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Artificial Charge Modulations in La-doped $SrTiO_3$ Superlattices

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A major obstacle to achieving high free-carrier densities in semiconductors is that electrically active dopants are, by definition, charged. The Coulomb repulsion between the charged impurities keeps these atoms widely spaced, preventing the formation of a good conductor [1]. In contrast, by choosing a material with a higher dielectric constant, and a lower dopant diffusivity, these problems can be overcome, and a wider range of physical (especially extremely non-linear) properties can be obtained within a common materials system. The ADF-STEM images of Fig. 1 illustrates that a monolayer of dopants in silicon, (2 different dopants on 2 different crystal orientations [2,3]) spreads out over almost 20 Ă, while in $SrTiO_3$, it can be confined to a single unit cell. The ability to stabilize mixed valence states is a unique feature of transition metal oxides as compared to conventional semiconductors, and this adds an effective screening term when considering the interactions between the charged dopant impurities.

We have explored perovskites based on $SrTiO_3$ as building blocks for atomic-scale superlattices. The A-site cations can be selected for a wide range of optical and electronic properties since the large unit cells make steps and dislocations energetically prohibitive. This leaves only point defects, which we have learned to control by varying the oxygen partial pressure during growth [4]. As a demonstration of our control we have produced charge-modulated superlattices (Fig. 2) in which the titanium valence is modulated from 4^+ to 3^+ by doping with La. The charge modulation can be imaged using EELS of the Ti L edge (Fig. 3) which provides a convenient valence fingerprint for the $(Sr/La)TiO_3$ system [5]. Using the 2k GIF as a spectrometer on our JEOL 2010F, the La M, O-K and fine structure of the Ti L edge can all be recorded simultaneously (Fig. 4). Figure 4 shows that the extra charge introduced by the La ions is screened by the Ti sites, with a screening length of few nm's. This lengthscale is key for understanding the screening of grain boundary charges in ceramics and more detailed measurements will be given. Figures 5,6 summarize the results.

Figure 5 show that every La dopant is compensated by a valence change of a Ti site. Hall effect measurements show carrier densities ($-1/R_He$, where R_H is the Hall coefficient and e is the electron charge) corresponding to 2/3's of the carriers being electrically active.

However, we find a critical thickness of 5 unit cells is needed for the bulk-like behavior of $LaTiO_3$ (which is expected to be an antiferromagnetic Mott insulator) to be recovered in the center (Fig. 6). Below this thickness, there is a crossover to a two-dimensional conducting regime. At greater thicknesses, the balance of surface to bulk energies is such that upon oxidation, La-rich faults develops and the system reverts to a 4^+ valence insulator. Nevertheless, the layers do not roughen and coherent La/Sr superlattices can be maintained for hundreds of periods. We expect that the kinetics and defect controls should be applicable to other perovskite superlattices.

References

[1] M. B. Johnson et al., *Phys. Rev. Lett.* **75**, (1995) 1606.
[2] P. H. Citrin et al., *Phys. Rev. Lett.* **83**, (1999) 3234.
[3] O. D. Dubon et al., *App. Phys. Lett.* **78**, (2001) 1505.
[4] A. Ohtomo et al., submitted to *App. Phys. Lett*.
[5] M. Abbate et al., *Phys. Rev. B.* **44**, (1991) 5419.

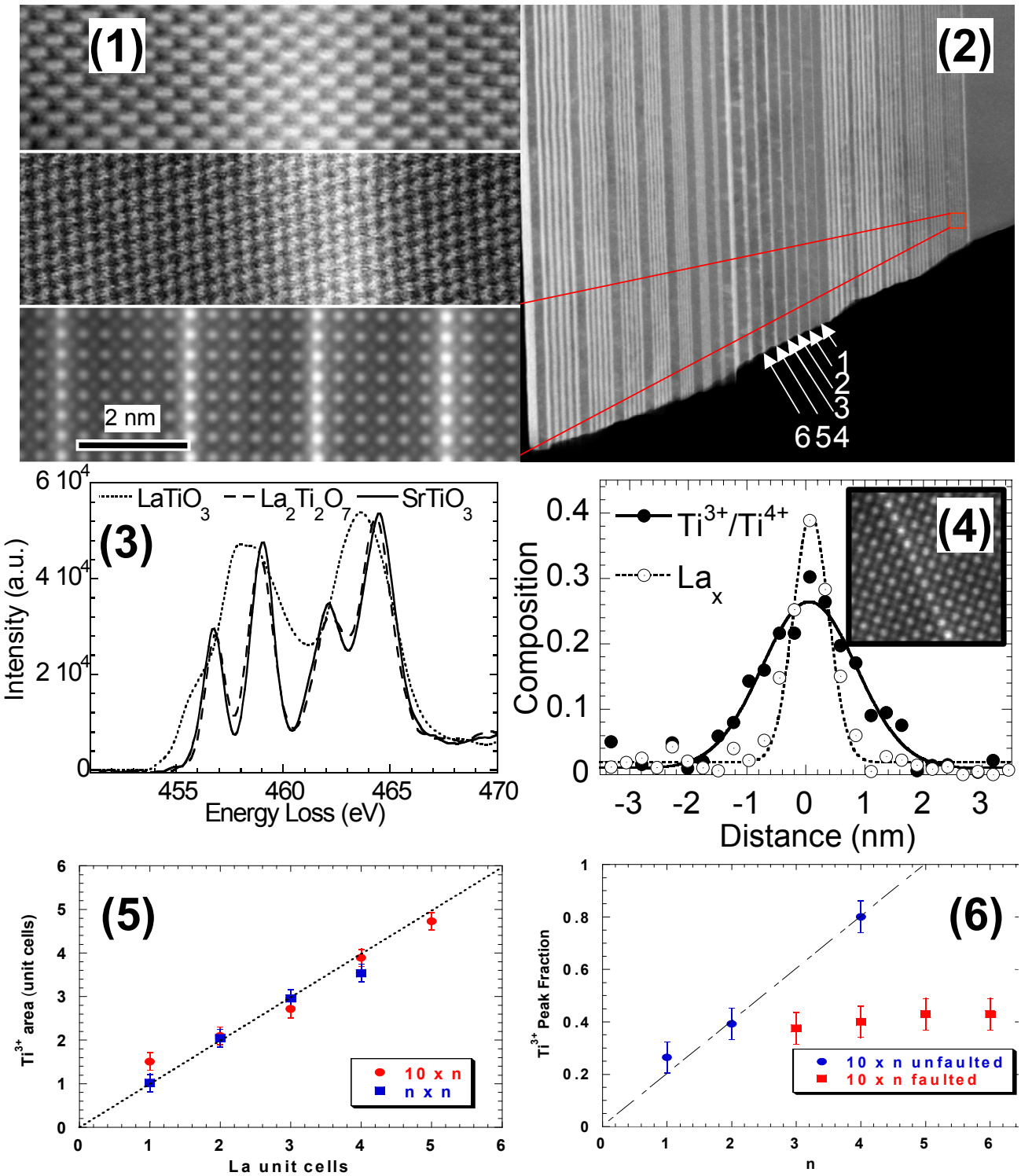

FIG. 1. A monolayer of dopants: (top) Sb in (100) Si (middle): As in (111) Si (bot): La in $SrTiO_3$.
FIG. 2. $LaTiO_3$ layers (5xn,10xn, nxn, etc., n=unit cells of $LaTiO_3$) in $SrTiO_3$ (500nm f.o.v.).
FIG. 3. Ti L edge fingerprints of Ti^{4+} ($SrTiO_3$, $La_2Ti_2O_7$) and Ti^{3+} ($LaTiO_3$).
FIG. 4. EELS profile across a $LaTiO_3$ monolayer. La modulates the Ti valence.
FIG. 5. EELS analysis for $(LaTiO_3)_n/(SrTiO_3)$ multilayers showing 1:1 Ti doping by La.
FIG. 6. Peak Ti^{3+}% for $(LaTiO_3)_n/(SrTiO_3)$. Bulk-like $LaTiO_3$ cannot be thinner than 5 layers.

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