The abnormal temperature-dependent rectification effect in BiFeO$_3$/YBa$_2$Cu$_3$O$_x$ heterostructures

Qianqian Yang, Huai Zhang, Qian Dai, Ruijuan Nie, Furen Wang
School of Physics, Peking University, Beijing 100871, People’s Republic of China

E-mail: qianyqq@pku.edu.cn

Abstract. We report the fabrication and properties of heterostructures formed by the BiFeO$_3$ (BFO) ferroelectric and YBa$_2$Cu$_3$O$_x$ (YBCO) superconductor. Four measurement configurations on BFO/YBCO heterojunctions are proposed and showed different I-V characteristics. Moreover, one type of BFO/YBCO heterostructures which had the strongest rectification effect at 15K, showed the abnormal rectification effect dependent on temperature. The rectifying effect enhanced with decreasing temperature below the superconducting transition temperature of YBCO. YBCO electrode played an important role in increasing the rectifying parameter because of the high density of states for quasi-particles in YBCO in the superconducting state.

1. Introduction
The discovery of high temperature superconductors (HTS) initiated studies about oxide heterostructures. The perovskite oxide heterostructures have attracted much attention owing to their exciting interface-related physics and excellent performances over polycrystalline materials.

Recently, BiFeO$_3$ (BFO) is widely known as a Pb-free ferroelectric and of large remnant polarization of up to 100 µC/cm$^2$ in its ground state (rhombohedral phase)[1]. It is found to have the diode effect, where BFO behaves like a semiconductor[2]. Ferroelectric bulk materials are traditionally regarded as insulators, but thin films are always treated as semiconductors as becoming thinner[3, 4]. The Bi-deficiency is the main reason for BFO films to become p-type semiconductor[5, 6] while n-type semiconductor BFO arises from the oxygen vacancy[7, 8]. HTS are expected to apply in electronic devices. However, the ordinary semiconductors such as Si and GaAs are difficult to combine with HTS because of the different crystal structures. This activated our interest in studying the BFO/YBCO heterostructures. In this paper, we propose the fabrication of the BFO/YBCO heterostructures. The properties of this heterostructures are of great potential for the development of new electronic devices such as diodes with very high rectifying parameters and transistors based on the Josephson field effect.

2. Experimental details
We have fabricated 180nm-thick BFO films epitaxially grown on 60nm-thick YBCO films on SrTiO$_3$ (STO) substrates by pulsed laser deposition (PLD). YBCO and Au as top electrodes are fabricated by PLD through a metal shadow mask. Silver (Ag) electrodes (~1 mm$^2$) were placed on the surface of YBCO, BFO and Au for measuring the electrical characteristics. The detailed growth parameters are summarized in Table 1. The growth rate for YBCO, BFO and Au are 0.067nm/pulse, 0.021nm/pulse, 0.015nm/pulse, respectively.
Table 1. PLD growth parameters of YBCO, BFO and Au thin films.

| Target-to-substrate distance (mm) | Deposition temperature (°C) | Deposition pressure (Pa) | Annealing time (min) | Annealing temperature (°C) |
|----------------------------------|----------------------------|-------------------------|----------------------|---------------------------|
| YBCO on STO                      | 50                         | 760                     | 26                   | 30                        | 430                      |
| BFO-1                            | 40                         | 650                     | 17                   | 5                         | 430                      |
| BFO-2                            | 40                         | 650                     | 6                    | 5                         | 430                      |
| YBCO on BFO                      | 50                         | 700                     | 26                   | 30                        | 430                      |
| Au                               | 40                         | Room temperature        | 2*10^{-5}            | -                         | -                        |

3. Results and discussion

Figure 1 shows the typical current-voltage (I-V) characteristics for a dc voltage loop ranging from 0→V_{max}→0→-V_{max}→0V of BFO/YBCO heterostructures. Here the Ag/Au and Ag/YBCO interface showed practically ohmic characteristics. Although the I-V curves in figure 1a and figure 1b are asymmetric for the forward and reverse biases, they are in the same order of magnitude and the current at V_{max} is small. The rectification behavior is mostly obvious in Au/BFO-2/YBCO as shown in figure 1d. The oxygen deposition pressure as fabricating BFO-2 is 6 Pa lower than that of BFO-1 with 17 Pa, which will increase the quantity of oxygen vacancies in BFO-2 films. The growth of top YBCO films in YBCO/BFO-2/YBCO (shown in figure 1b) results in the oxygen content of BFO increases and the oxygen vacancies are filled in BFO again, which is discussed in our previously reported paper[9]. The oxygen deficiencies are crucial to the rectification effect because they are the main reason for BFO films to become n-type semiconductors[7], as confirmed from the oxygen pressure experiment and annealing experiment[8].

![Figure 1: I-V characteristics of BFO/YBCO heterostructures with four measurement configurations at 15K.](image)

The rectifying parameter, r_p, is defined by, \( r_p = \frac{I_{+}^{\text{max}}}{I_{-}^{\text{max}}} \), where \( I_{+}^{\text{max}} \) and \( I_{-}^{\text{max}} \) denote the forward and reverse current at \( V_{+}^{\text{max}} \) and \( V_{-}^{\text{max}} \), respectively. Although the rectification behaviour is observed in in-plane BFO-2 films (as shown in figure 1c), the rectification parameter is just 10 much less than that of the Au/BFO-2/YBCO with \( r_p = 1100 \). YBCO electrode played an important role in increasing the rectifying parameter in Au/BFO-2/YBCO.

The conduction mechanism can be inferred by I-V curve dependent on temperature. For Au/BFO-1/YBCO and YBCO/BFO-2/YBCO with no rectification behavior, the \( I_{+}^{\text{max}} \) and \( I_{-}^{\text{max}} \) increased by increasing temperature, because more thermally activated charge carriers are generated in the film and
they participate in the conduction. The thermoionic emission is the most important process determining the current in a Schottky contact as a bias voltage is applied.

The rectifying effect is enhanced substantially with decreasing temperature below $T_c$. This is consistent with the change of the resistance of BFO film with the temperature.

The superconducting transition temperature ($T_c$) of YBCO is 89K. There is no rectification effect at room temperature. $\Gamma_{+\max}$ and $\Gamma_{-\max}$ firstly decrease with decreasing the temperature from room temperature. This is consistent with the change of the resistance of BFO film with the temperature. The rectifying effect is enhanced substantially with decreasing temperature below $T_c$ of YBCO, which is dependent on the $T_c$ of YBCO.

The similar results are observed in the other Au/BFO-2/YBCO heterstructure where $T_c$ of YBCO is about 40K. YBa$_2$Cu$_3$O$_x$ shows a significant $T_c$-x relationship, where the oxygen content x could be determined by the (00l) diffraction peak and controlled by changing the partial oxygen pressure during cooling in the deposition process[10, 11]. Figure 2b shows the I-V curves dependent on temperature for Au/BFO-2/ YBa$_2$Cu$_3$O$_{x=6.43}$ heterostructure. The resistance versus temperature curve of YBCO film is shown in the inset of figure 2b. We can see the rectification effect also diminishes above the $T_c$.

Although the rectification effect is recently observed in BFO capacitors, all the heterojunctions showed the rectification parameter decreased with the temperature below $T_c$ [2, 12]. This excluded the impact of Au and BFO interface and BFO films. Therefore, the BFO and YBCO interface is the main reason for the observed increase of the rectifying parameter.

The corresponding schematic energy band diagram at BFO/YBCO interface is shown in figure 3. For BFO, the band gap $E_g$ is 2.8 eV and the electron affinity is 3.3 eV[13], and then the work function of n-type BFO should be less than 4.7 eV. The work function of YBCO is about 6.1 eV[14]. Because the BFO has higher Fermi level than YBCO, the electrons of BFO would move spontaneously into YBCO at the interface. This results in the upward-bend conduction band CB and valence band VB of BFO. At the BFO/YBCO interface, transport current at temperature below $T_c$ is possibly from the

**Figure 2:** The measurement is carried out in the configuration of figure 1d. (a) $\Gamma_{+\max}$ and $\Gamma_{-\max}$ versus temperature curves of Au/BFO-2/YBCO heterostructures. The inset shows the resistance versus temperature (R-T) curve of YBCO. (b) I-V curves of Au/BFO-2/ YBa$_2$Cu$_3$O$_{x=6.43}$ heterostructure. The insets show the R-T curve (top) and $\Gamma_{+\max}$ versus temperature curve (bottom) separately.

The ferroelectric polarization of BFO is considered to have an effect on the rectification behavior. In the pseudo cubic crystal structure, the spontaneous polarization direction lies close to (111), and the values measured along a-axis and c-axis are projections of (111) onto these orientations and thus equal[1]. Therefore, the ferroelectric polarization should play the same role in the temperature dependent I-V curves of the in-plane BFO and out of plane BFO (Au/BFO-2/YBCO). $\Gamma_{+\max}$ of in-plane BFO-2 films increased with increasing the temperature. The ferroelectric polarization didn’t reduce rectification parameter with increasing the temperature. Nevertheless, in Au/BFO-2/YBCO, the rectification parameter decreased as the temperature increased. Figure 2a shows the temperature dependence of the rectifying I-V curve behavior in the out of plane configuration (inset of figure 1d). The superconducting transition temperature ($T_c$) of YBCO is 89K. There is no rectification effect at room temperature. $\Gamma_{+\max}$ and $\Gamma_{-\max}$ firstly decrease with decreasing the temperature from room temperature. This is consistent with the change of the resistance of BFO film with the temperature. The rectifying effect is enhanced substantially with decreasing temperature below $T_c$ of YBCO, which is dependent on the $T_c$ of YBCO.

For BFO, the band gap $E_g$ is 2.8 eV and the electron affinity is 3.3 eV[13], and then the work function of n-type BFO should be less than 4.7 eV. The work function of YBCO is about 6.1 eV[14]. Because the BFO has higher Fermi level than YBCO, the electrons of BFO would move spontaneously into YBCO at the interface. This results in the upward-bend conduction band CB and valence band VB of BFO. At the BFO/YBCO interface, transport current at temperature below $T_c$ is possibly from the...
correlated charge carriers and quasi-particles. Electrons from the conduction band of the BFO can approach the interface due to the decrease of the band-bending under the forward bias. The electrons and the holes can recombine at the interface. The superconductor opens an energy gap near the Fermi energy below the superconducting transition temperature. Meanwhile, the density of state for quasi-particles of YBCO increases with decreasing temperature below $T_c$ substantially, which directly increased the current.

Figure 3: Schematic energy band diagram of BFO/YBCO heterostructures under forward bias (a) and reverse bias (b) at the superconducting state ($T < T_c$).

4. Conclusions
The BFO/YBCO heterostructures are fabricated by PLD on STO substrates. Four measurement configurations on BFO/YBCO heterostructures are proposed and showed different I-V characteristics. The oxygen vacancies in BFO films are crucial to the observation of the rectification effect in BFO. Especially, the rectification effect in Au/BFO-2/YBCO is enhanced with decreasing the temperature below $T_c$, which is attributed to the BFO/YBCO interface.

5. References
[1] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A. Pyatakov, A. Zvezdin, and D. Viehland, Appl. Phys. Lett. 84, 5261 (2004).
[2] T. Choi, S. Lee, Y. Choi, V. Kiryukhin, and S.-W. Cheong, Science 324, 63 (2009).
[3] Y. Watanabe, Phys. Rev. B 57, R5563 (1998).
[4] M. Dawber, K. Rabe, and J. Scott, Rev. Mod. Phys. 77, 1083 (2005).
[5] Z. Zhang, P. Wu, L. Chen, and J. Wang, Appl. Phys. Lett. 96, 232906 (2010).
[6] T. R. Paudel, S. S. Jaswal, and E. Y. Tsymbal, Bulletin of the American Physical Society 57 (2012).
[7] S. Clark and J. Robertson, Appl. Phys. Lett. 94, 022902 (2009).
[8] C.-H. Yang et al., Nature Mater. 8, 485 (2009).
[9] Q. Yang, X. Ma, Q. Dai, H. Zhang, R. Nie, and F. Wang, Physica C 492, 181 (2013).
[10] J. Jorgensen et al., Phys. Rev. B 36, 3608 (1987).
[11] J. Ye and K. Nakamura, Phys. Rev. B 48, 7554 (1993).
[12] H. Li, K. Jin, S. Yang, J. Wang, M. He, B. Luo, J. Wang, C. Chen, and T. Wu, Journal of Applied Physics 112, 083506 (2012).
[13] S. Clark and J. Robertson, Appl. Phys. Lett. 90, 132903 (2007).
[14] T. Hirano, M. Ueda, K.-i. Matsui, T. Fujii, K. Sakuta, and T. Kobayashi, Jpn. J. Appl. Phys. 31, 1345 (1992).