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Anisotropic superconductivity induced by periodic multiferroic domain patterns

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Abstract

The competition between order parameters, such as ferroelectricity, ferromagnetism, and superconductivity, is one of the most fascinating topics in condensed matter physics. Here, we report intriguing anisotropic superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films induced by a multiferroic, BiFeO_3 , with periodic domain patterns. The anisotropic superconductivity was investigated by transport measurements and supported by phase-field simulations, and then the detailed local electronic structures were revealed by cross-sectional scanning tunneling microscopy. We found that the oxygen redistribution in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ modulated by the ferroelectric polarization in BiFeO_3 was the key mechanism driving this anisotropic superconductivity. The presented heteroarchitecture of a high-temperature superconductor and a domain-engineered multiferroic provides a new approach to tune superconductivity and offers potential advantages for the design of future multifunctional devices.

Introduction

The reversible switching ability of order parameters is a distinguishing key feature of spontaneous ordering in ferroics. Among the numerous ferroic systems that have been explored, multiferroics have recently aroused great scientific interest due to the coexistence and intriguing coupling between order parameters, allowing the modulation of one through another^{1–5}. BiFeO_3 (BFO) has played an important role in this field after the discovery of its large ferroelectric polarization ($\sim 100 \mu\text{C}/\text{cm}^2$)⁶ and multiferroic characteristics above room temperature^{7,8}, making it appealing for practical applications⁹. Perovskite BFO possesses the space group of $R3c$ with spontaneous ferroelectric polarization along pseudocubic $\langle 111 \rangle$ directions and in the G-type antiferromagnetic ordering; as a result of the free energy competition, the ferroics form domains^{9,10}. In BFO, three different angles (71° , 109° , and 180°) can be found between the ferroelectric

polarization in adjacent domains. In addition, domain walls in the BFO possess rich physical properties, such as magnetoresistance and exchange bias^{11,12}. Recently, progress in the domain engineering of BFO has been extensive, leading to the control of periodic domain patterns with long-range ordering, which can be used for the both fundamental research and the exploration of potential applications.

Moreover, the tangled ferroic orders in multiferroics result in the ability to provide a unique environment to the heterostructures via various coupling mechanisms. By precisely controlling domain patterns, a ferroic system can improve the electric, magnetic, and structural coupling to adjacent layers. For example, studies performed by Heron et al.^{13,14} and Trassin et al.¹⁵ show an excellent demonstration of the electrical control of ferromagnetism with the $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{BFO}$ heterostructure via a one-to-one correlation of the ferroelectric in the BFO and ferromagnetic domains in the $\text{Co}_{0.9}\text{Fe}_{0.1}$. In addition, uniaxial magnetic anisotropy and anisotropic magnetoresistance have been observed in a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ layer grown on a periodic 71° BFO domain pattern, where the magnetic easy axis of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and ferroelectric

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polarization of the BFO show parallel coupling via structural coupling^{16,17}. Thus, the utilization of periodic multiferroic domain patterns can be a way to trigger very intriguing phenomena. In this study, a model system based on a combination of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) and multiferroic BFO with carefully designed domain configurations are introduced. The superconductivity in the YBCO layer was thoroughly explored upon undergoing long-range-ordered electrostatic, elastic, and antiferromagnetic perturbations provided by neighboring multiferroic BFO domain patterns. Surprisingly, anisotropic superconductivity was discovered in the YBCO layer. The insights of this emerging phenomenon were unveiled by cross-sectional scanning tunneling microscopy (STM) and supported by phase-field simulations. Such a result provides an elegant approach to tune the local superconductivity of a superconductor, which has great potential to trigger additional device applications based on high-temperature superconductors.

Materials and methods

Thin film growth and characterization

YBCO/BFO films with thicknesses between 15 and 180 nm were grown on single-crystal $(110)_\text{O}$ DyScO_3 (DSO) substrates by pulsed laser deposition from 650–700 °C at an oxygen pressure of 100 mTorr. The samples were cooled at a rate of 20 °C/min at an oxygen pressure of 600 Torr and dwelled at 500 °C for 60 min. The typical deposition rate was ~2 nm/min with a laser repetition rate of 10 Hz. The focused laser power density on the target surface was ~2 J/cm². The structural details of the samples were studied by synchrotron-based X-ray diffraction techniques. The RSMs of the heterostructures were performed using a PANalytical X'Pert Pro 4-circle X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54 \text{ \AA}$), recorded with a series of θ – 2θ scans with different ω offsets and collected at beamline BL-17B1 at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan.

The ferroelectric domain structures were characterized at room temperature by piezoresponse force microscopy (PFM, Veeco Multimode). The tips used for the PFM imaging were Ti-Pt-coated cantilevers with an elastic constant of 4.5 N/m and a resonance frequency of 120–190 kHz.

Transport measurement

The transport measurement was performed in a physical property measurement system (Quantum Design). The resistance measurements were obtained during both heating and cooling paths with an applied current of 1 μA within a temperature range from 300 to 2 K with a cooling rate of 1 K/min.

Scanning tunneling microscopy

The experiments used DSO as the substrates for the STM study. A 30-nm BFO layer was deposited prior to the growth of the 35–45 nm YBCO layers. Finally, a 500 nm amorphous Al-doped ZnO (AZO) buffer layer was deposited on the YBCO to prevent a tip crash during the STM measurements. The samples were cooled down to 25 K and then cleaved in situ in an ultrahigh vacuum chamber with a base pressure of 5×10^{-11} Torr. All STM measurements were performed at 25 K.

Results and discussion

In the rhombohedrally distorted perovskite BFO, there are eight possible directions for ferroelectric polarization that point along the pseudocubic $\langle 111 \rangle$ directions, corresponding to four structural variants. The formation and control of ferroelectric domain patterns in (001)-oriented rhombohedral perovskite films have been well established in earlier theoretical and experimental studies^{18–20}. The heteroepitaxial constraints can lead to periodic nanoscale arrays of ferroelastic domains, such as the 109° and 71° domain configurations in BFO films. The same approach was adopted in this study with the $\text{DyScO}_3 (110)_\text{O}$ (DSO, where “O” denotes the orthorhombic system) substrates, and the detailed growth process can be found in our previous work²⁰ and the Methods section herein. PFM was employed to reveal the nicely ordered 109° and 71° domain patterns (Fig. 1a, d, respectively). We note that the ferroelectric polarization configurations are different in the 109° and 71° patterns shown in Fig. 1b, e. In the 109° pattern, the out-of-plane polarizations are periodically pointing up and down; on the other hand, in the 71° pattern, the out-of-plane polarizations are uniformly pointing down. Detailed PFM images of both domain patterns are shown in S1 in the Supplementary Materials. The YBCO layers were deposited on these BFO films to form heteroepitaxial systems. The structural information of the heterostructures was extracted from a series of X-ray diffraction reciprocal space maps (RSMs) shown in Fig. 1c, f. The normal scan (00L) shows a high-quality, single-phase, and c -oriented YBCO and BFO layer in S2. For the underlying BFO films, the typical diffraction characteristics of 109° and 71° domain patterns can be observed in the asymmetric RSMs along the $\text{DSO } (222)_\text{O}$ reflections. For the 109° domain pattern, the normal vector of the atomic planes in the 109° domain pattern has an angle difference ($\sim 0.68^\circ$) between the neighbor domains^{20,21}. Thus, we can observe a horizontal splitting of the $(012)_\text{pc}$ reflection (where “pc” denotes the pseudocubic system) (Fig. 1c) with the 109° domain pattern, whereas the peak splitting cannot be observed for the same reflection in the 71° domain pattern (Fig. 1f). On the other hand, for the 71° domain pattern, the normal vector of the atomic planes and lattice constant are the same

Fig. 1 Model domain-wall architecture. **a, d** PFM images of ordered arrays for 109° and 71° domain patterns, respectively. **b, e** Schematic of the heterostructure of the 109° and 71° domain-wall arrays, respectively. **c, f** Reciprocal space mapping of the (012)_{pc} peaks from BFO and DSO and (016)_{pc} and (015)_{pc} peaks from YBCO for 109° and 71° cases, respectively.

Table 1 Lattice parameter of the YBCO layer of 109° and 71° cases, respectively.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
109° case	3.84 (6)	3.85 (5)	11.68 (0)
71° case	3.87 (2)	3.88 (7)	11.71 (0)

between the domains, resulting in a single BFO peak, as shown in Fig. 1f. These measurements show that the BFO layer retained its domain structure after the consecutive deposition of the YBCO layer. The corresponding BFO lattice parameters were extracted and are presented in Table 1 of the supporting materials. In addition, the {105} and {106} YBCO diffraction peaks can also be observed in these RSMs. The YBCO layer maintained its orthorhombic structure (Fig. 1c, d) and possessed a mono-domain structure instead of twinned structures, presenting an elongated *a*-axis compared to that of the bulk YBCO to achieve a coherent strain with the BFO film and DSO substrate. In bulk orthorhombic YBCO, the Cu-O chains are typically formed along the *b*-axis between the CuO₂ planes. These chains provide conducting

channels for charge carriers, causing an anisotropic in-plane conductivity. Thus, the anisotropic lattice structure of YBCO can contribute to a low anisotropic transport behavior due to the direction of the Cu-O chains. However, when the temperature was lower than the critical temperature (*T_c*), the YBCO only shows isotropic superconductivity²². Here, we stress that the YBCO layers in this study exhibit single-crystal features; therefore, we can exclude any anisotropy that may be induced by grain boundaries or the bicrystal effect²³. We also note that the existence of vicinal steps or terraces in the BFO films should be excluded in this anisotropic superconductivity discussion because the terrace does not have a particular correlation with the direction the 71° domain walls (shown in S3). The ultimate goal of this study is to create anisotropic superconductivity in the heterostructures of YBCO/BFO by perturbing the pairing of Cooper pairs or modulating the doping level in the YBCO layer in only one direction via the long-range stripy domain patterns in the BFO layer at the nanoscale.

To explore the proposed anisotropic superconductivity, transport measurements were carried out on two sets of heterostructures: YBCO/BFO with 109° (denoted as the “109° case”) and 71° domain patterns (denoted as the “71°

case"). The DC resistance of the YBCO layers was extracted from the voltage drop measured by a four-terminal apparatus with a 1 μ A current flowing parallel ($[010]_{pc}$ in the 109° case and $[100]_{pc}$ in the 71° case and denoted as a "parallel geometry," shown as the black arrow in the inset of Fig. 2a, b, respectively) and perpendicular ($[100]_{pc}$ in the 109° domain pattern and $[010]_{pc}$ in the 71° domain pattern and denoted as a "perpendicular geometry," shown as the red arrow in the inset of Fig. 2a, b, respectively) to the domain walls in all samples. The temperature dependence of the resistance (300–2 K) is shown as the black and red curves for the two different measurement geometries in Fig. 2a, b with the data normalized to the resistance at 300 K. The trend of the R – T curves indicates that these YBCO films were underdoped^{24,25}. Interestingly, a large anisotropy with greater than a 20 K difference in the offset temperatures was found for the two measured geometries, which maintained similar onset temperatures (~ 80 K). The anisotropic behavior discovered in these heterostructures is defined as an "easy axis" for superconductivity, where a direction with a higher T_c can always be observed. It is very intriguing to see that the easy axis for superconductivity in our system is always parallel to the direction of the domain walls in the BFO layer ($[100]_{pc}$ in the 109° case, and $[010]_{pc}$ in the 71° case), suggesting that the anisotropic superconductivity is strongly correlated to the domain patterns in the BFO layer.

One possible hypothesis is that the ferroelectric field effect from the BFO layer modulates the carrier distribution in the YBCO layer, resulting in an anisotropic distribution of the doping level in the YBCO^{26,27} during the growth process since BFO has a high Curie temperature of ~ 1100 K. The controlled YBCO thickness dependence transport measurements support an interface effect (shown in S4). The anisotropic superconductivity vanishes beyond 48 nm of the YBCO. This suggests that the magnetic proximity effect might not be the dominant factor due to the short-range nature of the exchange interaction, yet the oxygen redistribution or elastic relaxation might play a very important role in our case. These hypotheses are further verified by a combination of phase-field simulations and cross-sectional STM (XSTM).

The superconductivity of YBCO is very sensitive to the oxygen doping level, which suggests that the oxygen content in the YBCO film determines the T_c . Phase-field simulations were employed to investigate the distribution of oxygen vacancies in the YBCO layer under the influence of periodic BFO domain patterns (see S5–S7 in the Supplementary Materials for details). In the simulation results, the 109° domain patterns show a periodic configuration of upward and downward polarizations. Under the influence of the electrostatic potentials, the oxygen vacancies can diffuse at high temperatures during growth, leading to the redistribution of the oxygen in the YBCO layer, as shown in Fig. 3a. Such a redistribution of the

Fig. 3 Distribution of oxygen vacancies and shear strain component. **a, b** Normalized distribution of hole concentration for the 109° and 71° cases, respectively. The concentration was normalized with respect to the concentration at zero electrostatic potential. **c, d** Distribution of ε_{23} for the 109° and 71° cases, respectively.

oxygen can result in different T_c in the YBCO regions correlated to the two domains in the BFO layer, which can be understood to consist of two parts with different resistances, namely a high- and low- T_c region. With the two types of regions connected in parallel, the superconductivity was determined by the high- T_c region for the parallel geometry (easy axis), whereas for the perpendicular geometry, the two types of regions are serially connected, and the overall T_c was determined by the low- T_c region (hard axis). On the other hand, for the 71° case, with a homogenous downward polarization in the BFO layer (see S1 in Supplementary Materials), the distribution of the oxygen vacancies is almost uniform along the in-plane direction, except the area in proximity with the domain walls, as shown in Fig. 3b, and in Fig. 3d due to the shear strain induced by 71° domain walls²⁸. However, this shear strain domain wall is not significant in the 109° case, as shown in Fig. 3c. This extra strain perturbation can distort the structure of the YBCO, resulting in a suppression of the T_c near the domain walls. This is consistent with the RSM result in Fig. 1f, where the YBCO is partially relaxed due to the lattice mismatch. Similar to the argument for the 109° case, the parallel geometry

shows a higher T_c than that of the perpendicular geometry. Thus, in both the 109° and 71° cases, an anisotropy in the superconductivity is very expected and needs to be further investigated by a spatially resolved characterization technique.

To reveal the mechanism of the anisotropic superconducting behavior, XSTM was employed to study the local electronic structure across the interfaces of the heterostructures. Both the 109° and 71° cases were investigated at 25 K. The geometry of the XSTM measurement is schematically illustrated in Fig. 4a. All samples were cleaved in an ultrahigh vacuum chamber to obtain a clean cross-section morphology, as shown in Fig. 4b, and then transferred to the XSTM chamber. The protection of the YBCO layer from moisture and the STM tip can be assisted by the deposition of a conducting layer, namely, AZO, on top of the YBCO layer. The experimental details of the XSTM measurements can be found in the Supplementary Materials (S8 and S9) and Materials and methods section. To explore the local electronic structures in the cross-sections of the YBCO/BFO heterostructures, the locations of the domains and domain walls (71° and 109°) in the BFO layer were mapped first.

Fig. 4 XSTM study of 109° and 71° cases. **a** Schematic of experimental configuration used for XSTM measurements. **b** STM morphology of the YBCO/BFO heterostructure obtained at a sample bias of +2.0 V. **c, f** Spectroscopic image of the YBCO/109° BFO domain wall and YBCO/71° BFO domain wall. The sample bias was acquired at **c** −500 mV and **f** +200 mV individually. **d, g** YBCO tunneling spectra acquired near the interfaces of YBCO/109° BFO domain wall and YBCO/71° BFO domain wall. **e, h** Energy gap 2Δ as a function of distance away the interface of YBCO/109° BFO domain wall and YBCO/71° BFO domain wall.

Based on our previous STM study of BFO domain walls²⁹, the locations of the 71° and 109° domain walls can be determined from the mapping of the tunneling conductance (Fig. 4c, f), where the yellow dotted line highlights the edges of the 109° (71°) domain wall and the red dotted line indicates the interface between the YBCO and BFO layers. With this map, we can then investigate the

electronic structures in the YBCO layer at the nanoscale. The detailed electronic structures of the YBCO layer were explored in three locations in each sample individually: the areas adjacent to the BFO domains (marked by red and purple rectangles (denoted as DM1' and DM2')) and the area adjacent to the BFO domain wall (marked by an orange rectangle (denoted as DW)). The sizes of the

energy gap of the YBCO at these locations can be estimated from the differential I - V (dI/dV) curves shown in Fig. 4d, g³⁰. Interestingly, the energy gaps extracted at the three locations show an obvious difference in size: they were 46, 42, and 36 mV for DM1, DW, and DM2, respectively, in the 109° case; and they were 36, 31 and 37 mV for DM1', DW, and DM2', respectively, in the 71° case. It is very important to note that the size of the YBCO energy gap measured adjacent to the DW area is between that of the two domains in the 109° case, while the sizes of the YBCO energy gap measured adjacent to the domain areas in the 71° case have very similar values, and the energy gap at DW is smaller than that for both of them. The variation in the energy gap size suggests different T_c values in these regions^{31,32}. These results support the anisotropic superconductivity found in the transport and can be well explained by the ferroelectric field and strain effects induced by the BFO domain patterns during the YBCO growth.

In the 109° case, the neighboring domains in the BFO layer have opposite polarization components along the out-of-plane direction, which are pointing away from and toward the YBCO layer. Here, we argue that during YBCO growth, the periodical electrostatic boundary condition caused a redistribution of oxygen because BFO has a high Curie temperature (~1100 K), where the ferroelectric domain formed during deposition, leading to a modulation of the YBCO doping levels. As a consequence, two different sizes of energy gaps, 46 and 36 mV, are observed (Fig. 4d). The polarization directions of the BFO domains corresponding to the DM1 and DM2 areas can also be determined to be pointing away from YBCO for DM1 and pointing toward YBCO for DM2 based on the underdoped YBCO layer. As the transition area between the domains, the domain wall exhibits a negligible out-of-plane component for the ferroelectric polarization^{33,34}. Thus, the size of the energy gap measured in the DW region falls between the DM1 and DM2 regions. As the measured spectra were acquired away from the YBCO/BFO interface, the difference between the energy gap sizes of the DM1 and DM2 regions diminishes ~28 nm away from the interface (Fig. 4e). Based on these results, the YBCO regions in the domains with different out-of-plane ferroelectric components correspond to two different T_c s, resulting in anisotropic superconductivity. On the other hand, it is a different story for the 71° case. The neighboring domains in the BFO layer have the same polarization components along the out-of-plane direction, both pointing away from the YBCO layer, which leads to the same doping level in the YBCO regions in the DM1' and DM2' areas. Thus, the strain effect becomes the dominant mechanism and causes the difference in the size of the energy gap between the DM' and the DW regions. A similar relaxation effect can also be observed with a

decreased relaxation length of ~21 nm (Fig. 4h). In this case, the anisotropic superconductivity is very likely to be induced by the domain walls. These results are in good agreement with the results predicted by the phase-field simulations. In both cases, the periodic domain patterns caused periodic modulations of inhomogeneity (nanoscale phase separation of YBCO), which directly led to the anisotropic superconductivity.

Conclusion

In summary, we successfully demonstrated an artificially created anisotropic superconductivity induced by the periodic domain pattern in BFO with YBCO/BFO heterostructures. The anisotropic transport behavior can be observed in both the 109° and 71° cases with the superconducting easy axis always along the domain wall direction in the BFO. Two mechanisms—the strain effect and the ferroelectric field effect during YBCO growth—lead to this anisotropic superconductivity. The formation of nanoscale phase separation based on an intimate contact between the superconductor and multiferroic suggests that new device architectures, such as a self-assembled Josephson junction (superconductor/normal metal/superconductor), can be achieved and ultimately lead to new multifunctional devices.

Acknowledgements

This work is supported by the Ministry of Science and Technology of Republic of China (Grant Nos. MOST 106-2119-M-009-011-MY3, 106-2628-E-009-001-MY2, 106-2218-E-009-021, 106-2923-M-009-003-MY2, 107-2112-M-001-042-MY3, 107-2218-E-007-050). Prof. Y.P. Chiu acknowledges the support from the Ministry of Science and Technology of Republic of China (under contract no. MOST 106-2628-M-002-011-MY3, MOST108-2633-M-001-001). The work at Penn State was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award FG02-07ER46417 (F.X. and L.-Q.C.).

Authors' contributions

Y.-L.H. and Y.-H.C. designed the experiments. Y.-L.H. carried out materials synthesis, characterization, and electrical measurements. J.-C.L. conducted electrical measurements. B.-C.H. and Y.-T.W. conducted XSTM measurements. F.X. carried phase-field simulations. R.H. performed HR-TEM imaging. H.-J.L. performed HR-XRD measurements. Y.-L.H. and Y.-H.C. wrote the paper. All authors made contributions to writing the manuscript. The work was conceived and guided by Y.-H.C. All authors discussed the results and commented on the manuscript.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Supplementary information is available for this paper at <https://doi.org/10.1038/s41427-019-0178-y>.

Received: 16 July 2019 Revised: 5 September 2019 Accepted: 16 September 2019.

Published online: 6 December 2019

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