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Photovoltaic property of domain engineered epitaxial BiFeO₃ films

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The effect of domain structure on the photovoltaic response of BiFeO₃ vertical capacitors is investigated, by domain engineering using vicinal SrTiO₃ substrates. It is observed that the open-circuit photovoltage remains unaffected by the domain structure, consistent with the photovoltaic effect being driven by the polarization modulated band bending at the metal/BiFeO₃ interface. Nevertheless, the enhancement of short-circuit photocurrent is achieved and attributed to the conducting domain walls. Furthermore, we have estimated and compared the magnitudes of photoconductivity of domains and domain walls in BiFeO₃ thin films, which can be used to explain the photocurrent improvements. These findings cast some light on the role of domain walls in ferroelectric photovoltaic effects and provide a simple route towards enhanced efficiency. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905000>]

Photovoltaic effect in BiFeO₃ (BFO) has spurred renewed interest in ferroelectric photovoltaic cells recently due to its switchable and non-volatile nature. It holds great promise for novel optoelectronic devices.^{1–4} Furthermore, what causes the above-bandgap photovoltage observed remains debated.^{5–7} Yang *et al.* discovered that the open-circuit voltage (V_{oc}) of the planar BFO capacitor is proportional to the number of 71° domain walls in between the two electrodes (domain walls parallel to the electrodes).⁵ Contrarily, if the domain walls are perpendicular to the electrodes, no sizable photovoltage is observed at room temperature, except for a large photoconductivity. The authors thus propose that the effect arises from the electrostatic potential steps at the 71° domain walls due to the polarization discontinuity. Similar effect was reported for BFO films containing periodic 109° domain walls, albeit with much smaller V_{oc} .⁸ However, Bhatnagar *et al.* recently observed that the above-bandgap V_{oc} scales up roughly exponentially with decreasing temperature irrespective of the geometry and type of domain walls.⁶ They suggest that the intrinsic bulk photovoltaic (BPV) effect is responsible for the abnormally high V_{oc} in BFO thin films, whereas the domain walls act as shunts due to their higher conductivity, thus reducing the V_{oc} values.

We note that most of the previous reports focus on domain wall effect in BFO epitaxial films using lateral device configuration. Only a few studies deal with vertical capacitor geometry, which is more relevant to applications. Recently, Yan *et al.* reported dynamics of photogenerated surface charge on BFO films by using scanning Kelvin probe microscopy (SKPM) technique.⁹ Although they claimed that the V_{oc} value increases linearly with the number of domain walls, no direct evidence was provided.

In order to clarify how domain walls contribute to the photovoltaic effect of BFO in the vertical capacitor geometry, it is necessary to control the domain configurations.

Vicinal substrates have been widely used to engineer the ferroelectric domain structures in BFO thin films.^{10–13} A miscut substrate can generate highly ordered steps on the surface, which may serve as the nucleation sites for adatoms during film growth. This anisotropic strain condition will thus favor certain domain variant(s) while suppressing the others. In this study, we grow high quality epitaxial BFO heterostructures on vicinal SrTiO₃ (STO) substrates with different miscut angles. The influences of miscut angle on the ferroelectric properties, especially the domain structure and photovoltaic properties of the BFO films, are investigated. In addition, the photoconductivities of the domain bulk and domain wall are estimated using a simple model, which is useful for the better understanding of the photovoltaic effect in BFO thin film.

A series of (001)-oriented STO substrates with various miscut angles (0°, 1°, 2°, and 4°) along [110] direction are selected for the film deposition. All BFO films and electrodes are deposited by pulsed laser deposition (PLD).¹⁴ La_{0.7}Sr_{0.3}MnO₃ (LSMO) and Pt electrodes are used as bottom and top electrodes (Pt/BFO/LSMO/STO). Precision LC Ferroelectric tester (Radiant Technologies) is used for ferroelectric measurements. The piezoelectric force microscopy (PFM) and SKPM studies are conducted using a commercial atomic force microscope (AFM, Asylum Research MFP3D). The macroscopic photovoltaic properties of the films are obtained using a low-noise probe station and a pA meter/direct current (DC) voltage source (Hewlett Package 4140B) under the illumination of a halogen lamp (energy density ~20 mW/cm²) through the top electrodes. In this study, forward (reverse) bias is defined as a positive voltage applied to the bottom (top) electrode, and the polarization pointing from the bottom (top) electrode to the top (bottom) electrode is defined as upward (downward) polarization, abbreviated as P_{up} (P_{down}).

Fig. 1 shows the evolution of the topography and in-plane (IP) domain structure of BFO thin films on STO substrates with different miscut angles, which are taken with the

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FIG. 1. (a)–(d) Topography AFM images of as grown BFO films on STO substrates with different miscut angles along [110] direction. (e)–(h) The corresponding IP PFM images in the same areas as those in (a)–(d). The insets of (e)–(h) are schematic drawing of evolution of IP polarization variant selections by the substrates.

AFM cantilever pointing along the $[1-10]$ direction. Uniform yellow tone in the out-of-plane (OP) PFM images indicates that the polarization points upward in all as grown BFO films (Figs. 3(a) and 3(b)). For the BFO films grown on exact STO with no miscut, the corresponding topography is featured by a crisscross structure with the edges parallel to $[100]$ or $[010]$ direction, whereas the domain patterns are characterized by random combinations of all the four possible domain variants, as schematically shown in the inset of Fig. 1(h). Based on the OP and IP PFM images, nearly all the domain walls are identified as 71° domain walls (see supplementary material¹⁵ for details), which is similar to the previous report.¹⁶ When the miscut angle is 1° along $[110]$ direction, the surface topography shows no considerable anisotropy except for slightly increased roughness compared with the no miscut case. However, the polarization variant along the miscut direction is favored, whereas the two

variants perpendicular to it are suppressed and the variant against it is eliminated. As the miscut angle is increased to 2° , the surface topography of BFO films has a saw-tooth step pattern with the amount of the domain walls greatly reduced. Further increase in the miscut angle to 4° does not change the topography, and nearly monodomain structure can be observed in the films. From the above results, we can conclude that with increasing miscut angle of the substrate, the amount of domain walls gradually decreases.

The effect of substrate miscut on the ferroelectric properties of BFO films can be demonstrated by measuring polarization-electric field (P - E) hysteresis loop, as shown in Fig. 2(a). It is known that the macroscopic ferroelectric switching behavior is the collective effect of domain nucleation and domain wall motion, and the domain engineering by the miscut substrate should thus affect the ferroelectric switching behavior of BFO. For the nearly monodomain

FIG. 2. (a) P - E loops for all the samples using vertical Pt/BFO/LSMO/STO capacitor structure. (b) The switchable polarization (ΔP) as a function of applied electric field for all the samples.

BFO film on 4° miscut STO, an almost perfect square-like P - E loop is achieved, with a remanent polarization value of $\sim 60 \mu\text{C}/\text{cm}^2$, suggesting complete ferroelectric switching under external electric field. On the other hand, it has been shown that domain walls in BFO are more conductive than the domain bulks,^{17–19} and more domain walls mean larger effective conductivity of the films. As expected, the BFO films display more opened and slanted P - E loops with the decreasing miscut angle. Meanwhile, the coercive field also increases gradually with the decrease of substrate miscut angle, indicating that elastic domain walls may hinder the reversed domain growth.^{12,20} To further investigate the ferroelectric properties, positive-up-negative-down (PUND) measurements are conducted with pulse width of 50 μs (Fig. 2(b)). The switchable polarization (ΔP) values for all BFO films are nearly the same, indicating that full switching of the polarization can be achieved in all samples. The switching process of the BFO films on 4° STO substrate is very sharp, while those on STO substrates with smaller miscut angles shows more gradual transition, consistent with the P - E loops.

Now, let us discuss how domain structure, i.e., domain walls, affects the photovoltaic properties in vertical BFO

capacitors. SKPM is a useful technique to study the surface potential and space charge distribution in thin films.^{9,21} It has been demonstrated that the photogenerated carriers in BFO films can be separated by the internal field and accumulate at the surface of the film, which can thus be detected and analyzed using SKPM.⁹ In this scenario, the surface potential difference of BFO film between under light and in dark (defined as Δ_{SP}) reflects the photogenerated voltage across the film, which can be regarded as V_{oc} in vertical tip/BFO/LSMO structures. As compared with conventional current-voltage (I - V) measurement, SKPM study reveals the areal distribution of photovoltaic response across the film. Figs. 3(a) and 3(b) are OP PFM phase images with electrically written patterns of BFO films on 4° and 0° STO, respectively. We apply +9.9 V (−9.9 V) dc voltage on the AFM tip to switch the OP polarization to P_{down} (P_{up}). Here, the OP PFM images remain the same before and after illumination, and the polarization states can be stable for at least several weeks. The corresponding SKPM images are given in Figs. 3(c) and 3(d), which are taken two days after the electrical writing in order to reduce the effect of injected charges introduced by the writing process. The cross section profile is used to calculate Δ_{SP} . In Fig. 3(e), we summarize the Δ_{SP} in

FIG. 3. (a) and (b) OP PFM phase images with electrically written patterns of BFO films on (a) 4° and (b) 0° STO substrates. (c) and (d) Corresponding SKPM images (including both in dark and under light parts) in the same areas. (e) The surface potential difference between under light and in dark (Δ_{SP}) in different regions, for the all samples.

STO substrate miscut angle	4°	2°	1°	0°
As grown Δ_{SP} (V)	-0.063±0.006	-0.066±0.007	-0.063±0.007	-0.065±0.008
+9.9V Δ_{SP} (V)	0.089±0.010	0.086±0.008	0.081±0.010	0.089±0.008
-9.9V Δ_{SP} (V)	-0.064±0.008	-0.067±0.006	-0.062±0.006	-0.063±0.004

Δ_{SP} =Surface potential (light on) - Surface potential (light off)

FIG. 4. Photovoltaic responses of BFO films on STO substrates with different miscut angles. (a) The typical I - V curves under illumination for all samples. (b) The values of V_{oc} and I_{sc} as a function of STO substrate miscut angle.

three different regions, namely, as-grown, +9.9 V, and -9.9 V regions, for all samples. Following the report of Bhatnagar *et al.*,⁶ it is natural to expect that the Δ_{SP} value will decrease as the substrate miscut angle decreases, since domain walls may act as shunts. However, the Δ_{SP} values of our samples are nearly independent of substrate miscut angle. Furthermore, the Δ_{SP} values are the same in the two P_{up} regions (as grown and -9.9 V written regions), while slightly different Δ_{SP} values are observed for the P_{down} region. Besides SKPM measurement, we also tried using conductive AFM to reveal current distribution with or without illumination. Unfortunately, similar to the previous report,²² we do not have the resolution to separate domain wall conduction from the domain contribution.

Therefore, in order to investigate the photovoltaic properties more accurately, macroscopic photovoltaic measurements using vertical Pt/BFO/LSMO capacitors are performed. Fig. 4(a) shows the typical polarization dependent photovoltaic responses of the samples, and Fig. 4(b) shows the dependence of the V_{oc} and short-circuit photocurrent (I_{sc}) on the substrate miscut angle. Although the V_{oc} values are larger than those obtained by SKPM, which can be attributed to the different light sources in these two measurement systems, they are again nearly the same in all samples for P_{up} or P_{down} state. Furthermore, the I_{sc} value increases with decreasing miscut angle of the substrate, which can be ascribed to increase the conductivity of the BFO films. It is clear that in the vertical structure, the domain walls do not affect the photovoltage but are crucial to the photocurrent. It is accepted that the switchable photovoltaic effects in metal/BFO/metal thin film capacitors originate from the energy band bending at the metal/BFO interface, which can be modulated by the polarization charge.^{23,24} In the Pt/BFO/LSMO structures,

the photocarriers are generated in the film and separated by the energy band bending (i.e., built-in field) at the Pt/BFO interface to produce the photovoltage. Therefore, if the ferroelectric polarization does not change, V_{oc} should be a constant as shown in this study.

To understand how the domain walls affect the photocurrent in BFO films, we try to estimate the domain wall and domain photoconductivities in our samples. In the low field region (-0.15 V to +0.15 V, Fig. 4(a)) of the I - V curves under illumination, the capacitors show Ohmic-like behavior. Schematic illustration of the vertical device is shown in Fig. 5(a), with 71° domain walls tilting approximately 45° from the substrate surface. The equivalent circuit is shown in Fig. 5(b), and the effective photoconduction is given by

$$1/R = 1/R_D + 1/R_{DW}, \quad (1)$$

where R_D and R_{DW} are domain and domain wall resistances under illumination. We have $1/R_{DW} = \sigma_{ph} S_{DW}/L$, with σ_{ph} being the photoconductivity and S_{DW} being the cross sectional area of domain walls, so

$$1/R = 1/R_D + \sigma_{ph} S_{DW}/L. \quad (2)$$

Here, L is $d/\sin 45^\circ$ and d is the film thickness, 130 nm. Furthermore, we can obtain the domain wall density by outlining the domain walls in Figs. 1(e)–1(h), and S_{DW} can be calculated using a reasonable domain wall width of 2 nm.^{17,25} The photoconduction $1/R$ as a function of S_{DW}/L is given in Fig. 5(c) for both P_{up} and P_{down} cases. From Eq. (2), the slope of $1/R \sim S_{DW}/L$ represents photoconductivity of 71° domain walls, and the fitting leads to 2.5 nS/cm and 3.9 nS/cm for P_{up} and P_{down}, respectively. Note that this is a rough analysis, as the actual domain structures may be altered during

FIG. 5. (a) Schematic illustration of the vertical Pt/BFO/LSMO/STO structures. (b) A schematic drawing of equivalent circuit for the corresponding structure. (c) The fitting results of domain wall photoconductivity in BFO films for both P_{up} and P_{down}.

the polarization switching and the effect of built-in electric field possibly due to asymmetric electrodes, strain effects or growth conditions are not taken into consideration here, resulting in slight difference of the photoconductivities between P_{up} and P_{down} states. Besides, the estimated photoconductivities vary with respect to the domain wall width we choose. However, we can estimate that the photoconductivity of 71° domain walls in BFO films is of the order of 10^{-9} – 10^{-8} S/cm. Moreover, the photoconductivity of domains is about 10^{-11} – 10^{-10} S/cm, which can be estimated from the intercepts of the lines in Fig. 5(c) based on Eq. (2). It is clear that the photoconductivity of 71° domain walls is two orders of magnitude larger than that of domains in BFO films. The domain walls, with higher conductivities,^{4,17–19} act as conducting paths for photo-generated carriers and increase the I_{sc} value.

In summary, we have studied the domain structures, ferroelectric properties, and photovoltaic responses of BFO thin films on vicinal STO substrates with different miscut angles. The V_{oc} value remains constant regardless of the domain configurations, consistent with it being governed by the electrode/BiFeO₃ interface band bending. On the other hand, I_{sc} can be enhanced due to the contributions of conducting domain walls.

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