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

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In the artificially tailored heterostructures of certain materials, a polar discontinuity across the interface introduces a large energy cost. The total energy of such systems may be reduced either by electronic reconstruction leading to the interface phases or by simple atomic reconstruction by inter-site cation mixing. While most of the experiments and theoretical calculations assume an abrupt interface, in this work, we consider the La/Sr inter-site disorder across the interface of SrTiO₃/LaTiO₃ heterostructures and study its energetics and electronic structure properties. The calculations find that inter-site mixing of La/Sr atoms across the interface also reduces the total energy. However, the extent of such disorder is found to be dramatically minimized by allowing the interfacial atoms to relax fully and that for such systems, the changes in the electronic structure are negligible. © *2011 American Institute of Physics*. [doi:10.1063/1.3629786]

Control of oxide film growth at the level of unit cell dimensions has opened a route in materials design.[1] One such manifestation is the observation of a two dimensional electron gas (2DEG) at the interface of two insulating oxide perovskites,[2–5] 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 $(Sr^{2+}O^{2-})$ and $(Ti^{4+}O_2^{2-})$ layers along crystallographic [001] direction and is, thus, nonpolar while LaTiO₃ (or LaAlO₃) is polar due to the alternating $(La^{3+}O^{2-})^+$ and $(Ti^{3+}O_2^{2-})^-$ 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[6] or by an atomic reconstruction at the interface by creation of oxygen vacancies in the substrate[7,8] and/or inter-site cationic disorder across the interface.[9–14] For an atomically abrupt interface, elementary electrostatic considerations suggest an electronic reconstruction via transferring a fraction of an electron per unit cell from $(La^{3+}O^{2-})^+$ to $(Ti^{4+}O_2^{2-})^0$ layers, thereby establishing charge neutrality at the interfacial layers. The model elegantly accounts for the strong ionic relaxations at the interface,[15] 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.[16] However, the model invariably assumes an ionic picture which is in contrast to the nature of chemical bonding in LaTiO₃.[17] 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.[17]

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.[6,9–13,18] Support for the inter-site mixing follows from the diffraction experiments where about 1–2 multilayers of disordered $Sr_{1-x}La_xTiO_3$ layers with significant lattice deformations has been observed.[9,18] 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.[6] Since La at Sr sites in SrTiO₃ would be an *n*-type dopant,[19,20] 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.[9]

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,[21] 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,

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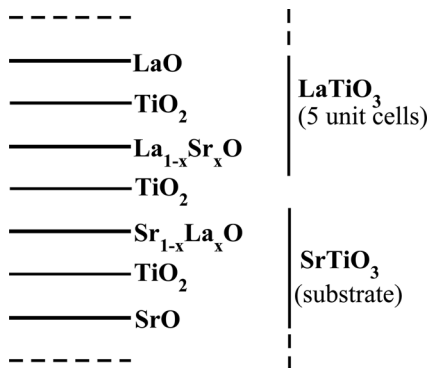
FIG. 1. The schematic representation of the LaTiO$_3$/SrTiO$_3$ heterostructure, used in the present work, showing La/Sr inter-site disorder across the TiO$_2$ interface.

FIG. 2. (Color online) The relative total energy difference (ΔE) of the disordered systems with respect to the atomically abrupt structure, in units of meV/atom. The blue filled circles represent the results from the unrelaxed structure, while the red filled squares are those for the fully relaxed structures.

interfaced with 5 unit cells of LaTiO$_3$. 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 $l_{max} = 3$ inside the atomic spheres. The multi-pole moments of the electron density have been determined up to $l_{max} = 6$ 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 LaTiO$_3$/SrTiO$_3$, we employ the full-potential linearized augmented plane wave method (FP-LAPW).[24] The basis set is determined by the following parameters: $R_{MT}K_{max} = 7.0$, $l_{max} = 10$, and $G_{max} = 24$, with 28 k-points in the irreducible Brillouin zone. The effects of local lattice relaxation at the interface of LaTiO$_3$/SrTiO$_3$ 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 TiO$_2$ layer which is closest to the LaO layer, near 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 $x \sim 0.6$, across TiO$_2$ 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
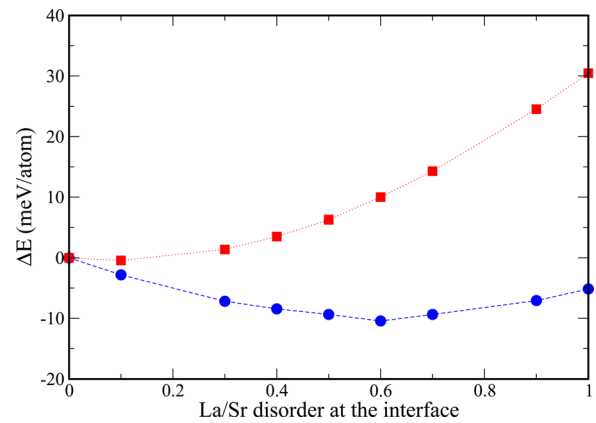
inter-site mixing (~ 10 meV/atom) are comparable. However, for the fully relaxed structure, the CPA calculations find that the minimum in the total energy shifts towards lower La/Sr disorder concentrations. The total energy is minimum for the $x = 0.1$ by -0.43 meV/atom with respect to that of the fully relaxed atomically abrupt configuration ($x = 0.0$). These results imply that the polar discontinuity at the LaTiO$_3$/SrTiO$_3$ 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 TiO$_2$ layers, we show in Fig. 3 the density of states of three TiO$_2$ 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 $x = 0.0$
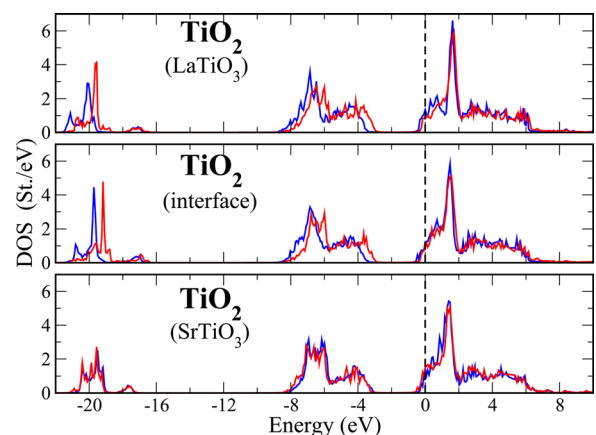

FIG. 3. (Color online) Layer resolved TiO$_2$ density of states of the LaTiO$_3$/SrTiO$_3$ using GGA, for $x = 0.0$ (blue curves) and $x = 0.1$ (red curves) for the atomically relaxed interface (see text). The middle panel represents the DOS of the TiO$_2$ terminated interface, while the upper and lower panels represent the DOS of TiO$_2$ layers in the LaTiO$_3$ and SrTiO$_3$ motifs, which is adjacent to the interface. The zero on the energy scale represents the Fermi energy (dashed line).

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 only little changes in the electronic structure properties of the $LaTiO_3/SrTiO_3$ system.

In summary, we have studied the effects of inter-site cationic La/Sr disorder across the interface of $LaTiO_3/SrTiO_3$ heterostructures using CPA. We find an intricate dependence of La/Sr disorder and lattice relaxation effects, with the local relaxation mainly accounting for the thermodynamical stability of the system, and by a factor of three larger in comparison to the inter-site mixing of the La and Sr ions 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,[27–29] that can allow a proper relaxation of the ions at the interface, can minimize the cationic inter-site 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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