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Improvement of ferroelectric fatigue endurance in multiferroic (Ba0.5Sr0.5)TiO3/(Bi1.05La0.05)FeO3/(Ba0.5Sr0.5)TiO3 sandwich structures

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Improvement of ferroelectric fatigue endurance in multiferroic $(Ba_{0.5}Sr_{0.5})TiO_3/(Bi_{1.05}La_{0.05})FeO_3/(Ba_{0.5}Sr_{0.5})TiO_3$ sandwich structures

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We report the improved ferroelectric properties in dielectric/multiferroic/dielectric sandwich structures composed of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) and $Bi_{1.05}La_{0.05}FeO_3$ (BLF). Compared with the single BLF film, the trilayer structures exhibit a lower dielectric loss and weaker frequency dependence of dielectric properties. At room temperature, the remnant polarization and saturation polarization of the trilayer structures are 34.3 and 46.9 $\mu C/cm^2$, respectively. More interestingly, the polarization of BST/BLF/BST trilayer exhibits a fatigue-free characteristic of up to 10^9 switching cycles. Applying Dawber's model, the concentration of oxygen vacancies and barrier energy of oxygen vacancies migration in BST/BLF/BST trilayer are calculated as 6.1×10^{17} cm^{-3} and 1.33 eV, respectively. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841672]

$BiFeO_3$ (BFO) materials exhibit a distorted perovskite structure with rhombohedral symmetry.[1] It belongs to the R3c space group with unit cell parameters $a=0.5634$ nm and $\alpha=59.348°$.[2,3] One of the striking features of BFO materials is the coexistence of ferroelectric ($T_C=1123$ K) and antiferromagnetic orderings ($T_N=643$ K) at room temperature.[4,5] Until now, many attempts have been made to improve the multiferroic properties of BFO by substituting ions into the *A*-site (Bi^{3+}) and *B*-site (Fe^{3+}), such as Mn^{2+}, Mn^{3+}, Cr^{3+}, Nd^{3+}, Ti^{4+}, and Nb^{5+}.[6–10] Among these substitutions, the doping of lanthanum (La^{3+}) on BFO films $(Bi,La)FeO_3$ can lead to a reduction of the leakage current,[11] improvement of polarization switching reliability,[12] and suppression of inhomogeneous magnetic spin structure.[13]

It was considered that the ferroelectric fatigue is related to the pinning of oxygen vacancies or other point defects during ferroelectric domain switching.[14] As an efficient way, the concentration of oxygen vacancies accumulated in ferroelectric films can be reduced by using oxide as electrode. Some oxide/ferroelectric/oxide trilayer structures, for example, $(Ba,Sr)TiO_3/Pb(Zr,Ti)O_3/(Ba,Sr)TiO_3$,[15] $(Bi,La)Ti_3O_{12}/Pb(Zr,Ti)O_3/(Bi,La)Ti_3O_{12}$,[16] and $(Pb,La)TiO_3/Pb(Zr,Ti)O_3/(Pb,La)TiO_3$,[17] exhibit better fatigue endurance characteristics. Recently, improved dielectric properties were found in $BiFeO_3/Pb(Zr,Ti)O_3$ multilayer[18] and $BiFeO_3/(Bi,La)Ti_3O_{12}$ bilayer.[19] However, the physical origin of the improved ferroelectric properties in these structures not been discussed yet. No investigation has been done on a sandwich structure composed of oxide/multiferroic/oxide. In this letter, a multiferroic trilayer composed of a $Bi_{1.05}La_{0.05}FeO_3$ (BLF) and two $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) layers are studied. It was found that, compared with the single BLF film, the dielectric/ferroelectric properties of BST/BLF/BST sandwich structure can be improved. More surprisingly, the polarization of BST/BLF/BST trilayer exhibits a fatigue-free characteristic of up to 10^9 switching cycles.

The BST and BLF layers were deposited in sequence on (111) $Pt/Ti/SiO_2/Si$ substrates using pulse laser deposition (PLD) with ceramic targets of $(Ba_{0.5}Sr_{0.5})TiO_3$ and $(Bi_{1.05}La_{0.05})FeO_3$. A excimer laser (Lambda Physic, $\lambda=248$ nm) of 1.5 J/cm^2 and 2 Hz was used to fabricate the films. The temperature of substrate and oxygen pressure during the growth of BST films were kept at 670 °C and 0.3 mbar, respectively, whereas the BLF film was deposited under 0.4 mbar oxygen pressure at a substrate temperature of 620 °C. After the fabrication, the samples were annealed for 10 min at an oxygen pressure of 0.8 mbar and cooled down to room temperature to prevent the loss of bismuth. The thicknesses of the BST and BLF layers were controlled to be 20 and 200 nm, respectively. For the electrical characterization, circular Pt top electrodes with a diameter of 0.1 mm were deposited on the surface of the films by sputtering.

Both the BST/BLF/BST trilayer and BLF film are randomly-oriented on $Pt/Ti/SiO_2/Si$ substrate according to XRD patterns (not shown). Figure 1(a) shows the frequency dependence of dielectric properties of the BST/BLF/BST trilayer and BLF film from 100 to 1 MHz. The measurement is carried out at room temperature with amplitude of 200 mV. Generally, the dielectric constant of both films decrease gradually the increasing the frequency of up to 10^6 Hz. A higher dielectric permittivity at lower frequency region is expected due to the increasing polarization contribution (consisting of interface, dipolar, ionic/atomic, and electronic) at the lower frequencies.[20] However, compared with the BLF film, permittivity of BST/BLF/BST structure exhibited a relatively weak frequency dependence. The dielectric constant of the trilayer structures is almost uniform at $\varepsilon\sim180$ throughout the measurement frequency. Furthermore, it is found that the dielectric loss of BST/BLF/BST trilayer exhibits less frequency dispersive characters than that of the BLF thin film, especially in high frequency region (>100 kHz). At 1 MHz, the dielectric loss of the BST/BLF/BST and BLF films are 0.16 and 0.27, respectively. In the

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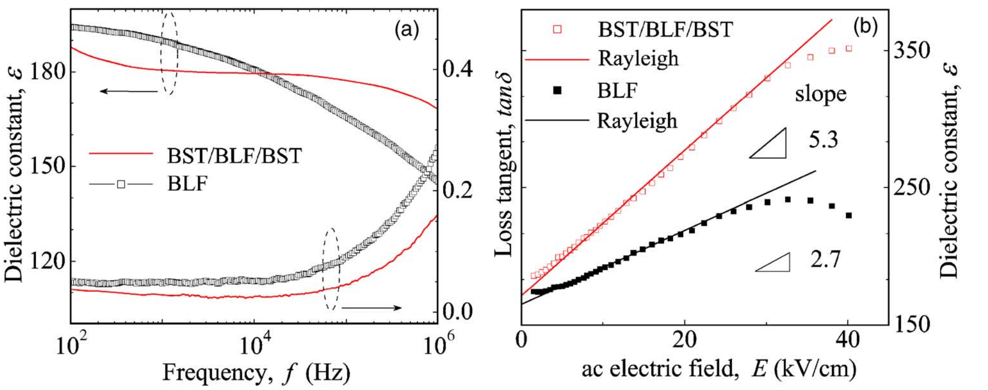

FIG. 1. (Color online) (a) Frequency dependence of the dielectric constant and loss tangent for the BST/BLF/BST trilayer structures and BLF thin film and (b) ac electric-field dependence of the dielectric constant for both capacitors performed at 100 kHz.

high frequency regime, it is suggested that the dielectric dissipation in thin films are related to the defect concentration (V_{O}^{2+}, V_{Bi}^{3-}, Fe^{2+}, etc.), interfacial polarization, and film-electrode interface. Thus, the less frequency dispersive characters in BST/BLF/BST trilayer indicate better interfacial state and lower defect concentration, which is attributed to the introduction of BST buffer layers between BLF film and Pt electrode.

The concentration of defects in BST/BLF/BST and BLF films are further analyzed through the dielectric constant (ε_E) versus ac field (E_{ac}), as shown in Fig. 1(b). Under the subswitching field, the ac field dependence of the permittivity in ferroelectric film is described by Raleigh's law,

$$\varepsilon_{(E)} = \varepsilon_0 \times \varepsilon_{\mathrm{init}} + \alpha \times E_{\mathrm{ac}}, \qquad (1)$$

where $\varepsilon_{\mathrm{init}}$ is the initial permittivity due to the reversible domain wall contributions, and α is the Rayleigh coefficient due to the irreversible displacement of domain wall. By fitting the experimental data, the values for $\varepsilon_{\mathrm{init}}$ and α of the BST/BLF/BST trilayer and of the BLF film are 177 and 165 cm/kV, and 5.3 and 2.7 cm/kV, respectively. According to Boser's discussion,[21] the value of $1/\alpha$ is proportional to the concentration of defects that affect the motion of ferroelectric domain wall. Compared with the single BLF film, the Raleigh coefficient of BST/BLF/BST trilayer reflects the total contribution from BLF and BST layers. The high value of α indicates the low concentration of defects which serves as the pinning sites for the domain wall movement in BST/BLF/BST sandwich structure.

Figure 2 shows the ferroelectric hysteresis (P-E) loops of the Pt‖BST/BLF/BST‖Pt and Pt‖BLF‖Pt capacitors under a maximum field of 430 kV/cm. Ferroelectric loops are measured with a 500 Hz triangle wave signal at room temperature by a commercial RT66A system (Radiant Technologies, USA). Interestingly, the shape of hysteresis loop of the BST/BLF/BST trilayer is much like a rectangle, whereas a tilted loop is observed in the single BLF film. The P-E loops clearly indicate that the BST/BLF/BST trilayer posseses a better ferroelectric character than the BLF film. The remnant polarization ($2P_r$) and saturated polarization ($2P_s$) are 34.3 and 46.9 $\mu C/cm^2$ for the BST/BLF/BST trilayer and 23.3 and 31.4 $\mu C/cm^2$ for BLF film, respectively, which are close to $BiFeO_3/PbZr_{0.5}Ti_{0.5}O_3$ multilayer ($2P_r \sim 25\ \mu C/cm^2$).[18] A high polarization in BST/BLF/BST trilayer may be attributed to a relatively low concentration of defects, since BST layer acts as a buffering layer to block the oxygen vacancy migration between BLF and Pt layers during electrical measurement. The coercive field ($2E_c$) for the BST/BLF/BST trilayer and BLF film are 307 and 236 kV/cm, respectively. A high E_c in BST/BLF/BST trilayer structure may be associated with the complicated interfaces in sandwich configuration, which requires a higher electric field to be saturated accordingly. Similar phenomenon has been reported in the trilayer films of $Ba_{0.5}Sr_{0.5}TiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$.[15]

To further clarify the influence of BST buffer layer on the BST/BLF/BST trilayer structures, the fatigue behaviors of both the trilayer and single film are investigated. Figure 3 illustrates the normalized polarization as a function of the switching cycles for Pt‖BST/BLF/BST‖Pt and Pt‖BLF‖Pt capacitors measured at room temperature. The fatigue test is performed using a bipolar with a pulsed width of 8.6 μs and an amplitude of 227 kV/cm at a frequency of 50 kHz. It is interesting to note that the BST/BLF/BST trilayer structure

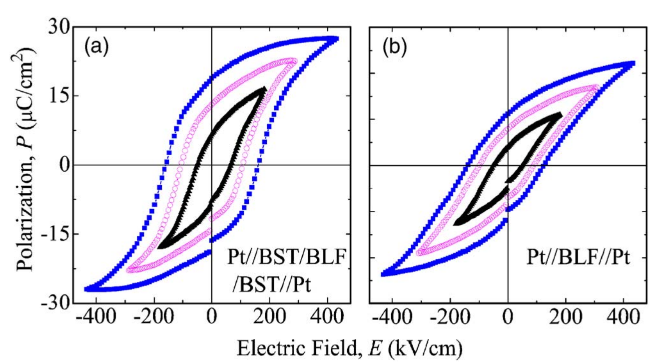

FIG. 2. (Color online) Ferroelectric hysteresis loops of (a) Pt‖BST/BLF/BST‖Pt capacitor and (b) Pt‖BLF‖Pt capacitor under different external fields at 500 Hz and room temperature.

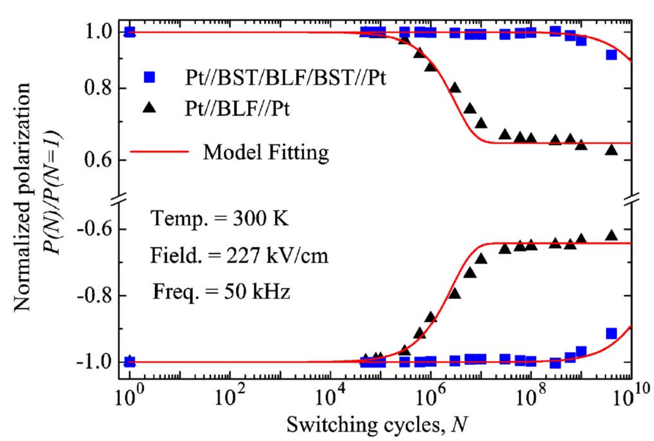

FIG. 3. (Color online) Polarization fatigue measurements for the Pt‖BST/BLF/BST‖Pt and Pt‖BLF‖Pt capacitors performed at room temperature. The red curves are the fitting results according to Dawber's model.

TABLE I. Fitting parameters of Eqs. (2)–(4) from the polarization switching data.

Films	A	B	η (cm^{-3})	ΔE (eV)
BST/BLF/BST	0.224	0.776	6.1×10^{17}	1.33
BLF	0.357	0.643	2.7×10^{19}	1.02

exhibits a superior ferroelectric fatigue endurance of up to 10^9 switching cycles. However, the BLF film shows a significant degradation of the reversible polarization after about 10^6 switching cycles. Dawber and Scott[22] have developed a model to describe the long-range diffusion of oxygen vacancies and the aggregation to the region near the film-electrode interface during the switching process. Accordingly, the relationship between the polarization $P(N)$ and switching cycles N is given as

$$P(N) = A \exp[-6D \exp(\Delta S/k)\exp(3aE_A/2)q\mu\varepsilon_s^{-1}Nf^{-1}] + B, \tag{2}$$

where E_A is the maximum field near the interface region and ε_s is the dielectric constant of the film. The definitions of A, B, ΔS, a, and f can be derived from their work. Deduced from Fig. 1, the values of ε_s for the BST/BLF/BST trilayer and the BLF film at 50 kHz are $179\varepsilon_0$ and $171\varepsilon_0$, respectively.

The temperature-dependent coefficient D describes the density of oxygen vacancies close to the region where pinning occurs and may flow into the region under the cycling process as[23]

$$D = \frac{1}{\eta}\exp\left[\frac{0.7\ \text{eV}}{k}\left(\frac{1}{T} - \frac{1}{300}\right)\right], \tag{3}$$

where η is the oxygen vacancy concentration at 300 K. Another temperature dependence parameter μ describes the mobility of the oxygen vacancies as[22]

$$\mu = \mu_0 \exp\left[-\frac{\Delta E}{k}\left(\frac{1}{T} - \frac{1}{500}\right)\right], \tag{4}$$

where μ_0 is 10^{-9} cm^2/Vs and ΔE is the barrier energy for oxygen vacancies migration.

We apply this model to the polarization switching results, as shown in the Fig. 3. The fitting parameters are summarized in Table I. Obviously, the evaluated values of vacancy concentration (η) in BST/BLF/BST trilayer is much lower than that of BLF film. More importantly, the energy barrier (ΔE) of BST/BLF/BST trilayer ($\sim$1.33 eV) is higher than that of BLF film ($\sim$1.02 eV), indicating a low mobility of the oxygen vacancies in BST/BLF/BST trilayer. As for the physical origin, the BST oxide layer is responsible for the low η and high ΔE in BST/BLF/BST trilayer, which acts as a diffusion layer by suppressing the migration of oxygen vacancies in trilayer structure. This conclusion is in agreement with that of the dielectric behaviors.

In summary, the randomly oriented BST/BLF/BST sandwich films are grown on (111) $Pt/Ti/SiO_2/Si$ substrate by PLD. As compared to the single BLF film, the BST/BLF/BST sandwich structures exhibit better dielectric and ferroelectric properties at room temperature. More strikingly, the BST/BLF/BST trilayer shows good fatigue resistance characteristic of up to 10^9 switching cycles. The improved fatigue properties in the BST/BLF/BST trilayer are assigned to the lower concentration ($\sim 10^{17}$ cm^{-3}) and the higher barrier energy ($\sim$1.33 eV) of oxygen vacancies or defects than those in the single BLF film. The BST layer may act as a diffusion barrier layer for the electromigration of oxygen vacancies or defects from BLF ferroelectric layer to Pt electrode during measurements. The BST/BLF/BST multiferroic trilayer was demonstrated as a promising structure for high density memory application.

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