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High charge carrier density at the NaTaO₃/SrTiO₃ hetero-interface

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The formation of a (quasi) two-dimensional electron gas between the band insulators NaTaO₃ and SrTiO₃ is studied by means of the full-potential linearized augmented plane-wave method of density functional theory. Optimization of the atomic positions points to only small changes in the chemical bonding at the interface. Both the p-type (NaO)[−]/(TiO₂)⁰ and n-type (TaO₂)⁺/(SrO)⁰ interfaces are found to be metallic with high charge carrier densities. The effects of O vacancies are discussed. Spin-polarized calculations point to the formation of isolated O 2*p* magnetic moments, located in the metallic region of the p-type interface. © 2011 American Institute of Physics. [doi:10.1063/1.3625951]

Heterostructures of perovskite oxides have attracted a lot of interest due to the possibility of novel functionalities.^{1–}

³ For example, a metallic interface (IF) is formed between the polar LaAlO₃ (LAO) and non-polar SrTiO₃ (STO) wide band gap insulators.^{4,5} The (quasi) two-dimensional electron gas (2DEG) shows a remarkable charge carrier density of $3.3 \times 10^{14} \text{ cm}^{-2}$ (Refs. 6 and 7) and other unusual properties related to magnetoresistance, superconductivity, magnetism, and metallic-insulator transitions.^{3,8,9} It is found that O vacancies play a very important role for understanding the physics of the IF. Park *et al.*¹⁰ have demonstrated theoretically that introduction of 25% O vacancies into the SrO layer at the p-type (AlO₂)[−]/(SrO)⁰ IF leads to metallicity, while 50% O vacancies yield an insulating state with a small band gap, which is consistent with a value of 32% as estimated experimentally.^{9,11}

The rich physics of the LAO/STO heterostructure has initiated various studies of IFs of other perovskite oxides. Only recently, a 2DEG has been reported experimentally for the n-type IF between STO and LaGaO₃.^{12,13} This IF shows superconductivity below $T_C \approx 150 \text{ mK}$, similar to LAO/STO.⁸ Metallicity is also observed for DyScO₃/STO heterostructures when a critical thickness of 6 DyScO₃ layers is reached.¹⁴ The experiments indicate that the O pressure (i.e., O vacancy concentration) can be used to control the formation of the 2DEG. The CaHfO₃/STO heterostructure behaves similarly.^{15,16} Interestingly, a metallic ferromagnetic IF appears in the LaMnO₃/STO heterostructure, although LaMnO₃ is a Mott insulator with A-type antiferromagnetic order.¹⁷

The KTaO₃/STO (KTO/STO) heterostructure shows very close relations to LAO/STO, despite the fact that at the (KO)[−]/(TiO₂)⁰ IF 0.5 holes per unit cell are transferred,¹⁸ while at the (LaO)⁺/(TiO₂)⁰ IF 0.5 electrons are transferred. The formation of metallic states at the (KO)[−]/(TiO₂)⁰ IF has been explained in terms of charge transfer between the Ti and O atoms, an effect which should also be important for related IFs such as LAO/STO.¹⁹ However, the 2DEG in this case is found to have a charge carrier density of $0.5 \times 10^{13} \text{ cm}^{-2}$, which is considerably less than in LAO/STO, for example. Therefore, we are interested in the question whether the chemical similarity of Na and K (same valence) can be exploited to

improve the charge carrier density, while maintaining the less involved mechanism for the creation of the 2DEG.

This work is devoted to a theoretical investigation of NTO/STO hetero-interfaces. The electronic structures of bulk NTO and STO are well studied experimentally and theoretically, which does not apply to the NTO/STO heterostructure. After discussing the details of our calculations, we will first address the two component materials NTO and STO and then focus on the heterostructure.

We use the full-potential linearized augmented plane-wave method of density functional theory as implemented in the WIEN2k package.²¹ For the exchange-correlation potential, we apply the generalized gradient approximation (GGA). Relativistic effects are taken into account fully for the core states, while the scalar relativistic approximation is used for the valence states (i.e., spin-orbit coupling is neglected). For the wave function expansion inside the atomic spheres, a maximum value of $\ell_{\text{max}} = 12$ is used, together with a plane-wave cutoff of $R_{\text{mt}}K_{\text{max}} = 7.0$ and $G_{\text{max}} = 24$. For the self-consistent calculations, a $19 \times 19 \times 19$ k-space grid which comprises 55 points within the irreducible wedge of the Brillouin zone is employed. Our basis set consists of the valence states Na 3*s*, 3*p*, 3*d*, Sr 5*s*, 5*p*, Ta 5*d*, 6*s*, Ti 3*d*, 4*s*, 4*p*, and O 2*s*, 2*p*. The muffin-tin sphere radii R_{mt} (in atomic units) are chosen as 2.5 for both Na and Sr, 1.98 for both Ta and Ti, and 1.75 for O. For ensuring correct results, all these parameters have been checked carefully for convergence. We have fully optimized the NTO/STO heterostructure by relaxing the atomic forces.

The bulk electronic structures of the two perovskites STO and NTO have been discussed in Refs. 20 and 22. The compounds crystallize in cubic structures with space group no. 221 ($Pm\bar{3}m$) and lattice constants 3.905 Å and 3.931 Å, respectively.^{4,23} Hence, the lattice mismatch is less than 1%. The experimental band gaps of STO and NTO are 3.2 eV and 4.0 eV, respectively. Due to the well-known shortcomings of the approximations required to handle the exchange-correlation potential, our calculated GGA band gaps for STO and NTO are 1.89 eV and 3.11 eV, respectively. These values are in a good agreement with previous band structure calculations.^{20,24,25} We model the NTO/STO heterostructure by means of the supercell approach, using the average value of the experimental lattice constants of STO and NTO (i.e.,

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FIG. 1. (Color online) Schematic representation of the NTO/STO heterostructure with TiO₂ terminated (p-type) and SrO terminated (n-type) IFs. Periodic boundary conditions apply.

3.918 Å) for the lattice matching. We stack 6 unit cells of NTO (~ 2.4 nm thickness) and 10 unit cells of STO (~ 4 nm thickness) along the (001) direction and employ three-dimensional periodic boundary conditions. Our supercell thus contains a TiO₂ terminated p-type (NaO)⁻/(TiO₂)⁰ IF as well as a SrO terminated n-type (TaO₂)⁺/(SrO)⁰ IF. A schematic representation of the supercell is shown in Fig. 1.

It is known that the electronic structure can depend critically on the structural details of the IF.²⁶ To be save, we consequently have optimized the structure of our system by atomic force minimization. However, due to 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 IFs. The Na-Na and Sr-Sr bond lengths remain virtually the same and also the changes in the Na-Ta and Sr-Ti bond lengths (3.384 Å in the bulk) are small. We obtain 3.382 Å for the Na-Ta and 3.386 Å for the Sr-Ti distance. The same applies to the Na-O and Sr-O bond lengths (2.763 Å in the bulk), which adopt values of 2.758 Å and 2.764 Å, respectively. The Ta-O and Ti-O bond lengths (1.954 Å in the bulk) shrink to 1.947 Å and 1.948 Å, respectively. Therefore, the structural relaxation cannot explain a metallic IF state, in contrast to other heterostructures. In turn, the NTO/STO heterostructure is a suitable candidate for a 2DEG with little additional complexity due

to a strong structural relaxation. The good lattice match points to a high probability of epitaxial growth.

Figure 2 shows partial densities of states (DOSs), which result from projections on the atoms in the vicinity of the IFs. Figures 2(a) and 2(b) refer to the (NaO)⁻/(TiO₂)⁰ IF, whereas Figs. 2(c) and 2(d) address the (TaO₂)⁺/(SrO)⁰ IF. The DOSs clearly indicate metallic IF states in both cases. The metallicity of the p-type IF mainly traces back to a partial occupation of the O 2*p* states in the TiO₂ layers. However, there are also remarkable O 2*p* contributions of atoms in the neighbouring NaO and TaO₂ layers, giving rise to rather sharp DOS peaks at the Fermi energy (E_F). We note that the Ti 3*d* and Ta 5*d* states do not contribute to the metallicity. The sharp DOS peaks at E_F could be indicative of IF magnetism in this system. In order to clarify this question, we have performed spin-polarized calculations. Our results show no magnetic moment ($<0.01 \mu_B$) for the Ti and Ta atoms, while significant moments of $0.08 \mu_B$ and $0.03 \mu_B$ arise for the O atoms in the NaO and TiO₂ layers. Therefore, we encounter a situation of isolated moments within the metallic region of the p-type IF.

Turning to the n-type IF, the metallic states show only very little O 2*p* admixtures due to hybridization. Figures 2(c) and 2(d) clearly indicate that the metallicity is carried by the Ti 3*d* and Ta 5*d* orbitals, mediated by the neighboring O 2*p*

FIG. 2. (Color online) Partial DOS as obtained for the relaxed NTO/STO heterostructure: (a)/ (b) p-type IF and (c)/(d) n-type IF, see Fig. 1.

orbitals. Due to the electronic reconstruction at the $(\text{TaO}_2)^+ / (\text{SrO})^0$ IF, the Ti 3d and Ta 5d states shift considerably to lower energy, cross E_F , and, therefore, become partially occupied. Due to the symmetry breaking induced by the crystal field, the Ti 3d and Ta 5d states split into $d_{3z^2-r^2}$, d_{xy} , and $d_{x^2-y^2}$ and degenerate $d_{xz} + d_{yz}$ symmetry components. We find that the IF metallicity is due to the filling of the d_{xy} and $d_{xz} + d_{yz}$ states, while the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states remain unoccupied, since they do mediate direct overlap with O atoms and, therefore, appear at higher energy.

Further evaluation of the DOS allows us to determine the electron and hole counts and the charge carrier densities. At the p-type IF, we find 0.22 O 2p holes in the TiO_2 layer, 0.08 O 2p holes in the NaO layer, and 0.04 O 2p holes in the TaO_2 layer. The corresponding charge carrier densities are $13.8 \times 10^{13} \text{ cm}^{-2}$, $5.2 \times 10^{13} \text{ cm}^{-2}$, and $2.5 \times 10^{13} \text{ cm}^{-2}$, respectively. At the n-type IF, the fillings of the Ti 3d and Ta 5d orbitals amount to 0.10 and 0.11 electrons, respectively, corresponding to charge carrier densities of $6.2 \times 10^{13} \text{ cm}^{-2}$ and $7.0 \times 10^{13} \text{ cm}^{-2}$. We observe that the charge carrier density at the NTO/STO IFs is significantly improved as compared to the KTO/STO heterostructure. Experimental data are not available for our system. Besides the higher charge carrier density, the calculated electronic structure is fully in line with previous findings for the KTO/STO heterostructure.¹⁹ This particularly is true for the mechanism leading to the creation of metallic states.

We have also analyzed possible effects of O vacancies by reducing the O content by 25% both in the TiO_2 and SrO layers. To this aim, a $2 \times 2 \times 12$ supercell is studied. As expected, the occupations of the Ti 3d and Ta 5d orbitals increase as additional electrons are set free when the O vacancies are introduced.

The formation of the 2DEG in our system appears to be thoroughly captured by the occupation changes of the transition metal d and O 2p orbitals. We find that in the vicinity of the n-type IF, the transition metal atoms gain electrons, while the O atoms gain holes at the p-type IF, see Fig. 2. This behavior is similar to that known from the KTO/STO heterostructure. We notice that the metallic states are restricted to a very narrow region around the IF. For the n-type IF, the charge transfer is strongest within the first TiO_2 layer and first TaO_2 layer off the IF, which thus are mainly responsible for the conductivity, and decreases rapidly when the distance to the IF increases. The second TiO_2 and TaO_2 layers are on the verge of metallicity, while atoms further away show an insulating behavior (not shown here). The total width of the metallic region amounts to 11.7 Å (perpendicular to the IF), which is almost the same as for the KTO/STO heterostructure. In contrast, in the case of the p-type IF, we find O 2p holes in a slab of 7.8 Å width around the IF.

In conclusion, we have studied the electronic properties of the NTO/STO heterostructure by full-potential band structure calculations based on density functional theory. Due to a minor IF lattice strain, our structural optimization leads only to small modifications of the bond lengths. Metallicity is found for the TiO_2 terminated p-type $(\text{NaO})^-(\text{TiO}_2)^0$ IF as well as for the SrO terminated n-type $(\text{TaO}_2)^+ / (\text{SrO})^0$ IF.

The charge carrier density is high with values of up to $13.8 \times 10^{13} \text{ cm}^{-2}$ and $7.0 \times 10^{13} \text{ cm}^{-2}$ for the p-type and n-type IFs. A detailed analysis of the site-projected partial DOSs indicates that the metallic IF states mainly originate from the Ti 3d and Ta 5d orbitals in the case of the n-type IF, while the O 2p orbitals are responsible for the 2DEG in the case of the p-type IF. Hybridizations always are found to be very small. The 2DEG forms in very narrow slabs of about 11.7 Å and 7.8 Å thickness for the n-type and p-type IFs, respectively. Our spin-polarized calculations show no magnetic moment on the Ti and Ta atoms, while significant moments are formed on the O 2p orbitals at the p-type IF.

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