Energetics and electronic structure of La/Sr disorder at the interface of SrTiO3/LaTiO3 heterostructure

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Control of oxide film growth at the level of unit cell dimensions has opened a route in materials design. One such manifestation is the observation of a two dimensional electron gas (2DEG) at the interface of two insulating oxide perovskites, such as LaAlO3/SrTiO3 and LaTiO3/SrTiO3. The formation of 2DEG results from the compensation of the polar discontinuity at the interface, which can be illustrated as follows: SrTiO3 has alternating (Sr2+O2−) and (Ti4+O2−) layers along the [001] direction and is, thus, nonpolar while LaTiO3 (or LaAlO3) is polar due to the alternating (La3+O2−) and (Ti3+O2−) layers. Thus, the polar discontinuity in such heterostructures is mainly induced by the alternating polarized layers of the La based system.

Several mechanisms have been proposed to explain the origin of electronic conductivity at the interface. These include electronic reconstruction, as suggested by the polar catastrophe model or by an atomic reconstruction at the interface by creation of oxygen vacancies in the substrate. Moreover, elementary electrostatic considerations suggest an electronic reconstruction via transferring a fraction of an electron per unit cell from (La3+O2−) to (Ti4+O2−) layers, thereby establishing charge neutrality at the interfacial layers. The model elegantly accounts for the strong ionic relaxations at the interface, switching of insulating to metallic ground states as a function of layer thickness, and the variation in the carrier density in samples that are synthesized at high O partial pressures. However, the model invariably assumes an ionic picture which is in contrast to the nature of chemical bonding in LaTiO3. By means of electron localization function, it has been shown that La–O and Ti–O bonds, in both cubic and orthorhombic forms of LaTiO3, have a certain degree of covalent nature associated with them.

An alternate mechanism that can avert the polar discontinuity at the interface is by an aliovalent cation exchange across the interface, i.e., an inter-site La/Sr disorder across the interface. Support for the inter-site mixing follows from the diffraction experiments where about 1–2 monolayers of disordered Sr1−xLaTiO3 layers with significant lattice deformations has been observed. Besides, the observation of a rough interface for the TiO2 terminated (n-type) also indicates a possibility of La and Sr inter-site mixing across the interface. Since La at Sr sites in SrTiO3 would be an n-type dopant, such a chemically disordered effect could also equally well explain the interface conductivity in such heterostructures.

The effect of cation inter-site disorder in heterostructures has received only little attention from theoretical calculations, perhaps, due to the requirement of large supercells which are computationally expensive. However, attempts were made to account for such interfacial La/Sr disorder in LaAlO3/SrTiO3 heterostructures, by using a simplified supercell in which a monolayer of LaO was embedded at the interface, between the TiO2 and the SrO layers. The resulting electronic structure showed substantial band bending at the interface.

In this work, we employ the coherent potential approximation (CPA) to model La/Sr disorder in LaTiO3/SrTiO3 heterostructures. CPA has not been used in such systems. We note that CPA describes the electronic structure properties of disordered bulk and interface alloys, besides being a very reliable approximation in treating metallic systems. Given that the interface of 5 (or more) LaTiO3 unit cells on SrTiO3 substrates induces a metallic state at the interface, CPA unequivocally tends to be a good approximation to study disorder in these systems. The chemical disorder is confined to the interfacial region and is schematically shown in Fig. 1.

The LaTiO3/SrTiO3 heterostructures are modeled by setting the lattice constant to that of the cubic SrTiO3 (a = 3.905 Å), with the SrTiO3 terminated by the TiO2 layer. Our model system comprises of 4 unit cells of SrTiO3,
interfaced with 5 unit cells of LaTiO₃. The ground state properties are calculated using the Green’s function method formulated in the atomic sphere approximation (ASA) (Ref. 22 and references therein). For better refinements in the alloy energetics, the ASA is corrected by the use of both the muffin-tin correction for the Madelung energy and the multi-pole moment correction to the Madelung potential and energy. These corrections bring significant improvement in the accuracy by taking into consideration the nonspherical part of the polarization effects.23 The partial waves in the Korringa-Kohn-Rostoker-ASA calculations are expanded up to \( l_{\text{max}} = 3 \) inside the atomic spheres. The multi-pole moments of the electron density have been determined up to \( l_{\text{max}} = 6 \) and then used for the multipole moment correction to the Madelung energy. For the exchange-correlation effects, we adopt to the generalized gradient approximation (GGA). The core states have been recalculated after each iteration. The atomic sphere radii of Sr/La, Ti, and O were kept as 1.511, 0.853, and 0.667 of the Wigner-Seitz radius, respectively. A Monhorst-Pack grid of \( 12 \times 12 \times 4 \) \( k \)-points was used to determine the total energies.

To study the lattice relaxation effects in LaTiO₃/SrTiO₃, we employ the full-potential linearized augmented plane wave method (FP-LAPW).24 The basis set is determined by the following parameters: \( R_{MTK}^{\text{max}} = 7.0, \ l_{\text{max}} = 10, \) and \( G_{\text{max}} = 24, \) with 28 \( k \)-points in the irreducible Brillouin zone. The effects of local lattice relaxation at the interface of LaTiO₃/SrTiO₃ are found to be similar to those reported earlier.15,25,26 The largest relaxation effects are determined for the Ti and O ions in the TiO₂ layer which is closest to the interface. Comparing the self consistently determined total energies of the relaxed and unrelaxed structures, we find an energy gain of about 12.2 meV/atom due to the local relaxation of atoms.

In Fig. 2, we show the relative total energy difference of the disordered systems with respect to the atomically abrupt structure for both relaxed and unrelaxed structures. For the unrelaxed structure, we find that the minimum in the total energy corresponds to \( x \approx 0.6, \) across TiO₂ interface. The decrease in the total energy between \( x = 0.6 \) and \( x = 0.0 \) is determined to be \(-10.6 \) meV/atom. Thus, on a given length scale, we find the energy gain due to the local lattice relaxation of an atomically abrupt interface (~12 meV/atom) and that of an atomically reconstructed interface through a La/Sr inter-site mixing (~10 meV/atom) are comparable. However, for the fully relaxed structure, the CPA calculations find that the minimum in the total energy shifts towards lower La/Sr disorder concentrations. The total energy is minimum for the \( x = 0.1 \) by \(-0.43 \) meV/atom with respect to that of the fully relaxed atomically abrupt configuration \((x = 0.0)\). These results imply that the polar discontinuity at the LaTiO₃/SrTiO₃ interface can be minimized by both lattice relaxation and chemical disorder.

To study the changes in the electronic structure due to the inter-site La/Sr intermixing across the TiO₂ layers, we show in Fig. 3 the density of states of three TiO₂ layers that are closest to the interface. The isolated deep valence states are essentially a composite of the O 2s states and La 5p states, while the states between \(-0.6 < E \) (Ry) \(< -0.2 \) mainly constitute the O 2p states with little admixture of the La/Sr and Ti states. The lower and the upper valence bands are separated by a pseudogap \((-0.2 < E \) (Ry) \(< -0.05 \) which manifests the separation of the bonding and anti-bonding states. With finite density of states at the Fermi energy, the metallic nature of the interface is established for both \( x = 0.0 \) and \( x = 0.1 \) as shown in Fig. 3.
and $x = 0.1$ case. As evident, one finds that the states in the vicinity of the Fermi energy are the least affected due to La/Sr disorder across the interface. The primary effect of disorder is mostly seen in the lower valence band ($E < -0.3$ Ry) where one finds significant re-distribution of states. These results suggest that a thermodynamic stability may be attained by local relaxation of atoms across the interface along with small mixing of the La/Sr atoms across the interface. However, the effects of such chemical disorder bring along with small mixing of the La/Sr atoms across the interface. The primary effect of disorder can be neglected in modeling such heterostructures using CPA. We find an intricate dependence of La/Sr disorder across the interface. Furthermore, we also find that such small levels of La/Sr disorder ($\sim 0.1$ at. %), which may persist across the interface, have only little effect on the occupied states near Fermi energy. We propose that developing growth techniques, such as pulsed laser interval deposition or interrupted deposition methods, that can allow a proper relaxation of the ions at the interface, can minimize the cationic inter-sites disorder at the interface, and that the effects of such chemical disorder can be neglected in modeling such heterostructures for future investigations.

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