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The Effects of Annealing on the Inter-Diffusion of Cations Across the $LaCrO_3/SrTiO_3$ interface, and the Formation of La Anti-site Defect Clusters

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Perovskite oxides can exhibit a wide range of physical and electronic properties depending upon the choice of cations and their arrangement. Interfaces between dissimilar oxides can give rise to characteristics not achievable in the bulk, giving rise to the potential to design unique oxide materials through the manipulation of interfaces. However, past results have indicated that not all interfaces can be grown with an abrupt transition [1]. Here we examine the interface for $LaCrO_3$ grown by molecular beam epitaxy on $SrTiO_3$(001) (LCO/STO). Past work has demonstrated that this polar/non-polar interface is not chemically abrupt [2], and that the extent of cation inter-diffusion scales with LCO film thickness. As thicker films are held at temperature for a longer time, a potential explanation was the kinetically-limited thermal diffusion of the cations.

To further investigate this effect, the extent of inter-diffusion has been measured for LCO/STO and STO/LCO/STO films as-grown at 650°C, and annealed for ~2 hours (roughly twice the growth time) and ~12 hours. Both growth and annealing are performed at 650°C. The interface is investigated by cross-sectional electron microscopy, including transmission electron microscopy (TEM), high angle annular dark field scanning TEM (HAADF-STEM), x-ray energy dispersive spectroscopy (EDS), electron energy loss spectroscopy (EELS). Cross sections were created using focused ion beam-based liftout techniques. Data are collected on a probe-corrected (for STEM, EELS, EDS) and an image-corrected (for HRTEM) FEI Titan 80-300, with a 0.13 sr EDAX detector and a Gatan QuantumER imaging filter. Results indicate that the extent of inter-diffusion does increase with annealing, based upon STEM-EELS spectra of the Ti L-edge, Cr Ledge, and La M-edge.

Additionally, LCO/STO films have been found to remain coherent and fully strained for up to 500-Å thick LCO films [3], well beyond the theoretical critical thickness. Furthermore, these films maintain crystal quality even for significant deviations from stoichiometry. It has been argued, based on first principles calculations, that the strain and non-stoichiometry might be mitigated by the favorable formation of cation anti-site defects. In one set of experiments, we examined the recrystallization of a partially amorphous LCO/STO film upon annealing. In addition to seeing the extent of intermixing increase with annealing time, a series of defects extending from the substrate to the film surface were observed, frequently associated with [100]type step-ledges one the STO substrate. With HAADF-STEM, the heavier A-site atomic columns are typically brighter than the B-site atomic columns. In proximity to the defect (Fig. 1a), the intensity at the B-site atomic columns is significantly higher than elsewhere in the LCO, suggesting that those atomic columns contain some unusual excess of La. Potential explanations include (1) planar clusters of anti-site defects, (2) a (110) stacking fault leading to a local overlap of A-and B-site columns in projection or a similar anti-phase boundary. These defects predominantly appear to be free of dislocations or the extra planes that would be necessary for

the case of a stacking fault. EELS mapping corroborates this observation, evidencing a clear increase in La at the location of these defects, and a deficiency of Cr (Fig. 1b), providing further evidence that these defects are La-anti-site clusters. While anti-site defects had been theorized, this would be the first direct evidence that they actually exist in these systems [4].

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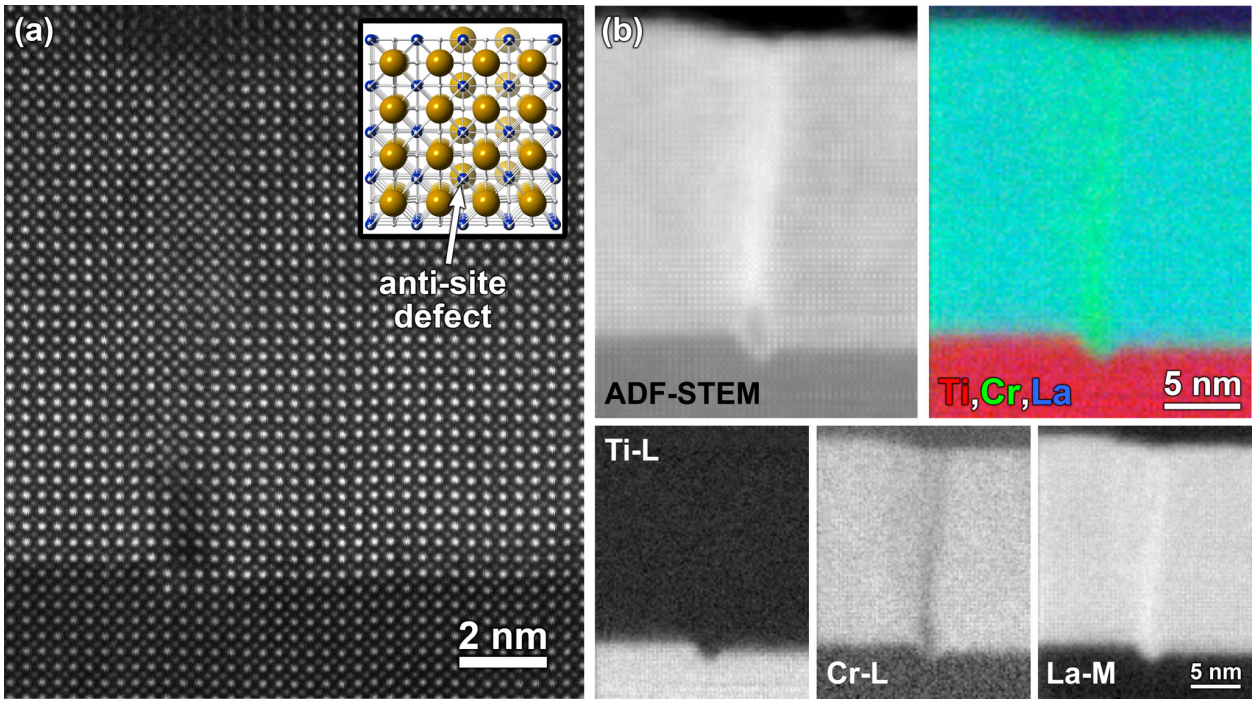

FIG. 1. (a) HAADF-STEM image of a typical defect in a recrystallized annealed LCO/STO film, extending from an STO step-ledge to the film surface, with an inste schematic diagram of LCO with a two unit-cell wide (110) La anti-site inclusion, one of the possible explanations for the observed contrast. (b) STEM-EELS maps of such a defect along with the simultaneously collected ADF-STEM image. The colored image is the combination of the Ti L, Cr L, and La M as red, green, and blue, respectively. There is frequently an inclusion above the step-ledge with a lower HAADF-STEM intensity but a composition consistent with the rest of the LCO defect, as seen in the above examples, suggesting an amorphous LCO inclusion. This is consistent with similar defects observed in La-rich LCO films grown on STO(001), suggesting a common strain relief mechanisms in the case of local non-stoichiometry.

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