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Dynamics of surface screening charges on domains of BiFeO$_3$ films

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The dynamics of surface screening charges on BiFeO$_3$ films with pre-written stripe domains was studied with surface potential measurements by Kelvin Probe Force Microscopy. The screening effect decays exponentially over time, and this decay is slower in the arrays with wider domains or larger intervals of domains, indicating that the in-plane diffusion of the surface screening charges plays a major role in the decay dynamics. The good agreement between experimental data and theoretical results based on diffusion-drift model confirms the mechanism of in-plane diffusion of the screening charges in the decay dynamics. Our work could provide a pathway to control the data stability of charge storage by artificially designing the ferroelectric domains. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Scanning probe microscopy (SPM) techniques such as piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM) have been widely utilized as an analyzing tool to evaluate the local domain structure and surface electric properties of materials. When an appropriate bias is applied on the ferroelectric materials by a SPM tip, the polarization can be switched locally. Then, the surface charges (electrons or holes) from the conducting tip are injected onto the surface of ferroelectric materials and screen polarized bound charges. Surface charge screening determines the stabilization of the ferroelectric domains and further influences the data storage density, signal reliability, and bit readout. The surface potential (SP) acquired by KPFM technique mainly comes from the overscreened charges for polarized domains. Recently, we proposed that SP can be utilized as a non-destructive readout method in ferroelectric memories. Therefore, it is crucial to understand the dynamics of tip-injected surface screening charges and their relaxation behavior. This understanding directly relates to the reliability towards memory and data-storage applications. So far, adsorption and desorption of the surface screening charges were seemed as a mechanism of SP decay process. Besides, sideways diffusion of screening charges and recombination with the opposite charges on adjacent domains has also been proposed to play important roles in the SP decay process. Moreover, charge diffusion along the out-of-plane direction followed by the injection into the bottom electrode, as a possible mechanism, has not been ruled out yet. Thus, the dynamics of surface screening charges on pre-written domains and the origin behind the SP decay process are still ambiguous, and need to be further studied at the present stage.

In this work, we investigated the dependence of the surface potential decay process on the domain scales and intervals. Stripes of alternately reversed ferroelectric domains with various widths and intervals on BiFeO$_3$ films were written by scanning probe microscopy technique. SP on the area with pre-written stripe domains was read out by Kelvin Probe Force Microscopy (KPFM).
II. EXPERIMENTAL DETAILS

High-quality epitaxial ferroelectric BiFeO$_3$ (BFO) films were fabricated on (001)-oriented SrTiO$_3$ (STO) substrates covered with La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) bottom electrodes, by the laser molecular-beam epitaxy (Laser-MBE). The LSMO with the thickness of 20 nm and the BFO of 30 nm were deposited successively on the substrate at the oxygen pressure of 40 Pa and 10 Pa, and at the substrate temperature of 610 °C and 580 °C, respectively. A XeCl 308 nm excimer laser was used with an energy density of 1.5 J cm$^{-2}$ and a repetition rate of 4 Hz. After the deposition, the samples were in-situ annealed for 20 min, and then cooled down to the room temperature. Surface topography, domain structure and surface potential were measured by the combination of atomic force microscopy (AFM), KPFM and PFM technique with a commercial test instrument (Asylum Research MFP3D). Pt-coated conductive tips (Olympus AC240, a spring constant of ~2 N m$^{-1}$ and a free air resonance frequency of ~70 kHz) were used for the AFM, the KPFM and the PFM scanning. During the surface potential measurement, the AFM tip is 10 nm over the surface scanning point by a point while the cantilever is ~15 µm above the surface. Therefore, it is reasonable to assume that the contribution of the cantilever to the SP signal is negligible. The relative humidity and temperature remained unchanged during the measurement process in order to avoid their effects on the dynamics of surface screening charges.

III. RESULTS

Figure 1(a) presents the schematic of local poling process of ferroelectric films by a conductive SPM tip. It is widely believed that an overscreened surface occurs during bias-induced domain switching. When a positive bias is applied on the ferroelectric films by a SPM tip, the ferroelectric polarization will points to the bottom electrode (downward-polarized). Electrons will be pulled away from the surface, and holes will accumulate and be trapped on the surface. In contrast, electrons will accumulate and be trapped when a negative bias is applied by the SPM tip. These tip-injected carriers can over screen the surface in the bias-induced domain switching process, and those overscreened charges can be measured by SP. Figures 1(b), 1(c), and 1(d) show the AFM topography image, the out-of-plane PFM phase image, and the KPFM potential image, respectively, at the same region of our BFO film. A typical crisscross topography for BFO grown on STO is demonstrated in the AFM topography image with a root-mean-square roughness of 9 Å over a 5×1 µm$^2$ area. We polarized this area with alternate +9 and -9 V bias. Well-defined domains with opposite polarization are demonstrated in the out-of-plane PFM phase image as shown in Fig. 1(c). The violet regions correspond to the downward-polarized domains, while the yellow regions correspond to the upward-polarized domains with the same polarization direction as the as-grown BFO/LSMO/STO. SP measurement right after the sample poling is shown in Fig. 1(d). The alternate bright and dark stripes correspond to the high and low SP regions, respectively. The line profile of the KPFM image marked by the red arrow in Fig. 1(d) was plotted by the black line in Fig. 1(e). The high and low SP correspond to the tip-injected positive and negative overscreened surface charges on the downward-polarized and upward-polarized domains, respectively. This overscreening effect after tip-induced switching is identical with the previous reports mentioned above. To quantitatively assess the dynamics of SP in the strips of alternately reversed domains, the line profiles of KPFM images at different time after poling were also plotted in Fig. 1(e). It is obvious that the SP decreased at the regions with high SP and increased at the regions with low SP. Therefore, the ΔSP decayed with time. Here, we define ΔSP as the difference between the average peak value and the average valley value as shown in Fig. 1(e). We attribute this decay to the reduction of tip-injected overscreened charges. Three possible mechanisms can be responsible for the reduction. The first one is the in-plane diffusion and the recombination with the opposite charges on adjacent domains. The second one is the diffusion along the out-of-plane direction and injected into the
bottom electrode. The third one is adsorption and desorption of the surface screening charges from the ambient air.

In order to clarify which one is the main reason for the decay of $\Delta SP$ and further understand the dynamics of overscreened surface charges, we wrote arrays of striped domains by applying alternately $+9$ and $-9$ V bias onto a series of rectangles with the widths ($w$) of 667, 500, 250, and 125 nm, respectively. The duration of bias is uniform with 4 ms/pixel and 64 pixel/µm in the present work. Figure 2(a), from top to bottom, shows the PFM phase images of the four arrays with reducing the domain width. The regions applying $+9$ V bias are down-polarized that correspond to violet rectangles in Fig. 2(a). The regions applying $-9$ V bias are up-polarized that are parallel to the as-grown direction of polarization. Therefore, we cannot recognize the regions applying $-9$ V bias from the background of PFM phase images. Figure 2(b) shows the corresponding KPFM potential images obtained right after electrically poling the striped domains. Alternate bright and dark strips correspond to the regions after applying $+9$ V and $-9$ V bias, respectively.

We extracted data from the KPFM potential images at different time after poling, and plotted the $\Delta SP$ evolution with time in Fig. 2(c). The initial values of $\Delta SP$ are 0.32, 0.35, 0.11, and 0.01 V.
FIG. 2. PFM phase images (a) and the corresponding KPFM potential images (b) of four arrays of domains with the domain widths of 667, 500, 250 and 125 nm. Time evolution of ∆SP (c) and normalized-∆SP (d).

for domains with the widths of 667 (∆SP_w=667 nm), 500 (∆SP_w=500 nm), 250 (∆SP_w=250 nm), and 125 nm (∆SP_w=125 nm), respectively. It is easy to understand that there are more screened charges on the surface of larger domains, therefore the initial values of ∆SPs is larger in wider domains. However, for both upward-polarized domains and downward-polarized domains, the initial surface density of screened charges is almost the same for different domain widths, since the duration and magnitude of bias are uniform throughout the poled process. Interestingly, the ∆SPs with smaller initial values decayed much faster than the ∆SPs with larger initial values. In other words, the ∆SPs decayed faster in the arrays with narrower domains. By fitting the data in Fig. 2(c) to an exponential decay function \[ \propto \exp(-t/\tau) \], with \( \tau \) being the time constant for decay, the time constants are 15.5, 13.2, 3.7, and 0.9 h for ∆SP_w=667 nm, ∆SP_w=500 nm, ∆SP_w=250 nm, and ∆SP_w=125 nm, respectively. To analyze the decay dynamics comparatively in arrays with different widths of domains, we normalized the values of ∆SP in Fig. 2(c) and plotted the time evolution of normalized-∆SP in Fig. 2(d). From Fig. 2(d), the ∆SP_w=125 nm almost completely decayed at 3.6 hours after poling. We cannot plot the ∆SP_w=125 nm points after 3.6 hour decay because the KPFM potential image of 125 nm striped domains was obscure and unable to distinguish after that. However, the ∆SP_w=250 nm, ∆SP_w=500 nm, and ∆SP_w=667 nm only decayed to 42%, 69%, and 72%, respectively, of their initial value. Therefore, we can conclude that the overscreened charges reduce faster in the region with narrower domains. We ascribe this phenomenon to the trapping effect from dipoles in the polarized region and the sideways diffusion, as the sideways diffusion depends on the in-plane diffusion distance and the trapping effect depends on the domain size.

To further distinguish the in-plane distance effect from the domain size effect on the ∆SP decay, we wrote arrays of striped domains by alternately applying +9 and -9 V bias onto a series of rectangles with the same scale of 125 nm × 600 nm. These arrays of rectangles were separated by 187, 125, 62, and 0 nm intervals (d) during the writing operation. Figure 3(a), from top to bottom, shows the out-of-plane PFM phase images of the four arrays with reducing the intervals. The violet regions corresponding to the downward-polarized domains were poled under +9 V
bias. The regions insert to the violet strips were poled under -9 V bias. It is worth mentioning that Ievlev et al. proposed intermittency, quasiperiodicity in probe-induced ferroelectric domain switching by decreasing the separation between the bias application locations on LiNbO$_3$ surface. They ascribed the abnormal domain switching to the interplay between tip and screening charge dynamics. Here, our well-defined striped domains in Fig. 3(a) imply that our BFO film has stable domain structure without such abnormal domain switching. Figure 3(b) shows the corresponding KPFM potential images right after the writing operation. The bright strips represent high SP regions with +9 V bias applied, while the dark strips represent low SP regions with -9 V bias applied. By extracting data from the KPFM potential images at various times after poling, we obtain the time evolution of $\Delta SP$ as shown in Fig. 3(c). We observe that even though the scale of rectangles and the magnitude of bias are uniform during the writing operation, the initial values of $\Delta SP$ are different in the four domain arrays with different intervals. As shown in Fig. 3(c), the initial values of $\Delta SP$ are 0.163, 0.126, 0.077, and 0.014 V for the domains arrays with the intervals of 187 ($\Delta SP_{d=187\text{ nm}}$), 125 ($\Delta SP_{d=125\text{ nm}}$), 62 ($\Delta SP_{d=62\text{ nm}}$), and 0 nm ($\Delta SP_{d=0\text{ nm}}$), respectively. We will discuss this phenomenon below in this article, while here we focus on the decay process. By fitting the data in Fig. 3(c) to an exponential-like decay function $[\times\exp(-t/\tau)+A_0$, where $\tau$ is the time constant for decay, $A_0$ is a constant], we can find that the $\Delta SP$ in some arrays decayed to a certain value rather than to zero. The certain values of $\Delta SP$ are 0.052, 0.031, 0.014, and 0.002 V for the $\Delta SP_{d=187\text{ nm}}$, $\Delta SP_{d=125\text{ nm}}$, $\Delta SP_{d=62\text{ nm}}$, and $\Delta SP_{d=0\text{ nm}}$. In turn, the time constants are 0.96, 0.61, 0.54, and 0.48 h for the four domains arrays. Therefore, the $\Delta SP$ decay slower and to a higher value in the domains arrays with larger intervals. For direct comparison, the time evolution of normalized-$\Delta SP$ is shown in Fig. 3(d). It is obvious that the $\Delta SP$ decayed to 59%, 42%, 31%, and 27% of their initial values for the $\Delta SP_{d=187\text{ nm}}$, $\Delta SP_{d=125\text{ nm}}$, $\Delta SP_{d=62\text{ nm}}$, and $\Delta SP_{d=0\text{ nm}}$, respectively, with an hour after poling.

**IV. DISCUSSION**

Based on the above measurements, we can conclude that the sideway diffusion of tip-injected overscreened charges is the main mechanism for the $\Delta SP$ decay process, rather than the mechanism

![PFM phase images (a) and the corresponding KPFM potential images (b) of four arrays of domains with the domain intervals of 187, 125, 62 and 0 nm. Time evolution of $\Delta SP$ (c) and normalized-$\Delta SP$ (d).](image-url)
of adsorption and desorption of the surface charges, nor the diffusion along the thickness direction in BFO thin films. To further verify the mechanism for above decay process, a numerical calculation based on a time-dependent drift diffusion model is carried out. The diagram of one-dimensional periodical polarized domain structure can be found in Ref. 8. The SP is determined by the distribution of surface charges which consists of the polarization bound charges and the screening charges. We set the out-of-plane direction as z-direction. We assume that alternating polarized domains are infinite along y-direction and are periodically arranged along x-direction. The surface screening charges can drift and diffuse towards the adjacent domains and recombine around domain boundaries, while the polarization charges remain still unchanged. Dynamic process of screening charges follows the drift-diffusion mechanism,

$$\frac{\partial}{\partial x} \left[ \varepsilon \frac{\partial \phi(x,t)}{\partial x} \right] = -e \left[ p(x,t) - n(x,t) \right]$$

$$\frac{\partial n(x,t)}{\partial t} = \frac{1}{e} \frac{\partial j_n(x,t)}{\partial x} - R(x,t)$$

$$\frac{\partial p(x,t)}{\partial t} = -\frac{1}{e} \frac{\partial j_p(x,t)}{\partial x} - R(x,t)$$

where $\phi$, $n$, $p$, $j_n$, and $j_p$ represent the electrostatic potential, the electron concentration, the hole concentration, the current density of negative screening charges, and the current density of positive screening charges, respectively; $e$ and $\varepsilon$ are the elementary charge and the dielectric permittivity; $R$ is the recombination rates of electron-hole pairs. The current density takes the form of drift and diffusion theory, and the SRH model is adopted to describe the recombination. Potential barriers of adjacent domains is as well taken into consideration, and the thermionic emission current is introduced to describe the current of screening charges moving across domain boundaries. The surface potential and its evolution can be calculated according to the charge distribution by solving the two-dimensional Poisson equation in our simulation. Parameters of domain and size of films are set according to different experimental configurations. Density of non-movable screening charges is set to be equal to the density of polarization charges. The initial state is assumed as that screening charges distribute uniformly in one domain. Then, screening charges begin to drift and diffuse, and surface potential begins evolving.

Figures 4(a) and 4(b) show the calculated normalized $\Delta SP$ evolution with time for different domain sizes and domain intervals, respectively. From Fig. 4(a) and 4(b), we can find out that the time constant increases with enlarging the domain scales and the domain intervals. With larger domain sizes or intervals, screening charges need to diffuse over a longer distance to recombine, and therefore it takes longer time for $\Delta SP$ to decay. The trapping effect from dipoles and the potential barrier (about 0.3 eV) at domain boundaries will hinder the diffusion of surface charges and make the $\Delta SP$ decay to a stable value. Besides, we believe that the tip-injected charge began to diffuse sideways once the tip contacted the surface with an applied bias. Due to the technological limitation,
we cannot polarize a region meanwhile detect the SP distribution at the same time. Therefore, the initial values of $\Delta SP$ in Fig. 3(c) were not the exact initial value, and were different in the four domains arrays because they were already decayed for a while. Thus, the calculated results cannot quantitatively reproduce this experimental decay process, but can show the tendency. These calculated tendencies are in good agreement with those of the experimental data from Fig. 2 and 3.

V. CONCLUSIONS

In conclusion, we have studied the dynamics of surface screening charges on ferroelectric BFO films using PFM and KPFM. Stripes of alternately reversed ferroelectric domains with different widths and different intervals on BiFeO$_3$ films were written by a conductive tip. The $\Delta SP$ between the adjacent reversed domains decayed exponentially right after poling, and this decay is slower in the arrays with wider domains or larger domains’ intervals. These results experimentally and theoretically confirm that the sideway diffusion of surface charges dominates the evolution of the screening charge decay process. The present results clarify the dynamics of surface screening charges on the widely researched BFO films, and offer a way to control the diffusion rate of surface screening charges on the ferroelectric surface. This is crucial to the stabilization of the ferroelectric domains, the data storage density, and non-volatile bit readout.

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