Significantly improved multiferrioc properties of $BiFeO_3/Pb(Zr_{0.52}Ti_{0.48})O_3$ bilayer films by magnetic field annealing

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1. Introduction

Multiferroic materials have attracted extensive attention due to the coexistence of ferromagnetic and ferroelectric properties in a certain temperature range. Such materials are promising for applications in specific devices including spintronics, multiple-state memories, and electric-field-controlled ferromagnetic resonance devices. Unfortunately, materials with simultaneous ferroelectric and magnetic properties are rare since the driving mechanism for ferroelectricity and magnetic ordering are in general incompatible. As a special case, $BiFeO_3$ (BFO) is well known for its unique ferroelectric mechanism, driven by the stereochemically active Bi $6S^2$ lone pair, which is compatible with the antiferromagnetic order of Fe ions. Importantly, BFO exhibits room-temperature (RT) multiferroic properties with the high ferroelectric Curie temperature (T_C = 1103 K) and antiferromagnetic Néel temperature (T_N = 643 K), which are crucial in practical application.

In spite of the RT multiferroicity in BFO, severe leakage behavior, large coercive field, and poor spontaneous magnetization may hinder its future application. To overcome these drawbacks, many methods have been attempted, including fabricating composites with other ferroelectric materials, doping with rare-earth or transition elements, and preparing single-crystal, epitaxial or polycrystalline BFO films. One of the most effective ways to decrease the leakage current density and enhance ferrolectricity is to utilize bilayer or multilayer BFO structures with other perovskite ferroelectrics that exhibit superior insulating property. As a familiar ferroelectric material, $Pb(Zr_x,Ti_{1-x})O_3$ (PZT) was extensively studied due to its well-known ferroelectric property and low conductivity. Therefore, we expect that the BFO/PZT bilayer structure can potentially provide a higher remanent polarization and still retain the magnetic properties of BFO, i.e., exhibiting multiferroic properties. High magnetic field treatment can affect the properties of materials. Studies on magnetic-field-annealing-induced changes in microstructures and physical properties of various alloys, ceramics, and films have been widely reported. For example, Ma et al. reported high-magnetic-field improvements on microstructure and superconducting properties of $YBa_2Cu_3O_7$ films.[1] However, to our best knowledge, there is no report on BFO-based films treated by high-magnetic-field annealing. In this paper, we report the fabrication and high-magnetic-field annealing of *(0l0)*-oriented BFO films deposited on $PbZr_{0.52}Ti_{0.48}O_3$ (PZT)-buffered $Pt/Ti/SiO_2/Si$ substrates, and the effect of high-magnetic-field annealing on microstructure, magnetic, and ferroelectric properties.

2. Experimental

Both the BFO and PZT layers were deposited by a sol-gel process. The BFO precursor solution was prepared from the starting materials of $Bi(NO_3)_3\bullet 5H_2O$ and $Fe(NO_3)_3\bullet 9H_2O$, which were mixed and dissolved in 2-methoxyethanol with a molar ratio of Bi/Fe = 1/1. An appropriate amount of $C_6H_8O_7$ (metal ions/$C_6H_8O_7$ molar ratio =1/1) was also dissolved in the above solution to complex the metal ions with the citrate ions. The concentration of the solution was adjusted to 0.3 M by adding 2-methoxyethanol as necessary. A commercially available Pt/Ti/SiO_2/Si wafer (Institute of Microelectronics, Peking University) was used as substrate. A bottom PZT film covered by BFO layers was deposited on the substrate by spin-coating and subsequent heat treatments. The spin coating was carried out at 3000 rpm for 40 s. The sample was heat-treated by pyrolysis at 400 ^{o}C for 5 min, followed by crystallization at 650 ^{o}C for 5 min after each coating. Upon coating the last layer of BFO, the sample was pyrolyzed at 400^{o}C for 5 min, then it was put in a high-magnetic-field furnace for annealing. The magnetic field annealing was conducted as follows. First, a magnetic field of 0, 5, or 10 T was applied after the films were put in the furnace; next, the furnace was heated to 650 ℃ and held for 5 min; finally, the external magnetic field was removed after the furnace was cooled to RT.

3. Results and discussions

Fig. 1 shows the XRD patterns (recorded with an XRD machine with Cu Kα radiation) of BFO/PZT bilayer films annealed at 0, 5, and 10 T magnetic fields. All the films are well crystallized and exhibit double diffraction peaks corresponding to the top BFO phase and the bottom PZT phase, as illustrated by the symbols of "⊕" and "◆" in Fig. 1, respectively. The XRD pattern obtained for BFO can be successfully indexed according to a pseudocubic unit cell. No trace of impurity phase can be detected for the films annealed in 0 and 5 T fields, whereas the films annealed in the 10 T field showed traceable amounts of $Bi_2Fe_4O_9$ and $Bi_{24}Fe_2O_{29}$ as low-level impurity phases (marked with *). In all the cases, XRD indicates a predominant (*0l0*) preferred orientation in BFO films. The textured BFO films prepared by the sol-gel method have also been observed by other researchers.

To evaluate the degree of texture for films annealed in various magnetic fields, rocking curves (recorded using an XRD machine with Fe Kα radiation) were measured for the BFO (010) diffraction peak, as shown in the inset of Fig. 1. Full widths at half maximum (FWHM) of 6.08, 5.78, and 4.10 ° were measured for samples annealed in 0, 5, and 10 T fields, respectively. The FWHM steadily decreases with increasing magnetic field, indicating that the texture and crystallinity are improved by applying an increased external magnetic field. This phenomenon is consistent with other reports on texture degree improvement in $YBa_2Cu_3O_7$ films induced by high magnetic fields. Moreover, the decrease in FWHM of the rocking curve proves the substantial improvement in the quality of BFO films by the high-magnetic-field annealing.

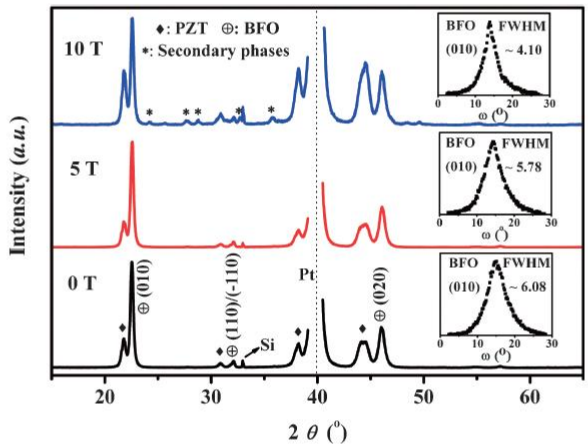

Figure 1 X-ray diffraction patterns of the BFO/PZT bilayer thin films annealed under different external magnetic fields. The inset along with each XRD pattern is the rocking curves of BFO (010) diffraction peak recorded for the corresponding films with Fe *K*α radiation.

Fig. 2 shows the typical micrographs of the surface of films annealed in different magnetic fields. Dramatic differences in density and grain size were observed. As shown in Fig. 2(a), the films fabricated without a magnetic field are composed of large grains of about 100 nm; correspondingly, a number of large pinholes are observed on the surface. Fig. 2(b) shows a more dense surface morphology of the films prepared at 5 T with a good distribution in the grain size of about 50 nm. As a result, the number of pinholes and their sizes are all obviously decreased. As for the films annealed at a magnetic field of 10 T, the surface morphology shown in Fig. 2(c) suggests that the film encompasses finer grains, which were evaluated to be about 20 nm from the high magnified images (not shown here). No small pinholes are observable, even though some anomalously distributed large grains can be seen on the surface. These results suggest that the grain size is evidently reduced and the film density is obviously improved by the magnetic field annealing, similar to those in other films prepared by high-magnetic-field annealing. To confirm the thickness of the BFO/PZT bilayer films, the cross-sectional SEM image of the 0 T films is shown in Fig. 2(d). It demonstrates that the films have a homogeneous thickness, and the total thickness of the bilayer film is about 542 nm.

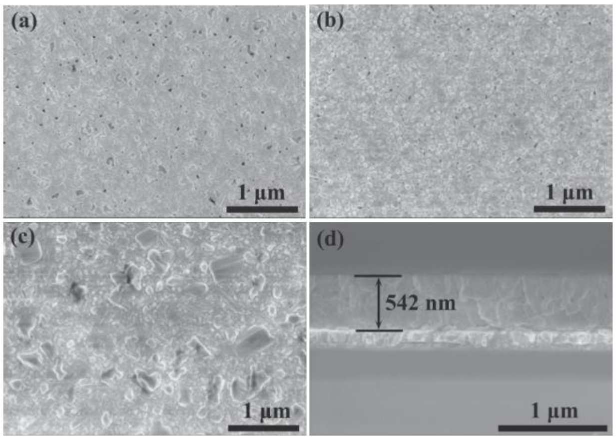

Figure 2 SEM images of the BFO/PZT bilayer thin films. (a) 0 T, (b) 5 T, and (c) 10 T; (d) Cross-sectional SEM image of the BFO/PZT bilayer prepared at 0 T.

Fig. 3 plots the magnetization hysteresis (*M-H*) loops measured with the magnetic field parallel to the film surface. These magnetization values are obtained after subtracting the diamagnetic signal from the Pt/Ti/SiO_2/Si substrate. As shown in Fig. 3, all the films exhibit distinct weak ferromagnetic hysteresis loops at RT. The saturation magnetizations (M_s) of the films annealed at 0, 5, and 10 T magnetic fields are 0.65, 2.19, and 4.18 emu/cm^3, respectively. It is worth noting that the magnetic properties are markedly improved by the applied external magnetic field during the annealing process. The maximum M_s obtained in the films annealed at 10 T is about 6 times as large as that of the films fabricated without imposing a magnetic field. The significant enhancement in magnetization may be attributed to the fact that magnetic annealing results in decreased grain size within nanoscale. The decreases in grain size might give rise to uncompensated spins and spin canting resulting from surface strain, so that the cycloid spin structure in BFO may be suppressed and the latent magnetization is released. In addition, the improvement in texture degree by magnetic field annealing may also contribute to the enhanced magnetization.

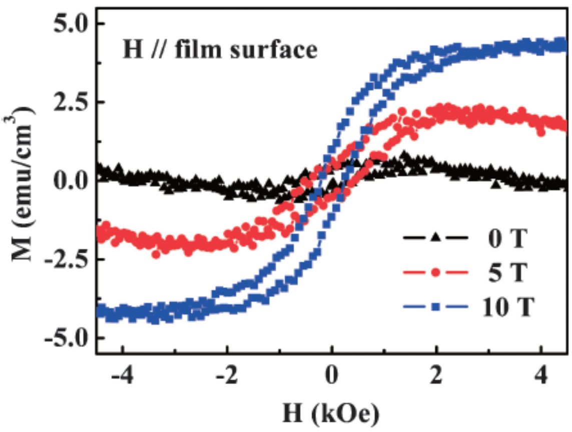

Figure 3 RT magnetization hysteresis (*M-H*) loops of all the BFO/PZT bilayer thin films fabricated at 0, 5 and 10 T, respectively.

Figure 4 shows the electric hysteresis (*P-E*) loops of the 0, 5, and 10 T films measured with a field sweeping frequency of 1 kHz. The films prepared without external magnetic fields exhibit a *P-E* loop with low polarization. Under the maximum applied electric field of 470 kV/cm, no electrical breakdown occurred, but its double remanent polarization ($2P_r$) value was small, ≈13 µC/cm^2. In contrast, both 5 and 10 T films showed well-saturated hysteresis characteristics with high $2P_r$ values of 77 and 55 µC/cm^2, respectively. It is found that through magnetic field annealing, the measured polarization values are enhanced by more than 3 times in the BFO/PZT bilayer films. $2P_r$ values observed in the 5 and 10 T films are much higher than those of the BFO/PZT multilayer films prepared by the chemical solution method. Moreover, the results are comparable to other

BFO-based multilayer or bilayer films in which a $2P_r$ value of ≈80 μC/cm^2 is reported. As a good insulating barrier, the presence of the ferroelectric PZT buffer layer will surely improve the ferroelectric behavior of the bilayer films. Nonetheless, considering that the fabrication techniques are similar for all the films except the different applied magnetic fields during the annealing process, it is certain that the improved ferroelectric properties of the BFO/PZT films are totally due to the magnetic field annealing process. All the effects arising from the magnetic annealing are illustrated by the rocking curves and SEM surface morphologies.

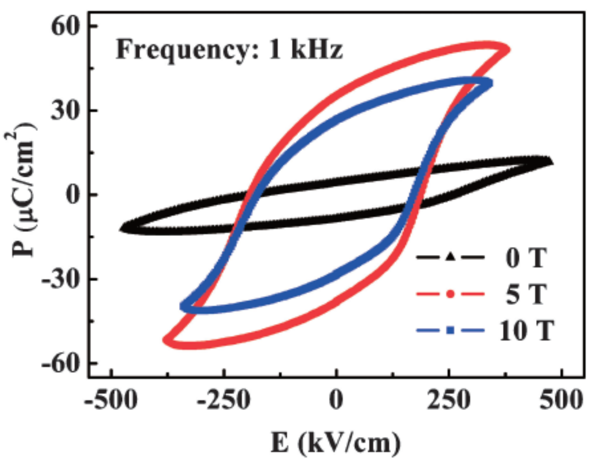

Figure 4 RT ferroelectric hysteresis (*P*-*E*) loops of all the BFO/PZT bilayer thin films fabricated at 0, 5 and 10 T, respectively.

Hence, the enhanced ferroelectric polarization can be understood from two different aspects, the enhanced texture and improved film surface quality by magnetic field annealing. It is well known that the epitaxial constraint with various orientations will induce dramatic changes in ferroelectric polarization. Therefore, several attempts by controlling the film orientation have been done to reduce the leakage current and enhance the ferroelectric polarization of BFO films. Our data demonstrated that the enhanced texture resulting from the high-magnetic-field annealing is directly correlated with the improved polarization. On the other hand, the SEM images in Fig. 2 reveal that the film density is enhanced by magnetic field annealing.

It has been reported that applying an external magnetic field during the film annealing can influence the nucleation rate of both ferromagnetic FePt and paramagnetic $YBa_2Cu_3O_7$ phase. In addition, it is demonstrated that the critical nucleus volume of the paramagnetic material is inversely proportional to the square of the external magnetic field (H^2). During the magnetic annealing process, BFO is paramagnetic because the annealing temperature of 650 ^{o}C is higher than its Néel point. Thus, we deduced that applying an external magnetic field during the film annealing at about 650 ℃ might influence the nucleation of BFO by decreasing the critical nucleus volume and increasing the nucleation number. As a result, the grain size would effectively decrease and the areal crystallinity would gradually increase with increasing magnetic field during the annealing process. These changes are in favor of improving the film quality, and thus lead to enhanced performances in magnetic-field-annealed BFO thin films.

4. Conclusion

We report a novel method of synthesizing multiferroic $BiFeO_3/Pb(Zr_{0.52}Ti_{0.48})O_3$ (BFO/PZT) bilayer films based on the use of a high magnetic field [2]. Simultaneously enhanced magnetization and electric polarization were observed at room temperature in the films annealed under an external magnetic field. Compared with the control samples annealed at zero field, the saturated magnetization and double remanent polarization were increased by a factor of 6 at room temperature. These results demonstrate that the strong magnetic annealing method is an alternative way to fabricate high-performance $BiFeO_3$ films.

References

[1] Y. W. Ma, K. Watanabe, S. Awaji, and M. Motokawa, Appl. Phys. Lett. 77 (2000) 3633.

[2] Shuxia Zhang, Zhongxia Duan, Xianping Zhang, Dongliang Wang, Zhaoshun Gao, Li Han, Yanwei Ma, S. Awaji, K. Watanabe, Appl. Phys. Express 5 (2012) 041802.