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The metallic interface between the two band insulators LaGaO₃ and SrTiO₃

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The formation of metallic interface states between the two band insulators LaGaO₃ and SrTiO₃ is studied by the full-potential linearized augmented plane-wave method based on density functional theory. Structural optimization of the atomic positions points to only small changes of the chemical bonding at the interface. The *n*-type (LaO/TiO₂) and *p*-type (GaO₂/SrO) interfaces turn out to be metallic. Reduction of the O content increases the conductivity of the *n*-type interface, while the *p*-type interface can be turned gradually from a hole doped into an electron doped state. © 2011 American Institute of Physics. [doi:10.1063/1.3604020]

Perovskite oxides interfaces (IFs) have attracted considerable attention due to a wide range of electronic and magnetic properties which do not exist in the individual bulk parent materials.^{1–3} Development of heterostructures incorporating such IFs is promising as it offers novel functionalities and device concepts. In particular, the recent discovery of a quasi two-dimensional electron gas (2DEG) at the IF between the oxide insulators SrTiO₃ (STO) and LaAlO₃ (LAO) had strong influence on this field.^{4–8} It was demonstrated that the 2DEG has a high electron density and carrier mobility, which makes it interesting for application in field-effect devices. At a very low temperature of ~200 mK, the LAO/STO IF becomes superconducting.⁹

Perovskite oxides (chemical formula ABO₃) consist of AO and BO₂ layers which alternate along the (0,0,1) direction. The layers can be both neutral and charged. For example, LAO consists of charged layers, while the layers are neutral in STO. When LAO is deposited on the top of STO, the polar discontinuity at the IF leads to divergence of the electrostatic potential when the number of LAO unit cells grows. To avoid the divergence, ideally speaking, half of an electron (per unit cell) is transferred across the IF, which fills the Ti 3*d* states partially and consequently leaves the IF metallic. Many studies have been performed to understand the mechanism behind the formation of the 2DEG.^{10–12} Nevertheless, various aspects of the physical picture of the LAO/STO IF remain open.^{13–19}

Only very recently, formation of a 2DEG has been found experimentally for the *n*-type IF between LaGaO₃ (LGO) and STO.^{20,21} This IF likewise becomes superconducting at low temperature (~150 mK).^{9,22} Interestingly, the lattice match of LGO with STO is much better than that of LAO with STO. While the electronic structures of bulk LGO (polar) and STO (non-polar) are very well studied both experimentally and theoretically, theoretical insight into the LGO/STO IF is missing, although it is desperately needed for understanding the IF properties.

In general, O vacancies are critical for the stability of a heterostructure and, beyond, play an important role for achieving a high conductivity.^{6–8,23,24} There is, however, experimental evidence that under sufficiently high O pressure electronic

reconstruction becomes the dominant effect.⁵ In the following, we discuss results of first principles calculations based on density functional theory in order to clarify the atomic relaxation and electronic structure of the LGO/STO IF, both without and including O vacancies. We present results for the electron doped IF (*n*-type) as well as for the hole doped IF (*p*-type).

We have performed both non-magnetic (NM) and ferromagnetic (FM) calculations using the full potential linearized augmented plane wave method, as implemented in the WIEN2K code.²⁵ This code is suitable for studying IF systems.^{26,27} For calculating the band structure, the exchange-correlation potential is parametrized in the local density approximation. Whereas the core states are treated fully relativistically, the scalar relativistic approximation (i.e., neglect of spin orbit coupling) is applied to the valence states. We have fully optimized the structures of all our LGO/STO IFs by relaxing the atomic forces, using the generalized gradient approximation which is known to describe the crystal structure very accurately. A maximum value of the angular momentum of $\ell_{max} = 10$ for the wave function expansion inside the atomic spheres and a plane-wave cutoff of $R_{mt}K_{max} = 6.0$ with $G_{max} = 18$ is sufficient. Furthermore, we apply a $15 \times 15 \times 1$ k-space grid which contains 36 points within the irreducible wedge of the Brillouin zone. The muffin-tin sphere radii (in atomic units) are set to 2.5 for both La and Sr, 1.94 for both Ga and Ti, and 1.72 for O. Self-consistency is assumed for a total energy convergence of less than 10^{-4} Ry.

STO has a cubic structure with the space group $Pm\bar{3}m$ (no. 221)²⁸ and experimental lattice constant 3.905 Å.²⁹ In contrast, LGO has a pseudocubic structure with experimental lattice constant 3.874 Å,²⁰ leading to a lattice mismatch at the IF of only 1%. The experiments indicate that the critical thickness of the surface LGO layer to leave the LGO/STO IF conducting is 4 unit cells,^{20,21} similar to the case of the LAO/STO IF. For this reason, we investigate a supercell with 4 unit cells of LGO and 8 unit cells of STO along the (0,0,1) direction. We use an average lattice constant of 3.884 Å for both the LGO and STO regions. We have checked that there is no discernible effect on our data for variation of the lattice constant between 3.864 Å and 3.905 Å. In order to resemble the experimental situation, we address an *n*-type IF

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FIG. 1. (Color online) Schematic representation of the (a) n -type and (b) p -type IFs.

(LaO/TiO₂). Beyond, we study a p -type IF (GaO₂/SrO). A schematic representation of both IFs is shown in Fig. 1. The effects of O vacancies are analyzed by means of a larger supercell which is obtained by doubling the above mentioned supercell both along the (1,0,0) and (0,1,0) directions. We note that for an experimentally metallic IF, we can expect correct results from our calculations, as metallic states are well described. However, for an experimentally insulating IF, a conjecture about the presence or absence of metallicity would not be valid due to the systematic underestimation of band gaps by the local density approximation.

It is known from the LAO/STO IF that the electronic structure might depend critically on structural details of the IF.³⁰ For this reason, it is necessary to optimize the atomic structure by atomic force minimization. However, by the minimal lattice mismatch between the component materials, the structure optimization in the present case results only in small modifications of the bond lengths at the IF. The Ti-O and Ga-O bond lengths (1.948 Å in the bulk) adopt values of 1.961 Å and 1.940 Å, respectively, while the Sr-O and La-O bond lengths (2.763 Å in the bulk) become 2.765 Å and 2.760 Å, respectively. For the LAO/STO IF significant changes in the chemical bonding due to buckling of the IF AlO₂ layer have been reported.³¹ On the contrary, the LGO/STO IF develops hardly any buckling during the structure optimization. This may be connected to the smaller lattice mismatch of only 1%. Due to the reduced buckling, as compared to LAO/STO, dipole effects do not play a relevant role in the LGO/STO heterostructure. The small structural relaxa-

tion allows us to attribute the thickness dependence of the electronic properties of the LGO/STO IF to charge transfer from the surface to the IF, which declines with increasing distance between surface and IF, i.e., with the film thickness.

Figure 2 shows the partial and orbitally resolved densities of states (DOSs) for the Ti and O atoms at the n -type IF. The DOS clearly reflects the metallic nature of the IF. We mention that metallicity is not a consequence of the structure relaxation since it is likewise found before the structure optimization. It is the charge transfer between the component materials which shifts the conduction states considerably to lower energy. As a consequence, they cross the Fermi energy (E_F) and leave the IF metallic. This fact perfectly resembles the experimental findings of Perna *et al.*²⁰ as well as Aruta *et al.*²¹ According to Fig. 2(a), the near- E_F states are mainly due to the Ti 3d orbitals. They are partially occupied with only small contributions of the O 2p orbitals. Due to the crystal field, the Ti 3d states split into $d_{3z^2-r^2}$, d_{xy} , $d_{x^2-y^2}$, and $d_{xz,yz}$ states. Fig. 2(b) clearly shows that the IF metallicity results from the filling of the Ti d_{xy} and $d_{xz,yz}$ states, while the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states remain empty. Note that the occupation of the d_{xy} states is significantly higher than that of the $d_{xz,yz}$ states. In general, the situation is similar to the n -type IF of the LAO/STO heterostructure.³¹

In order to exclude a possible magnetic ordering of the IF states, we have performed spin polarized calculations. In case of the LAO/STO IF, the magnetic ordering depends critically on the thickness of the STO slab. The calculated magnetic moments vanish above 9 layers.³² We find the spin majority and spin minority DOSs of the LGO/STO IF to be almost identical with a negligible magnetic moment of 0.007 μ_B at the Ti sites.

Besides the n -type IF, investigation of the p -type IF is equally interesting because it behaves very differently. In the present case, the p -type IF also develops a metallic IF state (before as well as after the structure optimization), which reproduces the behavior of the p -type LAO/STO IF.²³ Figure 3 shows that at the IF, the O 2p DOSs of O atoms both in the SrO and GaO₂ layers cross E_F , while the Ti 3d states are empty. While for the n -type IF the Ti 3d orbitals carry the 2DEG, we conclude that the O 2p states are responsible for the formation of the 2DEG in the case of the p -type IF. Experimental data for comparison are not available for the p -type LGA/STO IF. However, the results derived here are very similar to that of the well studied LAO/STO IF. While for the n -type IF the 2DEG extends 7.8 Å perpendicular to

FIG. 2. (Color online) Projected Ti 3d and O 2p DOSs at the fully relaxed n -type LGO/STO IF: (a)/(b) NM ideal and (c) NM 25%/50% O deficient.

FIG. 3. (Color online) Projected Ti 3d and O 2p DOSs at the fully relaxed p -type LGO/STO interface: (a) NM ideal, (b) NM 25% O deficient, and (c) NM 50% O deficient.

the IF plane (completely on the STO side), it extends only 5.9 Å for the p -type IF (about half on the STO and half on the LGO side).

It is widely accepted that O vacancies play an important role for the stability as well as the electronic properties of the IFs under consideration, see the discussion in Ref. 5, for example. Therefore, we introduce into our supercell different concentrations of O vacancies in order to systematically study the effects on the IF properties. We create configurations with 25% and 50% IF O deficiency by removing one and two O atoms, respectively, from either the TiO_2 layer (for the n -type IF) or the SrO layer (for the p -type IF). The results for the O deficient n -type IF are shown in Fig. 2(c). We again obtain metallicity, but with the Ti 3d states shifted considerably to lower energy. The occupation of these states thus increases, which is consistent with the fact that O vacancies enhance metallicity by providing extra electrons to the delocalized Ti 3d orbitals. The sharp DOS peaks near E_F are further enhanced when the O content is reduced, compare Fig. 2(c), which implies that the system destabilizes. Therefore, we suggest that the LGO/STO IF does not attract O vacancies, see the discussion in Ref. 20.

The behavior of p -type LAO/STO IF as a function of the O content has been discussed by Park *et al.*²³ It has been found that introduction of 25% O vacancies into the SrO layer at the IF leads to a metallic state, while 50% O vacancies yield an insulator with a small band gap. We note that the above vacancy concentrations are consistent with a value of 32% as estimated experimentally.^{4,5} However, for the LGO/STO IF, we do not obtain a finite band gap, even for the high vacancy concentration of 50%. The calculated DOSs for the p -type IF (25% and 50% O deficiency) are displayed in Figs. 3(b) and 3(c). Figure 3(b) demonstrates that the IF with 25% O deficiency is metallic. Although we observe a considerably shift to lower energy, the Ti 3d states remain empty. Figure 3(c) addresses the case of 50% O deficiency, indicating occupation of the Ti 3d states. As a consequence, the metallicity of the pure and 25% O deficient LGO/STO IFs is carried by the O 2p states, while the Ti 3d states are responsible in the case of 50% O deficiency. The different nature of the metallic states calls for an experimental investigation of the p -type IF as a function of the O deficiency.

To conclude, we have studied the electronic structure of the LGO/STO IF by all-electron band structure calculations based on density functional theory. Due to a small lattice

mismatch between the component materials, our structural optimization results only in minor modifications of the chemical bonding. Local magnetic moments at the IF can be excluded. We find the n -type IF to be metallic, which confirms recent experiments. Going beyond the experiment, we find the p -type IF to be likewise metallic. Analysis of the orbitally resolved DOSs indicates that the metallic states are due to the Ti 3d orbitals at the n -type IF. In contrast, the O 2p orbitals are responsible for the metallicity at the p -type IF. Expectedly, introduction of O vacancies into the n -type IF increases the metallicity. On the other hand, for the p -type IF, an increasing O deficiency counteracts the hole doping. For strong O deficiency (50%), this IF even can be driven into an electron doped state by populating the Ti 3d orbitals. Therefore, it is well suitable for a systematic study of a 2DEG with varying carrier density.

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