Switching kinetics in epitaxial BiFeO$_3$ thin films

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The switching kinetics in epitaxial (001)-, (110)-, and (111)-oriented BiFeO$_3$ thin films were investigated as a function of applied field and time. It was found that the ferroelectric switching behavior obeys the Kolmogorov–Avrami–Ishibashi theory only in the high field range. The detailed behavior depends on the film orientation. A comparison with standard systems, such as epitaxial Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ films, reveals some similarities as well as some differences. For instance, the presence of 109° and 71° ferroelastic domain walls might be ruled out as the source of the decrease in switched polarization at low applied fields, in contrast to what is the case for a/c domain walls in tetragonal Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$. © *2010 American Institute of Physics*. [doi:10.1063/1.3392884]

I. INTRODUCTION

The switching kinetics between the different stable polarization states in ferroelectric single crystals is usually described theoretically by the Kolmogorov–Avrami–Ishibashi (KAI) model.[1,2] Basically, the KAI model assumes nucleation of domains at independent nucleation centers followed by growth and coalescence of domains. The underlying processes are affected by extended structural defects and point defects.[3–6] It was previously shown that the switching kinetics in epitaxial tetragonal Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ [PZT(20/80)] ferroelectric thin films basically obeys the KAI model in many cases but the specific parameters or more generally the applicability of such a model for this case depends on the domain structure of the film.[6] A high density of 90° ferroelastic domain walls leads to a nucleation-limited switching model, which applies mostly to polycrystalline films,[7] rather than a KAI model.[6] In this letter we report on the switching kinetics in epitaxial BiFeO$_3$ (BFO) thin films.

BFO is a single phase multiferroic with transition temperatures well above room temperature (ferroelectric Curie temperature ~1103 K and antiferromagnetic Néel temperature ~643 K).[8,9] The lattice structure at room temperature is a rhombohedrally distorted simple cubic perovskite with polarization parallel to one of the four pseudo-cubic body diagonals ($\langle 111 \rangle$).[10] Due to the rhombohedral structure there are four different structural variants present in BFO leading to eight possible polarization directions and three different types of domain walls, namely 180° ferroelectric, 109° and 71° ferroelastic domain walls in which not only the polarization direction but also the direction of lattice distortion changes.[11,12] The polarization within the domains can be switched by an applied electric field. Polarization switching in BFO is especially important because it might also switch the antiferromagnetic orientation, necessary for magnetoelectric coupling.[13]

II. EXPERIMENTAL PROCEDURE

300 nm thick (001)-, (110)-, and (111)-oriented BFO films were grown on SrRuO$_3$/SrTiO$_3$ (SRO/STO) substrates with corresponding orientations by pulsed laser deposition. An epitaxial SRO top electrode was deposited and the resulting SRO/BFO/SRO trilayer was patterned into circular capacitors with an area of 750 μm^2 each. Details on growth process and structural investigations including x-ray diffraction (XRD) on similar films are published elsewhere.[15]

Ferroelectric hysteresis loops were measured by integrating the current response of a capacitor excited by a 1 kHz triangular voltage pulse applied with an aixACCT TF Analyzer 2000.

The polarization switching was performed using voltage pulse trains similar to Ref. 7, i.e., we used rectangular pulses. After establishing an initial, fully switched positive state (polarization pointing toward the bottom electrode) a negative switching pulse with variable width t between 20 ns and 1 s (rise time 5 ns) and variable amplitude of the switching field E between 100 and 250 kV/cm was applied. Subsequently, the switched polarization was measured by integrating the current during a positive pulse of high amplitude (2 μs, 330 kV/cm) which led to a fully switched positive state and was corrected for nonswitching contributions. Please note that we measured fully relaxed remnant switched polarization due to the time delay between switching and measuring pulse. The above described method is similar to the standard PUND (Positive switching pulse, Up voltage response, Negative switching pulse, Down voltage response).[14]
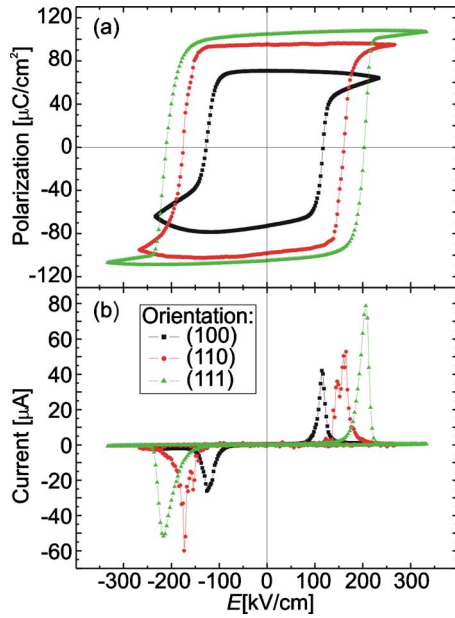
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FIG. 1. (Color online) Ferroelectric hysteresis measurement at 1 kHz for (001)-, (110)-, and (111)-oriented BFO films (squares, circles, and triangles, respectively); (a) polarization P and (b) corresponding current I vs electrical field E.

FIG. 2. (Color online) Switched polarization P as a function of switching time t for different electric fields E measured on 300 nm thick epitaxial BFO films with (a) (001), (b) (110), and (c) (111) orientations. Solid lines are fits to the KAI model. The applied fields are ■117 kV/cm, ●133 kV/cm, △150 kV/cm, ▼167 kV/cm, ◇183 kV/cm, ◁200 kV/cm, and ▷233 kV/cm (Not all measured curves are shown).

III. EXPERIMENTAL RESULTS

With respect to the structural properties and the domain structure, as probed by piezoresponse force microscopy (not shown here), the present BFO films resemble those measured in Ref. 15. All films were found to be single phase and fully epitaxial by XRD studies. The (111)-oriented film exhibits only one structural variant and 180° ferroelectric domain walls with an initial single domain state. The (110)-oriented film shows two structural variants whereas all four possible structural variants appear in the (001)-oriented film. In both (110)- and (001)-oriented films 109° and 71° ferroelastic and 180° ferroelectric domain walls can be observed. Therefore, depending on the film orientation, different ferroelectric (180°) or ferroelastic (71°and 109°) switching processes are allowed. The only difference to Ref. 15 is the mosaiclike domain structure shown by the present (001)-oriented film instead of a stripelike domain pattern shown by those films.[16]

Figure 1(a) shows the fully saturated polarization versus electrical field loops for the three different orientations and Fig. 1(b) the corresponding current versus electric field characteristics. Although there is a small contribution of leakage (visible in the opening of the polarization loops at high fields), the current peaks, which are given by the displacive current due to ferroelectric switching, are rather symmetric with respect to the voltage polarity. The coercive field is increasing from (001)- over (110)- to (111)-oriented BFO and the shape of the switching peaks is remarkably different for the different orientations.

The switching peak of (001)-BFO is rather symmetrical and the edges are smoothly decreasing and falling, respectively, whereas the current peak for (111)-oriented BFO is characterized by a smooth increase followed by a sharp drop. In contrast to both other orientations the (110)-BFO features two distinct current peaks and a rather steep increase fol-
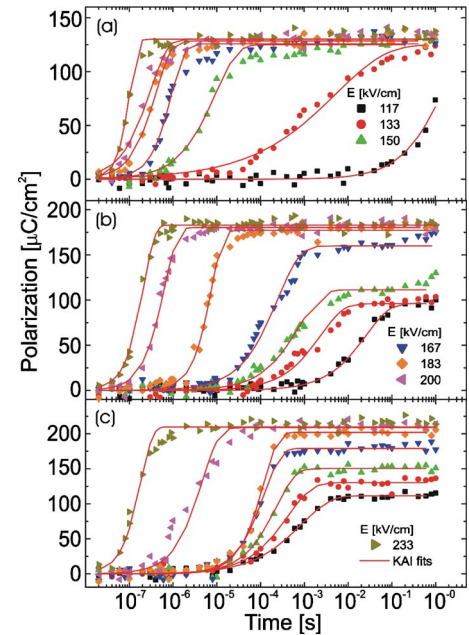
lowed by smoothly decreasing current. This difference in the switching current shape is a good indication of different switching kinetic but a detailed analysis is restricted to the squarelike pulses where a meaningful theoretical analysis is available.

Results of the switching measurements of the films are given in Fig. 2. The three BFO films show different remnant polarization P_s values due to different projections of the ⟨111⟩-polarization direction onto the film normal.[17] The measured saturated remnant polarization values, i.e., half the switched polarization for high fields and long exposure times, are 65 $\mu C/cm^2$, 90 $\mu C/cm^2$, and 105 $\mu C/cm^2$ for a (001)-, (110)-, and (111)-oriented film, respectively, which are in agreement with values from the ferroelectric loops [Fig. 1(a)] and the literature.[17–19]

IV. DISCUSSION

The switching data can be fit by the following equation of the KAI model,[1,2]

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

where P_s is the saturated polarization, t_0 is the characteristic switching time, and n is the effective dimension of domain growth, as shown by solid lines in Fig. 2. The electric field dependence of the fitting parameters P_s, t_0, and n is shown in Fig. 3. It should be pointed out that the KAI model cannot explain the low field data ($E < 170$ kV/cm) where $n < 1$ since n values smaller than 1 are not physically reasonable according to the KAI model. The KAI model assumes either a constant nucleation rate during switching (category I) or only latent nuclei and no new nucleation during switching (category II), leading to different effective dimensionalities.
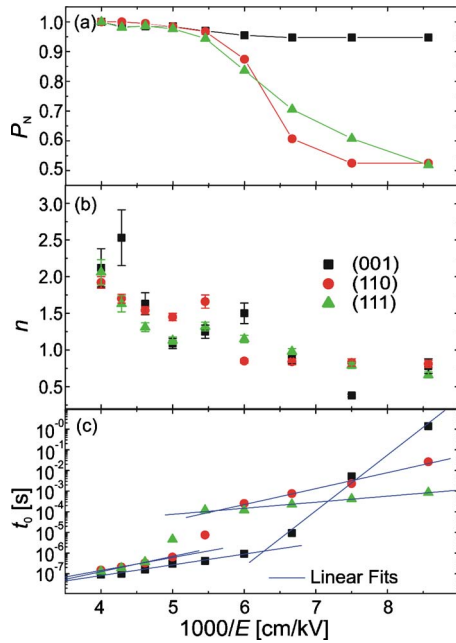
FIG. 3. (Color online) Field dependence of the fitting parameters; (a) normalized polarization P_N, (b) dimensionality factor n, and (c) characteristic time t_0 from the KAI model for (001)-, (110)-, and (111)-oriented BFO films from Fig. 2 (squares, circles, and triangles, respectively).

Noninteger n values can occur due to mixing of the two categories but values smaller than 1 cannot be achieved by any kind of mixing of the categories.[1,20]

For all three BFO orientations an in-depth analysis of the extracted effective dimensionality n [Fig. 3(b)] yields a decrease in n from about 2, i.e., bidimensional in-plane domain growth (assuming category II) or one-dimensional (1D) growth (assuming category I), for the case of high fields to about 1, i.e., 1D in plane domain growth (category II), at lower fields similar to previously reported behavior in epitaxial PZT(20/80) (Ref. 6) and PZT(40/60).[21] At even lower fields ($E < 170$ kV/cm) n drops substantially below 1, as discussed above. This cannot be explained by the KAI model but we may speculate that it is due to the internal fields which promote polarization switching at an early stage of the switching process and hinders it at a later stage.[20] Since n depends on the growth dimensionality and the nucleation rate,[22] the field dependency of n strongly suggests changing switching kinetics.

It is noteworthy that the polarization of the (001)-oriented film can be fully switched even at low fields ($E \approx 117$ kV/cm) after a sufficiently long waiting time ($t \approx 1$ s), whereas the polarization reversal in the (110)- and (111)-oriented films is complete only for high fields ($E > 170$ kV/cm). This could be related to the smaller coercive field for the (001)-oriented film (see Fig. 1). However, polarization saturates for all applied fields but with a lower switched polarization value at lower fields (Fig. 2). The electric-field dependence of the saturated switched polarization, namely fitting parameter P_s, is given in Fig. 3(a). The switched polarization is almost independent of the applied field E for the (001)-oriented BFO film but the switched polarization for the other two orientations decreases with decreasing field to about 50% of the high field value below a

TABLE I. Activation field α_1 and α_2 in the high and low field regimes, respectively, obtained from the fits (solid lines) in Fig. 2(c). For comparison, the values for epitaxial (001)-PZT are $\alpha_1 = 800$ kV/cm and $\alpha_2 = 1700$ kV/cm (Ref. 21).

Orientation	α_1 (kV/cm)	α_2 (kV/cm)
(001)	520	2700
(110)	630	770
(111)	740	290

certain threshold field [Fig. 3(a)]. This is particularly striking for the (111)-oriented film which contains only 180° ferroelectric domain walls. Therefore, the ferroelastic domain walls in BFO might be disregarded as the source of the decreased switched polarization with decreasing field. This is in contrast to the PZT(20/80) case where non-180° domain walls, i.e., ferroelastic domain walls, were found to hinder switching at low fields.[6]

According to Kubel and Schmid,[10] the 180° switching in BFO could be suppressed due to a large ion displacement related to the 180° switching. The same but to a smaller extend, applies to the 109° switching[10] and this could explain the similar effect in the (110)-oriented sample. This explanation is also in agreement with the observed coercive field dependence on the BFO-orientation (Fig. 1).

Other explanations could involve the depolarization field or back switching due to insufficient screening of the polarization after switching. Both mechanisms depend on the magnitude of polarization and are, therefore, more pronounced in (110)- and (111)-oriented films than in (001)-oriented films. The depolarization field lowers the actual field accessible for complete switching since it is antiparallel to the polarization direction. Due to the linear dependence of the depolarization field on the polarization[23] this could hinder a complete switching at low fields for (110)- and (111)-oriented samples. Concerning screening, more charge has to be redistributed for higher polarizations which might not be possible at low fields.

Since the microstructure has a strong impact on the ferroelectric properties[5] and the domain structure of the BFO is due to strain imposed by the substrate,[15] structural defects, e.g., dislocations, or the strain state, which is different for the different orientations,[15] might be another possible explanation for the reduced switched polarization at lower fields.

The decrease in n, the drop in switched polarization P_s and the transition between KAI and non-KAI switching are accompanied by discontinuities in the characteristic switching time t_0 for BFO films on (110) and (111) substrates, whereas t_0 is smooth for (001)-BFO films across the applied voltage range [Fig. 3(c)].

The empirical law,[24]

$$t_0 \propto \exp(\alpha/E), \tag{2}$$

with the activation field α could fit the data as shown in Fig. 3(c). The activation fields (see Table I) are comparable with those of epitaxial PZT.[6,21] Moreover, for all three film orientations the high and low field regions have different activation fields α_1 and α_2, respectively, as for the PZT. This might

be a strong evidence for a change in switching details since t_0 is known to depend on the precise details of the switching process.[21] As in the PZT case, we might assume that the change in switching kinetics in BFO is due to different nucleation rates in the low and the high field region.[21]

In the high field region (with complete switching for all orientations and KAI model like behavior) the activation field α_1 of the (111)-oriented film is higher than the activation fields α_1 of the two other directions as expected by Kubel and Schmid on the basis of atom displacement during switching.[10] In the low field region ($E < 180$ kV/cm) the (111)-oriented sample has the lowest activation field α_2 and reveals the shortest switching time but as discussed above, it does not exhibit complete polarization reversal and the fitting to the KAI model might not be reasonable and, therefore, the extracted characteristic switching times t_0 either.

V. CONCLUSIONS

In summary, we have demonstrated that the polarization switching in epitaxial BFO thin films obeys the KAI model only in the high field region, although we used epitaxial films, one of them without ferroelastic domain walls. This is somehow unexpected and the physical reasons are still unclear. Furthermore, the detailed parameters for the switching behavior are different for different BFO orientations and depend on the applied electrical field, e.g., we observe complete switching at low fields in (001)-oriented BFO but not in (110)- and (111)-oriented films. This is, especially for the (111)-oriented film with no ferroelastic domain walls and for (001)-BFO with ferroelastic domain walls, in contrast to the case of a/c domain walls in epitaxial PZT(20/80). The observed behavior could not be explained based on the ferroelastic domain walls but most likely on atom displacement during switching. Further investigations on the switching kinetics in epitaxial BFO films, e.g., a correlation between the microstructure and the switching, are necessary to clarify this behavior.

ACKNOWLEDGMENTS

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