Tailoring quasi-two-dimensional high conductivity and superconductivity areas at the interfaces of ferroelectric/dielectric heterostructures

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Abstract. The results of the investigations of high conducting and superconducting areas at the interfaces between ferroelectric oxide and insulating oxide are presented. The numerical simulations of BaTiO\textsubscript{3}/LaMnO\textsubscript{3} and BaTiO\textsubscript{3}/La\textsubscript{2}CuO\textsubscript{4} heterostructures have been performed. It is found that in the samples of the Ba\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3}/LaMnO\textsubscript{3} heterostructure the electrical resistance decreases significantly and exhibits metallic behaviour at low temperatures for the case when the c axis of ferroelectric film is directed along the normal to the surface of the single crystal. The superconducting behaviour with transition temperature $T_c$ about 30K has been found at the interface of the Ba\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3}/La\textsubscript{2}CuO\textsubscript{4} heterostructure. The proposed concept promises the ferroelectrically controlled interface conductivity and superconductivity.

1. Introduction

Unique properties of functional materials are achieved due to the effects associated with the complex composition of the interface structure. New materials include heterointerfaces between two insulating oxides, in which unique transport properties are observed because of strong electronic correlations. A high-mobility electron gas was discovered at the interface between two oxide insulators LaAlO\textsubscript{3} (LAO) and SrTiO\textsubscript{3} (STO) in Ref. [1]. It has attracted significant attention [1-10] due to a wide range of physical phenomena observed in this system. This type of heterointerfaces was comprehensively studied. In particular, it was found that the metallic phase (quasi-two-dimensional electron gas, q2DEG) was formed in the STO layers at the LAO/STO interface, when the number of LAO layers exceeded three [2]. The density of the charge carriers in this heterostructure reached the value of $3 \times 10^{13}$ cm\textsuperscript{-2}. Subsequently, the coexistence of a two-dimensional superconductivity and ferromagnetism was discovered in this system [3,4]. Such a system underwent a transition to a superconducting state at...
temperatures below 300 mK [3,4]. The creation of high-$T_c$ quasi-two-dimensional superconductivity at the interface was impossible up to now without tailoring the atomically perfect interfaces [11,12].

The polarization discontinuity at the interface is usually discussed [1,2,9,10] in order to describe the q2DEG in the LAO/STO heterostructure. Along the [001] direction, LAO slab represents an alternation of the differently charged layers of $(\text{LaO})^1$ and $(\text{AlO})^{2-}$. As it was shown experimentally, in the heterostructure with the TiO$_2$ interface layer the electric potential along the [001] direction appears due to the polarity disruption at the interface. Thus, the atomically flat quality of the interface between two components is utterly necessary since the effect is related to the strictly defined sequence of layers inside each slab. In this work, we study resistivity properties of two kinds of heterostructures: $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$/LaMnO$_3$ (BSTO/LMO) and $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$/La$_2$CuO$_4$ (BSTO/LCO). In the first case, we use LaMnO$_3$ (LMO) as a substrate, because antiferromagnetic LMO might be transferred to ferromagnetic state by increasing the concentration of free carriers. In the second case, we use La$_2$CuO$_4$ (LCO) as a substrate, because antiferromagnetic LCO might be transferred to a superconducting state by increasing the concentration of free carriers. The ferroelectric oxide $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (BSTO) was used as an overlayer in both heterostructures. For numerical simulations, we use BaTiO$_3$ instead of BSTO, because both materials have similar properties, but the simulations for BaTiO$_3$ are less complicated. As a result, we show that it is possible to use relatively simple techniques of sputtering of ferroelectric films in order to create q2DEG, which exhibits high conductivity and superconductivity at relatively high temperatures. It opens an opportunity to study the switching of such states by changing the polarization direction in the ferroelectric film.

2. Results and discussion

The numerical simulations [13-17] of the structural and electronic characteristics of the BaTiO$_3$/LaMnO$_3$ (BTO/LMO) and BaTiO$_3$/La$_2$CuO$_4$ (BTO/LCO) ferroelectric-antiferromagnet heterostructures have been performed. For density of states calculations and structural optimization, we use density functional theory [13]. Exchange and correlation effects were accounted by generalized gradient approximation [14]. Kohn-Sham equations were solved using the plane-wave basis set (PAW) [15] realized within the VASP code [16], which is a part of the MedeA® software of Materials Design [15]. We use the cut-off energy 400 eV. The force tolerance was 0.5 eV/nm and the energy tolerance for the self-consistency loop was $10^{-5}$ eV. The Brillouin zones were sampled including $5 \times 5 \times 1$ k-points. Since there are strong correlations between $d$ and $f$-electrons the GGA+$U$ correction were included to computational scheme [17]. The $U$ parameter was added to La $4f$, Ti $3d$, and Mn $4d$ orbitals ($U = 8$ eV, 2 eV, and 4 eV, respectively). The choice of $U$ for Ti and La atoms is based on Ref. [18]. Due to a high mismatch between BTO and LMO or LCO ($\approx 30\%$), the BTO unit cell was rotated by a $45^\circ$ before merging with LMO and LCO substrate. Because the substrate is compressive with respect to the film, the polarization of the ferroelectric BTO is directed perpendicular to the interface. Thus, the polarization has a discontinuity near the interface. Therefore, uncompensated charge is created at the interface on the ferroelectric side. This charge is screened by conduction charged carriers in thin layer on the surface of the substrate, forming the q2DEG state in this heterostructure.

The density of states of BTO/LMO heterostructure for the case when two layers of BTO were deposited on top of LMO substrate is shown in Figure 1. It is obvious that even two layers of BTO result in 0.3 eV band gap with a finite occupation of states near the Fermi-level. That behaviour is a characteristic of a weak metal. When number of BTO layers becomes larger than two, the band gap vanishes, and we expect the system to be a good metal at the interface. The density of states of BTO/LCO heterostructure for the case when two layers of BTO were deposited on top of LCO substrate is shown in Figure 2. The density of states of BTO/LCO heterostructure at the Fermi-level becomes also sufficiently large, approximately 5 eV$^{-1}$. The band gap vanishes, and we expect the system to behave as a good metal at the interface. Thus, BTO/LCO heterostructure can be superconductive.

The temperature dependence of the electrical resistance has been studied for heterostructures formed by antiferromagnetic LMO and LCO single crystals with epitaxial films of ferroelectric BSTO deposited on them by reactive sputtering of stoichiometric targets using RF plasma (RF-sputtering) method [19,20]
at 650°C. Here, we present the results of investigations of q2DEG in the interfaces between ferroelectric oxide and insulating oxide in BSTO/LMO and BSTO/LCO heterostructures.

The results of electrical resistance measurement of the BSTO/LMO heterostructure are presented in Figure 3. The measured resistance was compared to that exhibited by LMO single crystal without the film. It is found that in the samples with c-axis of the ferroelectric film perpendicular to the interface the resistance decreases significantly with lowering the temperature below 165 K, exhibiting metallic behaviour (Fig. 3). But in the samples with the c-axis of the ferroelectric film parallel to the interface the q2DEG is not observed [19]. Thus, the transition to the state with q2DEG at the interface, which is connected to a sharp change in the perpendicular component of the polarization at the interface, is demonstrated. When the magnetic field was applied perpendicularly to the interface, the resistance of BSTO/LMO interface started to change irreversibly. First steps of such changes are shown in Figure 3 (blue triangles). When the magnetic field was applied parallel to the surface, the q2DEG state disappeared. Thus, it is shown that the magnetic field effect on the resistivity of the BSTO/LMO interface is very strong.
Figure 3. Temperature dependences of the resistance $R(T)$ for $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3/\text{LaMnO}_3$ heterostructure before and after application of the magnetic field: red diamonds show $R(T)$ before application of magnetic field and blue triangles - after few cycles of application of magnetic field up to 1 T. Space distribution of surface charge near the interphase is shown in the insert.

The results of resistance measurements of the BSTO/LCO heterostructure are shown in Figure 4. The temperature dependence of the resistance in the wide temperature range shows that above 50 K it has semiconducting behaviour. At temperatures above 50K the main current flows through the substrate. The temperature dependence of the resistivity of LCO crystal is shown in Figure 4 by blue triangles. Below 50 K, the current flows mainly in the interface region. At low temperatures, the resistance decreases rapidly and superconducting behaviour is observed. It is confirmed by the observation of diamagnetic response in the susceptibility measurements in the BSTO/LCO heterostructure. The beginning of the transition to the superconducting state occurs around 40 K, similar to that observed in optimally doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals [11]. Thus, the interface between the ferroelectric and insulating oxides shows superconducting behaviour with $T_c$ higher than in LAO/STO heterostructure.

These results allow relatively simple interpretation. The abrupt change of the polarization $P$ at the interface leads to the formation of the surface charge with the density $\sigma_s = P_n$, where $P_n$ is the component of polarization perpendicular to the interface (see insert in Fig. 3). This charge must be screened; therefore, the charged layer forms at the opposite side of the interface. This charged layer may be considered as a surface doping. The characteristic charge density in this layer can be estimated as $n_s = \sigma_s/e = P_n/e$, where $e$ is the elementary charge. If we assume characteristic value of polarization as is in the bulk of ferroelectric ($P_n \approx 30 \mu\text{C/cm}$), we obtain $n_s \approx 10^{14}$ cm$^{-2}$. We estimate that the characteristic thickness of this layer is about 1-2 nm.

Figure 4. Temperature dependences of the resistance $R(T)$ for $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3/\text{La}_2\text{CuO}_4$ heterostructure for polarization directed perpendicular to ferroelectric film (red squares). Blue triangles show $R(T)$ for $\text{La}_2\text{CuO}_4$ single crystal without film.
3. Conclusion
In conclusion, the transition to q2DEG state in BSTO/LMO heterostructure was found below 165 K in the samples with polarization of the ferroelectric film perpendicular to the interface. It was shown that the resistance of the interface changed irreversibly, when the magnetic field was applied perpendicular to the interface. BSTO/LCO heterostructure was found to be superconductive. We showed that quasi-two-dimensional highly conductive and superconductive layers might be realized at the ferroelectric/dielectric interfaces obtained by relatively simple preparation techniques.

Acknowledgements
The reported study was funded by Russian Scientific Foundation, research project No. 18-12-00260. The authors from Kazan Federal University acknowledge partial support by the Russian Government Program of Competitive Growth of Kazan Federal University.

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