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 film on SrTiO$_3$ (001) by inserting ultra-thin "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$_3$ fil and the SrTiO$_3$ substrate, while maintaining crystallinity. This technique may provide a general approach for strain relaxation of perovskite film far below the thermodynamic critical thickness.

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A central issue in heteroepitaxial fil growth is the inevitable difference in lattice constants between the fil and substrate. Due to this lattice mismatch, thin film are subjected to microstructural strain, which can have a significan effect on the fil properties.[1] This challenge is especially prominent in the rapidly developing fiel 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-orde 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 misfi dislocations are still limited.

In this Letter, we report the fabrication of strain-relaxed $LaAlO_3$ (LAO) thin film on $SrTiO_3$ (STO) (001) using very thin "$SrAlO_x$" (SAO) buffer layers. Whereas for 1 or 2 pseudo-perovskite unit cells (uc) of SAO, the subsequent LAO fil 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 fil and the substrate. For 4 uc or greater, the perovskite epitaxial template is lost and the LAO fil 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 confirme 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 reflectio high-energy electron diffraction (RHEED). It should be noted that the thickness of the SAO layer was calibrated using the firs (and only) RHEED oscillation peak, as shown in Fig. 1(b). The transition of the strain state of the LAO film 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 homoepitaxial layer of STO was grown before the SAO to improve the RHEED oscillations during the subsequent growth.[9] After the SAO, a fi ed 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 fil directly deposited on STO. The out-of-plane lattice constants of these three film are found to be 0.374 nm, significantl shorter than that of bulk LAO (0.379 nm).[10] This is expected, since the LAO film 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 fil 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 significan in-plane difference is observed between the substrate and fil peaks, confirmin 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 fil is fully strained. Similar results were obtained for the film with 1 and 2 uc SAO insertion.

In contrast, the sample with a 3 uc thick SAO interlayer [Fig. 2(b)] shows a significan in-plane difference between the substrate and fil peaks. Both the in- and out-of-plane lattice constants of the LAO fil are found to be 0.381 nm, indicating that the LAO fil 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 fil 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 (b) show atomic force microscopy surface topography images of the LAO film without SAO and with a 3 uc SAO interlayer, respectively. Both film have atomically fla terraces with a root-mean-square roughness of $\approx$ 0.1 nm and clear 1 uc height ($\approx$ 0.4 nm) steps. Over a larger scale of 20×20 μm^2 the strained LAO film (SAO thickness = 0–2 uc) show microcracks associated with local relaxation. On the other hand, no such features were observed on the relaxed LAO fil (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 fiel (HAADF) imaging in an FEI Tecnai F20-ST scanning transmission electron microscope (STEM). Figures 4(a) and (b) show STEM images of the samples without an interlayer and with a 3 uc SAO interlayer, respectively, which are magnifie in Figs. 4(c) and (d). As expected from the XRD data, in both cases the LAO film are fully

crystalline and oriented. The LAO fil   with no SAO interlayer is clearly epitaxially grown on the STO substrate, with no obvious dislocations at the interface [Figs. 4(a) and (c)]. On the other hand, the LAO fil   with a 3 uc thick SAO interlayer shows many edge dislocations around the interface [Figs. 4(b) and (d)], relieving the lattice mismatch between the fil   and the substrate. We also see multi-domain structures in the relaxed LAO film consistent with the rhombohedral domains observed in bulk single crystals. This gives rise to the significan broadening of the XRD peak shown previously [Fig. 2(b)]. This multi-domain 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 XRD peak, was also confirme 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 artificia 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 specifi 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

REFERENCES

[1]D. G. Schlom, L.-Q. Chen, C.-B. Eom, K. M. Rabe, S. K. Streiffer, and J.-M. Triscone, Annu. Rev. Mater. Res. **37**, 589 (2007).

[2]H. Takagi and H. Y. Hwang, Science **327**, 1601 (2010).

[3]J. H. Lee, L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. Fitting Kourkoutis, J.-W. Kim, P. J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P. C. Hammel, K. M. Rabe, S. Kamba, J. Schubert, J. W. Freeland, D. A. Muller, C. J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D. G. Schlom, Nature (London) **466**, 954 (2010).

[4]K. Terai, M. Lippmaa, P. Ahmet, T. Chikyow, T. Fujii, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **80**, 4437 (2002).

[5]B. H. Park, E. J. Peterson, Q. X. Jia, J. Lee, X. Zeng, W. Si, and X. X. Xi, Appl. Phys. Lett. **78**, 533 (2001).

[6]T. Yamada, K. F. Astafi v, V. O. Sherman, A. K. Tagantsev, P. Muralt, and N. Setter, Appl. Phys. Lett. **86**, 142904 (2005).

[7]C. M. Folkman, R. R. Das, C. B. Eom, Y. B. Chen, and X. Q. Pan, Appl. Phys. Lett. **89**, 221904 (2006).

[8]Another 3 series of samples were grown to examine this issue, and the critical thickness of 3 uc was reproduced each time.

[9]J. Zhang, J. H. Neave, P. J. Dobson, and B. A. Joyce, Appl. Phys. A **42**, 317 (1987).

[10]In this Letter, all the Miller indices and the lattice constants of LAO are given for the pseudo-cubic perovskite unit.

[11]X. Luo and B. Wang, J. Appl. Phys. **104**, 073518 (2008).

[12]T. Ohnishi, M. Lippmaa, T. Yamamoto, S. Meguro, and H. Koinuma, Appl. Phys. Lett. **87**,

241919 (2005).

[13]J. H. Song, T. Susaki, and H. Y. Hwang, Adv. Mater. **20**, 2528 (2008).

[14]L. Fitting Kourkoutis, J. H. Song, H. Y. Hwang, and D. A. Muller, Proc. Natl. Acad. Sci. **107**, 11682 (2010).

[15]Y. B. Chen, M. B. Katz, X. Q. Pan, C. M. Folkman, R. R. Das, and C. B. Eom, Appl. Phys. Lett. **91**, 031902 (2007).

[16]K. Eisenbeiser, R. Emrick, R. Droopad, Z. Yu, J. Finder, S. Rockwell, J. Holmes, C. Overgaard, and W. Ooms, IEEE Electron Dev. Lett. **23**, 300 (2002).

[17]A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).

[18]N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nature Mater. **5**, 204 (2006).

FIGURE CAPTIONS

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

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

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

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 magnifie images of (a) and (b), respectively. In (d), a
Burgers circuit (box) and the Burgers vector (bold line) are also drawn, indicating an edge dislo-
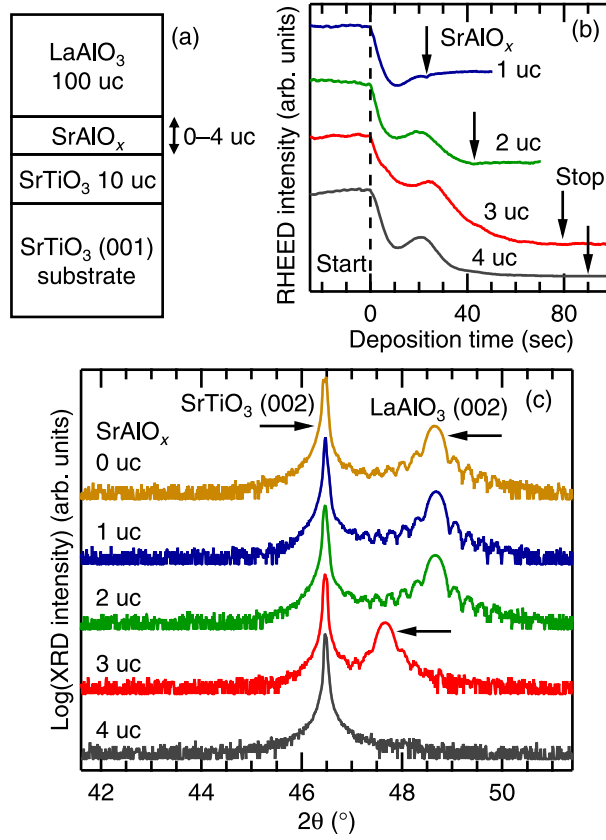cation.
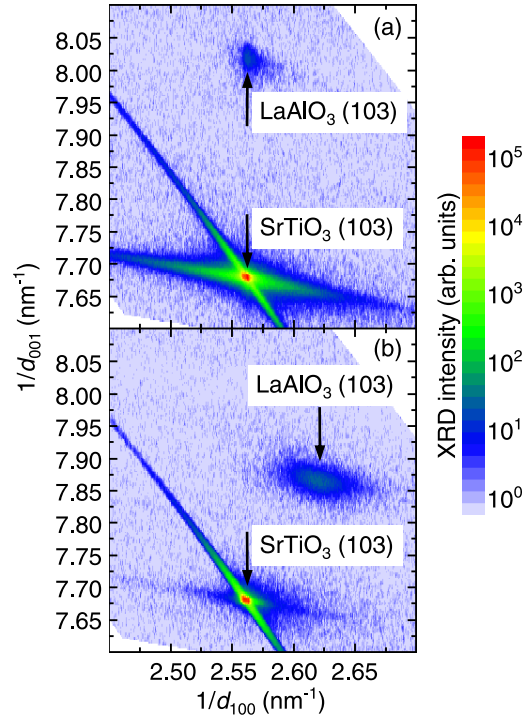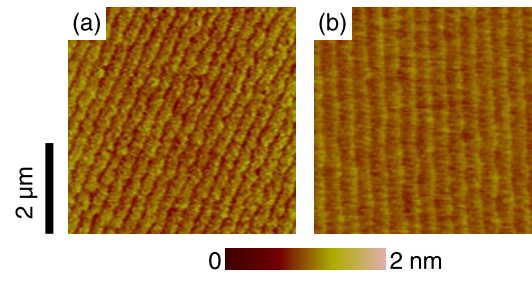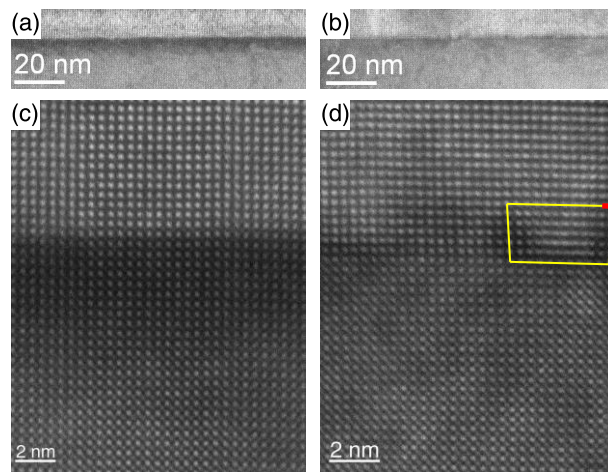
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