Dependence of BiFeO$_3$ thickness on exchange bias in BiFeO$_3$/Co$_2$FeAl multiferroic structures

X Zhang, D L Zhang, Y H Wang, J Miao*, X G Xu, Y Jiang*
State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, 100083, China

*Email: j.miao@ustb.edu.cn, yjiang@ustb.edu.cn

Abstract. We have grown BiFeO$_3$ (BFO) thin films with different thickness on Si/SiO$_2$/Ti/Pt(111) substrates by pulsed laser deposition. Half-metallic Co$_2$FeAl (CFA) films with a thickness of 5 nm were then grown on the BFO films by magnetron sputtering. Through the magnetic hysteresis loops of the BFO/CFA heterostructure, we observe a direct correlation between the thickness of the BFO film and exchange bias (EB) field. The EB field exhibits fluctuation behavior with a cyclical BFO thickness of 60 nm, which is close to the spiral modulation wavelength (62 nm) of BFO. It indicates the influence of spiral modulation on the EB in the BFO/CFA multiferroic structure.

1. Introduction
Multiferroics combining ferromagnetic and ferroelectric are a time-honored subject of study and have led to some of the most important technological advances to date [1]. One of the most widely studied multiferroic materials is BiFeO$_3$ (BFO), which possesses a rhombohedrally distorted perovskite structure at room temperature [2]. BFO has ferroelectric Curie and magnetic Néel temperatures at ~1100K and 647K, respectively [3-6], which indicates their potential applications in date storage, spintronic sensors, and so on [7, 8]. BFO has an antiferromagnetic spin ordering, but it also displays a weak ferromagnetic moment arising from a canted spin structure [9, 10]. Followed Wang et al., who have grown epitaxial BFO films on SrTiO$_3$(100) substrates [11], a great many studies have been done to grow high quality, fully epitaxial, and single phase thin films of BFO on various substrates [12-15].

Recently, electric-field control of magnetic exchange, and even spin polarization [16], has attracted much attention. Multiferroic materials, such as YMnO$_3$ and BFO, have been grown as the bottom antiferromagnetic layer in spin-valves [17], or the barrier layer in magnetic tunnel junctions [18]. In the devices, the magnetoelectric coupling was designed to tune the effective direction of the exchange bias (EB) by an electric field. Dynamic switching of the EB field with an applied electric field has been reported by Laukhin et al. focusing on YMnO$_3$ at very low temperatures [19]. Martin et al. [20] studied the asymmetric spin valves with BFO as the antiferromagnetic layer. However, till now there is few study on the influence of the BFO thickness on the EB.

In this letter, we study the effect of BFO thickness on the EB field in a BFO/Co$_2$FeAl (CFA) heterostructure and find that the EB field exhibits a fluctuation behavior with a cyclical BFO thickness of 60 nm, which is close to the spiral modulation wavelength (62 nm) of BFO. It indicates the influence of spiral modulation on the EB in the BFO/CFA multiferroic structure.

Published under licence by IOP Publishing Ltd
2. Experiment
The BFO films with different thickness were deposited on Si/SiO₂/Ti/Pt(111) substrates by pulsed laser deposition. The target was prepared by mixing Bi₂O₃ and Fe₂O₃ in a 1.2:1 stoichiometric ratio then sintering at 820 °C in air. The CFA films with a thickness of 5 nm were grown on the BFO films by magnetron sputtering. A 700 Oe local magnetic field was applied in order to induce an easy axis during the sputtering. 4 nm Ta films were then grown on the top of the heterostructure to protect the CFA films from oxidation. The structural characterization was performed using a M21XVHF22 X-ray diffractometer with Cu/Kα radiation. The surface morphology and cross section images were obtained using Scanning Electron Microscopy (SEM). Magnetic hysteresis loops were measured using an Alternating Gradient Magnetometer (AGM).

3. Results and discussion
As shown in figure 1(a), the X-ray diffraction (XRD) pattern of the BFO/Pt(111) structure demonstrates a high quality and single phase BFO film. An enhancement in (111) orientation is clearly observed due to the bottom electrode Pt(111) layer. According to the formula \( \alpha_{(111)} = I_{(111)}/[I_{(100)}+I_{(110)}+I_{(111)}] \), the calculated degree of (111) orientation is above 50%. Indeed, several different orientations have been reported for BFO thin films deposited by different techniques and on different buffers and substrates. It is proved that the (111)-oriented BFO thin films generally exhibit better ferroelectric behavior than those of other orientations [21-25]. Figure 1 (b) and (c) are the surface morphology and cross section of the BFO film. The BFO film shows a dense surface with grains which could be classified into two kinds of diameters of 30 nm and 100 nm. It can be seen from figure 1(c) that the grains were grown both perpendicular (left arrow) and parallel (right arrow) to the substrate surface. These results indicate the existence of differently oriented grains on the film surface. Lahmar et al. [26] also have got similar results. The parallel grains were considered to be formed as the result of local interaction between the film and the Pt-bottom electrode.

![Figure 1](image_url)

**Figure 1.** Structural analysis of the BFO films deposited on a Si/SiO₂/Ti/Pt (111) substrate. (a) XRD pattern; (b) SEM of the surface morphology; (c) SEM of the cross section.

We have fabricated the BFO/CAF heterostructures of Si/SiO₂/Ti/Pt(111)/BFO (t nm)/CFA (5 nm). Here t=100, 120, 140, 160, 180 and 200 nm, respectively. Figure 2 gives the magnetic hysteresis loops for these heterostructures measured at room temperature. The hysteresis loops are enlarged and shifted...
along the field axis compared to that of the CFA monolayer, which is shown in figure 3 (a),
demonstrating the presence of EB at the CFA/BFO interfaces. In figure 3 (b), when H is applied
perpendicular to the films, the M(H) shows a typical hard axis behavior.

Figure 2. Room temperature M-H loops of BFO/CFA structures
with different BFO thickness of (a) 100 nm, (b) 120 nm, (c) 140 nm,
(d) 160 nm, (e) 180 nm, and (f) 200 nm, respectively.

Figure 3. Room temperature M-H loops of (a) CFA monolayer and (b)
along perpendicular direction of BFO/CFA films.
Figure 4. The $H_{EB}$ vs. the BFO thickness of the BFO/CFA structures.

Figure 4 shows the correlation between the EB field ($H_{EB}$) and the BFO thickness $t$. The values of $H_{EB}$ are 6.8, 15.3, 9.4, 2, 14.6, and 10.7 Oe, for $t = 100, 120, 140, 160, 180$ and 200 nm, respectively. The $H_{EB}$ exhibits a fluctuation behavior with a cyclical thickness of 60 nm, which is close to the spiral modulation wavelength (62 nm) of BFO. The results are quite different from the work of Béa [18] and Nogués [27]. There are two reasons may explain the fluctuation of $H_{EB}$. Firstly, the different orientation of BFO, as shown in figure 1(c), could distract the interface effect. Nogués has also reported that the orientation of AFM layers are no longer stable above certain thickness, and this microstructural change leads to a decrease in $H_{EB}$. The lower value of $H_{EB}$ may also due to this reason. Secondly, the effect of the BFO spiral modulation structure has been unveiled when $H_{EB}$ has leveled off, which is concealed when $H_{EB}$ is changing abruptly. In other words, the BFO spiral modulation structure could affect $H_{EB}$, in a limited range.

4. Conclusion

In summary, we have grown the BFO/CFA heterostructures on Si/SiO$_2$/Ti/Pt(111) substrates and observed distinct EB behavior at room temperature. The $H_{EB}$ exhibits a fluctuation behavior with a periodic thickness of 60 nm, which may be caused by various orientation and the spiral modulation structure of the BFO films. The next work would be growing single oriented BFO film to demonstrate the correlation between the $H_{EB}$ and the BFO thickness.

ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China (Grant Nos. 50701005, 50831002, 50971025), the National Basic Research Program of China (Grant No. 2007CB936202) and the Key Grant Project of Chinese Ministry of Education (No. 309006).

References
[1] Prellier W, Singh M P and Mulugavel P 2005 J. Phys.: Condens. Matter 17 R804
[2] Schmidt R, Erenstein W, Winiecki T, Morrison F D and Midgley P 2007 Phys. Rev. B 75 245111
[3] Yun K Y, Ricinschi D, Kanashima T and Okuyama M 2006 Appl. Phys. Lett. 89 192902
[4] Kim D H, Lee H N, Biegalski M D and Christen H M 2008 Appl. Phys. Lett. 92 012911
[5] Ranjith R, Kundys B and Prellier W 2007 Appl. Phys. Lett. 91 222904
[6] Nakamura Y, Nakashima S, Ricinschi D and Okuyama M 2008 Functional Materials Letters 1 19
[7] Yuan G L, Or Siu Wing and Chan H L W 2007 J. Appl. Phys. 101 024106
[8] Wang H, Zheng Y, Cai M Q, Huang H T and Chan H L W 2009 Solid State Commun. 149 P641
[9] Sosnovska I, Peterlin-Neumaier T and Steichele E 1982 J. Phys. C 15 4835
[10] Blaauw C and van der Woude F 1973 J. Phys. C: Solid State Phys. 6 1422
[11] Wang J, Neaton J B, Zheng H, Nagarajan V, Ogale S B, Liu B, Viehland D, Vaithyanathan V, Schlom D G, Waghamre U V, Spaldin N A, Rabe K M, Wuttig M and Ramesh R 2003 Science 299 1719
[12] Béa H, Bibes M, Zhu X -H, Fusil S, Bouzehouane K, Petit S, Kreisel J and Barthélémy A 2008 Appl. Phys. Lett. 93 072901
[13] Chen Y C, Lin Q R and Chu Y H 2009 Appl. Phys. Lett. 94 122908
[14] Cheng Z X, Wang X L, Kimura H, Ozawa K and Dou S X 2008 Appl. Phys. Lett. 92 092902
[15] Tian W, Vaithyanathan V and Schlom D G 2007 Appl. Phys. Lett. 90 172908
[16] Garcia V, Bibes M, Bocher L, Valencia S, Kronast F, Crassous A, Moya X, Enouz-Vedrenne S, Gloter A, Imhoff D, Deranlot C, Mathur N D, Fusil S, Bouzehouane K and Barthélémy A 2010 Science 327 1106
[17] Dho J, Qi X D, Kim H, Macmanus-Driscoll J L and Blamire M G 2006 Adv. Mater. 18 1445
[18] Béa H, Fusil S, Bibes M, Cherifi S, Locatelli A, Warot-Fonrose B, Herranz G, Deranlot C, Jacquet E, Bouzehouane K and Barthélémy A 2006 Appl. Phys. Lett. 89 242114
[19] Laukhin V, Skumryev V, MartíX, Hrabovsky D, Sánchez F, Garcia-Cuenca M V, Ferrater C, Varela M, Lüders U, Bobo J F and Fontcuberta J 2006 Phys. Rev. Lett. 97 227201
[20] Martin L W, Chu Y H, Zhan Q and Ramesh R 2007 Appl. Phys. Lett. 91 172513
[21] Singh S K, Kim Y K, Funakubo H and Ishiwara H 2006 Appl. Phys. Lett. 88 162904
[22] Bai F M, Wang J, Wuttig M, Li J F, Wang N, Pyatakova A P, Zvezdin A K, Cross L E and Viehland D 2005 Appl. Phys. Lett. 86 032511
[23] Li J F, Wang J L, Wuttig M, Ramesh R, Wang N, Ruette B, Pyatakova A P, Zvezdin A K and Viehland D 2004 Appl. Phys. Lett. 84 5261
[24] Wu J G and Wang J 2009 J. Appl. Phys. 106 054115
[25] Wu J G and Wang J 2009 J. Appl. Phys. 106 104111
[26] Lahmar A, Habouti S, Solterbeck C H, Dietze M and Es-Souni M 2010 J. Appl. Phys. 107 024104
[27] Nogués J and Scholler I K 1999 J. Magn. Magn. Mater. 192 203