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Ferroelectric polarization switching kinetics process in Bi_{0.9}La_{0.1}FeO₃ thin films

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Bi_{0.9}La_{0.1}FeO₃ (BLFO) thin films with the thickness of ~500 nm were deposited on (001) oriented SrTiO₃ substrate with 30 nm LaNiO₃ as buffer layer. The switching kinetics process of ferroelectric BLFO thin films was investigated by using pulse voltages. The result shows that one dimension and two dimensions are the prior grown modes of BLFO domains in the polarization switching process. The dimensionality of the domain growth *n* increases linearly with applied voltage, and the grown model varies from 1 D (n = 1, implies needlelike growth) to 2 D (n = 2, planar growth) with electric pulses increasing. This is explained due to the increase in the density of nucleating domains at high fields where sideway growth is limited. The higher value of *n* can be an indication of non-homogeneous distribution of domain nuclei. Under all our experimental conditions that the switching time t_{sw} is instrumentally limited and therefore the intrinsic switching time of ferroelectric BLFO films is smaller than several nanoseconds. This very short polarization switching time can be explained dustor by nucleation increases with the temperature increasing under the same input voltage which in turn affects the he switching transient current and switching time. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4828880]

I. INTRODUCTION

Ferroelectric thin films of layered perovskite structure have emerged as a prospective material in the application of nonvolatile ferroelectric random access memories (NVFRAM), due to their low coercive field and leakage current, long retention, minimal tendency to imprint, and little fatigue.^{1–5} The prospects of producing nonvolatile memories with thin ferroelectric films have created considerable interest in such films. Since the speed of switching, in other words, of polarization reversal in ferroelectric thin films limits the speed of read-write memory devices, the switching time t_{sw} for polarization reversal of ferroelectric thin films capacitors is of direct relevance for such applications and should be as small as possible. Therefore, the study of switching kinetics is very important for their practical application.^{6–8} In particular, this understanding is essential for defining accelerated testing methods.

Multiferroics, which combine (anti)ferroelectricity and (anti)ferromagnetism, have great potential for practical applications in novel devices and various sensors.^{9,10} At room temperature, however, the number of candidate materials for multifunctional applications is very limited,¹¹ because most of the currently known materials exhibit a low magnetic-transition temperature (<273 K) in contrast to a high ferroelectric transition temperature (TC > 350 K).^{12–15} The large difference between the magnetic and ferroelectric transition temperature is clearly one of the obstacles to the

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exploitation of multiferroics in real applications at room temperature. From this point of view, BiFeO₃ (BFO) is the best candidate because it has both high antiferromagnetic $(T_{\rm N} = 640 \text{ K})$ and ferroelectric $(T_{\rm C} = 1100 \text{ K})$ transition temperatures.^{16–19} Thus, it is critical to understand the process of polarization switching in BFO-based thin films.

Herein, we investigate the switching time of La doped BFO ferroelectric films (BLFO). In general, the polarization switching in ferroelectric materials includes the nucleation of new domains, their growth, and then the combination.^{20–22} The reversal of the polarization is influenced by the rate of nucleation and the growth speed of new domains. Early studies of polarization switching in ferroelectrics revealed values of t_{sw} varying from a few nanoseconds to hundreds of seconds, depending on the material and the experimental conditions, e.g., electric (switching) field and temperature. We find that under all our experimental conditions the measured switching times are instrumentally limited and the intrinsic switching time is less than or comparable to the experimental resolution of several nanoseconds.

II. EXPERIMENTAL PROCESS

500 nm $Bi_{0.9}La_{0.1}FeO_3$ (BLFO) thin films were grown on LaNiO₃ buffered (LaNiO₃:LNO) STO (001) substrates using pulsed laser deposition (PLD). The target was prepared by mixing Bi_2O_3 , La_2O_3 , and Fe_2O_3 in a 1.1:0.1:1 stoichiometric ratio and sintering at 800 °C in air. The larger amount of Bi_2O_3 was used compensated for the easy volatilization of Bi. The films were grown at 650 °C under a low oxygen pressure of 15 Pa. The laser output was about 1.5 J/cm² with a

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repetition rate of 5 Hz. Typical film growth rate was around 8 nm/min. In order to ensure oxygen equilibrium, the films were slowly cooled to room temperature (2 °C/min) in the oxygen atmosphere of 100 Pa. For the ferroelectric measurements, a 200 nm thick Ag layer patterned with circles of 200 μ m diameter was deposited on BLFO as the top electrodes and LNO served as the bottom electrode. Structural characterization of the BFO films was performed using X-ray diffraction (XRD).

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the diffraction pattern of the films grown on LNO-buffered STO (001) substrates, which only reveals the (00*l*) (l = 1, 2, 3) peaks of BLFO and STO, indicating that the BLFO film was grown epitaxially. The peaks for the 30 nm thick LNO film are too weak to be resolved from the tails of the intense STO peaks. The inset of Fig. 1(a) shows the rocking curve of the BLFO (002) peak; the full width at half maximum is about 0.4° – 0.5° , which is slightly narrower than values.²³ The surface morphology of the as-grown BLFO films was examined using atomic force microscopy (AFM), as shown in Fig. 1(b). The film has a square like shape and small grain size of the order of 100 nm, as shown in the top part of Figure 1(b). The surface is reasonably smooth with a root mean square (RMS) roughness less than 6 nm, showed in the bottom part of Fig. 1(b). It can be seen



FIG. 1. (a) XRD spectrum of BLFO/LSMO/STO films with 2θ in the range of 10° – 80° , inset shows the rocking curve of (002) BLFO peak. (b) AFM image of BLFO surface, the top one is the morphology and the bottom is the roughness corresponding to the cross line. (c) Polarization versus voltage (P–V) curves of BLFO films at room temperature.

from Fig. 1(c) that the P-V curve of our BLFO film shows rectangular shape with remanent polarization of $\sim 80 \,\mu\text{C/cm}^2$, indicates good ferroelectric properties.

In order to investigate the polarization switching process, electric pulse was used to polarize the BLFO film, the schematic of measure circuit is shown in Fig. 2(a). Ag top electrode is connected to the positive pole of the pulse generator and LNO bottom electrode with a series resistance R_0 of 100 Ω is connected to the negative side, all of the negative sides are grounded. Inset of Fig. 2(b) is the sequence of pulse voltages applied to the ferroelectric capacitors. The response signals of the pulse switching are monitored as transient voltages across R_0 . The pulse width is also controlled to be much longer than the polarization switching time. The switching transient current I_{sw} can be described as

$$I_{SW}(t) = I_{R_0}(t) = \frac{V_{R_0}(t)}{R_0},$$
(1)

where $I_{Ro}(t)$ is the transition current across resistance R_0 which is equal to $I_{sw}(t)$ due to their in serial relations, $V_{Ro}(t)$ is the voltage across R_0 monitored by channel 1 of the oscilloscope.

Prior to identical positive pulses P1 and P2, BLFO films were polarized to upward state by a negative pulse P_0 , the response currents is shown in Fig. 2(b). It can be seen from Fig. 2(b) that the positive switching current I_{sw} caused by pulse P₁ is large and non-switching transient current I_{nsw} caused by pulse P₂ is very small. In order to evaluate the switching kinetics of BLFO films, the net switching current can be obtained by subtracting the non-switching transient curves from the switching transient curves. Figure 2(c)shows the net switching current obtained from Fig. 2(b). The net switching current transient as a function of time with the applied input voltage range from 3 to 30 V is shown in Fig. 2(d). It can be seen that the current maximum is found to shift towards the lower time with the increase in voltage. The current peak also becomes sharp and it increases with voltage increasing. Linear relationship with voltage higher than 10 V can be concluded, as shown in Fig. 2(e). The deviation below 10 V is mostly because of the broaden distribution of coercive electric field, which can be seen in Fig. 1(c). The switching time and charge density of BLFO film as a function of the input pulse voltages were investigated in detail. The switching time (t_{sw}) was defined as the time from the onset to the point where the net switching transient decreased to 10% of the peak current value.

Figure 2(f) shows the pulse voltage dependence of the switching time (t_{sw}) of BLFO film with the input pulse amplitudes ranging from 10 V to 30 V, which indicates that t_{sw} is linearly related to 1/V. Some of the previous work on the switching kinetics of ferroelectric single crystals and thin films suggested that the switching time depends on the applied pulse field (E) as $t_{sw} = aE^{-n}$ or $t_{sw} = b/(E-E_{th})$, where a, b, and n are constants and E_{th} is the threshold field.^{24–26} In our study, however, the switching time does not satisfy these power laws for field dependence, but significantly obeyed and linear dependence on the reciprocal of pulse voltage 1/V. Katayama *et al.* reported that PZT thin



FIG. 2. (a) The schematic of measuring polarization switching kinetic process. (b) Switching transient current (Isw) and not switching transient current (Insw) under bipolar pulses, inset is the sequence of the applied electric voltages. (c) Net switching transient current after subtracting Insw from Isw. (d) Time dependence of net switching transient current (I-t curve) with different pulse voltages. (e) Peak of the net switching transient current under different pulse voltages varying from 3 V to 30 V. (f) switching time versus the reciprocal of the voltage (t_{sw} - 1/V curve).

films deposited by CVD had the field dependence of the switching time, similar to our experimental results on BLFO films deposited by PLD.²⁷

Recently, analysis of the switching current transients in triglycine sulphate (TGS) single crystal based on the Avrami model has been reported.²⁷ The following equation^{27–29} for switching transients gives the current variation with time as

$$i(t) = (2P_s An/t_0)(t/t_0)^{n-1} \exp[-(t/t_0)^n], \qquad (2)$$

wherein *P*s is the spontaneous polarization, *n* is the dimensionality of the domain growth (n = 1 implies needlelike growth; n = 2, planar growth; and n = 3, spherical growth), A is the area of the sample electrode, and t_0 is the characteristic switching time. The theory assumes that the rate of nucleation is constant throughout the switching process. The theoretical fitting curves according to Eq. (2) and experimental data with the input voltage of 15 and 30 V are shown in Figures 3(a) and 3(b), respectively. The theoretical fitting for 15 V in Figure 3(a) has been obtained with the fitted parameters of n = 1.46, $t_0 = 1.2 \,\mu$ s, and $Ps = 46.9 \,\mu$ C/cm². The deviation of the fitting may be resulted from the interfacial capacitor and broaden distribution of coercive electric field.

The switching current peak I_{max} occurs at time t_m and the effective dimensionality n = 1.46, the ratio $u = t_0/t_m = 1.97$ is obtained here. Ishibashi and Takagi³⁰ theory for continuous nucleation predicted that for u = 2 and n = 1.5, the value of $I_{max}t_m/Qs$ should be 0.682. From Fig. 3(a), we find $i_m t_m/Qs = 0.72$ which is in reasonable agreement with the continuous nucleation model.³⁰ On the basis of this model, D = n-1, which gives D = 0.46, implying needle like domain growth in the BLFO thin film. Equation (2) is based on the Ishibashi and Takagi model,^{28,30} which is formulated for ideal infinite systems. This model often meets difficulties while describing the kinetics of transformation in real media having spatially non-uniform distribution of nuclei and finiteness of switched media. This may be the reason that the fitting curve of the decaying part of the switching current transient with the input voltage of 15 V is not in accordance with experimental data showed in Fig. 3(a). The switching transient at 30 V shows a good fit as shown in Fig. 3(b) with fitting parameters, n = 1.86, $t_0 = 0.64 \,\mu s$. The reason for this better fitting curve in higher input voltage can be ascribed to the fact that the broaden distribution of coercive field and interfacial effect can be ignored under high input voltage. Figure 3(c) shows the dimensionality of the domain growth *n*



FIG. 3. Experimental and theoretical fitting of switching transient current based on the Avrami model with voltage of 15 V (Fig. 3(a)) and 30 V (Fig. 3(b)). (c) The dimensions of domain growth with different pulse voltages.

as a function of input pulse voltage V. It can be seen that the value of *n* increases linearly with applied voltage, *n* increase from 1.2 at the voltage of 3 V to 1.86 at 30 V, indicating that the domain growth dimensionality shifts from lower dimension to higher one, the grown model varies from 1D (implies needlelike growth) to 2D (n = 2, planar growth) with electric pulses increasing. The result shows that one dimension or two dimensions were the prior grown modes of BLFO domains in the polarization switching process. This may be possible due to the increase in the density of nucleating domains at high fields where sideway growth is limited. The higher value of *n* can be an indication of non-homogeneous distribution of domain nuclei.²⁸

In general, the minimum time for a capacitor with the remanent polarization of $Pr = 80 \,\mu\text{C/cm}^2$ and electrode area of $S = 3.0 \times 10^{-4} \text{ cm}^2$ under the applied voltage of $V_{\text{appl}} = 20 \text{ V}$ is $t_0 = 2PrS/I_{\text{max}} = 240 \text{ ns}$ for the requirement of 2PrS charges to dissipate through the loading resistance of $R_0 = 100 \,\Omega$ with a maximum current of $I_{\text{max}} = V_{\text{appl}}/R_0$, where R_0 can be smaller but never be zero due to the existence of internal resistance of voltage source. With this consideration, it is quite doubtful for the usage of t_{sw} in modeling the data of switching speed of domains in thin-film capacitors as the intrinsic switching time, and the intrinsic switching time must be far smaller than t_{sw} because of the existence of loading resistance R₀, the resistance of LNO bottom electrode and the interfacial capacitance. In order to investigate the intrinsic switching time, the switching time was measured under different loading resistance, and the switching time concluded by extrapolation method should be more closed to the intrinsic value. The switching time under different loading resistance with input pulse voltages of 15 V and 30 V is shown in Figs. 4(a) and 4(b), respectively. It can be seen from Figs. 4(a) and 4(b) that the switching time depends linearly on loading resistance R₀, the switching time under zero loading resistance is concluded to be 163 ns and 18.5 ns by extrapolating with the input pulse voltage is 15 V and 30 V, respectively. Besides, the discharging time as well as the switching time is also limited by the capacitance C in the RC circuit, the capacitance dependence of switching time t_{sw} with the resistance of 100 Ω was shown in Fig. 4(c). It indicates that t_{sw} increases suddenly with capacitance below 10 nF then tends to be saturated. The switching time t_{sw} when the capacitance is zero is inferred to be 6 ns from Fig. 4(c). Although we cannot obtain the intrinsic switching time of BLFO thin film, it can be confirmed that the intrinsic switching time is much less than several nanoseconds concluded from extrapolating. This very short switching time is far smaller than values of present measurement.

The polarization reversal process in ferroelectrics depends not only on the electric (switching) field, the area of the sample electrode, and RC circuit but also on temperature. Figure 5(a) shows the current peak I_{max} as a function of input voltage ($I_{max} \sim V$ curve) under different temperature conditions, it can be found from Fig. 5(a) that, for one hand, I_{max} increases linearly with voltage in the whole voltage range below 300 K, but it trends to saturate in higher voltages above 300 K. For another hand, Imax increase with temperature increasing under the same input voltage. Larger current means that more domains can be switched in the same time, indicating that domains are easy to move in higher temperatures. As the limitation of the rising edge of the pulse and the charge-discharge time in the RC electric circuit, the maximum current will be limited and it cannot always increase with voltage. Therefore, Imax trends to be saturated in higher voltage above 300 K. Based on this reason, the switching



FIG. 4. The polarization switching time under different loading resistance with the pulse voltages of 15 V (a) and 30 V (b). (c) Switching time under different capacitance with the voltages of 30 V.

FIG. 5. (a) The peak of switching transient current versus voltage ($I_{max} - V$), (b) the switching time versus voltage ($t_{sw} - V$), (c) the saturated polarization versus voltage (P–V curve) under different temperatures.

time t_{sw} should increase with voltage because of the saturation current in high filed. In order to demonstrate this opinion and discuss how temperature affects the switching time, we plot t_{sw} – V curves under different temperatures. It can be seen that t_{sw} increases with temperature under the same input voltage, it means that domains switch more slow in higher temperature, another reason is that more domains can switch under higher temperatures. It is obviously that the 1st reason is impossible because of thermal disturbance and domain de-pinning in high temperature. Because I_{max} trends to be saturated in higher voltage and more amount of domains switching above 300 K, the switching time must increase with voltage in higher field, as shown in Fig. 5(b).

The switched charge density can be calculated by integrating the net switching current density with respect to time

$$p_r = \frac{Q}{2S} \tag{3}$$

and

$$Q = \int_{t_0}^t I_{sw}(t)dt,\tag{4}$$

where S is the area of electrode and Q is the switched charge.

Figure 5(c) shows the pulse voltage dependence of the switched charge density (Psw) of BLFO film in different temperature. Generally, in ferroelectric materials, Qs increase with voltage and approaches to a saturation value for higher voltages, which is consistent with P-V results, showed in Fig. 1(b). It can be seen from Fig. 5(c) that polarization increases with temperature under same voltage, which agrees with the result reported by Dho *et al.*²³ On the other hand, the polarization P is harder to be saturated in high temperatures, this may be that leakage current increases with temperature. The polarization switching kinetics affected not only by pulse voltages but also on external factors such as temperatures. Under higher temperatures, domains are easier to switch considering the less pinned domain walls because of thermal disturbance; therefore, the saturation polarization increase with temperature and in turn affect the switching current and time.

IV. CONCLUSIONS

In conclusion, the pulse switching kinetics of ferroelectric BLFO thin films has been investigated. The result shows that one dimension or two dimensions is the prior grown mode of BLFO domains in the polarization switching process. The dimensionality of the domain growth *n* increases linearly with applied voltage, and the grown model varies from 1 D (n = 1, implies needlelike growth) to 2 D (n = 2, planar growth) with electric pulses increasing. This is explained due to the increase in the density of nucleating domains at high fields where sideway growth is limited. The higher value of *n* can be an indication of non-homogeneous distribution of domain nuclei. Under all our experimental conditions that the switching time t_{sw} is instrumentally limited and therefore the intrinsic switching time of ferroelectric BLFO films is smaller than several

nanoseconds. This very short polarization switching time can be explained as a switching mechanism controlled by nucleation rate. Considering the domain walls de-pinning and thermal disturbance, the saturated polarization increases with the temperature increasing under the same input voltage which in turn affects the he switching transient current and switching time.

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