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<td>Fang, Liang; You, Lu; Zhou, Yang; Ren, Peng; Lim, Zhi Shiuh; Wang, Junling</td>
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Switchable photovoltaic response from polarization modulated interfaces in BiFeO3 thin films

Liang Fang, Lu You, Yang Zhou, Peng Ren, Zhi Shiuh Lim, and Junling Wang

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Switchable photovoltaic response from polarization modulated interfaces in BiFeO₃ thin films

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The switchable photovoltaic effect in BiFeO₃ thin films capacitors has been studied extensively. However, the origin of the photovoltaic response is still under debate. Both bulk depolarization field and interface effects have been used to explain the observations. In this work, we fabricate BiFeO₃ epitaxial films on SrTiO₃ substrate with La₀.₇Sr₀.₃MnO₃ and Pt as electrodes. Much larger switchable photovoltaic response can be observed in the Pt/BiFeO₃/La₀.₇Sr₀.₃MnO₃ samples, as compared with La₀.₇Sr₀.₃MnO₃/BiFeO₃/La₀.₇Sr₀.₃MnO₃. Moreover, the photovoltaic voltage of the Pt/BiFeO₃/La₀.₇Sr₀.₃MnO₃ samples is nearly independent of the thickness of the La₀.₇Sr₀.₃MnO₃ bottom electrode. We suggest that the Schottky barrier modulation by ferroelectric polarization at the Pt/BiFeO₃ interface is mainly responsible for the photovoltaic effect, with very small contribution from the bulk depolarization field. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870972]

Ferroelectric photovoltaic effect has received considerable attention due to its potential for optoelectronics, energy conversion, and information storage.¹–³ It is often suggested that different from p-n junction based systems, ferroelectric photovoltaic is a bulk effect where the photo-generated carriers can be separated throughout the sample.⁶ However, both bulk depolarization field and interface effect have been used to explain experimental observations in the literature. Among the various ferroelectric materials, BiFeO₃ (BFO) is of particular interest because of its robust ferroelectricity and small band gap.⁷,⁸ Several groups have grown high-quality epitaxial BFO films on oxide substrates and studied the photovoltaic effect. For example, Yang et al. reported the photovoltaic effect in an all-oxide heterostructure with SrRuO₃ (SRO) and tin doped indium oxide (ITO) electrodes,⁹ and attributed the effect to the Schottky barrier-induced field (E_Sc) within the interface depletion layer between BFO and ITO. Note that the photovoltaic response of their samples could not be switched by the ferroelectric polarization. In contrast, Ji et al. demonstrated switchable photovoltaic effect in the same ITO/BFO/SRO heterostructure under visible light illumination.¹⁰ They attributed the photovoltaic response to the polarization-induced internal electric field (depolarization field, E_De) due to incomplete screening. More recently, Lee et al. reported switchable photovoltaic response in Pt/BFO/SRO heterostructure,¹¹ which was ascribed to the modulation of E_Sc by polarization charge at the Pt/BFO interface. On the other hand, Wang et al. studied Au/BFO/La₀.₇Sr₀.₃MnO₃ (LSMO) heterostructures and suggested that polarization modulation of E_Sc occurs at both the Au/BFO and BFO/LSMO interfaces.¹² Therefore, it is clear that a systematic investigation is needed to clarify the origin of ferroelectric photovoltaic effect in the BFO heterostructures. In this paper, we aim to answer two questions: (1) Between E_De and E_Sc, which one determines the photovoltaic response of the BFO thin film capacitors? (2) What is the difference between metal/BFO and oxide/BFO interfaces?

The model system that we choose for our investigation is BFO with LSMO and Pt as electrodes. LSMO is one of the most used bottom electrode materials for preparing BFO heterostructures due to its lattice matching with BFO and high conductivity. It is known that the work function of LSMO is almost the same as that of BFO.¹³,¹⁴ Moreover, since the polarization can be partially screened by the ionic displacement at the interface,¹⁵,¹⁶ the BFO/LSMO interface shows nearly flat-band condition, while Pt/BFO interface has a Schottky barrier.¹⁷ This allows us to identify the E_De contribution to the photovoltaic response using LSMO/BFO/LSMO samples. Afterward, we can then clarify the effect of different types of interface by replacing the top LSMO with Pt. In this study, LSMO/BFO/LSMO and Pt/BFO/LSMO heterostructures were fabricated using pulsed laser deposition (KrF excimer laser, λ = 248 nm) on (001)-oriented SrTiO₃ (STO) single-crystal substrates with a 4° miscut toward the [110] direction, as described in our previous report.⁵ LSMO bottom electrode with different thickness (15, 6, 4, 3, 2, and 1 nm) was deposited at 780°C with the oxygen partial pressure of 200 mTorr. The laser energy density and repetition rate were 2 J cm⁻² and 3 Hz, respectively. Following the deposition of the bottom electrode, epitaxial BFO film of around 100 nm was grown at 680°C and oxygen partial pressure of 50 mTorr. The laser energy density and repetition rate were 1 J cm⁻² and 10 Hz, respectively. For the electric and photovoltaic measurements, 10 nm-thick Pt and 15 nm-thick LSMO top electrodes (20 × 20 μm²) were patterned using standard photolithography process. It should be pointed out that in order to avoid the decompositions of the as-grown BFO films, the LSMO top electrode was grown at 650°C and under an oxygen partial pressure of 300 mTorr, followed by a chemical etching process.¹⁸

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The phase purity and crystallinity of the samples were examined by x-ray diffraction (XRD) on an x-ray diffractometer (XRD-6000, Shimadzu) using Cu Kα radiation. Piezoresponse force microscopy (PFM) measurements were carried out on a commercial atomic force microscope (MFP-3D, Asylum Research) using a Pt/Ir-coated tip. Ferroelectric properties were characterized using a commercial ferroelectric tester (Precision LC, Radiant Technologies). The current-voltage (I-V) behavior of the films was obtained using a low-noise probe station and a pA meter/direct current (DC) voltage source (Hewlett Packard 4140B) in dark and under the illumination of a Halogen lamp (energy density ~20 mW/cm²) through the top electrodes. In this study, forward (reverse) bias is defined as a positive voltage applied to the bottom (top) electrode, and the polarization pointing from the bottom (top) electrode to the top (bottom) electrode is defined as upward (downward) polarization, abbreviated as \( P_{up} \) (\( P_{down} \)). The transmission coefficients of the two top electrodes are measured by UV-Vis-NIR spectrometer (Cary 5000, Agilent). About 80% (35%) of the light is transmitted for LSMO (Pt) electrode in the visible spectrum, which is consistent with other reports.5,19

Figure 1(a) shows the XRD pattern of the BFO/LSMO(15 nm) heterostructure grown on STO substrate. Only peaks corresponding to (00l) reflections of BFO and those from the substrate are seen, indicating the epitaxial growth of the films. The inset shows the AFM image of the corresponding sample. The phase image of the out-of-plane piezoelectric response for the corresponding sample is shown in Figure 1(b). Stable ferroelectric domains with opposite polarities can be written by applying a voltage to the AFM tip, suggesting robust polarization switching.

Figure 2(a) shows the ferroelectric polarization-voltage (P-V) hysteresis loop of the LSMO(15 nm)/BFO/LSMO (15 nm)/STO sample. The sample shows a large, approximately 65 μC/cm², remanent polarization along the [001] pseudocubic direction. Note that the P-V hysteresis loop is nearly rectangular, indicating very low leakage current through the sample.11,20 The current-voltage (I-V) curves under illumination reveal a very small photovoltaic response for both polarization directions. The open-circuit photovoltage (\( V_{oc} \)) is 0.05 V and the short-circuit photocurrent (\( I_{sc} \)) is ~3.7 pA for the films with the upward polarization, while the \( V_{oc} \) is ~0.03 V and the \( I_{sc} \) is 4.3 pA for the downward polarization. Although the I-V curve shifts slightly to one side, which is likely due to the different deposition conditions for the two LSMO layers, it is reasonable to assume that the \( E_{De} \) contribution to the photovoltaic effect in this system can be neglected. By taking average of the positive and negative \( V_{oc} \) values, the contribution from the \( E_{De} \) to the photovoltaic can be estimated to be only 0.04 V in this system.

After identifying the \( E_{De} \) contribution to the photovoltaic effect, we turn to study the interface effect. Figure 3(a) shows the P-V hysteresis loop of the Pt(10 nm)/BFO/LSMO(15 nm)/STO sample, which is similar to that of the LSMO/BFO/LSMO sample. On the contrary, much larger polarization dependent photovoltaic response is observed, as shown in Figure 3(b). The \( V_{oc} \) is ~0.20 V and the \( I_{sc} \) is ~1.0 pA with downward polarization, and ~0.18 V/-1.44 pA for upward polarization. (Note that the Pt electrode only allows 35% light to be transmitted, as compared with 80% for the top LSMO electrode. This means that, for the same light intensity on BFO, the Pt/BFO/LSMO sample should have an even larger photovoltaic response.) Moreover, as shown in the inset of Figure 3(b), both \( V_{oc} \) and \( I_{sc} \) exhibit hysteretic behaviors similar to the P-V loop by sweeping the switching voltages, which confirms that the ferroelectric polarization switching is the driving force of the switchable photovoltaic effect. Qin et al. pointed out that, compared with Au top electrode,21 LSMO top electrode tends to have the screening charges more extensively distributed away from the interface and consequently the polarization screening effect is weakened. This leads to the significantly larger photocurrent in the LSMO/(Pb0.97La0.03) (Zr0.52Ti0.48)O3/Nb:STO sample. However, opposite results are observed in our study, where Pt/BFO/LSMO sample shows larger photovoltaic response. This suggests that bulk depolarization field effect is not the dominating factor in our system.

In order to further study, the depolarization field contribution to the photovoltaic effect, Pt/BFO/LSMO capacitors with different LSMO thicknesses were prepared. It is well
known that the electronic properties of ultra-thin LSMO films vary dramatically as thickness decreases, often resulting in a metal-insulator transition, which consequently affects the screening length at the ferroelectric/LSMO interface. Figure 3(c) shows the temperature dependence of resistivity for the LSMO films with different thicknesses. Clearly, the resistivity of LSMO films increases drastically over the whole temperature range upon reducing thickness. For 6 and 4 nm LSMO films, bulk-like metallic behavior is observed over the whole temperature range. A metal-insulator transition at low temperature is observed in the 3 nm LSMO film. Further reducing the thickness to 2 and 1 nm leads to pure insulating behavior throughout the whole temperature range. This change in transport characteristics is commonly observed in LSMO ultra-thin films, which has been attributed to a modified structure at the interface. Although the conductivity of ultra-thin LSMO films is low and the switching time is longer, such films can still serve as the bottom electrode.

Figure 3(a) also shows the $P-V$ hysteresis loops of the Pt(10 nm)/BFO/LSMO(2 nm) and Pt(10 nm)/BFO/LSMO(1 nm) samples, which were measured at 200 and 20 Hz, respectively. It should be noted that due to the large contribution from leakage current, remanent hysteresis loop (see Ref. 25 for details) was employed to obtain the true remanent polarization of the Pt(10 nm)/BFO/LSMO(1 nm) sample, which is reduced to $\sim 50 \mu C/cm^2$. Figure 3(d) shows the LSMO thickness dependence of the $V_{oc}$ and $I_{sc}$ for the Pt/BFO/LSMO heterostructures. The $V_{oc}$ value (average of positive and negative $V_{oc}$) is nearly independent of the LSMO thickness except for the 1 nm sample. Though it is not entirely clear why the Pt(10 nm)/BFO/LSMO(1 nm) shows smaller photovoltaic response, such phenomenon may be related to the reduced remanent polarization observed in the $P-V$ hysteresis loop. Nevertheless, the result clearly shows that bulk depolarization field is not the dominating factor in this system (otherwise, the sample with thinner bottom LSMO would show larger photovoltaic response due to poorer screening effect). We can conclude that the enhanced photovoltaic response in Pt/BFO/LSMO (>1 nm) system mainly comes from the Pt/BFO interface.

To better understand the effect of interface on the photovoltaic response, we turn to the energy diagram across the heterostructure. The work functions of LSMO and Pt are $\sim 4.7$ eV and 5.3 eV, respectively. The band gap of BFO is $\sim 2.8$ eV and its electron affinity is $\sim 3.3$ eV. Even though Bi vacancies may render BFO $p$-type, they are very inefficient dopants, so it is reasonable to assume that the Fermi level of BFO is close to the center of the band gap. Furthermore, it has been suggested that ferroelectric polarization can be screened by ionic displacement at the epitaxial interface, which in turn weakens the band bending effect. A nearly flat-band is then expected at the interface between BFO and Pt, which generates a positive photovoltage and a negative photocurrent, while a nearly flat-band forms at the interface between BFO and LSMO. When the polarization of BFO is reversed, the $E_{bi}$ direction is also reversed as shown in Figure 4(b), leading to a negative photovoltage and a positive photocurrent. This model is also consistent with that proposed by Yuan and Wang.

In conclusion, photovoltaic effect in LSMO/BFO/LSMO thin film capacitors has been investigated, revealing a relatively small contribution from the depolarization field. On the contrary, much larger switchable photovoltaic response is observed in the Pt/BFO/LSMO sample. Moreover, the photovoltaic properties of Pt/BFO/LSMO sample are nearly independent of the thickness of LSMO bottom electrode, although its resistance increases with decreasing thickness. The switchable photovoltaic response in the Pt/BFO/LSMO samples is mainly attributed to the
modulation of Schottky barrier at the Pt/BFO interface by the ferroelectric polarization. Note that in our samples, the BFO films are ~100 nm thick. In cases where the two interfaces are perfectly symmetric (e.g., the in-plane sandwich structure with BFO channel of hundreds of micrometers),\textsuperscript{5,27} the bulk photovoltaic effect may dominate the device response.

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\begin{figure}
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\caption{Schematic of the energy band diagrams and operational principle of the photovoltaic properties for the Pt/BFO/LSMO heterostructure (a) the upward and (b) downward polarization states of BFO. $E_F$, $E_C$, and $E_V$ represent Fermi level, valence band, and conduction band of BFO, respectively. The corresponding insets show the signs and directions of $V_{OC}$ and $I_{SC}$.
\end{figure}