Editors' Suggestion

Fabrication of High-Temperature Quasi-Two-Dimensional Superconductors at the Interface of a Ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ Film and an Insulating Parent Compound of La_2CuO_4

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We report the first observation of superconductivity in a heterostructure consisting of an insulating ferroelectric film ($Ba_{0.8}Sr_{0.2}TiO_3$) grown on an insulating parent compound of La_2CuO_4 with [001] orientation. The heterostructure was prepared by magnetron sputtering on a nonatomically flat surface with inhomogeneities of the order of 1–2 nm. The measured superconducting transition temperature T_c is about 30 K. We have shown that superconductivity is confined near the interface region. Application of a weak magnetic field perpendicular to the interface leads to the appearance of the finite resistance. That confirms the quasi-two-dimensional nature of the superconductive state. The proposed concept promises ferroelectrically controlled interface superconductivity which offers the possibility of novel design of electronic devices.

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Up to now the creation of high-T_c quasi-two-dimensional superconductivity (HTQ2DSC) [1–6] as well as a quasi-two-dimensional electron gas (Q2DEG) [7–13] at the interface was impossible without tailoring the atomically perfect interfaces [1–4,7–14]. The realization of the HTQ2DSC area is a long-term goal because of potential applications [15,16] and the possibility to study quantum phenomena in two dimensions [9,17,18]. Typical approaches to the realization of a quasi-two-dimensional superconducting layer rely on the creation of an "ultrathin" film of a known superconductor [15,16]. However it is important not only to get HTQ2DSC, but also to have the ability to control superconducting states by magnetic and electric fields. In this Letter we present the experimental realization of HTQ2DSC by increasing the carrier concentration in a thin layer of the parent compound of the high temperature superconductor (PCHTSC) at the interface with the ferroelectric. By simple consideration the additional current carriers at the interface occur due to electrostatic potential arising from polar discontinuity. It allows us to change the conduction properties of the heterostructures by switching the polarization in the ferroelectric. This approach allows us to get heterostructures with relatively simple technology because the requirements for the boundary condition are less stringent.

Tailoring Q2DEG and HTQ2DSC at the interface is impossible without the deep understanding of the nature of quasi-two-dimensional states. First, the Q2DEG was created at the heterointerfaces between two insulating oxides, $LaAlO_3/SrTiO_3$ [3], and unique transport properties were observed owing to strong electronic correlations [7–13]. In this case the system becomes superconducting below 300 mK [9]. Then the superconductivity at 30 K in bilayers of an insulator (La_2CuO_4) and a metal ($La_{1.55}Sr_{0.45}CuO_4$), neither of which is superconducting in isolation, was reported [1,2]. The interplay of superconductivity with the antiferromagnetic order was also studied in the metal-insulator cuprate superlattices [5,6]. The price for these results in both cases was that the interfaces should be atomically perfect [1,9,14]. In the second case it was considered [1,13] that the interface must be atomically perfect to obtain the superconductivity at the interface in copper oxides, because the coherence length is very short ($\xi = 1$–3 nm) [19]. In the case of a ferroelectric oxide deposited on the copper oxide, the conditions are not so stringent for the appearance of the effect: inhomogeneities of the order of ξ are possible if their envelope is much greater than ξ. Thus in this Letter we report the first observation of superconductivity in a heterostructure consisting of an insulating ferroelectric film ($Ba_{0.8}Sr_{0.2}TiO_3$) on an insulator single crystal (La_2CuO_4). Here the results were obtained on the heterostructure, created by the relatively simple method of magnetron sputtering and using more simple conditions for the interface. We show experimentally that it is possible to get Q2DEG on a nonatomically flat interface. And we obtain superconductivity with $T_c = 30$ K at the heterointerfaces between two insulating oxides, which is 100 times higher than T_c in

the $LaAlO_3/SrTiO_3$ heterostructure. We would like to underline that using a ferroelectric oxide in the heterostructures allows us to fabricate the interface of two insulating oxides with a different structure of elementary cells and to have a more simple rf-sputtering method for tailoring the heterostructure. Moreover, using a ferroelectric material as an upper layer of the heterostructure brings interesting new physics, which opens the possibility to change the properties of the heterostructures by switching the polarization in the ferroelectric layer.

In our investigation, a La_2CuO_4 (LCO) single crystal was grown using a traveling-solvent-floating-zone technique and was characterized by magnetic susceptibility and resistivity measurements. And then a $Ba_{0.8}Sr_{0.2}TiO_3$ (BSTO) ferroelectric oxide was deposited on the *ab* surface of the single crystal [see Fig. 1(a)] by reactive sputtering of stoichiometric targets using the rf plasma (rf-sputtering) method [20] at 650 °C and partial pressure of oxygen of 0.7 Torr (details of the deposition are in the Supplemental Material [21]). Therefore, we tried to combine the advantages of both approaches described above in order to get the superconducting properties of the interface in an easy way. We have used a LCO single crystal as a substrate in order to obtain a high T_c. We use a relatively simple method of creating the interface, and the typical surface roughness of a LCO single crystal determined from atomic force microscopy data before deposition is about 1–2 nm [with the size in the plane of approximately 200–300 nm, see Fig. 1(b)], which is slightly more than one unit cell in the *c* direction (1.3 nm in LCO). A heteroepitaxial BSTO ferroelectric thin film (thickness of 200 nm from atomic force microscopy data) was deposited on the LCO single crystal (001) substrate. BSTO belongs to the ferroelectric perovskites. In the ferroelectric phase below the Curie temperature of the ferroelectric phase transition ($T_c = 353$ K) [24] it has a tetragonal unit cell. The as-grown film shows built-in polarization in the [001] crystallographic direction which was determined by the x-ray measurements. The temperature dependences of magnetic susceptibility χ(T) and resistivity ρ(T) of the LCO single crystal are shown in Figs. 1(c) and 1(d). The peak in χ(T) clearly observed around 306 K corresponds to the Néel temperature below which a long-range antiferromagnetic order is formed. The temperature dependence of resistivity $\rho(T)$ [Fig. 1(d)] is usual for LCO [25,26]. Both of these results are typical for this system [25,26] and indicate a good quality crystal.

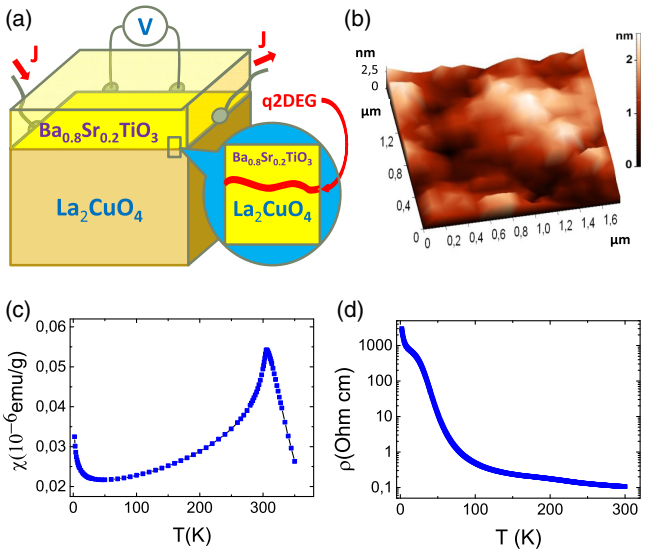

FIG. 1. The schematic structures of $Ba_{0.8}Sr_{0.2}TiO_3/La_2CuO_4$ (a) with Q2DEG (shown in red); AFM image of the La_2CuO_4 single crystal surface without the film (b) illustrates the inhomogeneity of the interface. The temperature dependence of the magnetic susceptibility (c), and the temperature dependence of the resistivity (d) of La_2CuO_4 single crystal (without ferroelectric film).

Resistance measurements on the interface of the heterostructure ware performed by a four contacts method. The electrodes were applied by using silver paste on the LCO surface at the boundary with the film as schematically shown in Fig. 1(a). The electrodes were in contact with the interface. The distance between potential electrodes was different in the different experiments. The distribution of the current, flowing by different routes at different temperatures, depends on the relation between the substrate conductance and the interface conductance. At high temperature the main current flows through the substrate. Below 50 K the current flows mainly in the interface region. The temperature dependence of the resistance of the $Ba_{0.8}Sr_{0.2}TiO_3/La_2CuO_4$ heterostructure in the wide temperature range [see Fig. 2(a)] shows that above 40 K the resistance has usual semiconducting behavior. At low temperatures [Figs. 2(a) and 2(b)] the resistance drops very rapidly and superconducting behavior is observed. Thus the interface between the ferroelectric and insulating oxides shows superconducting behavior with a high T_c of about 30 K (Fig. 2). The beginning of the transition to the superconducting state occurs around 40 K, similar to what is observed in bulk $La_{2-x}Sr_xCuO_4$ (LSCO) single crystals at optimal doping [25,26]. When a weak magnetic field is applied to the heterostructure in the direction perpendicular to the surface of the interface, the finite resistance of the interface appears and it increases with the increasing of the field (see Fig. 3) as it was predicted [27]. The magnetic field was applied perpendicular to the surface and parallel to the *c* axis of the LCO substrate at $T = 22.3$ K. The magnetic field dependence of the heterostructure resistance shows that nonzero resistance appears at a very low field. The H_{c1} for a thin layer of superconductor is very small and the magnetic field penetrates in the superconducting layer. In that case the system demonstrates flux-flow resistance. That confirms the quasi-two-dimensional nature of the superconductive state (see also Supplemental Material [21].) We did not perform the measurements in higher magnetic fields intentionally, since we know from previous

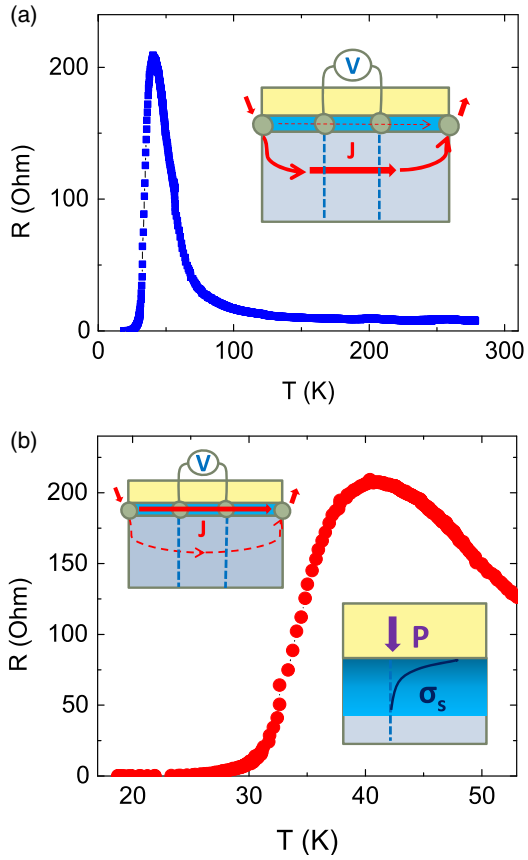

FIG. 2. The temperature dependence of the resistance of $Ba_{0.8}Sr_{0.2}TiO_3/La_2CuO_4$ heterostructure in the wide temperature range (a) and at low temperatures (b) (the results of the same measurements).

experience [28] that the effects of magnetostriction in relatively small magnetic fields can lead to partial peeling of the film from the substrate resulting in partial or complete disappearance of the observed effect. On the other hand, we believe that in our case, by analogy with

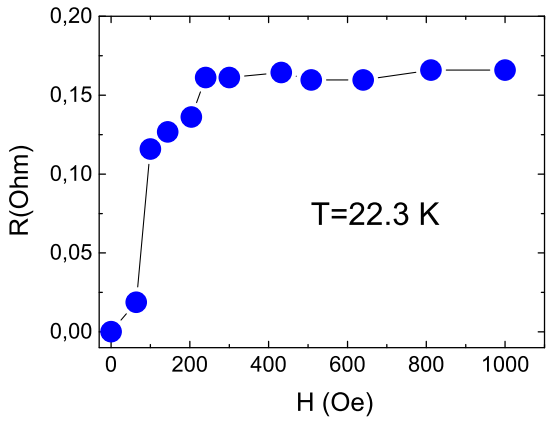

FIG. 3. The magnetic field dependence of the resistance of the $Ba_{0.8}Sr_{0.2}TiO_3/La_2CuO_4$ heterostructure.

LSCO, H_{c2} is of the order of 29–81 T, which is inaccessible for us.

The most common mechanism for Q2DEG is the polarization catastrophe (PC) model [12,17], which was also discussed for the case of the ferroelectric-dielectric interface [27–31]. The polar discontinuity at the interface leads to the divergence of the electrostatic potential. In order to minimize the total energy, it is necessary to shield the electric field arising from this. As a consequence, both the lattice system and the energy spectrum of the current carriers are restructured [27], and the increase of the current carriers' density occurs in a narrow interface area. This occurs in a self-consistent manner, so that rearranging the energy spectrum of the carriers and increasing their concentration in the interface region leads to the formation of a narrow metal region near the interface on the part of the LCO as shown in the right insert of Fig. 2(b). Our estimates show that if we assume that the polarization of the ferroelectric is $P = 30\ \mu K/cm^2$ (it gives $\sigma_S = 1.875 \times 10^{14}\ 1/cm^2$) and the screening length in LCO is $d_{Sc} = 0.45$ nm, then the concentration corresponding to the doping level, at which the superconducting state is observed in $La_{2-x}Sr_xCuO_4$ ($x = 0.05$–0.26), will be achieved in a narrow region of LCO in the second-third interface layers of the CuO_2 planes (details are presented in the Supplemental Material [21]).

In addition to this possibility, the occurrence of HTQ2DSC is possible due to the impact of cation interdiffusion (primarily Ba or Sr from BSTO to LCO) and oxygen nonstoichiometry. Barium or strontium diffusion is unlikely due to a low diffusion coefficient at 650 °C [32]. Reduction of oxygen during deposition of the film is also unlikely, since the process is carried out at elevated oxygen pressure. For that matter, an introduction of additional oxygen in this process would be more likely. But the following three experimental facts argue against this. The first is that Q2DEG was created at the interface of the $Ba_{0.8}Sr_{0.2}TiO_3/LaMnO_3$ heterostructure [28]. It would be unlikely that a change in the oxygen concentration in $LaMnO_3$ could lead to the appearance of Q2DEG, because it was shown experimentally for this case that the occurrence of Q2DEG is related to the direction of polarization in the ferroelectric, and arises only in the case of polarization directed perpendicular to the interface [28]. Our sample was obtained by the same technology using the same equipment. The second is that the application of the magnetic field, which partially destroys the contact at the interface between $Ba_{0.8}Sr_{0.2}TiO_3$ and $LaMnO_3$, leads to Q2DEG disappearance. From this fact it was concluded that the occurrence of Q2DEG is related to the proximity effect, rather than to diffusion processes. And the third fact is illustrated in Fig. 4. Here we applied electrodes for resistance measurements on the back side (single crystal side) of the heterostructure, and electrodes were not in contact with the interface (see upper left insert in Fig. 4). In this case the superconducting state is not observed directly.

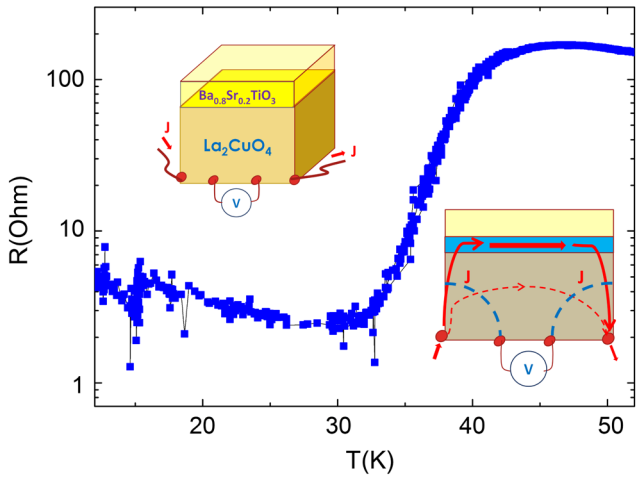

FIG. 4. The temperature dependence of the resistance of the $Ba_{0.8}Sr_{0.2}TiO_3/La_2CuO_4$ heterostructure from the substrate side. The temperature dependence of the heterostructure resistance is measured by electrodes deposited on the La_2CuO_4 surface opposite to the surface with the film.

The resistance decreases below a certain temperature but not below 4 Ohm. We believe that the current line distributions are strongly different at different temperatures (see lower right insert in Fig. 4) and depend on the relation between conductance of the substrate and the interface. At high temperature the main current flows through the substrate. Below 50 K the current flows mainly in the interface region, and the resistance shows qualitatively the same behavior as the resistance measured with the electric contacts at the top [Fig. 2(b), see also Supplemental Material [21]]. But superconductivity is not observed directly because the surface of substrate is not superconducting. It means that the oxygen does not penetrate the surface layer during the film deposition. The possibility of the reduction of oxygen in the interface area during deposition had been also discussed for the case of bilayers $La_2CuO_4/La_{1.55}Sr_{0.45}CuO_4$ [1,2]. It was concluded that "Interstitial oxygen in $La_2CuO_{4+\delta}$ is mobile and, in particular in very thin films, it diffuses out of the sample on the scale of hours or days" [1].

All these findings strongly indicate that we observed superconductivity in heterostructures consisting of an insulating ferroelectric film ($Ba_{0.8}Sr_{0.2}TiO_3$) grown on an insulating single crystal with [001] orientation (La_2CuO_4). This heterostructure was created by magnetron sputtering on a nonatomically flat surface. Our results open a new page in creating interfaces with Q2DEG and HTQ2DSC, since it has been shown experimentally that it is possible to create HTQ2DSC by a relatively simple method at the boundary of the ferroelectric and parent compound of the high temperature superconductor (PCHTSC). We believe that these results will have a large impact in the field and will be interesting for a broad scientific community, because a large number of new heterostructures may be fabricated by this technique, and a large number of different groups may use this method. Note, that with this technique we obtain superconductivity with $T_c = 30$ K, which is 100 times higher than T_c in $LaAlO_3/SrTiO_3$ heterostructures.

In conclusion Q2DEG is formed at the interface, which becomes the HTQ2DSC state when the temperature is lowered below 30 K. The HTQ2DSC arises from strongly increasing carrier density localized in the interface area in copper oxide while the polar discontinuity at the interface leads to the divergence of the electrostatic potential due to the polarization catastrophe [7,12]. This allows us to control the interface superconductivity by applying an electric field, as it was done in the case of the ionic liquid [33]. It opens the possibilities to use these phenomena in a novel design of electronic devices.

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