Polarization Switching Behaviors in Multiferroic BiFeO$_3$(001) Thin Film Capacitors under In-plane Magnetic Field

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(Received 9 July 2009)

We investigated the polarization switching behaviors of epitaxial BiFeO$_3$(001) films under magnetic fields. The polarization switching behaviors in the BiFeO$_3$(001) films were well described by using the Kolmogorov-Avrami-Ishibashi model and by assuming Lorentzian distribution functions of the logarithm of the characteristic switching time. These results were attributed to domain wall pinning effects, probably due to interaction between domain walls and defects or antiferromagnetic domains in the films. Finally, from the magnetic-field dependence of the polarization switching behaviors, we found that the ferroelectric and the antiferromagnetic domains in the BiFeO$_3$(001) films were weakly coupled, leading to a shift in the polarization switching behaviors.

PACS numbers: 77.80.Fm, 77.80.Dj, 77.55.+f
Keywords: BiFeO$_3$, Multiferroic, Magnetoelectric, Ferroelectric, Polarization switching
DOI: 10.3938/jkps.56.503

I. INTRODUCTION

Multiferroic materials, in which at least two ferroic orderings, such as ferroelectricity and ferromagnetism, coexist and interplay, are of great interest for application of nano-scale multi-functional devices [1–5]. Especially, BiFeO$_3$ (BFO) with a ferroelectric Curie temperature ($T_C$) of $\sim$1,100 K and an antiferromagnetic Neel temperature ($T_N$) of $\sim$640 K is a remarkable multiferroic material due to its ferroelectric polarization being comparable to that of Pb(Zr,Ti)O$_3$ (PZT) [6–10]. So far, there have been many efforts to probe and enhance magnetoelectric coupling in BFO films [11,12]. Recently, Zhao et al. [11] showed that antiferromagnetic domains in BFO films could be manipulated by using ferroelectric polarization switching with a piezoelectric force microscope. Oppositely, the ferroelectric properties could be also controlled by using a magnetic field, and the multi-functionality of BFO films will have much larger potential. Therefore, it is important to investigate whether ferroelectric domain dynamics can be affected by an external magnetic field or not.

In BFO(001) films, four structural variants formed by the rhombohedral distortion of oxygen octahedra lead to eight possible polarizations [13,14]. Each polarization with a different structural variant lies along the [111] direction. On the other hand, since magnetism in BFO(001) films is coupled with ferroelectricity, spins in the 3d orbital of the Fe cation are antiferromagnetically aligned along the [110] direction on the [111] planes [11,12,15]. For example, [111] and [111]-polarized ferroelectric domains have spins aligned along the [110] and the [110] directions, respectively. It is probable that
the realignment of spins by a magnetic field alters the ferroelectric domain configuration inside the BFO(001) films.

Polarization switching behavior is useful for detecting changes in the domain configuration in ferroelectric films. Recently, there have been some reports on polarization switching behavior in epitaxial and polycrystalline PZT films [16–20]. In epitaxial PZT films, the polarization switching behavior could be explained by using the Kolmogorov-Avrami-Ishibashi (KAI) model [16,19]. However, in polycrystalline PZT films, the polarization switching behavior could be well described by using a Lorentzian distribution of the logarithm of the characteristic switching times, not by using the simple KAI model [17,18]. The distribution of the switching times was ascribed to the variation in the local field caused by the random defect dipoles in the polycrystalline PZT films, which is expected to change the ferroelectric switching behaviors if ferroelectric domains in BFO(001) films are affected by the different antiferromagnetic domains. In this work, we studied the changes in the ferroelectric polarization switching behaviors in multiferroic BFO(001) films under in-plane magnetic fields.

II. EXPERIMENTS

Epitaxial BFO(001) thin films of 240 nm in thickness were grown on SrRuO$_3$/SrTiO$_3$(001) substrates through pulsed laser deposition with a KrF excimer laser ($\lambda$=248 nm) [10]. To characterize the crystal structures of the BFO/SrRuO$_3$ heterostructures on SrTiO$_3$ substrates, we carried out $\theta$-2$\theta$ scans with a Bruker AXS D8 advanced high resolution x-ray diffractometer (HRXRD). To confirm the ferroelectricity of BFO(001) films, we measured the polarization-electric field ($P$-$E$) hysteresis loop at 77 K at 2 kHz with a TF analyzer 2000.

The ferroelectric polarization switching of the BFO films was investigated by using the voltage pulse sets shown in Fig. 1 to measure the non-switching polarization ($P_{ns}$) and the switching polarization ($P_{sw}$). First, to measure $P_{ns}$, the poling pulse A1 and the read pulse A2 with the same pulse width of 15 $\mu$s and amplitude of 15 V were sequentially applied to the BFO(001) films. After a few seconds, the write pulse B with a pulse width of $t_w$ and an amplitude of $V_{ext}$ was applied to reverse the pre-poled ferroelectric domain partially. Finally, $P_{sw}$ was measured by applying the read pulse A3. From the difference between the measured $P_{sw}$ and $P_{ns}$, the switched polarization ($\Delta P$) could be obtained as a function of $t_w$.

We observed the changes in the polarization switching behaviors along the direction of the magnetic spins for magnetic fields from 1.0 T to $-1.0$ T, by using a low-temperature probe-station with a superconducting magnet. The superconducting magnet was operated at $\sim$4 K, and the temperature was stably maintained without quenching. Then, the superconducting magnet was heated up to 77 K to carry out the polarization switching experiment in the BFO(001) films.

III. RESULTS AND DISCUSSION

Figure 2(a) shows HRXRD $\theta$-2$\theta$ scan of the BFO/SrRuO$_3$ heterostructure on the SrTiO$_3$(001) substrate. Because peaks with different orientations were not observed, the BFO layer and the SrRuO$_3$ bottom
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Fig. 3. (Color online) (a) Normalized time ($t$)-dependent switched polarization $\Delta P(t)$ under various external voltages ($V_{ext}$) at (a) 77 and (b) 10 K. (c) $V_{ext}$-dependent $w$ at 77 and 10 K.

electrode were found to have been grown epitaxially on the SrTiO$_3$(001) substrate. From the inset of Fig. 2(a), it is clear that BFO(002) and SrRuO$_3$(002) peaks with different $d$-spacings exist around the SrTiO$_3$(002) peak. Also, we found that the BFO(001) films had square-like $P$-$E$ hysteresis loops without imprints, as shown in Fig. 2(b). The $P$-$E$ hysteresis loop measurements were carried out at 77 K to reduce the leakage current effects in the BFO(001) films [10]. A high remnant polarization of $65 \sim 70 \mu C/cm^2$ and a coercive field of $\sim 250$ kV/cm were observed.

The polarization switching behaviors of epitaxial BFO(001) films were obtained at 77 and 10 K as shown in Figs. 3(a) and 3(b), respectively. The solid dots correspond to the normalized $\Delta P(t)$ measured under various $V_{ext}$ while varying $t_w$ from 200 ns to 1 s. Interestingly, we found that the polarization switching behaviors in the BFO(001) films were well described by using the modified KAI model, as represented by the solid lines: $\Delta P(t) = 1 - \int F(\log t_0) \exp[-(t/t_0)^n]d(\log t_0)$, where $n$ is the domain dimensionality and is equal to 2 and $F(\log t_0)$ is the Lorentzian distribution function of the characteristic switching time $t_0$ proposed by Jo et al. [17]. They claimed that in polycrystalline PZT films with random defect dipoles, the local field variation due to random quenched dipole defects could induce such a Lorentzian distribution of the characteristic switching time. Thus, the good agreement between the solid dots and the lines suggests that ferroelectric domains in BFO(001) films have such randomly quenched dipole defects, which affect domain switching. In BFO(001) films, four structural variants exist, resulting in eight polarization directions [13,14] and domains. Some of the domain walls may be pinned by defects or magnetic domains in the BFO films, giving rise to a randomness of the BFO films, and that randomness may result in switching behaviors similar to those in polycrystalline PZT films.

In general, the randomness in ferroelectric films is affected by the ferroelectric domain structure and the defects inside the film. In the polarization switching behavior, the randomness is expressed as $w$, the half width at the half maximum of the Lorentzian distribution function [17,18]. In other words, $w$ is closely related to the...
domain configuration and to the defects in the ferroelectric films. Figure 3(c) shows the $V_{ext}$ dependence of $w$ at 77 and 10 K, and $w$ values are nearly independent of $V_{ext}$, within the errors of the fitting parameters. However, at 77 K, the values of $w$ are much smaller than those at 10 K. This indicates that thermal activation of pinned domain walls contributes to decreasing the randomness of the system, giving smaller $w$ values. Thus, the polarization switching behaviors in BFO(001) films can be thermally controlled by depinning pinned domain walls. Note that there is no structural transition between 77 and 10 K because the Curie temperature of BFO is above room temperature.

Under an external magnetic field, possible changes in the magnetic domains in BFO(001) films can also induce variation in the polarization switching behaviors. We observed a magnetic-field dependence of the polarization switching behaviors in BFO(001) films at 77 K. First, we carried out the polarization switching experiment before the magnetic field was applied. Next, we observed the polarization switching behaviors under several in-plane magnetic fields, as shown in Fig. 4(a). Note that, since spins are antiferromagnetically ordered at zero magnetic field after the field was applied, the configuration of the magnetic domains has to be different from those before the field was applied. As a result, we found that the polarization switching behaviors were slightly shifted compared to that before the magnetic field was applied, as shown in Fig. 4(b). This change in the polarization switching behaviors by applying in-plane magnetic fields indicates that there is a weak magnetoelectric coupling between the ferroelectric and the antiferromagnetic domains in BFO(001) films.

To show clearly the variation of the polarization switching behaviors due to the in-plane magnetic field, we plotted the normalized $\Delta P(t)$ at the same switching time as a function of the magnetic field. Figure 4(c) shows that there are distinct gaps between the normalized $\Delta P(t)$ measured before and after the in-plane magnetic fields were applied. All of the normalized $\Delta P(t)$ under in-plane magnetic fields are smaller than that before the field was applied. Since the ferroelectric polarizations in BFO(001) films are orthogonal and coupled with antiferromagnetic spins, we can restrict the particular polarization switching through a spin realignment by using an in-plane magnetic field. Therefore, some ferroelectric domains constrained by using an in-plane magnetic field may be less switched than free ferroelectric domains, leading to a decrease in the total polarization.

IV. CONCLUSIONS

We investigated the polarization switching behavior in 240-nm-thick BFO(001) films epitaxially prepared by using pulsed laser deposition. The polarization switching behaviors in BFO(001) films was well described through a Lorentzian distribution of the logarithm of the switching time. The good agreement indicates that the broadening of the Lorentzian distribution may be mainly induced by the eight polarization variants in BFO(001) films. In addition, we observed that the polarization switching behaviors were thermally controlled, probably due to the depinning of pinned domain walls. Finally, from the magnetic-field dependence of the polarization switching behaviors, we suggest that the ferroelectric and the antiferromagnetic domains in BFO(001) films are weakly coupled, leading to a shift in the polarization switching behaviors. The realignment of spins induced by an in-plane magnetic field may restrict the polarization switching in some ferroelectric domains.

ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. 2009-0080567). T.H.K. acknowledges financial support, in part, from the Seoul Science Scholarship.

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