of the satellite peaks and the surrounding diffuse scattering are typical for an in-plane structural modulation with a periodic increase in the out-of-plane lattice constant. The observed separation corresponds to an expansion of the out-of-plane lattice constant of 0.15 ± 0.04%. Hence, there is an in-plane structural modulation in the LaAlO$_3$ film due to periodic distortions with an increased out-of-plane lattice constant.

The surface topography of the LaAlO$_3$ films was studied in order to identify possible origins of the observed structural distortions. Figure 2(a) shows an AFM image of a 15-nm-thick LaAlO$_3$ film. The only visible surface structure is the step-and-terrace structure due to the miscut of the substrate. From the AFM image, an average terrace width of 250 nm and a miscut direction $\beta = 16 \pm 5^\circ$, defined as the angle between the [010], axis of the substrate and the projection of the surface normal on (001), plane, are obtained. In order to probe a possible influence of the step-and-terrace morphology on the observed structural distortions, linear $q_x$ scans of the LaAlO$_3$ (001)$_{pc}$ reflection were made at different azimuthal angles, $\psi$, i.e. the angle between the in-plane direction probed by XRD and the [010], axis of the substrate, see Fig. 2(a). Figure 2(b) shows the observed $\Delta q_x$ as a function of $\psi$ (red crosses). The structural modulation has a twofold symmetry, with a maximum at $\psi = 15^\circ$, which equals the miscut direction of the substrate. Furthermore, the dashed line in Fig. 2(b) corresponds to 1/$d$, the reciprocal width of the substrate terraces as a function of $\psi$. The clear correlation testifies to the fact that the minimum

![FIG. 1. (Color online) (a) The in-plane lattice constant, $a$, as a function of film thickness. (b) Reciprocal space map around the LaAlO$_3$ (001)$_{pc}$ reflection of a 19-nm-thick LaAlO$_3$ film on (001) SrTiO$_3$. (c) X-ray diffraction linear $q_x$ scans of LaAlO$_3$ (001)$_{pc}$ reflection [red (lower) line] and (002)$_{pc}$ reflection [blue (upper) line]. Similar data was obtained for all thicknesses investigated in this study. (d) The separation in $q_x$ between the satellite and Bragg peaks as a function of in-plane lattice constant for as grown (circles).](image-url)
in-plane periodicity in the LaAlO$_3$ film is the same as the width of the substrate terraces and that the minimum periodicity is observed parallel to the miscut direction of the substrate. A similar correspondence was observed for all samples in this study having thicknesses between 8 and 19 nm. Figure 2(c) shows the minimum periodicity, as determined from the maximum satellite to Bragg peak separation, as a function of the terrace width of the substrate. This clear correlation shows that the in-plane periodicity is determined by the step-and-terrace structure of the substrate. An estimate of the length of the distortions perpendicular to the miscut direction can be obtained from the angular dependence. However, when $\Delta q_x$ is smaller than $2 \times 10^{-4}$ Å$^{-1}$, the satellite peaks and the Bragg reflection start to overlap, and the satellite peaks cannot be resolved. This paper therefore places a lower limit on the maximum distortion length along the terraces at approximately two times the terrace width.

LaAlO$_3$ being rhombohedral can have up to four structural variances when deposited on cubic SrTiO$_3$. Ferroelastic domain walls can accommodate strain, as, for example, seen for BiFeO$_3$ thin films. This is in agreement with the present data; the larger degree of coherency between the thin film and the substrate, as seen in Fig. 1(d), the larger the observed effect of periodic in-plane modulations. Such structural boundaries can form at the substrate step edges during sample growth and are in LaAlO$_3$ characterized by an absence of the rotation of the oxygen octahedra and a change in volume of the unit cell, as illustrated in Fig. 3(b), and it is given by:

$$\frac{I_{\text{satellite}}}{I_{\text{Bragg}}} = \frac{1}{\sqrt{n}} \sum_{m=1}^{\infty} \sum_{c=1}^{n} \frac{f_a e^{i2\pi q_z c a + m}}{\Delta_c c} \frac{f_b e^{i2\pi q_x c b}}{\Delta_b b} \frac{f_c e^{i2\pi q_y c c}}{\Delta_c c} \frac{f_d e^{i2\pi q_x c d}}{\Delta_d d},$$

where $f_a$ is the atomic form factor of the different atoms in the unit cell, $q_i$ the reciprocal lattice unit, $c$ the out-of-plane lattice constant of LaAlO$_3$, $\Delta c$ the observed lattice expansion and $n$ the number of unit cells in the LAO layer. Calculations of $\Delta F_{\text{LaAlO}_3}/F_{\text{SrTiO}_3}$ revealed an increase in $\Delta F_{\text{LaAlO}_3}/F_{\text{SrTiO}_3}$ with thickness, but failed to explain the observed trend, i.e., the blue line in Fig. 3(a). Oxygen vacancies are likely to be present at structural boundaries, and defects would result in a thickness independent contribution to $\Delta F_{\text{LaAlO}_3}/F_{\text{SrTiO}_3}$. Including oxygen vacancies in the LaO plane in these calculations it was possible to fit the observed trend. The red dashed line is a fit based on the inclusion of oxygen vacancies. From this fit, the oxygen content of unit cells at the boundary was found to be $2.5 \pm 0.1$. Fits using vacancies in the AlO$_2$ plane or a combination of both planes, which is more probable, rendered a higher vacancy concentration. These results give a lower limit for the oxygen content in the domain wall because complimentary cation vacancies, having a more pronounced contribution to the scattered x rays, also contribute to the satellite intensity.
We note that the assumptions underlying the calculation of $\Delta F_{\text{LaAlO}_3}$ can result in a scaling error. Therefore, the data was also fitted using an additional scaling factor. In this case, an improved fit was also obtained by including vacancies in the calculation.

B. Structural coupling across an epitaxial interface

Although structural distortions have been observed in epitaxial perovskite thin films, the interaction of such distortions with the substrate is less studied. In order to investigate possible coupling between the distortions in LaAlO$_3$ and the SrTiO$_3$ substrate, linear $q_z$ scans of the SrTiO$_3$ substrate were made along the [010]$_c$ direction on the (101)$_c$, (001)$_c$, and (002)$_c$ reflections before (dashed lines) and after (solid lines) the deposition of the LaAlO$_3$ films. As shown in Fig. 4(a), no satellite peaks were observed before the deposition, which confirms that the observed distortions discussed above originate in the LaAlO$_3$ layer. However, all three reflections showed satellite peaks with an identical separation in reciprocal space after the deposition. Reciprocal space scans revealed a clear separation in $q_z$ for the satellites to the LaAlO$_3$ and SrTiO$_3$ Bragg reflections, respectively. Thus, in agreement with that, the satellites to the SrTiO$_3$ reflection do not originate from LaAlO$_3$ reflections. Moreover, in Fig. 2(b) the measured $\Delta q_z$ for SrTiO$_3$ (blue circles) and LaAlO$_3$ (red crosses) are compared as a function of the azimuth angle, $\phi$. These observations are clear evidence that the lattice distortions in the SrTiO$_3$ substrate are caused by the distortions in the LaAlO$_3$ thin film. A possible cause for the observed structural coupling could be a compression of the SrTiO$_3$ lattice due to the LaAlO$_3$ reflection in $q_z$. Furthermore, it was not possible to observe a coupling from La$_0$Sr$_{0.7}$MnO$_3$ to SrTiO$_3$. This indicates that coupling into the substrate depends on the degree of distortion at the structural boundary as compared to domains of the thin films.

In Fig. 3, it was shown that the structure factor difference of the LaAlO$_3$ films increases with increasing film thickness. In order to study how this affects the distortions in SrTiO$_3$, the substrate satellite peaks were examined as a function of the LaAlO$_3$ film thickness. It is expected that the distortions are present only near the interface. Therefore, an exponential decay of the structure factor difference is introduced, as illustrated in Fig. 4(b). The integrated intensity of the SrTiO$_3$ satellites, $I_{\text{satellite}}^{\text{SrTiO}_3}$, is thus proportional to $\frac{1}{2} \Delta F_{\text{SrTiO}_3}^{\text{satellite}}$, where $|\Delta F_{\text{SrTiO}_3}|$ is the structure factor difference between the distortions in SrTiO$_3$ and the undistorted SrTiO$_3$, and $\lambda$ is the penetration depth of the distortions into the substrate. The integrated satellite intensity was determined by fitting the linear $q_z$ scans of the (001) reflection to Voigt functions and by multiplying the obtained area with the FWHM in $q_z$.

Figure 4(c) shows that $\sqrt{I_{\text{satellite}}^{\text{SrTiO}_3}}$, normalized to the maximum value, exhibits a near linear increase with the LaAlO$_3$ film thickness and becomes constant above approximately 15 nm. Since $\sqrt{I_{\text{satellite}}^{\text{SrTiO}_3}}$ is proportional to $|\Delta F_{\text{SrTiO}_3}|$, $|\Delta F_{\text{SrTiO}_3}|$ exhibits a similar dependence on SrTiO$_3$ film thickness as $\Delta F_{\text{LaAlO}_3}$. The linear increase can be explained in terms of a quadratic increase of the penetration depth with SrTiO$_3$ film thickness, a linear increase of the structure factor difference in SrTiO$_3$ with LaAlO$_3$ film thickness, or a combination of these. From the present data, it is not possible to distinguish between these scenarios. However, we note that the structure
factor difference for LaAlO$_3$ increased close to linearly with LaAlO$_3$ thickness.

In order to determine the penetration depth of this structural distortion, it is assumed that $\lambda$ is constant and that the ratio of the satellite peaks with respect to the Bragg reflection is the same for SrTiO$_3$ as for LaAlO$_3$. Based on these assumptions, an average $\lambda$ of 50 ± 20 nm was determined. Assuming a larger distortion in SrTiO$_3$, a reduced penetration depth would be obtained. This estimate thus serves as an upper bound on the conductance at the LaAlO$_3$/SrTiO$_3$ interface.

Furthermore, a linear fit of the thickness dependent data below 15 nm, see Fig. 4(c), suggests that thinner LaAlO$_3$ films will lower the conductivity of the LaAlO$_3$/SrTiO$_3$ interface in the LaAlO$_3$ film thickness range investigated. We therefore expect that the observed distortions in SrTiO$_3$, which increase with the LaAlO$_3$ film thickness, will also induce distortions in the SrTiO$_3$ substrate. Bell et al. indeed observed a decrease in conductivity with increasing film thickness. Nevertheless, more detailed studies are needed to clarify the implications of the observed distortions on the conductance at the LaAlO$_3$/SrTiO$_3$ interface.

In conclusion, our results show that the step-and-terrace structure of SrTiO$_3$ substrates can give rise to ordering of lattice distortions in LaAlO$_3$ thin films. It was demonstrated that the observed lattice distortions induce corresponding lattice distortions in the SrTiO$_3$ substrate. These results not only show that the crystal structure of a thin film depends on the substrate, but also show that the crystal structure of the upper atomic layers of the substrate is affected by the growth of a low-symmetry thin film. These results are important for devices based on perovskite materials having a lower symmetry than the substrate and for devices based on the interface conductivity in particular since similar distortions in the blanket of thin films affects their conductivity.

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31. It was not possible to investigate thinner LaAlO₃ films due to the limited intensity of the XRD setup.