

Atomic and Electronic Imaging of Oxide Heterostructures

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Electron energy loss spectroscopy (EELS) provides direct information on the local electronic structure of a material. In ionic systems, EELS measurements of formal valences give insight and place remarkable constraints on the structure and stability of heterointerfaces and defects. This is of considerable importance to the field of oxide electronics and ferroelectrics, where the growth of atomically-abrupt heterointerfaces has been a central goal. However, when the interfaces are between polar and nonpolar layers, electrical and atomic abruptness turn out to be mutually incompatible goals. This is the bulk analogy of the surface reconstructions found in polar systems where a material terminated along a bulk polar plane has a net charge and a divergent surface energy. Unlike conventional semiconductors, for multivalent oxides, physical roughness is not the only option – atomically abrupt interfaces are allowed if electrons can be redistributed at lower energy cost than it takes to redistribute ions. These extra electrons are detectable by EELS.

Recent work on SrTiO₃/LaAlO₃ [001] interfaces has found that Ti-La interfaces are conducting, but Sr-Al interfaces are insulating. Our EELS studies show that for the Ti-La terminated interface, excess electrons are found on the Ti sites, but not for the Sr-Al termination (where an extra 1/2 hole would be expected theoretically). Instead significant compensating oxygen vacancies are present and no free holes are found, probably explaining the electrical asymmetry. Controlling the interface termination lets us tune between insulator and conductor, trading chemical for electronic roughness[1].

When both sides of the interface contain mixed-valence ions, the interface can be atomically-abrupt, but electronically diffuse. Under these conditions, interface phases and charge-modulated structures can be constructed [2]. Structures that are thermodynamically unstable in the bulk can be stabilized by their interface energies in thin layers. As the layer thickness is increased, the structure can fault, in an attempt to recover its bulk valence (fig 1). For the LaTiO₃/SrTiO₃ however, the stable oxidized La-phase is the pyrochlore La₂Ti₂O₇ which has a unit cell of ~4 La layers along the [001] direction[3]. In thinner structures a new fault, that does not exist in the bulk, develops along the (001) plane in which a single layer of La sites splits into a double layer of a 1/2 occupied Ruddleson-Popper-like fault. This oxidation reduces the electron count on the neighboring Ti sites (Fig 2). While thin layers are stable against oxidation, they also do not have the bulk electron count, so the stable electron count is limited to ~40% of the bulk value after thermal annealing (Fig 3). The unfaulted structure is stable up to ~400C [4].

[1] N. Nakagawa, H. Y. Hwang, D. A. Muller, *Nature Materials* **5**, doi:10.1038/nmat1569 (2006).

[2] A. Ohtomo, *et al.*, *Nature* **419**, 378 (2002).

[3] A. Ohtomo, *et al.*, *Appl. Phys. Lett.* **80**, 3922 (2002).

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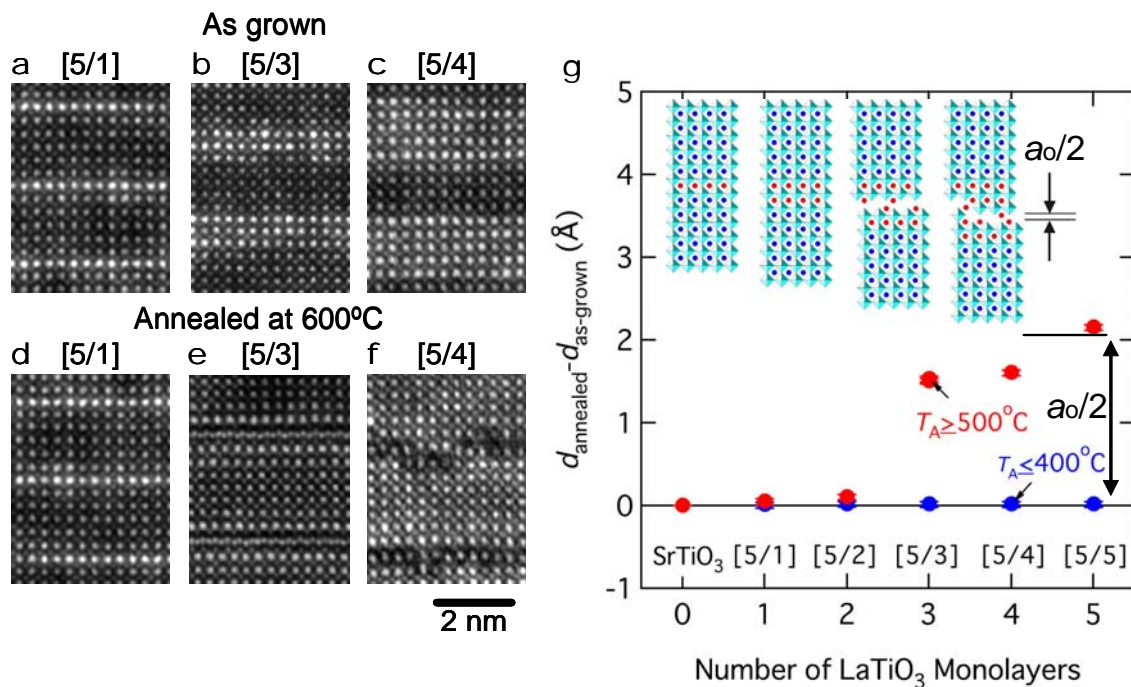


FIG 1. $(\text{SrTiO}_3)_5/(\text{LaTiO}_3)_n$ superlattice structures before (a,b,c) and after (d,e,f) annealing in oxygen. A fault opens up in the LaTiO_3 layer when more than 2 unit cells are present. (g) shows the expansion of the superlattice period as measured by x-ray diffraction.

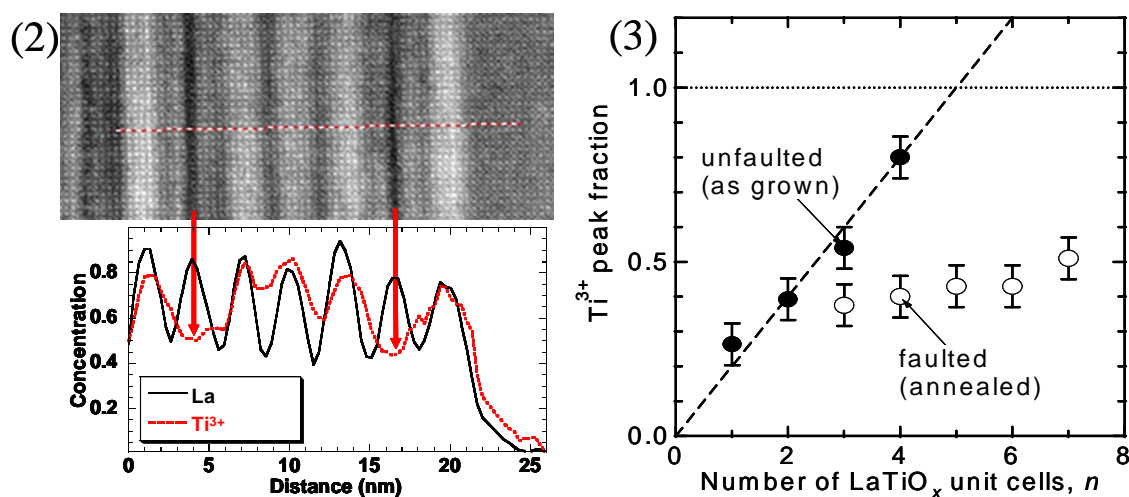


FIG 2. EELS profile across a partially annealed $(\text{SrTiO}_3)_5/(\text{LaTiO}_3)_4$ superlattice. La modulates the Ti valence (i.e. acts as a dopant) except when a fault occurs (arrows).

FIG 3. Peak Ti^{3+} fraction for $(\text{LaTiO}_3)_n/(\text{SrTiO}_3)$. Bulk-like LaTiO_3 cannot be thinner than 5 layers. Annealing introduces faults in the thicker structures, leading to more fully-oxidized Ti (i.e. Ti^{4+}) sites.