Interface and domain engineering for enhanced reliability in ferroelectric-based memory

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**INTERFACE AND DOMAIN ENGINEERING FOR
ENHANCED RELIABILITY IN FERROELECTRIC-
BASED MEMORY**

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School of Materials Science and Engineering

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Abstract

In a ferroelectric random access memory (FeRAM), the two logic states, “1” and “0”, are represented by the spontaneous polarization directions in the ferroelectric material, which can be altered by an external electric field. FeRAM has many advantages, such as high speed and excellent data retention, over magnetic hard disk drive and flash memory. However, one drawback of the conventional FeRAM is that the reading process may erase the stored information and a re-write step is needed. This is because the read-out in a conventional FeRAM is achieved by sending a voltage pulse larger than the coercive field to the memory cell and detecting the current. For the past decade, researchers have been exploring various concepts for non-destructive read-out of FeRAM. In 2013, we have demonstrated the feasibility to use the ferroelectric photovoltaic response as the read-out signal of FeRAM, as both the signs of open-circuit voltage (V_{oc}) and short-circuit photocurrent (I_{sc}) depend on the polarization direction in the ferroelectric layer. Such a photovoltaic effect-based FeRAM features a non-destructive reading process, giving rise to low energy consumption and increased lifetime of the memory. In this study, we further investigate the fundamentals of fatigue in ferroelectric materials and clarify the origin of switchable photovoltaic effect, aiming to improve the performance of the proposed novel FeRAM.

Polarization fatigue, i.e. the reduction of switchable polarization after repetitive electrical cycling, poses a serious problem for the performance and the lifetime of ferroelectric-based devices. The first part of this work is to study the mechanism of the polarization fatigue in a typical ferroelectric material, BiFeO₃. By using planar BiFeO₃-based capacitors, we have carried out *in-situ* study on the domain evolution and space charge redistribution in the ferroelectric layer during fatigue measurements. It is found out that charge injection/accumulation at the electrode/film interface is responsible for domain pinning and the macroscopic polarization fatigue in BiFeO₃ films. Furthermore, the Schottky barrier at the electrode/BiFeO₃ interface is likely to play a crucial role in the charge injection/accumulation process by deep-trapping the injected electrons under the

localized high electric field. Lowering the barrier height, with either oxides or low work function metals as the electrodes, effectively suppresses or even eliminates the electron accumulation due to the high detrapping rate, and thus improves the fatigue performances of the device. The systematic study on vertical BiFeO_3 -based capacitors using different top electrodes further supports the Schottky barrier-controlled charge accumulation model for polarization fatigue.

With the mechanism of polarization fatigue clarified, we move on to improving the ferroelectric photovoltaic response in BFO systems. Through controlling the interface conditions, we have studied the origin of the switchable ferroelectric photovoltaic effects in BFO heterostructures and both effects from bulk depolarization field and interface have been explored. In vertical $\text{Pt/BiFeO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ capacitors, the polarization modulated built-in field at the Pt/BiFeO_3 interface plays the dominating role in separating the photo-excited carries and producing photovoltages, whereas the contribution from bulk depolarization field proves to be relatively small. After clarifying the origin, we have also investigated the photovoltaic property of domain engineered epitaxial BiFeO_3 films. Consistent with the photovoltaic effects being driven by the built-in field at the Pt/BiFeO_3 interface, the domain structures in BiFeO_3 films do not affect the V_{oc} values in the vertical heterostructures. However, the improvements of I_{sc} can be achieved by increasing the domain wall density, which is attributed to the larger photoconductivity of the domain walls. In addition, preliminary results on the enhancements of the photovoltaic responses by chemical substitution have also been obtained, though the mechanism is still unclear.

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List of Abbreviations

AFM	atomic force microscopy
BFO	BiFeO_3
E_{bi}	built-in field
E_{c}	coercive field E_{c}
FeRAM	ferroelectric random access memory
IP	in-plane
I_{sc}	short-circuit current
ITO	indium tin oxide
LSMO	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$
OP	out-of-plane
P_{r}	remanent polarization
P_{down}	downward polarization
PFM	Piezoelectric force microscopy
PLD	pulsed laser deposition
PUND	positive-up-negative-down
P_{up}	upward polarization
SCLC	space charge limited current
SKPM	scanning Kelvin probe microscopy
SRO	SrRuO_3
STO	SrTiO_3
TEM	transmission electron microscopy
XRD	x-ray diffraction
UV	ultraviolet
V_{oc}	open-circuit voltage
XPS	X-ray photoelectron spectroscopy
ε_{r}	dielectric constants
ΔP	switchable polarization

Δ_{SP}

surface potential difference

Chapter 1 Introduction

1.1 Ferroelectric Materials and BiFeO₃

1.1.1 Introduction to Ferroelectric Materials

Ferroelectric materials possess a spontaneous polarization that can be changed from one direction to another by an external electric field.[1] They are usually normal dielectrics at a high temperature and transform to ferroelectrics when cooled to below a critical temperature.[2] This transition temperature is called the Curie temperature (T_c). Most of the widely studied ferroelectric materials have a perovskite structure whose chemical formula is ABO_3 . A and B are different cations whose valences can be widely ranged (i.e., $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$). Typically, the radius of A is larger than that of B.

In the perovskite structure, A-site cations are located at the eight corners, oxygen anions at the face centered positions, and B-site cation at the body center of the cell.[3] For ferroelectrics, at T_c , the cubic structure is distorted to tetragonal, orthorhombic or rhombohedral with the cations and oxygen anions slightly shifted in opposite directions, resulting in a spontaneous electric dipole moment. The transition from paraelectric to ferroelectric phase often leads to dramatic changes in the properties of the material, including the dielectric, elastic, thermal and other properties.[2]

Generally, the spontaneous polarization is not homogeneously oriented throughout the whole sample. Instead, multiple ferroelectric domains, each of which contains uniform polarization direction, form to minimize the electrostatic energy and/or to reduce the

elastic energy induced by mechanical stresses. The boundaries separating adjacent ferroelectric domains are defined as ferroelectric domain walls. The symmetry of the phases, in both paraelectric (above Curie temperature) and ferroelectric (below Curie temperature) states, determines the types and distributions of domain walls.[4] Ferroelectric domain walls have distinguishing features because of their different symmetry from the domains. Over the past few years, there have been a large number of reports focusing on the unique properties of ferroelectric domain walls and their potential applications.[5-13]

With the application of an electric field to the ferroelectric materials, the spontaneous polarization within each individual domain tends to be reoriented in favor of this external field. Initially, the directions of spontaneous polarization within individual domains throughout the whole ferroelectrics are different, and thus the overall net polarization is nearly zero. Under external electric field, however, a polar state with nonzero net polarization is achieved, owing to the reorientation of the ferroelectric domains. The interesting property of ferroelectrics is that polarization remains nonzero after external electric field is removed, though a certain number of domains will still switch back to original orientation.

One of the most important features of ferroelectric materials is the ferroelectric hysteresis loop (polarization-electric field loop, or P - E loop) as a consequence of polarization switching by an external electric field, [2, 14] as schematically shown in Figure 1-1. At the initial stage (point A), the as-prepared ferroelectrics possess an overall zero net polarization. After external electric field is applied, the polarization of each domain tends

to be reoriented along the direction of the electric field, and the polarization value increases with the field (period BC). Saturated polarization is reached if the electric field is further increased and all the domains are aligned (point D). If the electric field starts to decrease from its maximum, some domains will switch back. When the electric field decreases to zero, however, a certain number of domains still stay in the direction of the field and this gives rise to a nonzero polarization (point E). The polarization value at this stage is called remanent polarization (P_r). Reversed field is required to reach a zero polarization again (point F), and the value of the electric field needed is called coercive field (E_c). Further increase of the negative electric field will lead to an opposite alignment and saturation (point G) of the polarization. When the negative field is reduced to zero, a cycle of the polarization-electric field curve will be completed, giving rise to the ferroelectric hysteresis loop. In good ferroelectric samples, the values of P_r and E_c are intrinsic properties and thus unaffected by the history of the external electric field.

Figure 1-1. Typical ferroelectric hysteresis loop (polarization-electric field, or P - E loop) and the alignment of polarization orientation at each stage. Adapted from Ref [2].

1.1.2 Polarization Switching and Domain Structures in BiFeO_3

Our research throughout this study focuses on one particular ferroelectric material, BiFeO_3 (BFO). Over the past decade, no other single ferroelectric material has attracted more attention than BFO.[15-17] The Curie temperature of BFO is far above room temperature, which is around 1100 K, meaning that the ferroelectric state is stable even at a raised temperature. Along the $[111]_{\text{pc}}$ (here the subscript pc refers to pseudocubic) direction, Bi^{3+} and Fe^{3+} cations can be displaced from their centrosymmetric positions, resulting in a polar distortion.[18] The resulted spontaneous polarization along $[111]$ direction is as large as $\sim 100 \mu\text{C}/\text{cm}^2$. Eight different directions of spontaneous polarization are possible in BFO, shown as $P_i^\pm$ ($i=1, 2, 3$ and 4) in Figure 1-2.

The ferroelectric domain walls are defined by the angle between the polarization vectors of the two adjacent domains that are separated by the wall. By this way, there exist three types of domain walls in BFO, namely 71° wall ($P_i^\pm/P_{i\pm 2}^\mp$ and $P_i^\pm/P_{i\pm 1}^\pm$), 109° wall ($P_i^\pm/P_{i\pm 1}^\mp$ and $P_i^\pm/P_{i\pm 2}^\pm$) and 180° wall ($P_i^\pm/P_i^\mp$), as indicated in Figure 1-2. Similarly, under external electric field, three different kinds of polarization switching (i.e. 71° , 109° and 180° switching) can take place.[19]

Piezoelectric force microscopy (PFM) technique is useful to detect the ferroelectric domains, which is based on the atomic force microscopy (AFM) setup. We will introduce the working principle of this technique in following chapter. During the scanning, probe cantilever is placed along the face diagonal of the pseudocubic BFO unit cell. Both in-plane (IP) and out-of-plane (OP) PFM images are needed to efficiently detect and identify all the eight possible orientations of spontaneous polarization. The color code of our PFM images (both IP and OP) and the types of domain walls in BFO samples are schematically drawn in Figure 1-2.

Figure 1-2. Schematic of the polarization directions in BFO and color code of our PFM setup. (a) and (b) show the PFM imaging of IP and OP working mode, respectively.

1.2 Polarization Fatigue in Ferroelectric Materials

1.2.1 Introduction to Ferroelectric Random Access Memory

Compared to traditional non-volatile memories such as hard disk drive and flash memory, ferroelectric random access memory (FeRAM) has its own advantages in speed and energy saving.[20] In an FeRAM, the two logic states, “1” and “0”, correspond to the polarization up and down states in ferroelectric materials.[21] Figure 1-3 is the structure of typical 1 transistor-1 capacitor (1T-1C) and 1 transistor (1T) FeRAM cells. During the write process, an electric field higher than E_c is applied to the ferroelectric capacitor to bring the polarization to a known direction, either up or down, to represent one of logic states. The read process requires an electric field higher than E_c as well. If the directions of the polarization in the ferroelectrics and the external electric field are the same, a low nonswitching current is expected. If the polarization is opposite to the applied field, a higher nonlinear current will be generated due to the contribution of polarization

switching. 1T based FeRAM benefits from its simpler structure and larger cell density.[22] However, the data retention time is the major problem that limits its potential commercialization.

Figure 1-3. Schematic drawing of FeRAM cells based on (a) 1T-1C and (b) 1T.

1.2.2 Mechanisms of Polarization Fatigue

Endurance, i.e. the write/read cycles a memory cell can withhold before failure or breakdown takes place, is one of the most important parameters for the performance of a memory. In ferroelectric materials, after a certain number of repetitive electric cycling, some parts of the domains will be pinned and cannot respond to external field. Macroscopically, the remanent polarization, or the switchable polarization reduces gradually. The reduction of switchable polarization is defined as polarization fatigue in ferroelectrics. Figure 1-4 shows the typical behavior of polarization fatigue in BFO. It is obvious that polarization fatigue in the ferroelectric layer is detrimental to the performance and the lifetime of ferroelectric-based devices, including FeRAM. To suppress or even eliminate polarization fatigue, the fundamental mechanism should be

studied thoroughly. [23-25]. To date, the mechanism of the polarization fatigue is still under debate and different models have been proposed.

Figure 1-4. Typical polarization fatigue in ferroelectric materials. (a) P - E loops before and after repetitive electrical cycling. (b) Switchable polarization as a function of number of electrical cycles.

1.2.2.1 Defects Redistribution Mechanism

Oxygen vacancies are the most common and relatively mobile defects in perovskite ferroelectric materials and the defects redistribution mechanism is the most widely adopted model to explain the fatigue behavior in ferroelectrics.[26-29] It was suggested by Scott *et al.* that, upon repetitive electrical cycling, oxygen vacancies are arranged into two dimensional planes and cause domain pinning and give rise to macroscopic polarization fatigue.[26] Theoretical calculations also indicated that the development of charged domain walls would efficiently reduce the electrostatic energy of isolated charged defects (i.e. oxygen vacancies) as shown in Figure 1-5.[30] During the electrical cycling of fatigue measurements, the clusters of charged defects lead to domain pinning around them. Based on this mechanism, the improvement of fatigue performance by

donor doping in ferroelectric materials[31] can be attributed to the reduction of oxygen vacancy concentration. However, if the oxygen vacancy redistribution is indeed the origin of polarization fatigue, the fatigue performance should be monotonically dependent on the partial oxygen pressure, which is not consistent with some of the experimental results.[32] Moreover, temperature dependent activation energy of the fatigue endurance is far smaller than that of the mobility of oxygen vacancies,[33] which is also inconsistent with the defects redistribution mechanism.

Figure 1-5. The energy of charged defects (i.e. oxygen vacancies). The electrostatic energy of isolated oxygen vacancies is reduced by formation of charged domain walls. Adapted from Ref [30].

1.2.2.2 Charge Injection Mechanism

Another proposed mechanism of polarization fatigue is the charge injection model.[34-36] It is suggested that high energy electrons can be injected from electrode to the semiconductor thin film by high electric field created at the interface and these injected charges have the capacity to strike the ions in the thin film to generate charged defects.

Thus domain pinning will be formed and stabilized by the charged defects, finally giving rise to macroscopic polarization fatigue. Charge injection fatigue model was proposed by Mihara *et al.* [34] and then supported by Du *et al.* [37] through improving the fatigue performance in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ film with an inserted SiO_2 layer between $\text{Pb}(\text{Zr,Ti})\text{O}_3$ film and Pt electrode, which supposedly hinders the charge injection at the film/electrode interface. Theoretical calculations by Tagantsev also supported charge injection fatigue model.[36] As illustrated in Figure 1-6, the injected charges at the dielectric/ferroelectric interface are set as σ . Because of a spatial variation of polarization, negative bound charges and positive free charges emerge (Figure 2-7b), forming a plane capacitor. The size effect of switching and small signal permittivity and their links with enhanced fatigue property can also be explained by charge injection fatigue model. [35, 36]

Figure 1-6. The model used to describe effects of charge injection on polarization switching of a ferroelectric device. (a) Sandwich structure used for modeling, consisting of a ferroelectric layer with a thickness of L and a dielectric layer with a thickness of d and dielectric constant of ϵ_d . Gray regions represent electrodes. (b) A nearby-electrode variation of polarization where x is the distance to electrode. Adapted from Ref [36].

1.2.2.3 Local Phase Decomposition Mechanism

More recently, Lou *et al.* observed local phase decomposition in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films during electrical bipolar switching, where the original perovskite phase transformed to a pyrochlorelike structure.[38] The pyrochlorelike phase can be changed to the original perovskite structure by annealing, accompanied by the rejuvenation of the fatigued $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films. In order to explain their experimental results, a switching-induced charge injection fatigue mechanism is proposed, in which charge injections initially

occurred at the film/electrode interface and then local phase decomposition further caused the polarization fatigue in ferroelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films. Figure 1-7 shows the very early stage of electrical switching. When the first half of ac field is applied, the unscreened bound charges at the tip of the needle like domain and the screened charges near the film/electrode interface give rise to huge electric field, which is high enough to generate extremely high leakage current induced by charge injections and thus cause local phase decomposition near the nucleation sites. Both the parallel-device structure formed by pyrochlorelike structure and the reduction of available nucleation sites are possible to cause polarization fatigue, i.e. harder polarization switching in ferroelectrics.

Figure 1-7. Schematic of the very early stage of electrical switching. An extremely high electric field is generated due to the unscreened bound charges at the tip of the needle like domain and the screened charges near the film/electrode interface. Adapted from Ref [38].

1.3 Switchable Ferroelectric Photovoltaic Effects in BiFeO₃

1.3.1 Introduction to Ferroelectric Photovoltaic Effects in BiFeO₃

BFO has a direct bandgap of ~ 2.7 eV, which is within the visible light range. Photovoltaic effect in epitaxial BFO heterostructures has attracted considerable interest due to its potential applications in the solar energy conversion and optoelectronic devices.[39-43] Our recent study has demonstrated the feasibility of ferroelectric photovoltaic effect based non-volatile memory using BFO capacitors.[44] In this device, the read-out signals are the polarization direction dependent signs of open-circuit voltage (V_{oc}) or short-circuit current (I_{sc}). The advantages of this concept include high operating speed (less than 10 ns for write), lower power consumption (with write voltage ~ 3 V) and excellent fatigue performance (the prototype device can withstand more than 10^8 write cycles). One significant advantage of such photovoltaic effect-based FeRAM over conventional FeRAM is that the reading process is nondestructive and no rewrite process is necessary, leading to lowered energy consumption and enhanced lifetime.

In traditional pn junction based photovoltaic cells, light absorption induces electron-hole pairs, which then are separated by the internal field within the micrometer-thick depletion layer.[45, 46] In such cases, the largest V_{oc} is limited to be the band gap of the specific semiconductor. In BFO thin films, however, a fundamentally different mechanism is expected. Despite that a large number of reports have focused on the photovoltaic effect in BFO capacitors,[39-43] the underlying origin of the switchable ferroelectric photovoltaic response in BFO is still under debate. Both bulk (i.e. bulk depolarization

field or structural asymmetry)[47-50] and interface effects (i.e. polarization induced energy band bending at electrode/BFO interface)[40, 51-53] have been proposed.

1.3.1.1 Bulk Effects

The bulk photovoltaic effect can be dated to the 1950s,[54] and there have been plenty of reports on this effect in ferroelectric materials such as BaTiO₃[55-57] and LiNbO₃. [58-60] It is suggested that the photo-excited carriers are separated throughout the whole volume of the ferroelectrics. After photovoltaic effect of BFO was first reported in 2009,[39] some researchers have tried to explain its origin using bulk effects. The complication of bulk effects implies that different mechanisms may be taken into consideration. Specifically, both bulk depolarization field and structural asymmetry can play important roles in the origin of bulk photovoltaic effect in BFO.

Ji *et al.* investigated the photovoltaic effect in BFO thin films using SrRuO₃ (SRO) and indium tin oxide (ITO) as electrodes.[47] They separated the substantial V_{oc} into non-switchable and switchable parts, where the value of the latter is around twice as large as that of the former. The internal field (labeled as E_{bi} in Figure 1-8), arising from impurities in BFO films, was proposed to be responsible for the non-switchable V_{oc} . On the other hand, since the effects of the Schottky barriers at the two electrode/BFO interfaces cancel each other, they attributed the photovoltaic effect to bulk depolarization field, which can be interpreted as the tilted band in the bulk region in Figure 1-8, that helps separate the photo-generated carriers and leads to switchable photovoltage. The same group later reported photovoltaic effect perpendicular to polarization direction (i.e. [111] direction), which excluded the photovoltaic origin from depolarization field as well as interface band

bending, and therefore supported the structural asymmetry induced bulk photovoltaic effect.

Figure 1-8. Energy band diagram of SRO/BFO/ITO capacitors. The unflat band in the bulk BFO region (depolarization field) is responsible for photo-carriers separation and photovoltaic effect. Adapted from Ref [47].

1.3.1.2 Interface Effects

The energy band bending at the electrode/BFO interface is another widely adopted mechanism to explain the switchable photovoltaic effect in BFO heterostructures. Though many factors, such as Schottky barrier and non-uniformly distribution of defects, might exist when considering the ferroelectric/electrode interfaces, the basic picture of this mechanism was well described by Yuan and Wang.[53] Owing to the incomplete screening of the polarization charge, a depletion layer might form at the electrode/BFO interface, in which a gradient of charges (opposite to polarization bound charges) exists within the ferroelectric material. As a result, we can expect an energy band bending at the interface and a built-in field in it, which is responsible for the diode behavior from

current-electric field (I - E) curves in Figure 1-9. Under illumination, the built-in field assists the separation of photo-generated carriers (both electrons and holes), resulting in open-circuit photovoltage. Note that for the interface effect, the energy band is bent only at the interface but remains flat in the bulk region. In other words, the driving force of separating photo-excited carriers is the built-in field that solely exists at the interface. If surface bound charge changes after polarization switching, the built-in electric field should reverse and both V_{oc} and I_{sc} would change their signs.

Figure 1-9. The role of energy band bending at the electrode/BFO interface in switchable ferroelectric photovoltaic effect. Adapted from Ref [53].

1.3.2 Domain Engineering in Ferroelectric Photovoltaic Effects

Recent studies have demonstrated that certain types of domain walls in BFO can conduct whilst the domain themselves remain insulating.[6, 61, 62] This has led to the idea that the ferroelectric switching behavior and leakage issue can be improved by domain

engineering. Meanwhile, it has been demonstrated that the photovoltaic property of BFO films can also be tuned by controlling the ferroelectric domain configuration.[50, 63] For example, Yang *et al.* observed that in the BFO films with 71 ° stripe domains and lateral electrode configuration, the V_{oc} value increases linearly with the total number of domain walls along the net polarization direction (perpendicular to the domain walls).[63] However, if the domain walls of BFO are perpendicular to the electrodes, there is no sizable photovoltaic effect at room temperature, but only a photoconductive effect can be detected. The authors proposed that the effect might arise from the structurally driven electrostatic potential steps at the nanometer-scale domain walls. As indicated in Figure 1-10, the periodic band structure in the whole sample results in a zero net electric field in the dark, and thus there is no net voltage (Figure 1-10b). Under illumination, however, a high local field is created by the built-in potential at the walls, which was supported by *ab initio* calculations and therefore, a small photovoltage is achieved at each domain wall. Moreover, the schematic band diagram in Figure 1-10c demonstrates a structure equivalent to a series circuit, meaning that the net voltage is proportional to the number of domain walls given that the domain walls are parallel to the electrodes. As a consequence, an abnormally large photovoltage, which can be even larger than the bandgap of BFO, can be obtained with enough number of domain walls between the two electrodes. Our previous work also found the similar switchable photovoltaic phenomena in the BFO films with 109 ° domain walls, though the output is much smaller.[64]

Figure 1-10. The mechanism of above-bandgap photovoltages in BFO films with striped 71 ° domain walls. (a) Polarization directions in 71 ° stripe domain walls. (b,c) The band structure in the dark (b) and under illumination (c). (d) The details of the separations of photo-carriers at the domain walls under illumination. Adapted from Ref [63].

More recently, Bhatnagar *et al.* observed the above-bandgap V_{oc} scaled up roughly exponentially with decreasing temperature irrespective of the domain wall geometry and the type of domain wall.[50] They pointed out that the domain walls are having a rather different role. The bulk photovoltaic effect was used to explain the results, and in bulk photovoltaic effect, the V_{oc} value is given by

$$V_{oc} = J_{ph} \left(\frac{1}{\sigma_d + \sigma_{ph}} \right) L \quad 1-1$$

where J_{ph} is the photocurrent density, σ_d and σ_{ph} are conductivities in the dark and under light and L is the channel width of the planar device. In the parallel structure (Figure 1-11a,c), it can be treated as series circuit with separated domains and domain walls. And the effective resistance of the device is the sum of all the domain and domain wall resistances. Therefore, a large V_{oc} is expected due to the low effective conductivity, based

on Equation 2-1. On the other hand, in the perpendicular geometry case (Figure 1-11b,d) and at room temperature, the domain walls are acting rather as shunts due to their intrinsically higher conductivity, and the V_{oc} values are thus low.

Figure 1-11. The schematic drawings of planar devices and the equivalent circuits of BFO thin films with stripe domain walls, for both parallel and perpendicular geometries. Adapted from Ref [50].

1.4 Objectives of Research

To enhance the reliability of ferroelectric-based non-volatile memories, including conventional FeRAM and the novel photovoltaic effect-based FeRAM, the purpose of this work is to investigate the mechanisms of polarization fatigue and switchable ferroelectric photovoltaic responses. One typical ferroelectric material, BFO, is chosen for the study. The main objectives include:

1. *To clarify the exact mechanism of the polarization fatigue in BFO.* There has been continuous debate on the roles of oxygen vacancy redistribution and electron injection, which is partially because that direct observation of domain evolution and

charge activities is prohibited in the conventional vertical sandwich structures. This forms the initial motivation of the first part of our study. In this study, we use the planar BFO-based capacitors and carry out the *in-situ* PFM and scanning Kelvin probe microscopy (SKPM) studies during fatigue measurements. By direct observations of the domain structure and charge distribution in ferroelectrics during fatigue measurements, we can clarify the mechanism of polarization fatigue. More importantly, improvements of fatigue performance can then be achieved by reducing the factors causing fatigue in the BFO-based devices.

2. *To investigate the mechanism of switchable ferroelectric photovoltaic effect.* Even though we proposed the photovoltaic effect-based FeRAM concept, we have noted that the read-out signals, especially the values of I_{sc} , are far smaller than that required for commercialized devices. Therefore, enhancing the ferroelectric photovoltaic effects is highly desirable, which makes it necessary to fully understand the underlying origin of the switchable photovoltaic responses in ferroelectric heterostructures. In this study, both the effects of bulk depolarization and interface will be investigated, by carefully controlling the interfaces in BFO based heterostructures.
3. *To enhance the switchable ferroelectric photovoltaic effect.* After clarifying the origin of photovoltaic effect in ferroelectric heterostructures, we will turn to the routes towards enhancing such effect. Since the ferroelectric domain configuration has been demonstrated to affect photovoltaic property of BFO films, we will try to improve the

photovoltaic response via domain engineering. Moreover, we note that in all the previous reports, only BFO films with lateral device configuration have been studied. None of earlier studies can give insight to if and how domain walls contribute to the photovoltaic effect in vertical capacitor geometry, which is more suitable for actual applications. In this study, we will investigate the influence of domain walls on the ferroelectric and photovoltaic properties of BFO in vertical capacitor geometry.

Chapter 2 Device Preparation and Characterization

2.1 Pulsed Laser Deposition (PLD)

All the films and electrodes used in this study were deposited using pulsed laser deposition (PLD). PLD is a widely used technique where high power pulsed laser beam is focused on the target of the desire material and vaporize the material.[65, 66] A typical PLD system is equipped with a vacuum chamber that is connected to gauges, controllers and other implements to control the growth environment.[1] Figure 2-1 shows the schematic of a PLD system. Thin film deposition is carried out inside the vacuum chamber where a target holder and rotator and substrate heater are equipped. During the deposition, laser beam is focused by the lens to make sure that energy density at the surface of material is high enough. A plume consisting of energetic atoms, molecules, electrons, ions and clusters is created upon laser ablation and then expands normal to the target surface towards the substrate. To obtain high quality films, the optimization of various parameters, such as laser energy and repetition rate, substrate temperature, oxygen partial pressure and appropriate substrates, is required.

Figure 2-1. Schematic of a PLD system. The inset shows the real-time image of the plume. Adapted from Ref [1].

2.2 Photolithography and Electrode Deposition

Standard photolithography and lift-off process was used to obtain patterned electrodes on the films. We take photolithography using positive photoresist as an example to demonstrate the basic principle and process (Figure 2-2). Thin films or substrates are firstly heated to drive off water layer on the surface. Buffer layer and positive photoresist is then spin-coated with uniform thickness on the sample. Before exposure to ultraviolet (UV) light, pre-baking is required to remove remanent photoresist solvent. The samples with buffer layer and photoresist are then covered by patterned photomask, followed by exposure to UV light for several seconds. The regions exposed to UV light will become reactive and can be dissolved by a special chemical, called the “developer”, whereas other areas remain nonreactive to the developer. PLD is used to deposit metal electrodes

on the samples with patterned photoresist. Electrodes with desired pattern are finally created on the samples after removing the nonreactive regions of the photoresist. Negative photoresist differs from the positive in a way that the exposed regions remain nonreactive and other parts are soluble in developer.

Figure 2-2. Simple schematic of photolithography process and electrode preparation.

2.3 Atomic Force Microscopy (AFM)-based Characterization

Techniques

AFM is a useful technique to image the specimen surface with high resolution on the order of nanometers.[67, 68] The schematic diagram of an AFM system is given in Figure 2-3. A cantilever with an extremely sharp tip at the end is used to scan the surface.

When the probe tip is brought closely to the surface, the force between the probe tip and the specimen surface will cause the deflection of the cantilever, which will be measured by a laser spot reflected from the cantilever onto a photodiode. In order to achieve a constant deflection, a feedback system is used to adjust the distance between the tip and the sample to maintain a constant tip-sample force. In such way, the recorded movement of the probe tip follows and reflects the surface morphology. There are three modes of operation for an AFM, namely contact mode, non-contact mode and tapping mode. In contact mode, the probe tip directly contacts the specimen surface and the feedback system adjusts the height of the tip according to the sample surface morphology to maintain a fixed deflection. In non-contact mode, on the other hand, the tip does not contact the sample surface. Instead, the cantilever oscillates near its resonant frequency and long range force, e.g. Van der Waals force, causes the change of the amplitude and frequency of cantilever oscillation, which acts as the feedback source. Tapping mode is also called AC mode or intermittent contact mode, which operates similarly to non-contact mode but differs in a way that the short-range forces such as dipole-dipole interactions and electrostatic forces cause the variation of the amplitude or frequency of cantilever oscillation due to the intermittent tip-sample surface contacts.

Figure 2-3. The simple schematic diagram of the basic set-up of AFM.

PFM[69] is an effective technique to study the domain structure in ferroelectric materials, working under the contact mode of AFM. With applied voltage, ferroelectric sample vibrates at the same frequency (ω) of the ac bias, with a phase delay φ .

$$D = D_{\omega} \cos(\omega t + \varphi) \quad 2-1$$

where D_{ω} is the amplitude of the ac voltage induced displacement. Two different types of PFM imaging, i.e. vertical and lateral PFM, are used to detect the OP and IP polarization components. The vertical PFM imaging makes use of the vertical deformation of the ferroelectric materials under electric field, which is related to d_{33} coefficient. As indicated in Figure 2-4a,b, the ferroelectric material will expand vertically if the applied electric field and the spontaneous polarization are in the same direction, and no phase delay occurs ($\varphi=0$). On the other hand, if these two are antiparallel to each other, vertical depression occurs and 180 °phase delay is to be detected. The shear coefficient, d_{15} , leads

to the lateral displacement, i.e. torsion, of the ferroelectric materials under electric field, which can be used to identify the IP component of the polarization, as shown in Figure 2-4c,d.

Figure 2-4. The working principles of PFM. (a-b) Vertical PFM: d_{33} coefficient dictates the vertical deformation of the ferroelectric material under applied electric field. (c-d) Lateral PFM: shear coefficient d_{15} determines the torsion of the ferroelectric material.

SKPM[70, 71] is another useful technique based on AFM, which acquires the contact potential difference (CPD) between the AFM tip and the sample surface. It is a dual pass method. In the first pass, the topography of the surface is obtained. During the second pass, the sample-tip distance is maintained as a constant, and voltage containing ac and dc components is applied to the tip. The electrostatic force, proportional to the tip-sample CPD, drives the cantilever to oscillate at the same frequency as the ac bias. The dc voltage is adjusted to zero the oscillation, which is, in turn, recorded to measure the CPD at the point. All nulling dc values obtained during the scanning are used to construct the CPD map. Since the CPD corresponds to the work function difference between the tip

and the sample, the scanned image reflects the distribution of the work function of the sample. More importantly, owing to the fact that space charge in the sample affects CPD value, the SKPM image can also represent the space charge distribution in the samples if any.

Chapter 3 Role of Schottky Barrier in Polarization Fatigue in BiFeO₃

In this chapter, I summarize our investigations on the mechanism of polarization fatigue in ferroelectrics using a planar capacitor, where direct observations of domain evolution and space charge distribution are obtained through *in-situ* PFM and SKPM scanning during fatigue measurements. Conventional vertical capacitors are also fabricated and their fatigue performances tested, to further support the fatigue model proposed based on our study of the planar devices. Our objectives are:

1. To clarify the origin of polarization fatigue in BFO thin film and the factors that control the process.

BFO is an exceptional material for the study of polarization fatigue since it has a large remanent polarization along [111] direction, giving rise to both large IP and OP components for a (001) oriented film, which allows us to fabricate both planar and vertical structures to investigate the polarization fatigue in BFO films. Our previous study[72] has confirmed the charge injection mechanism for polarization fatigue in BFO. However, the factors that affect the charge injection process are still unclear, which we will try to clarify in this work.

2. To improve the fatigue performance of BFO-based heterostructures.

Oxide electrode has been known to improve the fatigue performance dramatically. It was initially suggested that such improvement arises from the suppression of oxygen

vacancies.[73] However, since we have established that charge injection is the main cause of fatigue in BFO, this effect needs to be revisited. Our hypothesis is that the energy band bending at the electrode/ferroelectric interface is crucial, which suggests that Schottky barrier or Ohmic contact at the interface would lead to different fatigue performance. We will investigate this issue by replacing the traditional noble metal electrodes by oxides or low work function metals, and conduct fatigue measurement.

3.1 Introduction

Much work has been done to improve the fatigue performance in BFO.[74-77] The mechanism of the polarization fatigue in BFO, however, remains unclear until recently. In our previous study,[72] we demonstrated that charge injection, instead of defects (oxygen vacancies) redistribution, is the cause of domain pinning and macroscopic polarization fatigue in BFO thin films. The systematic PFM and SKPM studies were carried out to investigate the evolution of domain structures and charge distribution at different electrical cycling stages. We took advantage of the IP component of polarization in BFO (the spontaneous polarization is along [111] direction, as shown in Figure 1-2) and fabricated planar Pt/BFO/Pt capacitors. In such planar structures, it is possible to perform the microscopic scanning during fatigue measurements, since the surface of BFO film is located between, rather than beneath, the two contact electrodes.

Figure 3-1 summarizes the evolution of domain structures and simultaneously the redistribution of space charges in the planar Pt/BFO/Pt capacitor after electrical cycling. It was observed that domain pinning occurred at 10^{10} cycles for a planar capacitor with channel width of about 10 μm , accompanied by the accumulation of negative charges

(dark regions in the SKPM images) along the Pt/BFO interfaces, which made the device more conductive than the as-grown state. When the injected charges and pinned domains continuously migrate into the film and across the whole channel, after $\sim 6.7 \times 10^{10}$ cycles, reduced switchable polarization was observed and macroscopic fatigue took place. Therefore, we concluded that electrons are injected from the Pt electrode to the BFO films and cause the domain pinning and consequent polarization fatigue.

Figure 3-1. IP-PFM and SKPM images of planar Pt/BFO/Pt device after (a-c) 0, (b-e) 10^{10} and (g-i) 6.7×10^{10} switching cycles. The pinned domains are outlined in (d,e,g,h). Adapted from Ref [72]. (i) Macroscopic fatigue is observed after 6.7×10^{10} switching cycles, and large dark regions in SKPM image, indicating negative charges, are clearly observed in the channel.

Oxide electrodes are well known to improve fatigue performance of ferroelectrics.[73, 78, 79] As reported by Ramesh *et al.*, when Pt was replaced by $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as top electrode, the fatigue performance of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ film was dramatically enhanced.[73] The

suggested mechanism was that the concentration of oxygen vacancies is lowered at the electrode/film interface when oxide electrode is used, resulting in less domain pinning. However, this would not be the case if charge injection is causing fatigue in BFO.[72] In this section, we try to clarify how oxide electrode controls the charge injection process and improves the fatigue performance in BFO thin films. The significant role of Schottky barrier in charge injection process is proposed.

To understand how the charge injection process is affected by the type of contact electrodes, we have investigated different kinds of electrodes, including oxide ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, or LSMO), low work function metals (e.g. Fe and Ta) and high work function metals (e.g. Pt and Au), and studied the fatigue performances of the corresponding capacitors, including both planar and conventional vertical ones.

3.2 Experimental Procedure

We prepared planar BFO-based capacitors using three different electrodes, i.e. Pt, LSMO and Fe. (001) oriented SrTiO_3 (STO) single crystal substrate was used. To optimize the topography and domain structures of BFO thin films, we grew BFO films at 650 °C and under oxygen pressure of 100 mTorr. The laser energy density was $\sim 1 \text{ J/cm}^2$ and the repetition rate was 5 Hz, resulting in a deposition rate of $\sim 1 \text{ nm/min}$. BFO thin films with thickness of $\sim 40 \text{ nm}$ were used for the study. For the LSMO/BFO/LSMO capacitors, as the deposition temperature for high quality LSMO was 800 °C, and in order to protect the BFO film from decomposing at such a high temperature, we deposited LSMO first on STO substrate and then BFO was grown on the patterned LSMO electrodes. Note that the fatigue results of the capacitors with Pt electrodes on top and embedded are the same,

which excludes the device architecture as the cause of the different fatigue performances in planar BFO devices using the LSMO and metal electrodes.

The conventional vertical BFO-based devices were also fabricated and their fatigue performances tested. In the vertical structures, bottom LSMO electrodes were grown on (001) oriented STO substrate at 800 °C with oxygen pressure of 200 mTorr. And the following BFO films were deposited at 675 °C and under 50 mTorr oxygen pressure. To reduce the leakage current, we tried to deposit relatively thick BFO and simultaneously use small top electrodes. The thickness of BFO was about 100 nm and the areas of the top electrodes were 100 μm^2 .

Precision LC Ferroelectric tester (Radiant Technologies) is used to carry out *P-E* and fatigue measurements. During fatigue measurements, ± 100 kV/cm square electric pulses are applied to the device at a frequency of 10 kHz. A commercial AFM (Asylum Research MFP3D) is used to conduct the AFM, PFM and SKPM scanning and MikroMasch DPE 14 tips (Pt-coated, resonance frequency of ~ 160 kHz, and spring constant of ~ 5.7 N/m) are used.

3.3 Fatigue Study using Planar BiFeO₃-based Capacitors

As described in session 3.1, by using planar capacitors to conduct *in situ* PFM and SKPM scanning during the fatigue measurement, we can collect images that directly reflect the domain evolution and charge distribution during electrical cycling. Such images allow us to correlate domain pinning with local charges and elucidate the mechanism of polarization fatigue. The structure of the planar devices is schematically drawn in Figure

3-2. Both OP and IP PFM images are needed to identify the polarization direction from the eight possible ones. During the scanning, the probe cantilever is placed along the face diagonal of the BFO cell. The channel width for all planar devices used in the study is fixed at 5 μm for better comparison.

Figure 3-2. Schematic drawing of BFO based planar devices for fatigue and PFM/SKPM studies.

The basic properties of the BFO films are shown in Figure 3-3. XRD 2θ scan shows that the BFO thin film is subjected to an in-plane compressive strain by the STO substrate causing an elongated c-axis (Figure 3-3(a)). Topography image of BFO obtained by AFM reveals a smooth surface of the BFO sample with average surface roughness of $< 1.5 \text{ nm}$ (Figure 3-3(b)). Both the XRD and AFM results indicate the high quality of the BFO films.

Figure 3-3. Both (a) XRD and (b) AFM results show high quality of the BFO thin films.

3.3.1 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ vs. High Work Function Metals

3.3.1.1 Comparison between Planar BiFeO_3 Capacitors using Pt and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ as

Electrodes

To study the different fatigue performances of BFO films with metal and oxide electrodes, we have prepared and investigated BFO planar capacitors using Pt and LSMO as electrodes. Since all the BFO samples show uniformly upward polarization and the IP electrical cycling does not affect the OP polarization, it is reasonable that we only focus on the IP components when carrying out the PFM scanning. Figure 3-4 gives the IP PFM and SKPM images of Pt/BFO/Pt and LSMO/BFO/LSMO devices for the as-grown states (after initial electric switching), in which no obvious differences are observed. The similarity of the domain structures and charge distribution from PFM and SKPM images of the as-grown BFO samples is due to the same parameters used for film deposition and excludes the probability that the different phenomena after repetitive cycling between the two devices are led by the different properties of as grown devices.

Figure 3-4. IP-PFM and SKPM images of as-grown planar BFO capacitors using (a,b) Pt and (c,d) LSMO electrodes. The scanning size of all the images is $10\mu\text{m}\times 10\mu\text{m}$.

Now we compare the IP-PFM and SKPM images of the planar devices using Pt and LSMO electrodes after repetitive electrical cycling. As seen in Figure 3-5, it is clear that Pt/BFO/Pt device shows significant domain pinning after 10^{10} electrical cycles, whereas no domain pinning is observed for LSMO/BFO/LSMO device at the same number of cycles. Moreover, the SKPM images taken after the electrical cycling reveal no (or negligible) charge accumulation at the LSMO/BFO interface, but obvious injected electrons (dark region) at Pt/BFO interface. (In our SKPM setup, the positive and

negative charges are represented by bright and dark contrasts, respectively.) Note that the thin dark line along the LSMO/BFO interface is due to the sharp step edge in topography, which exists before the fatigue measurements.

Figure 3-5. (a,b,d,e) IP-PFM and (c,d) SKPM images of two different planar BFO devices using (a-c) Pt and (d-f) LSMO electrodes at 10^{10} electrical cycles.

The correlation between pinned domain and injected charges along the Pt/BFO interface clearly indicates that charge injection may be responsible for polarization fatigue. If this is the case, the macroscopic fatigue performance of planar LSMO/BFO/LSMO device should be improved by the suppression of electron injection and accumulation at the LSMO/BFO interfaces. To test this, we have also conducted the macroscopic fatigue measurements on these two capacitors and the results are given in Figure 3-6. Indeed, no macroscopic fatigue was seen for the LSMO/BFO/LSMO device after 10^{10} cycles. As a

comparison, considerable fatigue occurred in the 5 μm Pt/BFO/Pt planar capacitor at the same number of electrical cycles. At this stage, we have shown that using oxide electrodes can improve the fatigue performance in ferroelectrics dramatically, which is consistent with other reports. Furthermore, the *in-situ* PFM and SKPM study by taking advantage of planar device implies that the elimination of charge injection at the electrode/ferroelectric interface is likely the cause of the enhancements.

Figure 3-6. The fatigue behaviors of planar (a) Pt/BFO/Pt and (b) LSMO/BFO/LSMO capacitors.

3.3.1.2 The Role of Schottky Barrier in the Charge Injection Process

Now that we have demonstrated that LSMO electrode can improve the fatigue behavior in BFO by minimizing the accumulation of injected electrons, the question is: why is there no (or negligible) charge injection at the LSMO/BFO interface? In other words, what are the differences between the LSMO/BFO and Pt/BFO interfaces? The electronic structures at the two interfaces have to be investigated in order to answer the question. It is well accepted that there exists a Schottky barrier at the Pt/BFO interface, whereas an

Ohmic contact forms between LSMO and BFO. To support this conclusion, we have conducted detailed I - V study on the two capacitors.

Figure 3-7. The leakage current densities of planar BFO-based capacitors using LSMO and Pt as electrodes.

When oxide LSMO is used as electrodes in the planar capacitor, the leakage current density is much higher (Figure 3-7), which implies that a much lower barrier is expected at the LSMO/BFO interface. Furthermore, we have analyzed the conduction mechanisms of these two capacitors to understand the properties of these two interfaces.

Mainly three different mechanisms of leakage current in ferroelectric capacitors have been proposed, which are Schottky conduction (interface limited), Poole-Frenkel conduction (bulk limited) and space charge limited current (SCLC) conduction. In

Schottky conduction,[80] the equation of current density across the barrier (the Schottky barrier induced by the Fermi level difference between electrode and the ferroelectric) is

$$\ln \frac{J}{T^2} = \frac{\left[-q\varphi_b + q\sqrt{\frac{qV}{4\pi d\epsilon_0\epsilon_r}} \right]}{k_B T} + \ln (A^*) \quad 3-1$$

where J is the current density, T is the temperature, φ_b is the barrier height, q is the electronic charge, V is the applied voltage, d is the sample thickness, ϵ_r is the dielectric constant, k_B is the Boltzmann constant and A^* is the effective Richardson's constant.

The Poole-Frenkel mechanism is a bulk limited process,[81] and the conductivity of Poole-Frenkel conduction is given by

$$\sigma = C \exp \left[-\frac{E_I}{k_B T} + \frac{1}{k_B T} \left(\frac{q^3 V}{\pi \epsilon_0 \epsilon_r d} \right)^{\frac{1}{2}} \right] \quad 3-2$$

where C is a constant and E_I is the trapping ionization energy.

The SCLC conduction mainly describes the contribution from the trapped charges and the current density is[82]

$$J = \frac{9\mu\epsilon_0\epsilon_r}{8} \frac{V^2}{d^3} \quad 3-3$$

where μ is the mobility of the charges.

The fittings for both planar Pt/BFO/Pt and LSMO/BFO/Pt devices have been conducted according to all the three conduction models described above. The fitting results are

given in Figure 3-8. When Pt electrode is used, we observe linear fittings in the high field regions for all the three leakage current mechanisms. To evaluate which mechanism provides the best fitting, we extract the dielectric constants (ϵ_r) of BFO films and compare them to the reported value ($\epsilon_r=6.25$). [83] For planar Pt/BFO/Pt structure, the Schottky conduction fitting gives rise to the reasonable value of dielectric constant ($\epsilon_r=2.84$), comparable to the reported one, whereas Pool-Frenkel fitting leads to a large value ($\epsilon_r=20.4$) and SCLC yields an extremely small value ($\epsilon_r=3.4 \times 10^{-6}$). It is thus suggested that the leakage current in planar Pt/BFO/Pt capacitor is dominated by interface limited Schottky emission and a Schottky barrier forms at the Pt/BFO interface (the rectifying feature in the I - V curve of the vertical devices provides stronger evidence, which will be discussed later), consistent with the previous report [84]. For planar LSMO/BFO/LSMO, we can also obtain linear fittings according to all the three leakage current mechanisms. Nevertheless, the values of dielectric constants extracted based on both Schottky emission ($\epsilon_r=0.43$) and SCLC conduction ($\epsilon_r=0.002$) are unreasonably low, whereas the bulk limited Poole-Frenkel model produces the only acceptable value ($\epsilon_r=2.8$), suggesting that the leakage current in LSMO/BFO/LSMO is mainly bulk limited and LSMO/BFO interface features a flat band with negligible barrier.

Figure 3-8. Leakage current fittings for the planar (a-c) Pt/BFO/Pt and (d-f) LSMO/BFO/BFO devices using (a,d) Schottky conduction, (b,e) Poole-Frenkel and (c,f) SCLC models.

Moreover, vertical (Pt or LSMO)/BFO/LSMO devices are also fabricated (their fatigue behaviors will be discussed in the following section) and their conducting properties are measured. The Ohmic contact at the LSMO/BFO interface is confirmed by the nearly

linear I - V curve (Figure 3-9a). On the other hand, the rectifying feature of the I - V curve for Pt/BFO/LSMO device indicates a Schottky barrier at the top Pt/BFO interface. These observations are consistent with the leakage current fitting results for the planar devices.

Figure 3-9. I - V curves of vertical (a) LSMO/BFO/LSMO and (b) Pt/BFO/LSMO devices.

Based on the Schottky conduction mechanism for Pt/BFO interface, we have conducted the current-temperature (I - T) fitting using Equation 3-1. From the fitting result shown in Figure 3-10, the barrier height at the Pt/BFO interface is around 1.1 eV under the applied electric field during fatigue measurements. Based on this information, we propose that the possible reason for the fatigue improvement by LSMO electrode is that the Ohmic contact of the LSMO/BFO interface helps to transfer electrons across it freely and results in less charge accumulation during fatigue measurements. On the other hand, the Schottky barrier at the Pt/BFO interface facilitates the injections of electrons through the high local field in the depletion region and retains the injected charges as well.

Figure 3-10. The fitting of I - T curve based on Schottky conduction mechanism, indicating a barrier height of ~ 1.1 eV for the Pt/BFO/Pt device at the applied electric field.

Figure 3-11 is the key illustration of this chapter, which demonstrates the role of Schottky barrier in controlling the charge injection and accumulation process during fatigue measurements. As shown above, Pt forms a large Schottky barrier with BFO. When external electric field is applied to the device during electrical cycling, a large voltage drop is generated at the reversely-biased Pt/BFO interface, by which electrons from Pt electrode are driven to overcome the barrier and injected into the film. Once electrons are injected, the localized high electric field[34] within the depletion layer accelerates the injected electrons to be deep trapped and immobilized at the gap states, accompanied by the formation of charged defects.[85] When the electric field is reversed, the immobilized electrons are hardly detrapped. The external electric field, though significantly reduces, does not totally remove the Schottky barrier at the forward-biased Pt/BFO interface. Such remaining barrier prevents injected electrons from jumping back to the Pt electrodes

freely and reduces the detrapping rate, which also assists the electron accumulation. As a consequence, electron accumulation occurs upon repetitive electrical cycling, which gives rise to domain pinning and eventually macroscopic polarization fatigue in BFO films. On the contrary, the LSMO/BFO interface features a flat band structure and Ohmic contact is expected. The external field is nearly uniformly distributed across the whole film thickness, implying that the electrons can move freely both at the interfaces and in the bulk region. Even if the higher leakage current still leads to the injection of electrons into BFO film, it is unlikely for them to be accumulated at the interface since there exists no localized high field in this case. Instead, the application of opposite field during electrical cycling promotes the injected electrons to jump back to the LSMO electrodes. In other words, the high detrapping rate[35, 85] reduces the effective accumulation of injected electrons. Without local charges accumulation at the LSMO/BFO interface during fatigue measurements, domain pinning will be suppressed and fatigue performance improved.

Here we would like to clarify that charge injection is only the starting point. The injected charges have to remain in the film and accumulate to induce fatigue. Note that fatigue measurement usually involves bipolar voltage pulses. For Ohmic contacts, the electric field is uniform throughout the ferroelectric film for both polarities, so the injected charges under one pulse can easily escape from the traps back to the electrode under the following opposite bias, leading to fewer accumulated electrons and improving fatigue performance.

Figure 3-11. Energy band diagrams of planar BFO devices. The Schottky barrier at the Pt/BFO interface (a) assists the electron trapping and accumulation by localized high electric field within the depletion layer, whereas the Ohmic contact at the LSMO/BFO interface (b) gives rise to high detrapping rate and leads to no (or negligible) electron accumulation within the BFO film.

3.3.1.3 *Fatigue Behavior of Planar Au/BiFeO₃/Au*

It is widely reported that Pt electrode can act as an effective catalyst to promote the migration ionic species between solid oxides and Pt surface.[86-89] To rule out the possibility that the unintended chemical reaction at the Pt/BFO interface affects the fatigue performance, we also prepared planar BFO-based capacitor with Au as the contact electrodes and investigated its fatigue properties. Similar to Pt, Au is also a high work function metal and likely to form a large Schottky barrier with BFO at the interface. The fatigue performance of planar Au/BFO/Au is measured following the same procedure. After electrical cycling to 10^9 , we observe clear charge injection/accumulation and domain pinning at the Au/BFO interfaces from the SKPM and IP PFM images. Further electrical cycling is expected to lead to more charge accumulation, domain pinning across the whole channel and macroscopic polarization fatigue. Unfortunately, before macroscopic fatigue could be observed, the Au electrodes were burnt due to poor adhesion to BFO surface. Nevertheless, these data are sufficient to support our claim that the Schottky barrier are likely the cause of charge injection/accumulation and domain pinning, which occurs in both Pt/BFO and Au/BFO interfaces.

Figure 3-12. (a,b) IP PFM images and (c) SKPM image show domain pinning and charge injection in planar Au/BFO/Au device after electrical cycling.

3.3.2 Planar Fe/BiFeO₃/Fe Device: Improving Fatigue by Low Work Function

Metals

According to the our model that the Schottky barrier at the electrode/BFO interface controls the charge injection/accumulation process and subsequently the domain pinning, metals with low work functions should improve the fatigue behavior in BFO since they form a lower Schottky barrier with BFO than Pt does. One typical low work function metal, Fe, is used to test this prediction. The barrier at Fe/BFO interface may be lowered (or even eliminated) through one of the two following ways. 1) Fe has a work function of

~ 4.5 eV, which is similar to that of BFO (4.7 eV). This should lead to a much lower Schottky barrier at Fe/BFO interface. 2) Fe is an active metal with an oxidation free energy of ~ -500 kJ/mol.[90] An oxide layer is highly likely to form at the Fe/BFO interface. By either way, we anticipate a lower Schottky barrier with smaller energy band bending at Fe/BFO interface, similar to the situation at LSMO/BFO interface. Therefore, improved fatigue performance in planar Fe/BFO/Fe device is expected according to the Schottky barrier-controlled charge injection model.

Figure 3-13. The (a) IP-PFM and (b) SKPM of planar Fe/BFO/Fe in the as-grown state.

We have fabricated planar Fe/BFO/Fe capacitors using the same procedure and tested their fatigue behavior. Figure 3-13 gives the IP PFM and SKPM images for as-grown planar Fe/BFO/Fe device, showing no clear differences from those samples using Pt and LSMO as contact electrodes (Figure 3-4). After 10^{10} electrical cycles, the PFM images indicate a very small amount of domain pinning (Figures 3-14a,b) and SKPM image shows negligible injected electrons (Figure 3-14c) at the interface. The inset of Figure 3-

14c is the same SKPM image with reduced scale, in which the small amount of electron injection (dark contrast) can explain the little domain pinning at Fe/BFO interface. From the P - E loops before and after electrical cycles and the drawing of switchable polarization as a function of switching cycles (Figure 3-15), improvement of macroscopic fatigue performance is indeed achieved in planar Fe/BFO/Fe device as expected, since no polarization fatigue is observed up to 10^{10} cycles. These observations further confirm our model that Schottky barrier controls the charge injection process and the subsequent domain pinning. The methods towards lowering the Schottky barrier at electrode/BFO interface are efficient to improve fatigue properties of BFO-based heterostructures.

Figure 3-14. (a,b) IP-PFM images and (c) SKPM image of planar Fe/BFO/Fe device show a very small amount of domain pinning and charge injection after 10^{10} cycles.

Figure 3-15. The macroscopic fatigue property of planar Fe/BFO/Fe device. (a) P - E loops before and after electrical switching and (b) switchable polarization as a function of electrical cycles show no macroscopic fatigue up to 10^{10} electrical cycles.

3.4 Fatigue Study of Vertical BiFeO₃-based Capacitors

In the previous session, by using planar BFO-based devices, we have performed fatigue measurements and more importantly, the *in-situ* PFM and SKPM imaging during the macroscopic measurements. The significant role of the Schottky barrier at the electrode/BFO interface is proposed, which controls the charge injection/accumulation process and subsequently the fatigue behavior. For practical applications, however, the traditional vertical sandwich structures are more desirable, and therefore, it is necessary to carry out standard fatigue measurements using conventional vertical capacitors. The schematic structure of the vertical BFO-based devices used in this study is given in Figure 3-16, in which LSMO is used as the bottom electrodes.

Figure 3-16. The schematic drawing of vertical BFO-based capacitors using LSMO as bottom electrodes.

Like in planar devices, the fatigue behaviors of vertical devices using Pt and LSMO as top electrodes were tested and compared. The results are shown in Figure 3-17. With high work function metal Pt being the top electrode, macroscopic fatigue occurs rather soon. Upon only 10^4 switching cycles, significantly reduced switchable polarization is observed. On the other hand, vertical LSMO/BFO/LSMO shows improved fatigue performance, as no macroscopic fatigue appears up to 10^8 cycles. The enhancement of fatigue property in BFO by oxide electrode is in consistence with microscopic behavior observed in the planar devices.

Figure 3-17. The fatigue properties of vertical BFO-based devices using Pt and LSMO as top electrodes. LSMO/BFO/LSMO has a significant improved fatigue performance over Pt/BFO/LSMO device.

Table 3-1. Work functions of different metals and the Schottky barrier heights (for electrons, and estimated by the work function difference) at the metal/BFO interfaces

Metal	Work function	barrier height (eV)
Pt	5.65	0.95
Au	5.1	0.4
Fe	4.5	0*
Ta	4.25	0*

*For metals with work functions lower than BFO, downward energy band bending forms at interface, showing no Schottky barrier for electrons.

We note that the fabrication process of metal electrodes is much more simplified than that of oxide electrodes, since high temperature is often required for oxides deposition. We thus tested a series of metals as top electrodes in vertical BFO-based devices and the fatigue performances are investigated systematically. Two typical high work function metals, Pt and Au, and two low work function metals, Fe and Ta are deposited on a single high quality BFO thin film. The leakage current density of the devices is drawn as a

function of the work function of the metals (Figure 3-18a). It is clear that lower work function metals lead to higher leakage current and imply lower barrier heights at the metal/BFO interface. And Figure 3-18b shows a clear dependence of fatigue performance on the work functions of the top metals, which confirms the model we proposed based on studies of planar devices that lowering the barrier at the electrode/BFO interface can enhance the fatigue properties.

Figure 3-18. (a) Leakage current density and (b) fatigue performance in vertical BFO-based devices using a series of metal electrodes. The utilization of low work function metals can considerably improve the fatigue performance of BFO-based devices.

3.5 Conclusions

By taking advantages of the IP polarization component in BFO and using planar BFO-based devices, we have carried out *in-situ* PFM and SKPM studies to investigate the domain evolution and charge redistribution during fatigue measurements. It is observed that:

- I. Charge injection/accumulation at the electrode/BFO interface (dark regions in SKPM image) causes domain pinning and the macroscopic polarization fatigue in BFO thin film.
- II. Oxide electrodes can improve fatigue performance in BFO, consistent with previous reports. This is attributed to the suppression of electron accumulation at the electrode/BFO interface. Through systematic studies on the leakage current mechanism and analysis of energy band diagrams, we propose that the Schottky barrier at the electrode/BFO interface control the charge injection/accumulation process and thus the macroscopic fatigue behavior. The Schottky barrier assists the electron trapping and accumulation by localized high electric field, and lowering the Schottky barrier suppresses the accumulation of injected electrons due to higher detrapping rate. Based on this model, we predict that metals with low work functions can improve the fatigue performance in BFO, which has been proven using planar Fe/BFO/Fe device.
- III. Furthermore, the Schottky barrier-controlled charge accumulation model has also been verified using conventional vertical BFO-based capacitors, and the results clear show that lowering the Schottky barrier effectively improves the fatigue properties in BFO thin films.

Chapter 4 Mechanism of Switchable Ferroelectric Photovoltaic Effect in BiFeO₃ Heterostructures

In this chapter, I present our study on photovoltaic effect in BFO and its potential as an alternative non-destructive read-out method for FeRAM. The underlying mechanism of switchable ferroelectric photovoltaic effect in BFO heterostructures will be discussed. Our objectives are:

1. To distinguish between the effects of bulk depolarization field and interface on switchable photovoltaic response in ferroelectric materials.

Both bulk effects (bulk depolarization field and/or structural asymmetry) and interface effects have been proposed to explain the photovoltaic response in ferroelectric materials. We will carry out systematic study to separate the contributions from bulk depolarization field and interface energy band bending (i.e. the built-in field at the interface).

2. To understand the mechanism underlining the switchable ferroelectric photovoltaic effect.

The switchable photovoltaic effect must be related to changes in the energy band diagram across the heterostructures upon polarization switching. After clarifying the determining factors, we will try to elucidate how these factors affect the energy band diagram and the photovoltaic response.

4.1 Introduction

In previous chapters, we have shown that repetitive electrical switching will lead to the failure of ferroelectric-based devices by reducing, and finally eliminating the switchable polarization. By combining macroscopic fatigue measurement and microscopic PFM/SKPM imaging, we have established that charge injection at the electrode/ferroelectric interfaces is responsible for polarization fatigue. Based on this conclusion, we have predicted and proved that using low work function metals as electrodes would improve fatigue performance of BFO-based heterostructures.

When it comes to ferroelectric-based devices, such as FeRAM, besides improving the fatigue performance of the heterostructures, we can also redesign the device architecture. In conventional 1T-1C FeRAM, reading is done by sending an electric field larger than E_c and detect whether polarization switching occurs. This process is destructive to the stored information and a rewrite step is needed, which increases the number of polarization switching cycles. During the past decade, various non-destructive read-out methods have been proposed and tested. To this end, we have recently proposed the photovoltaic effect-based FeRAM concept [44] and demonstrated its operation using BFO capacitors. In this novel FeRAM, the read-out signals are the polarization direction dependent V_{oc} or I_{sc} . The advantages of this technique include high operation speed (less than 10 ns write and read time), lower power consumption and excellent fatigue performance (the prototype device can withstand more than 10^8 write cycles), as shown in Table 4-1. Particularly, the most significant advantage of photovoltaic effect-based FeRAM over conventional FeRAM is that the reading process is non-destructive and no

rewrite process is needed, which can increase the lifetime of ferroelectric-based memories, especially for those that require more reading cycles.

Table 4-1. Advantages of photovoltaic effect-based FeRAM over other memories. Adapted from Ref [44].

	Volatile Memory		Non-Volatile Memory				
	DRAM	SRAM	Flash (NAND)	MRAM magnetic	PCM phase change	FeRAM conventional	FeRAM photovoltaic
Cell element	1T1C	6T	1T	1T1C	1T1R	1T1C	1T1C
Feature size	50 nm	65 nm	90 nm	130 nm	65 nm	180 nm	50 nm
W/E time	<10 ns	0.3 ns	0.1 ms	20 ns	50 ns	10 ns	< 10 ns
Retention	64 ms	0	>10 y	>10 y	>10 y	>10 y	> 4 month * > 10 y ^
Write cycles	>10 ¹⁶	>10 ¹⁶	>10 ⁵	>10 ¹⁶	>10 ⁹	>10 ¹⁴	> 10 ⁸ * > 10 ¹⁴ ^
V_{write} /energy	2.5 V 5 fJ	2.5 V 0.7 fJ	15 V 10 fJ	1.5 V 100 pJ	3 6 pJ	0.9-3.3 V 30 fJ	~3 V < 5 fJ
V_{read}	1.8 V	1 V	2 V	1.5 V	3 V	0.9-3.3 V	0 V

*Based on our work in Ref. [44].

^Based on previous study on conventional FeRAM.

The feasibility of the photovoltaic effect-based FeRAM has been demonstrated using a 4×4 cross-bar array. In Figure 4-1a, the memory cells are represented by the junctions and upward and downward polarization directions are indicated in blue and red color, respectively. Figure 4-1b demonstrates the performance, particularly the V_{oc} values, of such architecture of memory cells, in which each of the 16 memory cells is fully operational and has a polarization direction dependent V_{oc} . However, it was noted in our previous study that the photovoltaic current is very small which could limit the practical realization of the concept. To improve the ferroelectric photovoltaic responses, it is imperative that we clarify the mechanism underlining this effect.

Figure 4-1. The feasibility of the photovoltaic effect-based FeRAM by 4×4 cross-bar structure. Adapted from Ref [44].

4.2 Experimental Procedure

Vertical BFO-based capacitors using LSMO as bottom electrodes were prepared. Firstly, the bottom LSMO electrodes of different thicknesses were grown on (001) oriented STO substrate (with 4 ° miscut along [110] direction) at 780 °C and under oxygen pressure of 200 mTorr. For the following BFO film (~100 nm) growth, the substrate temperature was fixed at 680 °C, with oxygen pressure of 50 mTorr, laser energy density at ~1 J/cm², repetition rate at 10 Hz and deposition duration of 50 minutes. Top Pt electrodes (~10 nm) were prepared by standard photolithography and lift-off process. And ~15 nm LSMO film was deposited on BFO at 675 °C and under oxygen pressure of 300 mTorr, followed by photolithography and chemical etching process[91] to form patterned top LSMO electrodes (20 μm×20 μm).

Precision LC Ferroelectric tester (Radiant Technologies) is used to carry out the *P-E* measurements. A commercial AFM (Asylum Research MFP3D) is used to conduct the AFM and PFM scanning and MikroMasch DPE 14 tips (Pt-coated, 160 kHz, and 5.7 N/m)

are used. A low-noise probe station and a pA meter/direct current (DC) voltage source (Hewlett Package 4140B) are used to conduct the macroscopic photovoltaic measurements, with a Halogen lamp (energy density $\sim 20 \text{ mW/cm}^2$) as the light source shining through the top electrodes.

The basic properties of the BFO film are shown in Figure 4-2. Both XRD and AFM results show high quality of the as-grown BFO film. Particularly, topography image indicates an average surface roughness of $\sim 3 \text{ nm}$ (inset of Figure 4-2a). The ferroelectric property is confirmed by PFM image, which indicates uniform out-of-plane polarization direction for the as-grown sample. This is consistent with literature report [92] and likely a result of the interface chemistry between BFO and LSMO grown on TiO_2 -terminated STO. By applying a dc bias to the tip during the scan, areas with opposite polarization directions can be created (Figure 4-2b).

Figure 4-2. The basic properties of the BFO film. Both (a) XRD and (inset) AFM results show high quality of BFO thin film. (b) The polarization can be easily switched by a dc bias on the AFM tip.

4.3 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$: Contribution from Bulk

Depolarization Field

As discussed in the previous chapter, LSMO forms Ohmic contact with BFO. Moreover, ionic displacement[93, 94] at the LSMO/BFO interface also helps to screen the polarization bound charges. As a consequence, a flat band with negligible energy barrier is expected at the LSMO/BFO interface, which makes LSMO/BFO/LSMO structure an ideal system to study the contribution of bulk depolarization field to ferroelectric photovoltaic effect in BFO, since neither of the two interfaces possesses an internal field. In other words, there exists no contribution from the interface effects in LSMO/BFO/LSMO system and therefore, all the photovoltaic response merely arises from the effect of the depolarization field. We have fabricated the vertical LSMO/BFO/LSMO capacitors with $20\ \mu\text{m} \times 20\ \mu\text{m}$ top LSMO electrodes by standard photolithography and chemical etching. The square hysteresis loop indicates low leakage

current and good quality of the capacitor. From the I - V measurement under illumination, a very small V_{oc} value, around 0.04 V (average for P_{up} and P_{down} states) is observed, which can be deemed as the contribution from bulk depolarization field. We thus can conclude that the bulk depolarization field has a relatively small contribution to the photovoltaic responses in BFO heterostructures.

Figure 4-3. (a) The ferroelectric hysteresis loop and (b) photovoltaic effect of LSMO/BFO/LSMO device. With flat band at both interfaces, only bulk depolarization field is acting as the driving force to separate the photo-generated carriers, whose contribution to photovoltaic effect in BFO thin films is very small.

4.4 Pt/BiFeO₃/La_{0.7}Sr_{0.3}MnO₃: Polarization Modulated Interface

Effects

After clarifying the effect of the bulk depolarization field, we can further study the interface effect on the ferroelectric photovoltaic in BFO heterostructures, by replacing the top LSMO electrode with Pt. It is accepted that a Schottky barrier exists at the Pt/BFO interface,[84] which is also well addressed in the previous chapter.

4.4.1 Photovoltaic Properties of Pt/BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ Capacitors

Similar to LSMO/BFO/LSMO, Pt/BFO/LSMO capacitor also shows square-like ferroelectric hysteresis loop (Figure 4-4a). The I - V curves under illumination (Figure 4-4b), however, demonstrate much larger V_{oc} values, around +0.20 V for P_{up} state and -0.18 V for P_{down} state. More importantly, both signs of V_{oc} and I_{sc} can be switched by the polarization directions in BFO films. Note that the transmission measurements show that only 35% of the light is transmitted through the Pt electrode, whereas LSMO top electrode allows 80% light transmission in the visible light range, which means that the V_{oc} value of Pt/BFO/LSMO might be even larger if the same light intensity is achieved at the top electrode/BFO interface. The inset of Figure 4-4b gives the photovoltaic properties under different pulse voltage applied to the bottom electrode. As expected, both V_{oc} and I_{sc} show hysteresis behaviors similar to the ferroelectric P - E loop, confirming that the switchable photovoltaic properties are driven by the ferroelectric polarization switching in BFO thin films. And after demonstrating that bulk depolarization field causes negligible photovoltaic response in BFO heterostructures, combined with the flat band (i.e. no internal field) at the LSMO/BFO interface, the significant photovoltaic effects in Pt/BFO/LSMO structures are believed to originate from the energy band bending at the Pt/BFO interface.

Figure 4-4. (a) The ferroelectric hysteresis loops and (b) photovoltaic effect of Pt/BFO/LSMO device. Large V_{oc} values for both P_{up} and P_{down} states are observed in such structure. The inset of (b) shows the photovoltaic properties as functions of pulse voltage applied to the bottom electrode, and the hysteresis behaviors of both V_{oc} and I_{sc} are closely related to ferroelectric hysteresis loop of BFO.

4.4.2 Effects of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thickness on Photovoltaic Properties

To further support our claim that the photovoltaic effect in Pt/BFO/LSMO structures originates mainly from the Pt/BFO interface rather than the bulk depolarization field or the bottom LSMO/BFO interface, we prepared a series of Pt/BFO/LSMO samples with different LSMO thicknesses, ranging from 1 nm to 6 nm. For ultrathin LSMO films, the electrical properties are highly dependent on the thickness.[95] As shown in Figure 4-5a, upon reducing thickness, LSMO films undergo a metal-to-semiconductor transition with a critical thickness of around 3 nm, and the resistivity is increased by several order of magnitudes. The photovoltaic properties of the Pt/BFO/LSMO capacitors, surprisingly, remain almost unaffected and both V_{oc} and I_{sc} values are nearly irrelevant to the bottom LSMO electrode thickness, except a slight decrease for 1 nm LSMO, which may arise from the incomplete polarization switching of BFO films, as shown in Figure 4-4a. It is thus logical to associate the enhanced photovoltaic responses in Pt/BFO/LSMO heterostructures with the top Pt/BFO interface. And again, the nearly independence of photovoltaic responses on bottom LSMO thickness leads to the conclusion that the contribution of bulk depolarization field can be neglected, otherwise, the samples with thinner LSMO electrode will lead to enhanced photovoltaic effect, due to weakened screening effect caused by lower conductivity.

Figure 4-5. Effects of bottom LSMO thickness on photovoltaic properties in Pt/BFO/LSMO heterostructures. (a) The conducting properties of LSMO films highly depend on the thickness. (b) The photovoltaic properties are nearly independent on the bottom LSMO thickness, further ruling out the dominant contribution of LSMO/BFO interface or the bulk depolarization field.

4.4.3 Mechanism of Switchable Photovoltaic Properties in

Pt/BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ Heterostructures

With the understanding that the photovoltaic response in Pt/BFO/LSMO heterostructures mainly arises from the Pt/BFO interface, it is possible to elucidate the energy band diagram change that leads to the switchable photovoltaic effect (Figure 4-6). Since it has been proven that neither of the LSMO/BFO interface and the bulk depolarization field plays a significant role in the photovoltaic effect, it is reasonable to assume that the energy band at the LSMO/BFO interface as well as in the bulk BFO region is flat (i.e. no internal field). On the other hand, energy band bending with a built-in field (E_{bi}), induced by incomplete screening of polarization bound charges or/and the work function difference between Pt and BFO, exists at the Pt/BFO interface, which separated photo-induced carriers under illumination to produce the photovoltaic response. More

importantly, this built-in field can be reversed by polarization switching. For P_{up} state in BFO, incompletely screened positive bound charge leads to a built-in field orientated from Pt/BFO interface towards BFO bulk, resulting in a lower potential at the top Pt electrode under illumination. When a short circuit is connected, the photocurrent flows from bottom LSMO to top Pt electrode in the circuit. If the BFO film is polarized downwards, however, V_{oc} (or I_{sc}) switches to the opposite direction, as the built-in field is reversed towards the Pt/BFO interface due to negative bound charges at the interface. The switchable V_{oc} and I_{sc} are clearly seen in Figure 4-4b.

Figure 4-6. The energy band diagrams of Pt/BFO/LSMO heterostructures under illumination. (a) For upward polarization in BFO, the built-in field at the Pt/BFO interface induced by incompletely screened positive bound charges is pointing downward and leads to a lower potential at the top Pt electrode under illumination. Once a short circuit is connected, the photocurrent flows from bottom LSMO to top Pt electrode in the circuit. (b) If the BFO film is polarized downwards, negative bound charges at the interface causes reversed built-in field and thus reversed V_{oc} and I_{sc} directions.

4.5 Conclusions

By using vertical BFO heterostructures and controlling the interface conditions including varying the top electrode materials and the thickness of the bottom LSMO electrode, we have carried out a systematic study to clarify the origin of the switchable photovoltaic effect in BFO heterostructures. The conclusions are:

- I. By studying the photovoltaic responses in LSMO/BFO/LSMO structure, in which the electrodes are symmetric and energy band is flat at the LSMO/BFO interfaces, the contribution from bulk depolarization field to the photovoltaic effect in BFO thin films is proven to be relatively small.
- II. Significant switchable photovoltaic responses with large V_{oc} values have been observed in Pt/BFO/LSMO heterostructures and polarization switching in BFO films is suggested to be the driving force of the ferroelectric photovoltaic effects. After further ruling out the role of the LSMO/BFO interface or the bulk depolarization field based on the nearly independence of photovoltaic properties on bottom LSMO thickness, we propose that the enhanced photovoltaic response in Pt/BFO/LSMO heterostructures originates from the Pt/BFO interface.
- III. We have elucidated the energy band diagrams across the Pt/BFO/LSMO capacitors. The built-in field at the Pt/BFO interface induced by incompletely screened polarization bound charge is crucial for the separation of photo-excited carriers. The polarization direction in BFO films determines the type of the bound charges at the Pt/BFO interface and the directions of V_{oc} and I_{sc} .

Chapter 5 The Enhancement of Photovoltaic Properties in BiFeO₃ Thin Films through Domain Engineering

The comprehensive understating of the switchable ferroelectric photovoltaic effect in the previous chapter is valuable for seeking methods to improve the photovoltaic properties, which is desirable for the applications of ferroelectric photovoltaic-based devices, such as photovoltaic effect-based FeRAM and solar cells. In this chapter, I summarize our efforts to tailor the ferroelectric photovoltaic responses in BFO-based capacitors via domain engineering. The objectives are:

1. To control the domain structures and domain wall densities in BFO thin films through substrate engineering.

Recent studies have proved the feasibility to create specific domain structures in BFO thin films, by substrate strain effect or vicinality control. We will grown BFO thin films on STO substrates with different miscut angles to control ferroelectric domain configuration and thus the ferroelectric switching behavior in BFO films.

2. To enhance the macroscopic photovoltaic response and correlate with the domain structures in BFO thin films.

The corresponding photovoltaic properties, including both V_{oc} and I_{sc} , of BFO-based capacitors on STO substrates will be investigated. We will answer the question of how photovoltaic responses in vertical Pt/BFO/LSMO capacitors are affected by domain structures, or more accurately, by domain walls.

5.1 Introduction

5.1.1 Domain Engineering in BiFeO₃ Thin Films

It has been widely reported that domain walls in BFO thin films possess many interesting properties, such as higher conductivity [6] and net magnetization.[96, 97] It is of significant importance to controllably design the domain structures in BFO thin films, for both fundamental physics study and potential applications in the next generation nanoscale devices.[98, 99] Conventionally, periodic domain structures are achieved by applying an external electric field through lithographically defined electrodes or by a direct writing process.[100, 101] If one wants to obtain sub-micrometer sized domain patterns, domain engineering using a scanning force microscope with an appropriate bias voltage has to be conducted.[102] However, this approach is limited to small regions and the scanning rate is usually slow. Here we introduce several novel methods to create periodic domain structures in BFO films over large areas.

5.1.1.1 Substrate Strain Effect

An early paper reported that for (001)-oriented rhombohedral films, 71 ° domain walls form along the (101) planes; on the other hand, 109 ° domain walls would form along the (100) planes.[103] Moreover, theoretical studies showed the possibility of controlling the domain structure by the heteroepitaxial strain in thin films.[104] Experimentally, Chu *et al.* developed an elegant method towards highly ordered one dimensional (1D) ferroelectric domains in La-doped BFO films.[105] Firstly, the orthorhombic (110) DyScO₃ single-crystal substrate was used to provide an anisotropic strain to exclude two of the possible structural variants. In addition, through careful control of electrostatic boundary conditions, i.e., the existence of a SrRuO₃ conducting layer (and its thickness),

either 109° or 71° 1D periodic domain walls can be selectively created (Figure 5-1c). The schematics of highly ordered 71° and 109° domain walls are given in Figure 5-1a,b.

Figure 5-1. Schematics of periodic (a) 71° and (b) 109° domain patterns. (c) Evolution of domain fractions. Adapted from Ref [105].

5.1.1.2 Domain Control in BiFeO_3 through Substrate Vicinality

Another method of controlling the ferroelectric polarization variants in BFO films is to use various STO substrates. The ferroelectric domain structures of BFO films deposited on STO substrates with different orientations have been studied.[106] The IP PFM results

of (001), (110) and (111)-oriented BFO thin films are shown in Figure 5-2. For (001)-oriented BFO thin films, due to the degenerate energy levels of the domains, twinned domain structures are obtained to relax the elastic energy of the films. For (110)-oriented BFO thin films, on the other hand, two ferroelectric variants over large areas are observed, as a result of the combined effects of compressive strain and the self-poling due to film-substrate interface. Finally, for (111)-oriented BFO thin films, since the polarization variants perpendicular to the film surface have the lowest energy for films grown under compressive strain, a single domain with a downward polarization is observed.

Figure 5-2. The effects of substrate orientations on the polarization variants in BFO thin films. (a) Schematic drawing of the vicinal substrates. (b-d) IP-PFM images of BFO films on (b) STO (001), (c) (110), and (d) (111) substrates. Adapted from Ref [106].

If one wants to further control the domain structures in BFO thin films, a break in symmetry of the ferroelectric variants is necessary, which can be achieved by using vicinal STO substrates. Jang *et al.* [107] carried out the domain engineering study by employing exact (with negligible miscut) and 4 ° miscut STO (the miscut is along [100] direction) substrates with coherent SrRuO₃ bottom electrodes. The domain selections by miscut substrate during film growth are schematically shown in Figure 5-3. On the exact substrate, three dimensional island-growth is expected and all the four polarization variants are possible since the biaxially isotropic strain leads to no preference of any specific rhombohedral distortion (Figure 5-3a). On the other hand, on the miscut substrate, the small terrace width gives rise to step flow growth of BFO thin films, suppressing the formation for r_2 or r_3 domains assisting the formation 71 ° domain walls with r_1 and r_4 stripe domains (Figure 5-3b). Later Shelke *et al.* [108] grew BFO thin films on (100) vicinal STO substrate with 4 ° miscut along [110], which is more effective in breaking the symmetry among the polarization variants and assists the growth of BFO films with highly selected variants. It was suggested that the domains are intermediate between stripe and fractal geometry, making the switching of polarization much easier. Therefore, such BFO thin films display largely reduced coercive field (74 kV/cm), compared to the films on plain (100) and (110) substrates, or even on the substrates with miscut along [100].

Figure 5-3. The schematics growth modes and domain formations of BFO films on (a) exact and (b) miscut STO substrates. Adapted from Ref [107].

5.1.2 Conduction at Domain Walls in BiFeO₃ Films

Separating the ferroelectric domains, domain walls themselves have their own symmetry and thus distinguishing properties.[6, 96, 97] One of the most fascinating properties of domain walls in BFO films is their conductive nature, whereas the domains appear insulating.[6] Two main reasons have been proposed to explain the conduction at the domain walls. First, as shown in Figure 5-4, a decrease of local band gap is seen at all the three types of domain walls.[109] And the 180° wall shows the largest reduction of band gap, indicating that the 180° domain wall is the most conductive. On the other hand, the least conduction is expected for 71° domain walls. And this reduction of band gap across the domain walls is suggested to be associated with the change of Fe-O-Fe bond

angle, whose local distortion controls the orbital overlap. Another factor that leads to the conductive nature of the domain walls is the electrostatic potential steps at the domain walls.[110] It is found that the component of the polarization normal to the domain wall shows small changes due to the gradual rotation of the polarization vector across the wall region, which can induce these electrostatic potential steps, and consequently, the conduction at the domain walls.

Figure 5-4. Local band gap across all the three types of ferroelectric domain walls in BFO. a_0 is the pseudocubic lattice constant of BFO, $a_0=0.389$ nm. Adapted from Ref [109].

5.2 Experimental Procedure

STO substrates with different miscut angles along [110] direction were used to achieve different domain structures in BFO films. Bottom LSMO electrodes were grown on different STO substrates at 780 °C and under oxygen partial pressure of 200 mTorr, followed by BFO films (~130 nm) deposited at 655 °C and under 50 mTorr oxygen partial pressure. During the BFO growth, the laser repetition rate was fixed at 10 Hz and energy density at ~ 1 J/cm². The top Pt electrodes were patterned using standard photolithography and lift-off process and the size is 20 $\mu\text{m} \times 20 \mu\text{m}$.

A commercial AFM (Asylum Research MFP3D) is used to conduct the AFM, PFM and SKPM scannings and MikroMasch DPE 14 tips (Pt-coated, 160 kHz, and 5.7 N/m) are used. Precision LC Ferroelectric tester (Radiant Technologies) is used to carry out *P-E* and positive-up-negative-down (PUND) measurements. A low-noise probe station and a pA meter/direct current (DC) voltage source (Hewlett Package 4140B) are used to conduct the macroscopic photovoltaic measurements, with a Halogen lamp (energy density $\sim 20 \text{ mW/cm}^2$) used as the light source through the top electrodes.

5.3 Domain Engineering in Epitaxial BiFeO₃ Films through Substrate Vicinity

Figures 5-5a-d show the topography of as-grown BFO thin films on (001)-oriented STO substrates with different miscut angles, namely 4° , 2° , 1° and 0° , along $[110]$ direction (in the next, we call them 4° , 2° , 1° and 0° STO, for simplification). All the samples exhibit smooth surface, though the roughness increases with the miscut angle, accompanied by the saw-tooth step pattern from the substrates. In all samples, no clear protrusions and holes are observed, indicating high quality of the films and absence of 3D growth mode. The corresponding IP PFM images are given in Figures 5-5e-h. The AFM cantilever is placed along $[1-10]$ direction to effectively identify the IP polarization directions in BFO films. Note that the uniform OP PFM contrast indicates the upward direction for all the samples (Figures 5-8a,b). With the combination of OP and IP PFM images, most of the domain walls are identified as 71° domain walls (we will discuss this later). It is clear that with decreasing substrate miscut angle, the domain structures tend to be more

complicated and the wall density increase dramatically. Using 4° STO, nearly single domain BFO film with few domain walls (Figure 5-5e) is obtained, since the interface between the bottom electrode and BFO at the step edge favors one of the eight degenerate polarization directions. As the miscut angle of substrates decreases, the selection of preferential distortion of the unit cells is weakened gradually (shown schematically in the inset of Figures 5-5e-h), and thus complicated domain structures with a large number of domain walls are expected, which is confirmed by our IP PFM images (Figures 5-5f-h), where a monotonic increase of domain wall concentration is observed. On 0° STO, the biaxially isotropic strain leads to no selection among the four structural variants during BFO deposition and thus combinations of all the four polarization variants in BFO films are observed.

Figure 5-5. (a-d) The topography and (e-h) IP domain structures of as-grown BFO thin films on STO substrates with different miscut angles. The insets in (e-h) indicate the selection of preferential polarization through STO substrate miscut angle.

To further confirm the types of domain walls in our samples, we have conducted more detailed IP PFM scanning and the results are given in Figure 5-6, in which two BFO samples (on 0° and 2° miscut substrates) are chosen as examples. The uniform OP contrast excludes the existence of 180° domain walls. For more accurate identification of the IP polarization directions, we physically rotate these two samples and scan the same areas. Technically, during the first scanning, the AFM tip is placed along $[1-10]$, followed by a second scan then where the samples are physically rotated by 90° and the AFM tip is along $[110]$. By combining the IP PFM measurements before and after physically rotating the samples, we are able to identify the exact types of the domain walls (Figure 1-2). Following the color code of our PFM, both 71° and 109° domain walls are outlined in Figure 5-6e,f. It is clear that in both samples, nearly all the domain walls are 71° , with negligible 109° domain walls.

Figure 5-6. PFM images of as-grown BFO thin films grown on 0° and 2° STO substrates. (a-b) The OP PFM images show upward polarization direction of the films, ruling out the existence of 180° domain walls. (c-d) The IP PFM images of BFO films with AFM tip placed along [1-10] direction. After physically rotating the samples by 90°, the domain structures in the same regions

are shown in (e-f). The combination of (c), (e) and (d), (f) can identify the exact types of the domain walls.

5.4 Ferroelectric Properties of Epitaxial BiFeO₃ Films

In order to correlate the domain structures with macroscopic properties, we have fabricated vertical Pt/BFO/LSMO/STO capacitors and conducted the ferroelectric measurements accordingly. The typical *P-E* loops of these capacitors with different STO substrates are given in Figure 5-7a. For nearly single domain BFO on 4° STO, an almost perfect square-like *P-E* loop is obtained, with a remanent polarization value of ~60 $\mu\text{C}/\text{cm}^2$, comparable to that of the theoretical value of BFO film on (001)-oriented STO substrate (~63 $\mu\text{C}/\text{cm}^2$), which implies complete switching of the ferroelectric polarization in BFO film under external electric field. When STO substrates with smaller miscut angles are used, we observe more open loops, indicating higher leakage current in these capacitors than that in Pt/BFO/LSMO/4° STO. And such higher leakage current may originate from the conductive domain walls in these films, which we will discuss in details later. Moreover, the coercive field increases gradually with decreasing substrate miscut angle, consistent with previous reports that complex domain structures increase the energy barrier for domain nucleation[108, 111] and thus a larger external field is needed to complete the polarization switching. When we compare the values of remanent polarization among different capacitors, however, they seem to be independent of domain structures in BFO thin films, all around 60 $\mu\text{C}/\text{cm}^2$.

Figure 5-7. The macroscopic ferroelectric properties of BFO thin films on STO substrates with different miscut angles. (a) P - E loops of the BFO samples. The switchable polarization remains unaffected by the STO miscut angle, though smaller miscut angles cause larger coercive field and more open loops. (b) The results of PUND measurements are in good agreement with the P - E loops.

To quantify the remanent polarization more accurately, PUND measurements have been carried out, in which the switchable polarization (ΔP) is given as a function of applied electric field. Again, the same ΔP value is observed for all the samples. These results are different from previous work by Jang *et al.*, [107] where drastically lower ΔP was observed for BFO film on STO substrate with smaller miscut angle along [100]. They attributed the incomplete ferroelectric switching in BFO films on exact STO to the existence of 109° domain walls, which impedes domain wall motions. In this work, however, negligible 109° domain walls are seen from the PFM images, and therefore ferroelectric switching in all samples is complete and the ΔP values in different capacitors remain the same. Such complete switching, in turn, implies that almost all the domain walls in our BFO films are 71° domain walls.

5.5 Photovoltaic Responses of Domain Engineered BiFeO₃ Films

In the previous chapter, we have shown that polarization modulated band structure within the depletion layer at the Pt/BFO interface induces the switchable photovoltaic effect in Pt/BFO/LSMO heterostructures. According to this mechanism, a built-in field (E_{bi}) is generated at the metal/ferroelectric interface due to the incompletely screened polarization bound charges, which effectively separates the photo-generated carriers and produces V_{oc} . In the BFO heterostructures, if the value of the switchable polarization is the same, the magnitude of E_{bi} remains unchanged, and consequently, V_{oc} value should be a constant. Recently, SKPM has proven to be a useful technique to study the surface potential, and reflect the space charge distribution in the films. For the photovoltaic effects in BFO films, the photo-generated carriers, separated by E_{bi} under illumination, will accumulate at the surface and can be detected and analyzed by SKPM. In this sense, the surface potential difference of BFO film between under light and in dark (which we define as Δ_{SP}), derived from SKPM images, reflects the photo-generated voltage across the film and can be treated as V_{oc} in vertical tip/BFO/LSMO structures. Furthermore, SKPM study can reveal the areal distribution of photovoltaic response across the film.

Figure 5-8. (a-b) The OP PFM and (c-d) The corresponding SKPM images of BFO thin films with electrically written patterns, on (a,c) 4° and (b,d) 0° STO substrates. The SKPM images include both dark and illuminating conditions, in which the potential differences reflect the photo-generated voltage across the film.

Figure 5-8 shows the measurements of V_{oc} by SKPM, for which BFO films on 4° and 0° STO are chosen as examples to demonstrate the working principles of this method. Figures 5-8a,b are OP PFM phase images of BFO films with electrically written patterns, where the application of +9.9 V (-9.9 V) dc voltage on the AFM tip during scan in contact mode can switch the OP polarization to downward, P_{down} (upward, P_{up}). The corresponding SKPM images in the same areas are given in Figures 5-8c,d, which were

taken two days after the electrical writing, to reduce the impact of injected charges during the writing process. Then a line across both the “light on” and “light off” parts is drawn, whose profile can be used to calculate Δ_{SP} . Table 5-1 summarizes the Δ_{SP} values in three different regions, namely as-grown, +9.9 V written and -9.9 V written regions, for all the four samples, from which we can see that the Δ_{SP} values in each region is nearly independent of STO substrate miscut angle. Moreover, in the two P_{up} regions (i.e. as-grown and -9.9 V written regions), Δ_{SP} values are also the same. All these results indicate that V_{oc} is generated solely by the energy band bending at the metal/BFO interface and the internal field in it, and unaffected by domain structures and even the switching history in vertical BFO capacitors. The slight difference of Δ_{SP} between P_{up} and P_{down} may result from the effect of remaining injected charges, which can be seen from the different contrasts in “light off” parts in Figures 5-8c,d. It should be mentioned that our conclusion here is different from the results observed in lateral device configuration by Bhatnagar *et al.*, [50], according to which more conducting samples generate smaller V_{oc} values. However, our conclusions are consistent with the model based on the polarization modulated interface effects. In addition to SKPM measurement, conductive AFM can also be used to reveal current distribution under light and in dark. However, we do not have the resolution to distinguish between the conduction contributions from domains and domain walls, similar to another recent report.[112]

Table 5-1. Summary of Δ_{SP} values in different regions in BFO films on different STO substrates.

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

To correlate with the microscopic studies and better understand the effect of domain walls on photovoltaic responses in BFO films, we have fabricated conventional vertical Pt/BFO/LSMO capacitors and carried out the macroscopic photovoltaic measurements. Even though the domain wall conductivities vary according to the type of the wall, namely 180 °, 109 ° and 71 °, it is well accepted that all the domain walls are more conductive than the domains in BFO films.[6, 61, 110] Combined with the fact that the density of domain walls (most are 71 ° domain walls) increases with decreasing STO substrate miscut angle (Figures 5-5e-h), we predict that the effective conductivity in BFO films will increase as amount of domain walls increases. Indeed, our I - V measurements under illumination show larger slopes when STO substrates with smaller miscut angles are used, giving rise to larger I_{sc} (Figure 5-9a). The V_{oc} values, on the other hand, are nearly the same in all samples for P_{up} or P_{down} states, which is consistent with our SKPM study. The difference of the absolute V_{oc} values between SKPM study and I - V measurements may arise from the different light sources in these two systems. The trend of V_{oc} and I_{sc} as a function of STO substrate miscut angle is shown in Figure 5-9b for clearer illustration. At this stage, we can conclude that the effect of domain walls on the photovoltaic properties in vertical BFO heterostructures is reflected in enhancement of I_{sc} ,

by improving the effective photoconductivity of BFO films, while keeping the interface band bending conditions and the V_{oc} values intact.

Figure 5-9. The photovoltaic performances of BFO films on STO substrates with different miscut angles. (a) The typical I - V curves of all the four samples under illumination, clearly showing similar V_{oc} values but increasing I_{sc} values with reduced miscut angles. V_{oc} and I_{sc} values as functions of miscut angle are drawn in (b).

5.6 Domain and Domain Wall Photoconductivities

The domain wall conductivity is one of the most fascinating properties in ferroelectrics, due to its potential application in next generation nanoscale electronics.[6] Our systematic study on the photovoltaic responses with different domain wall (71°) densities makes it feasible to evaluate the magnitude of 71° domain wall photoconductivity in BFO thin films. Within low field regions from -0.15 V to $+0.15$ V, the Schottky emission conduction mechanism is not dominant, and the capacitors show Ohmic-like behavior, which is supported by the linear I - V curves shown in Figure 5-9a. In addition, we can get the domain wall densities in different samples by outlining them as shown in Figures 5-5e-h. Schematic illustration of the vertical device structure is shown in Figure 5-10a, with

71 ° domain walls titling approximately 45 ° from the film surface. The equivalent circuit is schematically shown in Figure 5-10b, and the effective photoconduction of this parallel circuit is given by

$$1/R = 1/R_D + 1/R_{DW} \quad 5-1$$

where R_D and R_{DW} are photoresistances of bulk domain and domain wall. We also have

$1/R_{DW} = \sigma_p S_{DW} / L$ by definition with S_{DW} being the cross sectional area of domain

walls and σ_{ph} the photoconductivity of 71 ° domain wall, so

$$1/R = 1/R_D + \sigma S_{DW} / L \quad 5-2$$

Here, L can be estimated by $d/\sin 45^\circ$, and d is the film thickness, 130 nm. Besides, we can calculate S_{DW} using a reasonable domain wall width of 2 nm,[6, 113] together with the domain wall densities derived from Figures 5-5e-h.

Figure 5-10. (a) The schematic drawing of vertical Pt/BFO/LSMO devices and (b) the equivalent circuit.

The photoconduction $1/R$ as a function of S_{DW}/L is given in Figure 5-11, for both P_{up} and P_{down} states. From equation 5-2, the slope of $1/R \sim S_{DW}/L$ represents photoconductivity, and through fitting we obtain photoconductivities of 2.5 nS/cm and 3.9 nS/cm, for P_{up} and P_{down} , respectively. We emphasize that this is a rather rough analysis, since the real domain structures might be far more complicated than that shown in Figure 5-10a during polarization switching and we do not consider other factors such as growth conditions, strain effects or the asymmetric electrodes, from which slight difference of the photoconductivities between P_{up} and P_{down} states may arise. Besides, the chosen width of domain walls also affects the value of estimated photoconductivities. From equation 5-2, there is an inverse relationship between the estimated domain wall photoconductivity and

chosen domain wall width, based on the $\sigma_{ph}S_{DW}$ term. This means that the photoconductivity of 71° domain walls would be 5 ($=2.5 \times 2$) nS/cm (P_{up}) and 7.8 ($=3.9 \times 2$) nS/cm (P_{down}) if domain wall width is chosen as 1 nm, and 1.3 ($=2.5/2$) nS/cm (P_{up}) and 2 ($=3.9/2$) nS/cm (P_{down}) if domain wall width is 4 nm. However, we can safely conclude that the photoconductivity of 71° domain walls in BFO films is of the order of 10^{-9} - 10^{-8} S/cm. As a comparison, the bulk BFO photoconductivity is of the order of 10^{-11} - 10^{-10} S/cm, which can be derived from the intercepts of the fitting lines in Figure 5-11 based on equation 5-2. It is obvious that the photoconductivity of 71° domain walls is two orders of magnitude larger than that of bulk BFO. Acting as conducting paths for photo-excited carriers, the conductive domain walls increase the I_{sc} values.

The predominance of 71° domain walls has also been reported previously,[114] in which both uncharged head-to-tail and charged head-to-head domain walls are mapped. The domain patterns in our case, however, are not so complicated and our PFM images (Figure 5-6) show a predominance of uncharged (head-to-tail) 71° domain walls (with only a small amount of charged domain walls). However, even for uncharged domain walls, there exist electrostatic potential steps due to the gradual rotation of the polarization vector across the wall region. Such intrinsic polarization discontinuity will couple to specific types of defects, which serve as intrinsic doping to the domain walls. In this sense, the charged and uncharged domain walls can be deemed as heavily and lightly doped regions, respectively. Thus, as pointed out above, a specific type of domain wall should facilitate the conduction of one carrier and reduce the recombination.

Figure 5-11. The fitting results of 71 ° domain wall photoconductivities for both upward and downward polarization directions, giving rise to the values on the order of 10^{-9} - 10^{-8} S/cm.

5.7 Conclusions

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. It has been shown that:

- I. Substrate vicinality can be used to control ferroelectric domain configuration and thus the ferroelectric switching behavior in BFO films. The selection of preferred ferroelectric distortions is weakened with reduced miscut angle in STO substrates, giving rise to more complicated domain structures and higher domain wall densities.

- II. The corresponding photovoltaic properties of vertical capacitors are also investigated. Both SKPM study and macroscopic ferroelectric measurements show that V_{oc} is irrelevant to domain configurations and governed solely by energy band bending at metal/BFO interface, further confirming the interface effect in ferroelectric photovoltaic response as proposed in the previous chapter. On the other hand, I_{sc} can be enhanced due to the contributions of conducting domain walls to the effective photoconductivity of the samples.
- III. Lastly, the photoconductivities of both domains and domain walls (71 %) have been estimated, through mapping the domain wall densities from PFM images and fitting the photoconduction using the equivalent circuit. A much larger photoconductivity of domain walls assists the conduction of photo-generated carriers and explains the increased I_{sc} values.

The enhancement of photovoltaic responses in BFO films shown above is valuable for understanding the exact role of domain walls in ferroelectric photovoltaic devices, as well as offering a simple way towards enhancing the photovoltaic efficiency.

Chapter 6 Summary and Future Work

6.1 Summary

Along the way to commercialization of ferroelectric-based non-volatile memories, the main drawbacks include polarization fatigue and destructive read-out process, both increasing the probability of device failure over time. The main objective of this work is to investigate the mechanisms of polarization fatigue and switchable ferroelectric photovoltaic responses in BFO-based heterostructures. Various methods to improve the fatigue performance and to enhance the ferroelectric photovoltaic response have been investigated. The main conclusions are:

1. By using *in-situ* PFM and SKPM scanings to investigate the domain evolution and charge redistribution during fatigue measurements in planar BFO-based devices, it is concluded that charge injection/accumulation, rather than defects redistribution, is responsible for domain pinning and the macroscopic polarization fatigue in BFO-based capacitors.
2. The improvement of fatigue performance by oxide electrodes are shown to arise from the suppression, or even elimination of electron accumulation at the electrode/BFO interface due to higher detrapping rate of injected electrons. On the other hand, the Schottky barrier at the electrode/BFO interface assists the electron trapping and accumulation by localized high electric field, and consequently, promotes the domain pinning and polarization fatigue. Lowering the Schottky barrier, e.g, by using low work function metals, improves the fatigue performance dramatically. This Schottky

barrier-controlled charge injection model is further supported by fatigue study in vertical BFO-based capacitors.

3. To reduce the unnecessary polarization switching caused by destructive read-out method in conventional FeRAM, we have proposed a novel photovoltaic effect-based FeRAM, where the ferroelectric photovoltaic responses (V_{oc} or I_{sc}), are used to read the stored information nondestructively. We have conducted systematic study to clarify the origin of the switchable photovoltaic effect in BFO heterostructures, through controlling the interface conditions, including varying the top electrode materials or simply the thickness of bottom electrodes in vertical BFO heterostructures. It is proposed that the Pt/BFO interface, or more specifically, the built-in field at the Pt/BFO interface caused by incompletely screened polarization bound charge, plays the crucial role in separating photo-generated carrier and producing photovoltage. The directions of photovoltage and photocurrent can be reversed by polarization switching induced reversal of the built-in field.
4. After understanding the origin of switchable photovoltaic effect in BFO, we have further enhanced such effect via domain engineering. Substrate vicinality is used to control ferroelectric domain configuration in BFO films and it is found that decreased miscut angle in STO substrates leads to more complicated domain structures and larger domain wall densities. Both SKPM study and macroscopic ferroelectric measurements are carried out and the results suggest that V_{oc} is almost unaffected by domain configurations, consistent with the interface effects of ferroelectric photovoltaic responses proposed above. Furthermore, enhanced I_{sc} is observed and

attributed to the much larger photoconductivity of domain walls, which offers a relatively simple way towards enhancing the photovoltaic efficiency.

Besides being valuable for better understanding on complicated physical phenomena in ferroelectric materials, these investigations also provide insights on the improvements of the reliability of ferroelectric-based non-volatile memories, including both conventional FeRAM and the novel photovoltaic effect-based FeRAM.

6.2 Future Work

6.2.1 Effects of Electrode Materials on the Photovoltaic Response in BiFeO_3

Heterostructures

It has been proven that the switchable photovoltaic response in BFO is governed by the energy band bending at the metal/BFO interface. Moreover, the metal/BFO interface is highly dependent on the metal materials. It is naturally expected that the photovoltaic property will be affected by the electrode materials. A series of metal electrodes have been used in the vertical metal/BFO/LSMO heterostructures and the photovoltaic properties have been tested. The typical *I-V* curves under illumination are given in Figure 6-1.

Figure 6-1. The typical I - V curves of vertical BFO-based capacitors under illumination with different metals as top electrodes.

To understand that how electrode materials affect the photovoltaic effects in BFO heterostructures, the switchable V_{oc} (the sum of the absolute V_{oc} values for P_{up} and P_{down}) values as functions of different properties of the metals, including electronegativity, work function and oxidation free energy, are drawn in Figure 6-2. It is clear that only when oxidation free energy of the metals is chosen as the variable, a linear dependence of V_{oc} value is observed. This implies that an oxide layer may exist at the metal/BFO interface and reduces the interface barrier height and the photovoltaic effect. However, more direct evidences from advanced techniques, such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), are needed to support this hypothesis.

Figure 6-2. The switchable V_{oc} as functions of (a) electronegativity, (b) work function and (c) oxidation free energy of the metal electrodes.

6.2.2 Enhancements of Photovoltaic Responses in BiFeO_3 by Chemical Substitution

Unfortunately, varying the top electrodes in BFO heterostructures does not significantly improve the photovoltaic responses. To further improve the ferroelectric photovoltaic effect, we have to investigate the intrinsic properties of the ferroelectric layer. Chemical substitution in BFO has been reported to improve ferroelectric properties and enhance piezoelectric and dielectric performance.[115, 116] In the future, we plan to conduct a systematic study to reveal the effect of rare earth substitution on the photovoltaic properties in BFO. The preliminary results of photovoltaic responses of La-doped BFO ($\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$, $x=0.1, 0.2, 0.3$ and 0.4) are provided in Figure 6-3. Both V_{oc} and I_{sc}

increase significantly with La concentration, reaching the maximum values at $x=0.2$, then decrease. For heavily doped BFO ($x=0.3$ and 0.4), P - E loops and PUND measurements show no switchable polarization, and consequently, I - V curves under illumination reveal no photovoltaic effect. This further supports that the polarization switching is the main driving force of ferroelectric photovoltaic response in BFO films. However, the fact that lightly doped BFO shows enhanced photovoltaic response even though the switchable polarization is reduced is very interesting and the mechanism is still unclear. Initial study shows no changes in the band gap and interface barrier height upon doping. We propose that local polar instability caused by the La doping could lead to non-polar regions in the film where large unscreened depolarization field exists. This local depolarization field effectively separates the electron-hole pairs and increases photocarrier lifetime. More experimental results and theoretical simulations are needed to clarify the exact mechanism of the improvements of photovoltaic effects by chemical substitution.

Figure 6-3. (a,b) Ferroelectric and (c,d) photovoltaic properties of La-doped BFO films.

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