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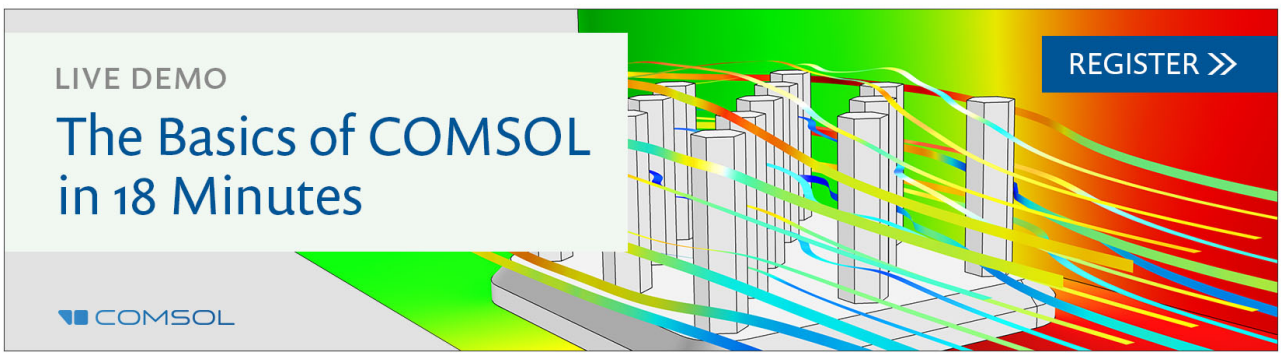

Nanometer-scale epitaxial strain release in perovskite heterostructures using "$SrAlO_x$" sliding buffer layers

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We demonstrate the strain release of $LaAlO_3$ epitaxial films on $SrTiO_3$ (001) by inserting ultrathin "$SrAlO_x$" buffer layers. Although $SrAlO_x$ is not a perovskite, nor stable as a single phase in bulk, epitaxy stabilizes the perovskite structure up to a thickness of 2 unit cells (uc). At a critical thickness of 3 uc of $SrAlO_x$, the interlayer acts as a sliding buffer layer, and abruptly relieves the lattice mismatch between the $LaAlO_3$ film and the $SrTiO_3$ substrate, while maintaining crystallinity. This technique may provide a general approach for strain relaxation of perovskite films far below the thermodynamic critical thickness. © *2011 American Institute of Physics*. [doi:10.1063/1.3583459]

A central issue in heteroepitaxial film growth is the inevitable difference in lattice constants between the film and substrate. Due to this lattice mismatch, thin films are subjected to microstructural strain, which can have a significant effect on the film properties.[1] This challenge is especially prominent in the rapidly developing field of oxide electronics, where much interest is focused on incorporating the emergent physical properties of oxides in devices.[2] Although strain can be used to great effect to engineer unusual ground states,[3] it is often deleterious for bulk first-order phase transitions, which are suppressed by the strain and symmetry constraints of the substrate. While there are some reports discussing the control of the lattice mismatch in oxides using thick buffer layers,[4–7] the materials choice, lattice-tunable range, and control of misfit dislocations are still limited.

In this letter, we report the fabrication of strain-relaxed $LaAlO_3$ (LAO) thin films on $SrTiO_3$ (STO) (001) using very thin "$SrAlO_x$" (SAO) buffer layers. Whereas for 1 or 2 pseudoperovskite unit cells (uc) of SAO, the subsequent LAO film is strained to the substrate, at a critical thickness of 3 uc the SAO interlayer abruptly relieves the lattice mismatch between the LAO and the STO, although maintaining the relative crystalline orientation between the film and the substrate. For 4 uc or greater, the perovskite epitaxial template is lost and the LAO film is amorphous. These results suggest that metastable interlayers can be used for strain release on the nanometer scale.

All of the samples studied were grown by pulsed laser deposition using a KrF excimer laser, with an energy of 28 mJ imaged to a spot of area 1.5×1.5 mm^2 using an afocal zoom stage. Each sample was grown on a TiO_2-terminated STO (001) substrate, at a growth temperature of 700 °C and an oxygen pressure of 1×10^{-5} Torr. For SAO deposition, a composite polycrystalline target of $Sr_3Al_2O_6$ and $SrAl_2O_4$ was prepared by bulk solid state synthesis. The target's constituent materials were confirmed by powder x-ray diffraction (XRD).

Figure 1(a) shows a schematic illustration of the sample structure. The thickness of each layer was monitored *in situ* using reflection high-energy electron diffraction (RHEED). It should be noted that the thickness of the SAO layer was calibrated using the first (and only) RHEED oscillation peak, as shown in Fig. 1(b). The transition of the strain state of the LAO films with SAO thickness described below was quite reproducible using this calibration, regardless of the details of the growth rate.[8] In this set of experiments, a 10 uc ho-

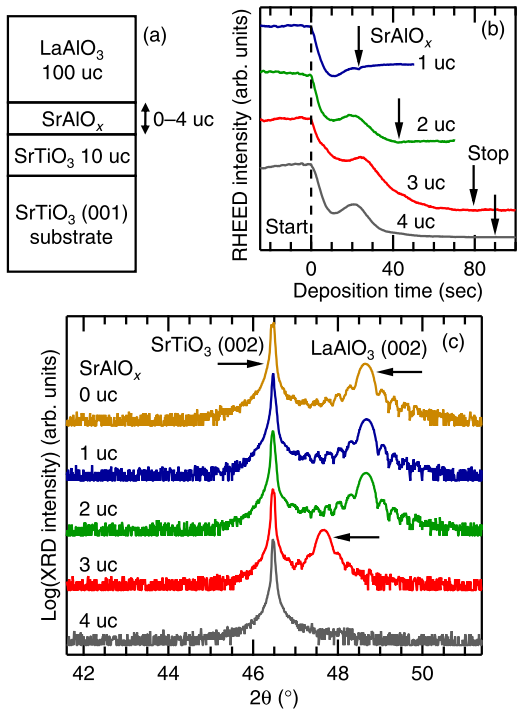

FIG. 1. (Color online) (a) Schematic illustration of the sample structure. (b) RHEED oscillations during the growth of SAO layers. (c) XRD θ–2θ patterns of the samples from (b) after additional LAO growth.

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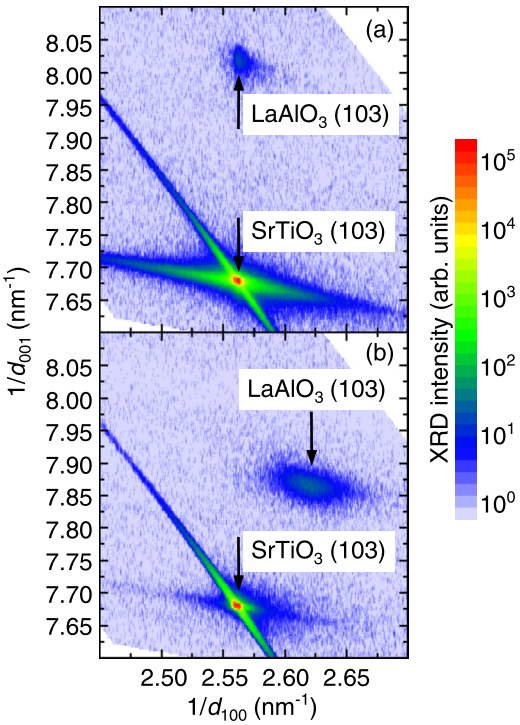

FIG. 2. (Color online) XRD reciprocal space maps of the samples with (a) no SAO interlayer and (b) a 3 uc SAO interlayer.

moepitaxial layer of STO was grown before the SAO to improve the RHEED oscillations during the subsequent growth.[9] After the SAO, a fixed thickness of 100 uc LAO was grown using a single crystal target. For 0–3 uc SAO, clear RHEED oscillations were observed during LAO deposition; for 4 uc SAO, they could not be observed, and the LAO thickness was estimated by calibrations of the deposition rate.

Figure 1(c) shows the XRD θ–2θ patterns of the samples with various SAO thicknesses. Clear LAO (002) peaks[10] are observed from all the samples except for the 4 uc thick SAO interlayer sample, which was amorphous. In contrast, the samples with 1 and 2 uc thick SAO interlayers show essentially the same diffraction patterns as that of the LAO film directly deposited on STO. The out-of-plane lattice constants of these three films are found to be 0.374 nm, significantly shorter than that of bulk LAO (0.379 nm).[10] This is expected, since the LAO films are subjected to tensile strain by the STO substrates (lattice constant=0.3905 nm), and in reasonable agreement with calculations of the Poisson ratio.[11] The Laue fringe peaks and the full width at half maximum (FWHM) of the LAO (002) peaks are in good agreement with the nominal thickness of 100 uc, indicating that the out-of-plane lattice constant is homogeneous throughout the LAO films.

Most notably, the 3 uc SAO sample also shows a clear LAO (002) peak, but at a much smaller angle. The out-of-plane lattice constant is found to be 0.381 nm, 0.5% larger than that of bulk LAO. In this case also, the Laue fringe peaks, although less pronounced, and the FWHM suggest that the LAO film is quite homogeneous.

To further investigate the structure of these films, we measured the off-axis XRD peaks. Figure 2 shows reciprocal space maps in the vicinity of the STO (103) and the LAO (103) peaks for two of the samples. For the sample without SAO [Fig. 2(a)], no significant in-plane difference is observed between the substrate and film peaks, confirming that the LAO in-plane lattice constant is locked to the STO substrate. No satellite peak associated with strain distribution is observed, indicating that the LAO film is fully strained. Similar results were obtained for the films with 1 and 2 uc SAO insertion.

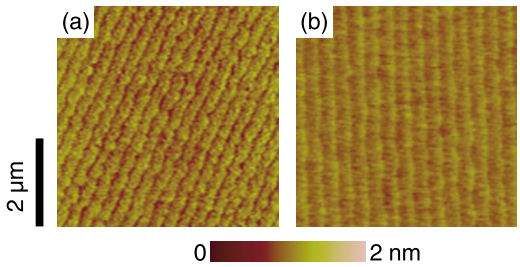

FIG. 3. (Color online) Atomic force microscopy surface topography of the LAO films with (a) no SAO interlayer and (b) a 3 uc SAO interlayer.

In contrast, the sample with a 3 uc thick SAO interlayer [Fig. 2(b)] shows a significant in-plane difference between the substrate and film peaks. Both the in- and out-of-plane lattice constants of the LAO film are found to be 0.381 nm, indicating that the LAO film is free from strain in the plane, and its crystal structure is essentially that of the bulk. The small (0.5%) difference between the relaxed LAO film lattice constant and the bulk value is due to slight cation off-stoichiometry in the film, which can be tuned by varying the laser ablation conditions.[12–14]

Figures 3(a) and 3(b) show atomic force microscopy surface topography images of the LAO films without SAO and with a 3 uc SAO interlayer, respectively. Both films have atomically flat terraces with a root-mean-square roughness of ≈0.1 nm and clear 1 uc height (≈0.4 nm) steps. Over a larger scale of 20×20 μm^2 the strained LAO films (SAO thickness=0–2 uc) show microcracks associated with local relaxation. On the other hand, no such features were observed on the relaxed LAO film (SAO thickness =3 uc), suggesting that the lattice mismatch is relieved in the SAO interlayer even on a macroscopic scale.

To visualize the nanoscale changes occurring at the 3 uc critical thickness, cross sectional samples were studied by high-angle annular dark field (HAADF) imaging in an FEI Tecnai F20-ST scanning transmission electron microscope (STEM). Figures 4(a) and 4(b) show STEM images of the samples without an interlayer and with a 3 uc SAO interlayer, respectively, which are magnified in Figs. 4(c) and 4(d). As expected from the XRD data, in both cases the LAO films are fully crystalline and oriented. The LAO film with no SAO interlayer is clearly epitaxially grown on the STO substrate, with no obvious dislocations at the interface [Figs. 4(a) and 4(c)]. On the other hand, the LAO film with a 3 uc thick SAO interlayer shows many edge dislocations around the interface [Figs. 4(b) and 4(d)], relieving the lattice mismatch between the film and the substrate. We also see multidomain structures in the relaxed LAO film, consistent with the rhombohedral domains observed in bulk single crystals. This gives rise to the significant broadening of the XRD peak shown previously [Fig. 2(b)]. This multidomain state may also have a partial contribution to the strain relaxation, and might be eliminated by employing high miscut substrates.[7,15] The LAO above the 4 uc thick SAO layer, which showed no

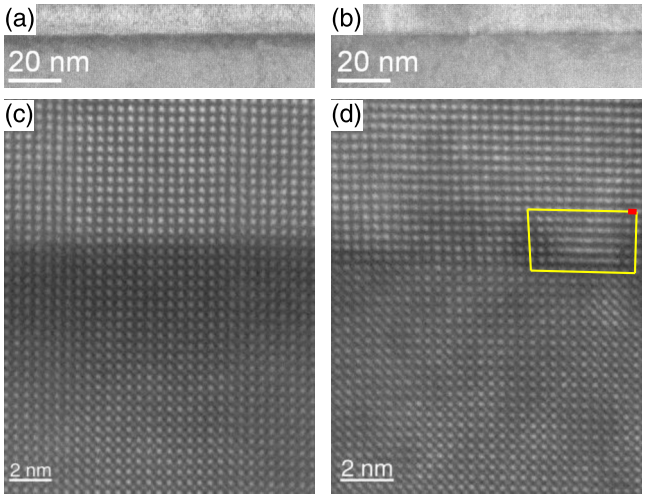

FIG. 4. (Color online) HAADF STEM images of the samples with (a) no SAO interlayer and (b) a 3 uc SAO interlayer. (c) and (d) are magnified images of (a) and (b), respectively. In (d), a Burgers circuit (box) and the Burgers vector (bold line) are also drawn, indicating an edge dislocation.

XRD peak, was also confirmed to be amorphous on a microscopic scale by STEM (not shown).

These results demonstrate that at the 3 uc critical thickness, the SAO interlayer acts as a sliding buffer layer for the LAO film. A similar process has been reported for GaAs growth on Si substrates, where STO grown on the Si forms both an epitaxial template and an amorphous SiO_2 layer, creating a sliding buffer that relieves the lattice mismatch between the substrate and the subsequent GaAs film.[16] Our results provide a complementary approach to conventional perovskite strain buffer layers,[4–7] with a potential advantage for growing oxide artificial heterostructures with nanoscale precision, since the SAO buffer layer is very thin (~1 nm) compared to typical values (~10–100 nm).

Finally, we note that SAO is also of interest for controlling the termination of LAO/STO (001) interfaces, which originally motivated our exploration of this material. It has been shown that this interface becomes conducting when LAO is deposited directly on the TiO_2-terminated STO surface, whereas one monolayer of SrO inserted before the LAO makes the interface insulating.[17] In the context of superlattice fabrication, heterostructures with all conducting interfaces could be grown by using 1 uc $LaTiO_3$ at the transition between LAO and STO.[18] The converse is not possible using SrO, which is only half of a perovskite unit. By using 1 uc SAO in analogy to $LaTiO_3$ insertion, insulating single interfaces and LAO/STO superlattices could be formed. While this specific background motivated the development of SAO here, we note that this idea should be generalizable to use metastable interlayers to control both the interface electronic structure and the strain state of the film.

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