Structural, electronic, and magnetic properties of ferroelectric/dielectric heterostructures

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Abstract. We present the results of structural, electronic, and magnetic properties of BaTiO3/LaMnO3 heterostructure by means of first-principles calculations. We demonstrate the possibility of highly conducting layer formation at the heterostructure composed of perovskite ferroelectric BaTiO3 and antiferromagnet manganite LaMnO3. We also analyse magnetic properties and an impact of ferroelectric polarization onto the conducting properties. Experimental results of magnetic field effect on Ba0.8Sr0.2TiO3/LaMnO3 heterostructure are presented as well. Effect of illumination of the Ba0.8Sr0.2TiO3/LaMnO3 heterostructure is also demonstrated.

1. Introduction

A high-mobility electron gas was found at the interface between two nonmagnetic wide-band gap insulating oxides LaAlO3 (LAO) and SrTiO3 (STO) in 2004 [1]. After that, similar heterointerfaces involving two insulating nonmagnetic oxides were comprehensively studied [1-12]. In particular, it was found that the metallic phase, so-called quasi-two-dimensional electron system (q2DES), was formed in the STO layers next to the LAO/STO interface, when the number of LAO overlayers exceeded three [2,3]. Such a system underwent a transition to a superconducting state below 300 mK [4]. Remarkably, this superconducting state coexisted with a magnetic state being stable up to the room temperature. It was concluded, that the primary mechanism responsible for the q2DES formation was the electronic reconstruction followed by structural reconstruction. Later, q2DES was found in other non-magnetic dielectrics. Their common feature is that the creation of q2DES might be due to either the polar nature of one of the components or due to defects or dopants. The polarity can be due to a sequence of the differently charged layers as in the LAO, or due to the ferroelectric material used as an overlayer [3,4]. The main advantage of using ferroelectric material in the heterostructure is a possibility to change the direction of the polarization in the ferroelectric layer and thus to control properties of the interface.

The most common mechanism for describing the q2DES formation is the polarization discontinuity model [1,12]. The important feature related to the 2DES formation is the local polarity of layers inside the LAO slab. LAO can be considered as a sequence of (LaO)\(^+\) and (AlO\(^-\)) layers. The conductivity occurs as soon as the field towards the surface exceeds the field, which arises due to the buckling, or in other words, when the number of LAO overlayers exceeds the critical value. In the present work, we have chosen the BaTiO3/LaMnO3 (BTO/LMO) heterostructure, where BTO has (BaO)\(^0\) and (TiO\(^2\)) layers.

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neutral layers. Thus, there is no polarity due to charge sequence, but there is a ferroelectric polarization due to Ti atoms displacements out of the octahedron centre in the BTO slab. Moreover, the direction of this polarization might be switched by an external electric field. Based on first-principles band structure calculations, we demonstrate the possibility of conducting layer formation at the interface composed of perovskite ferroelectric BTO and antiferromagnet manganite LMO. We briefly introduce the employed computational method and first results of modelling of structural, electronic, and optical properties of BTO/LMO heterostructure with different numbers of layers. We also present the experimental results of magnetic field effect and the effect of illumination onto the $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$/LaMnO$_3$ heterostructure.

2. Simulation and experimental details

For the density of states (DOS) calculations and structural optimization, we use density functional theory (DFT) [12]. Exchange and correlation effects were accounted by generalized gradient approximation (GGA) [13]. Kohn-Sham equations were solved using the plane-wave basis set (PAW) [14] realized within the VASP code [15], which is a part of the MedeA® software of Materials Design [14]. The cutoff energy was chosen to be 400 eV. The force tolerance was 0.5 eV/Å and the energy tolerance for the self-consistency loop was $10^{-4}$ eV. The Brillouin zones were sampled including $5 \times 5 \times 1$ k-points. Since there are strong correlations between $d$ and $f$-electrons in our system, the GGA+$U$ correction were included to our computational scheme [16]. The $U$ parameter was added to La 4f, Ti 3d and Mn 3d orbitals ($U=8$ eV, 2 eV, and 4 eV, respectively). The choice of $U$ for Ti and La atoms was based on our previous research [17]. In the case of BTO/LMO, heterointerface components represent two insulating oxides with different structures and parameters of elementary cell. Due to a high mismatch between BTO and LMO ($\approx 30\%$), the BTO unit cell was rotated by a $45^\circ$ before merging with LMO substrate, since the $\sqrt{2}a_{\text{BTO}}=0.5657$ nm, resulting in less than 1 % mismatch with LMO substrate’s in-plane cell parameter. It means that the substrate is compressive with respect to the film. As a result, the polarization axis of the ferroelectric BTO will be directed perpendicular to the interface. For modelling, the heterostructure the LMO central slab was enlarged by a factor of 1.5 in $z$-axis direction and bounded by a varying number of BTO layers with interface BaO or TiO$_2$ layers on both sides. Such a unit cell guarantees the absence of artificial dipoles and additional polarity, which might arise due to a non-symmetric structure. In order to avoid interaction of surfaces and slabs with their periodic images, a 20 nm vacuum region was added. In plane, $a$ and $b$ cell parameters were fixed to lattice parameters of LMO substrate, whereas the rest atom positions were allowed to relax during the optimization procedure. Since the substrate is compressive with respect to the film, the polarization axis of the ferroelectric BTO will be directed perpendicular to the interface.

The temperature dependence of the electrical resistance has been studied for heterostructures formed by antiferromagnetic LaMnO$_3$ single crystals with epitaxial films of ferroelectric $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (BSTO) deposited on it by reactive sputtering of stoichiometric targets using RF plasma (RF-sputtering) method [18, 19] at 650°C. In this work, we present a review of the investigation of conducting state and show the effect of illumination on the interface resistance between ferroelectric oxide and insulating oxide in the BSTO/LMO heterostructure.

3. Results and discussion

The DOS spectrum of BTO/LMO heterostructure with three BTO overlayers deposited on top of the LMO substrate is shown in Figure 1. In this case, Ti states cross the Fermi-level with sufficiently large DOS intensity (about 10 $\text{eV}^{-1}$). The band gap vanishes for the spin-up component, and we expect that the system is a good metal. A distinctive feature of the DOS with two and three BTO overlayers is the fact that in the first case the resulted magnetic state is antiferromagnetic, whereas in the second case it is ferromagnetic. Possibly, that is related to the number of free charge carriers. In the case of three BTO overlayers, the DOS at the Fermi-level and charge carriers’ concentration are higher. Consequently, indirect ferromagnetic exchange through charge carriers becomes efficient for the ferromagnetic ordering at the interface. It can be well observed from Figure 1, where DOS with spin up and down differ significantly (mainly due to Mn atoms shown by green colour).
Figure 1. DOS spectrum of the BTO/LMO heterostructure with three BTO over layers on top of the LMO substrate. Solid and dashed curves correspond to spin-up and down components.

It also follows that band gap vanishes for the heterostructure with relatively small number of BTO over layers. Thus, we expect the interface area to absorb the light having the energy less than the band gap of LMO, in other words, photon energies considerably less than 1.8 eV. Besides, there is a metallic state, which might lead to the absorption in the terahertz spectral region. Thus, light absorption experiments in the terahertz spectral region might shed the light on the conductive properties. It is utterly important during such experiments to distinguish two contributions: the first one is related to the absorption by charge carriers in the conductive area, the second one is related to the optical phonon absorption in the region of 10-20 THz, if such phonons exist. Note, that the aforementioned line of reasoning is based on our assumption and so far not on experimental evidence. We applied magnetic field of different values and measured the temperature dependences of the heterostructure resistance by four contact method in the magnetic field and after switching it off.

After each cycle of the magnetic field application the resistance changed irreversibly. Temperature dependences of the resistance R(T) for the BSTO/LMO heterostructure after application of magnetic field are shown in Figure 2. Blue triangles show R(T) after few cycles of application of the magnetic field parallel to the c-axis of LMO and red diamonds show R(T) after few cycles of application of the magnetic field perpendicular to the c-axis of LMO. The inset shows a space distribution of the surface charge in the vicinity of the interphase. When the magnetic field is applied parallel to the c-axis of LMO, the resistance of the BSTO/LMO heterostructure sharply decreases after few cycles of the magnetic field application, but when the magnetic field is applied perpendicular to the c-axis, the resistance increases after few cycles of the magnetic field application.

Figure 2. Temperature dependences of the resistance R(T) for the BSTO/LMO heterostructure after application of magnetic field: blue triangles show R(T) after few cycles of application of the magnetic field up to 1 T parallel to the c-axis of LMO and red diamonds show R(T) after few cycles of application of the magnetic field perpendicular to the c-axis of LMO. Space distribution of surface charge in the vicinity of the interphase is shown in the insert.
When the magnetic field is applied perpendicular to the $c$-axis, the resistance of the BSTO/LMO heterostructure shows semiconducting behaviour. The resistance measurements for these samples are shown in Figures 3 and 4. In particular, Figure 3 shows temperature dependences of the resistance for BSTO/LMO heterostructures under light radiation and without it. The resistance of the sample under radiation is more than 10 times higher than the resistance measured without radiation. The light absorption by the film affects the charge distribution in the BSTO/LMO heterostructure. Thus, we observe a negative photoconductivity. To understand the nature of resistivity increasing under the light radiation, we have measured time characteristics $R(t)$. As it is shown in Figure 4, the resistance saturates in less than 10 seconds after switching the light on. The resistance recovers with the same relaxation time after switching the light off.

Since we found rather slow relaxation processes, we assume that charge dynamic is associated with relaxation processes in the ferroelectric film (relaxation processes in the metallic regions should be much faster). Under illumination, the free electron-hole pairs are generated in ferroelectric film. These pairs screen the polarization. This process leads to the depletion of the interface region. To clarify all these issues, further experiments with switching the polarization of the film in the strong electric field are necessary.

4. Conclusion

The results of structural, electronic, and optical properties calculations of BaTiO$_3$/LaMnO$_3$ heterostructure composed of different number of layers based on first-principles calculations and theoretical consideration were presented. A possibility of a conducting state at the interface formation was shown. The transition to a metallic state in Ba$_{0.8}$Sr$_{0.2}$TiO$_3$/LaMnO$_3$ heterostructure was observed when the polarization of the ferroelectric film was perpendicular to the surface of the heterostructure. The resistance of the heterostructure strongly decreased, when a magnetic field was applied perpendicular to the surface of heterostructure. The effect of illumination of the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$/LaMnO$_3$ heterostructure was observed. Therefore, the resistance of the heterostructure may be controlled by the light. This example shows that highly conductive state can be created at the ferroelectric/dielectric interfaces using the relatively simple technique of preparation.
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