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Electronic Properties of a Two-Dimensional Electron Gas at the Interface between Transition Metal Complex Oxides

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Abstract—The structural and electronic properties of heterostructures based on transition metal oxides containing strongly correlated electrons are compared. The investigated structures are $LaAlO_3/SrTiO_3$ (LAO/STO), $LaAlO_3/BaTiO_3$ (LAO/BTO), and $BaTiO_3/SrTiO_3$ (BTO/STO). The role of structural relaxation in the formation of a two-dimensional electron gas at the interface of two dielectrics is revealed. The contribution from different orbitals and atoms to conductivity is analyzed, along with the correlation between structural distortions induced by the dipole moment in an LAO layer and conductivity.

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In 2004, Ohtomo and Hwang [1] reported an observation of a high-mobility electron gas at an interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO). Since then, heterointerfaces of these two nonconducting and nonmagnetic oxides have been observed in numerous studies. It was found that a metallic phase of nanometer thickness (a two-dimensional electron gas, 2DEG) forms in STO layers in structures with more than three LAO layers and interface LaO and TiO_2 layers. This phase becomes superconducting at temperatures below 300 mK [3]. The electron density in such heterostructures can be as high as 3×10^{13} cm^{-2}. In addition, ferromagnetism was observed in a LAO/STO heterostructure in [4].

Since STO is often used as a substrate, combinations of it and other compounds were examined in searching for emerging conductivity. A 2DEG was also observed at interfaces between other nonmagnetic dielectrics (e.g., $KTaO_3/SrTiO_3$ [5]). In addition, a 2DEG was found at the interface with antiferromagnetic $LaTiO_3$ [6] having a maximum density of 3×10^{14} cm^{-2}.

Several authors have assumed that the emergence of conductivity is related to structural (and thus electronic reconstructions), but a clear explanation and model of this phenomenon have yet to be presented. The aim of this work was therefore to examine the relationship between electronic correlations, structural distortions, and electronic reconstructions in LAO/STO and $LaAlO_3/BaTiO_3$ (LAO/BTO) heterostructures, which contain polar LaO and AlO_2 layers, and the BTO/STO heterostructure, in which the layers are electrically neutral but the emergence of ferroelectric polarization in BTO, which can switched as a result of external influences, may be expected.

The density functional theory approach [7] employed in VASP [8] was used as a research tool. Since strong correlations between the electrons of *d*-orbitals must be considered in modeling the electronic properties of transition metal oxides, we chose the GGA + *U* approximation for this, with corrections introduced as proposed by Dudarev [9]. Parameter *U*–*J* was added to the La 4*f* and Ti 3*d* orbitals ($U = 8$ and 2 eV, respectively). The magnetic nature of the material was ignored. Exchange and correlation effects were accounted for by using the GGA-PBE generalized gradient approximation [10]. Kohn–Sham equations were solved using the basis of plane waves (PAW) implemented in VASP, which was integrated into MedeA [11]. The cut-off energy was set at 400 eV, the residual forces were 0.05 eV Å^{-1}, and the energy convergence was 10^{-5} eV. The Brillouin zone was sampled using a $5 \times 5 \times 1$ grid.

The unit cell of heterostructures contained a central region of $SrTiO_3$ or $BaTiO_3$ (4.5 unit cells with boundary TiO_2 layers) surrounded from both sides by four $LaAlO_3$ layers with boundary LaO at the interface and AlO_2 at the surface (halves of unit cells are shown in Fig. 1). This structure ensured lack of polarity and a dipole moment induced by asymmetry. To avoid interaction between surfaces and their periodic copies, a 20 Å vacuum region was introduced into the calculations. Lattice constant $a = b = 3.905$ Å was taken from the experimental data for cubic bulk $SrTiO_3$. The experimental conditions of heterostructure growth were thus reproduced [1]. These lattice parameters

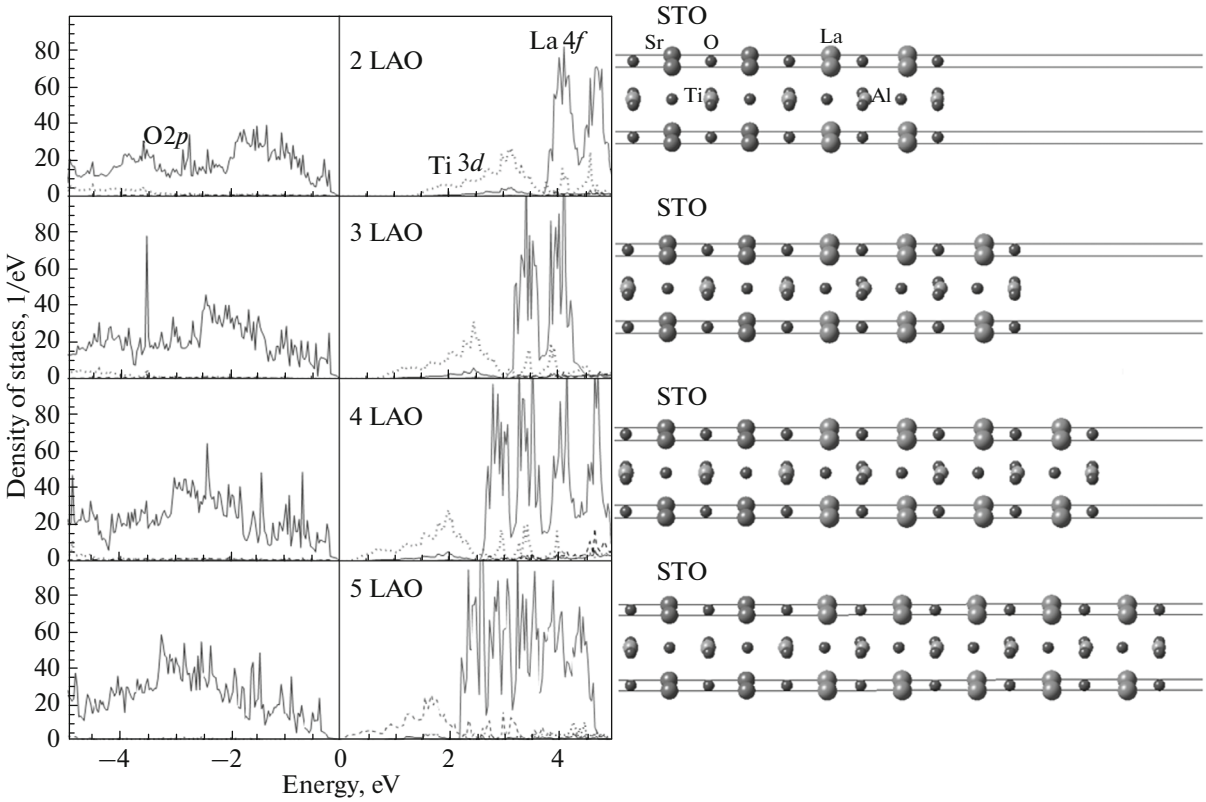

Fig. 1. Density of states spectra for the nLAO/4.5STO/nLAO n-type heterostructure (n = 2, 3, 4, 5) and the corresponding halves of unit cells.

were fixed in heterostructure optimization in order to imitate the rigidity of the STO substrate.

Let us discuss the obtained results. It was demonstrated in [12] that introducing the parameter of Coulomb repulsion in a heterostructure into calculations is essential not only for simulating electronic properties, but also for optimization. In order to examine the electronic properties of the heterostructure and determine the point of transition into a conducting state, the densities of states of heterointerfaces with different numbers of LAO layers were calculated for an ideal cell and after structural optimization. In the case of ideal atomic positions ($a = b = \Delta c = 3.905$ Å, where Δc is the distance between atomic layers), all heterostructures with an arbitrary number of LAO layers are conductors. Their conductivity is induced by the overlap of surface O 2p states and interface Ti 3d states. The optimization procedure has a critical effect on the electronic properties: a gap between surface O 2p levels and interface Ti 3d levels forms (see Fig. 1 for LAO/STO and Fig. 2 for LAO/BTO). This gap shrinks as more LAO layers are added. The dependence of the bandgap width on the number of LAO layers is then linear, which agrees with the polarization catastrophe theory. It is important that structural distortions arise during optimization. These wave-like distortions are seen clearly in Figs. 1 and 2: Aluminum atoms emerge out of oxygen planes (with the displacement of atoms near the interface (Fig. 3) being the largest). This strong lattice polarization balances out the dipole electrical field in LAO, which is induced by the alternate arrangement of oppositely charged layers, and keeps the system dielectric as long as it contains less than five LAO layers. Electronic rearrangement then occurs, electronic states overlap, and the spectrum of the density of states starts to resemble that of an ideal heterostructure.

The properties of LAO/STO and LAO/BTO are similar in three ways: (1) the transition to a conducting state occurs when the number of layers goes from four to five (Figs. 1 and 2), and conductivity is established by the overlap of surface oxygen states and levels of interface titanium; (2) the displacement of aluminum (and titanium) from oxygen planes becomes more prominent near the interface; (3) an increase in the number of layers results in the suppression of the dipole electrical field in LAO, which is reflected in the off-plane displacement of Al atoms (minimum displacement for a conducting heterostructure) and Ti atoms (maximum displacement for a conducting heterostructure).

The primary difference between the properties of LAO/STO and LAO/BTO heterostructures is the nature of displacements in the STO (or BTO) layer. This may be attributed to the ferroelectric properties

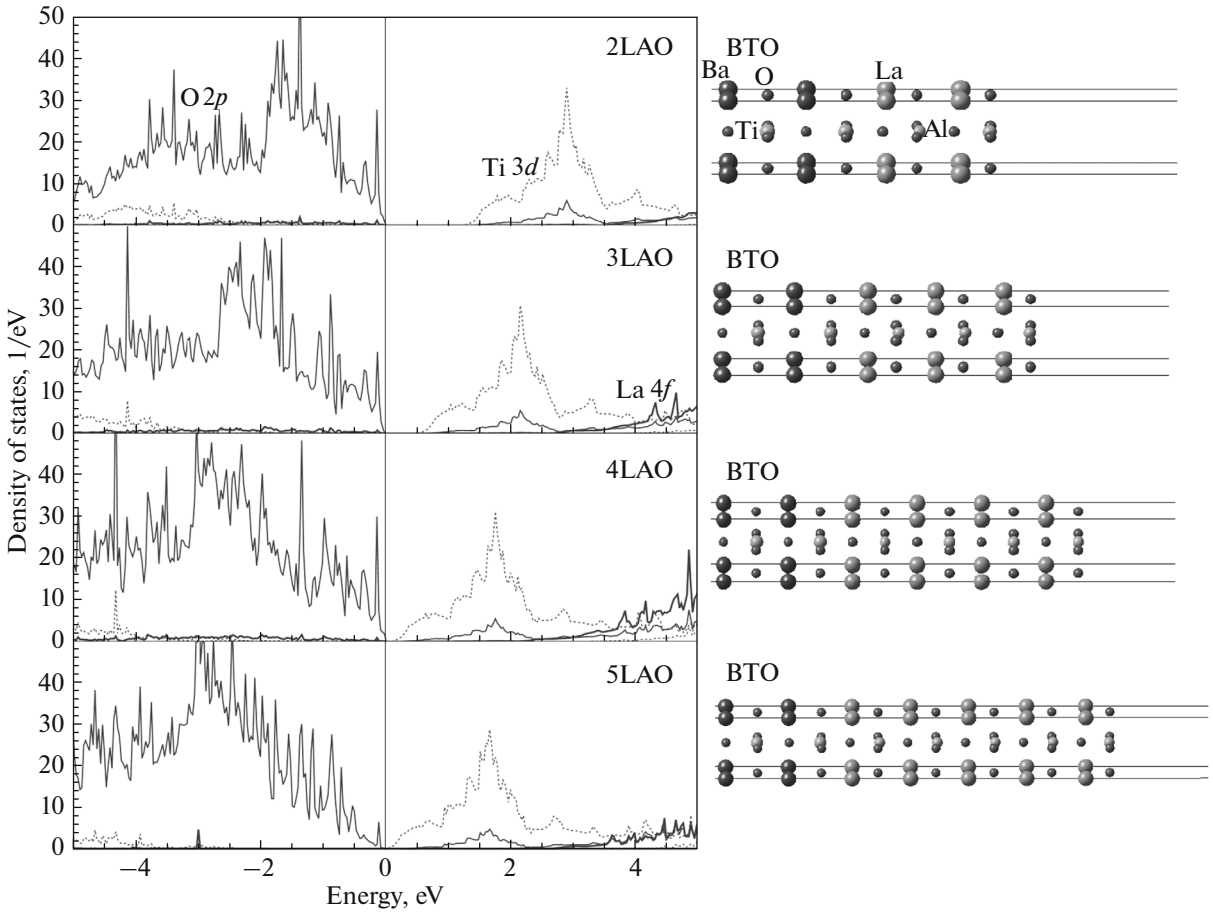

Fig. 2. Density of states spectra for the *n*LAO/4.5BTO/*n*LAO *n*-type heterostructure ($n = 2, 3, 4$) and the corresponding halves of unit cells.

of the BTO layer, where the displacement of Ti atoms is considerably larger (Fig. 3).

Let us consider the case of STO/BTO. Both components of the heterostructure are composed of electrically neutral (in the ion approximation) layers: $Sr^{2+}O^{2-}$ and $Ti^{4+}O_2^{2-}$. This is why no atomic displacement is observed (Fig. 4). Although the bandgap width shrinks slightly (from 0.8 eV with two BTO layers to 0.65 eV with five layers), two-dimensional conductivity does not emerge in these structures. However, the bandgap closes in a model heterostructure with Ti atoms in the BTO layers being displaced in a similar manner to Al atoms in the LAO layer of LAO/STO.

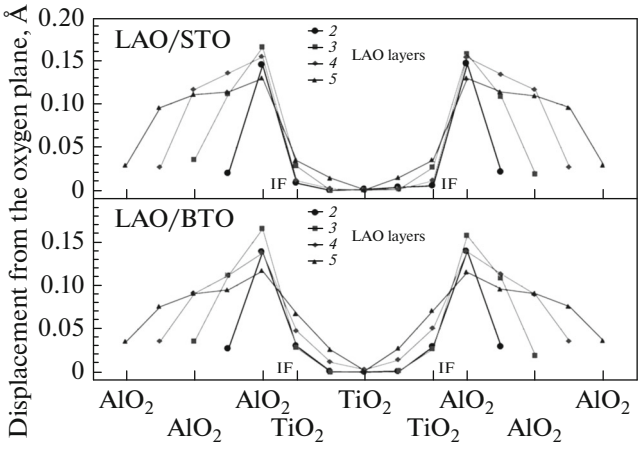

Fig. 3. Displacement of Al and Ti atoms from oxygen planes in *n*LAO/4.5STO/*n*LAO and *n*LAO/4.5BTO/*n*LAO, where *n* is the number of layers.

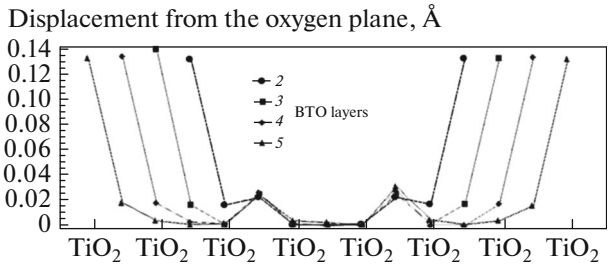

Fig. 4. Displacement of Ti atoms from oxygen planes in the *n*BTO/4.5STO/*n*BTO heterostructure, where *n* is the number of layers.

Magnetic order with a magnetic moment of 0.3782 μ_B then arises.

It is worth noting that additional effects possibly associated with the spatial rearrangement of charge carriers at the interface were ignored in the above modeling. However, we have revealed the formation of a 2DEG at the interface of two dielectrics and determined the contribution from structural relaxation to this phenomenon.

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