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Tunable photovoltaic effects induced by different cooling oxygen pressure in Bi_{0.9}La_{0.1}FeO₃ thin films



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ABSTRACT

The photovoltaic effects in Bi_{0.9}La_{0.1}FeO₃ thin films are found to be strongly dependent on the oxygen concentration which can be manipulated by cooling oxygen pressure. Switchable photovoltaic effects can be observed without any electric field applied in low oxygen pressure cooled samples, however, it is hard to detect with high oxygen pressure cooled samples, until the occurrence of polarization flipping by applied electric field. This switchable photovoltaic effects can be explained well by the variation of the Schottky barrier at the metal–Bi_{0.9}La_{0.1}FeO₃ interface resulting from the combination of oxygen vacancies and polarization. The sign of photocurrent could be independent of the direction of polarization when the modulation of the energy band induced by oxygen vacancies is large enough to offset that induced by polarization. The photo-current induced by the electro migration of oxygen vacancies is variable due to the diffusion of defects such as oxygen vacancies or the recombination of oxygen vacancies with hopping electrons. Our work provides new ideas for tuning the photovoltaic effect in ferroelectric materials. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

Multiferroic materials, which combine two or more the properties of ferromagnetism, ferroelectricity and ferroelasticity, offer extra degrees of freedom in the information storage process, which may either simplify the operation of present device structures or offer new architecture [1,2]. Among them, single-phase multiferroic BiFeO₃ (BFO) is the most extensively investigated because of its high ferroelectric Curie temperature ($T_{\rm C}$) of ~1100 K and an antiferromagnetic Néel temperature (T_N) of ~640 K [3,4]. Recently, the photovoltaic (PV) effect observed in BFO has received increasing interest due to its small band gap (~2.8 eV), large open circuit voltage (Voc), and switchable diode and PV effects [5–10]. It was found that the direction of photo-current was strongly depended on the polarization switching, the direction of the PV effects can be reversibly switched by applying an alternating electric field, and the sign of photo-current is opposite to the polarization direction [7,8]. Thus, it is believed that polarization flipping should play an essential role in the observed PV effects [5,7,8]. However, several sensitive experiments show that the migration of positively charged oxygen vacancies (V_{OS}) under an external electric field is as essential as the polarization flipping to produce the switchable PV effects [5], and even the critical parameter for defining such phenomenon in BFO based thin films [11]. It also indicated that the sign of photocurrent is independent of the direction of polarization, but it is always opposite to the voltage direction of the last treatment [11]. Obviously, whether the oxygen vacancies or the polarization or both of them affect the PV effects is quite elusive. Besides the oxygen vacancies and polarization, the formation of a Schottky barrier at the metal–semiconductor interface is also reported to have a contribution to the PV effect [12–14]. Therefore, it is of great value to disentangle how oxygen vacancies, polarization, and Schottky barriers affect the PV effects of ferroelectric films.

This paper is mainly to report the influences of V_{os} on the photovoltaic effects in Bi_{0.9}La_{0.1}FeO₃ thin films. Here, the small amount of La is added to stabilize the perovskite structure. The density, diffusion, and distribution of V_{os} are manipulated by the partial pressure of oxygen during cooling after growth.

2. Experiment

Using pulsed laser deposition, 500 nm thick $Bi_{0.9}La_{0.1}FeO_3$ (BLFO) and 30 nm $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films (used as a bottom electrode) were epitaxially grown on (001)-SrTiO_3 (STO) single crystal substrates. The conductive metallic oxide LSMO was chosen as bottom electrode because the pseudocubic crystal lattice is ~0.3878 nm for LSMO thick film, ~0.3905 nm for STO crystal substrate and



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~0.3965 nm for BFO crystal [4.15.16]. Therefore, with small lattice parameter mismatch and stress, one can expect epitaxial growth. BLFO thin films were grown at 650 °C and 15 Pa, as we depicted previously [14,16]. The other laser parameters during depositions were (i) laser source: KrF excimer laser with λ = 248 nm, (ii) repetition frequency: 5 Hz, (iii) energy density was about 1.5 J/cm². Typical film growth rate was around 9 nm per minute. Following the growth, these samples were then cooled to room temperature at 5 °C/min in 500, 20, or 0.5 Pa Po₂ in order to induce different oxygen concentrations. For the conductive characteristics measurements, 200 nm thick Ag layer as the top electrodes was deposited by PLD through a shadow mask with an area of 3×10^{-4} cm². Structural characterization of these BLFO films was performed using X-ray diffraction (XRD)analysis (Rigaku D/max-2550/PC with Cu K radiation) at a scan speed of 0.05° s⁻¹. The roughness and the ferroelectric domains of BLFO surfaces were studied using Scanning Probe Microscopy (SPM, with AFM and PFM model)(Seiko, Nanonavi II, E-Sweep, Japan), Pt coated Si was used as tip, ac-voltage (64 kHz, 3000 mV) was applied for domains measuring. The ferroelectric properties were investigated using an RT6000 ferroelectric tester (Radiant Technology) at 10 kHz for BLFO samples. The oxygen concentration of the samples was analyzed using X-ray Photoelectron Spectroscopy (XPS, Thermo ESCA 250, Mg target). Green laser with the wavelength of 532 nm (100 mW/cm²) was used as excitation light source for the photovoltaic effect (PVE) measurement. Current-voltage characteristics were measured using a Keithley 2611 source meter. The polarity of bias is defined as negative or positive according to the negative or positive voltage applied to the Ag top electrode.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of BLFO films cooling at different oxygen pressures. The patterns can be fully indexed using the standard XRD data, which reveals high quality, epitaxial films that appear to be single phase. All the 002 diffraction peaks of BLFO films are slightly higher than the 45.770° expected for BFO ($\delta \sim 0$) crystal (inset of Fig. 1(a)), suggesting all the samples are weakly strained. Besides, a slightly shift of the BLFO (002) diffraction peak is observed with varying cooling pressure, correspondingly, the out-of-plane lattice strains $\varepsilon_{001} = (c_{\text{bulk}} - c_{\text{film}})/c_{\text{bulk}}$



Fig. 1. XRD spectrum of BLFO/LSMO/STO films cooled under different Po_2 , where the 002 peaks are amplified in insets and the dashed lines located at 45.770° expected for bulk like BFO.

varies from -0.082% to -0.561% when the cooling oxygen partial pressure decreases from 500 Pa to 0.5 Pa. However, Basu et al. and Yuan et al. did not observed noticeable shift of the BFO diffraction peak with varying cooling Po₂ from 760 Torr to 0.01 Torr in BFO/SRO/STO heterostructures [15,17]. Generally, the diffraction peak shift is always observed in oxygen deficient perovskite manganite [18–20]. Therefore, for one hand, it is possible that as V_{0} s induces the slightly expanded of *c* axis of LSMO films, which in turn increase the in-plane compressive stress between BLFO and LSMO films, thus results the expansion of *c* parameter of BLFO films. For another hand, as BFO belongs to perovskite structures, the same as LSMO, therefore, different oxygen vacancies will result in different out-of-plane lattice parameters. In order to estimate the approximate V_{0s} in BLFO films in different cooling Po₂, oxygen concentration was determined by fitting oxygen peak in the measured spectrum using XPS, as shown in Fig. 1(b). One can see from Fig. 1(b) that oxygen concentration increases with the cooling Po₂ increasing. It means that there are V_{0} s in BLFO films and V_{0} s increases with the cooling Po₂ decreasing. Obviously, low Po₂ cooling will greatly enhance the V_0s concentration [15,17]. It is



Fig. 2. (a) Typical AFM image of BLFO/LSMO/STO (001) films. (b) Out of plane PFM images of BLFO films. The films were poled through PFM tip scanning of the film surface with a positive voltage of +10 V with a square area $2 \times 2 \, \mu m^2$. After that, the polarization in the center $1 \times 1 \, \mu m^2$ area is scanned with $-10 \, V$. Finally, the piezoelectric phase image was carried out by applying an ac voltage (frequency 64 kHz, amplitude $3 \, V$ peak-to-peak) to the PFM tip with a square area $5 \times 5 \, \mu m_2$.

reported that the oxygen concentration is determined to be 5.14×10^{17} and 5.44×10^{17} at./cm³ for as-deposited and annealed BFO films, respectively, while the ideal oxygen concentration for stoichiometric BFO film is estimated to be 5.79×10^{17} at./cm³ [21].

Fig. 2 shows the ferroelectric properties of these BLFO films using a combination of atomic force microscopy (AFM), piezoresponse force microscopy (PFM), and polarization-electric field (P-E) hysteresis loop measurements. AFM imaging (Fig. 2(a)) reveals smooth films-average root mean square roughness (RMS) of 5.5 nm. Additionally, PFM was used to probe the ferroelectric nature of the films. By applying a voltage to the tip during the scan, we were able to reversibly switch the polarization for all films regardless of cooling Po₂ (Fig. 2(b)). The ac voltage for imaging domain structure has amplitude of 3 V (peak to peak) and a frequency of 64 kHz. First, the samples were poled by +10 V with the areas of $2 \times 2 \text{ um}^2$, then poled it by -10 V with $2 \times 2 \text{ um}^2$ in center. It can be seen that the polarization orientation can either point down toward the bottom electrode (imaged as white contrast in the outof-plane PFM image) or up (imaged as black). Films used in this experiment are almost entirely upward polarized in the as-grown state with the exception of small downward pointing domains. Self-polarization is easy to form in ferroelectric films with a stress gradient or an internal bias field (E_{bias}) due to a non-uniform distribution of oxygen vacancies. Ji et al. and Basu et al. have reported self-polarization in the virgin BFO films [6,17]. It is reasonable that self-polarization with a polarized up state exists in the as-deposited films. P-E hysteresis loop measurements reveal high quality, square-like hysteresis loops with a saturation polarization of \sim 60 μ C/cm² for all the films, as shown in Fig. 3. A bigger leakage current can be found in Fig. 3(c) with the lowest cooling Po₂ of 0.5 Pa, indicating the existence of defect states such as V_{0S} is the main cause of high leakage current in BLFO films [5,22].

Fig. 4(a)-(c) shows the dark and illumination *J*–*V* curves of the virgin BLFO thin films. The dark current density at zero bias is so

small (<10 nA/cm²) that it could be reasonably neglected. A distinct PV response is observed under illumination. The open circuit voltage (V_{oc}) and the corresponding shorted circuit photo current (I_{sc}) are shown in the insets of Fig. 4(a)–(c). It shows that for the thin films cooled at 500 Pa, 20 Pa and 0.5 Pa, V_{oc} can reach up to 0.12 V, 0.15 V and 0.18 V, respectively. The corresponding J_{sc} can reach up to 2.25 $\mu\text{A/cm}^2$, 22 $\mu\text{A/cm}^2$ and 80 $\mu\text{A/cm}^2$, respectively. Both V_{0c} and J_{sc} increase with Po₂ decreasing, which manifests the important effect of V_{os} on the V_{oc} and J_{sc} . Time-dependent J_{sc} for the as grown BLFO film capacitors is shown in Fig. 5(a)-(c), exhibiting good retention and stability over multiple cycles. Furthermore, all the J_{sc} is positive value and it is increase with the cooling Po_2 decreasing. This distinct J_{sc} is mainly because that all the films cooling in different Po2 is upward polarized in the asgrown state. Some authors have reported switchable PV effects by applying an alternating electric field, and the sign of photocurrent is opposite to the polarization direction [7.8]. Therefore, it is not strange that all our as-grown films show positive photocurrent.

Fig. 6(a)–(c) shows time-dependent photocurrent for the poled BLFO film capacitors. It can be found that I_{sc} is positive when BLFO is in upward polarization state (UPS, poled by -30 V), while it can be switched to negative when BLFO is in downward polarization state (DPS, poled by +30 V), indicating switchable Isc with switching the polarization. However, it is found that the PV effect for the poled BLFO samples cooled in 500 Pa Po₂ exhibits good retention and stability over multiple cycles yet it is not stable especially in low cooling Po_2 (Fig. 6(c)). The photo-currents both in UPS and DPS all decrease rapidly firstly, then slow down, and at last reach a value slightly lower than those of the initial values. For the positively poled samples, the direction of the photo-current can be switched back to its original direction (Fig. 6(c)). The time-dependent photo-current curves can be fitted well by exponential decay with a relaxation time τ = 4.05 s and 8.98 s for UPS and DPS, respectively. Qin et al. [23] has found a switchable photovoltage



Fig. 3. P-E loops of the as-grown BLFO/LSMO/STO (001) thin films.



Fig. 4. J-V curves under dark and illumination for the virgin BLFO/LSMO/STO (001) films cooled at (a) 500 Pa, (b) 20 Pa, (c) 0.5 Pa Po₂.



Fig. 5. Time-dependent photocurrent for the as-grown BLFO/LSMO/STO (001) films cooled at (a) 500 Pa, (b) 20 Pa, and (c) 0.5 Pa Po₂.



Fig. 6. Time-dependent photocurrent for the negatively poled (-30 V) and positively poled (+30 V) with light on and off for the BLFO/LSMO/STO (001) films cooled at (a) 500 Pa, (b) 20 Pa, and (c) 0.5 Pa partial pressure of oxygen.

in WO₃ doped PZT ferroelectric polycrystalline films, the photovoltage decreases during UV illumination. They suggested that the Schottky barriers and polarization screening due to the trap of photo induced charges at ferroelectric–metal interfaces would determine the magnitude, stability, and polarity of the photovoltage. Moubah et al. [11] have also observed a decay of photocurrent under illumination in single domain BFO crystals with oxygen vacancies introduced by prolonged exposure to high-power white light in the presence of an electrical field much lower than its coercive field. They attributed the photocurrent decay to the photo induced electron–hole pairs. Pintilie et al. [24] observed a switchable photocurrent on PZT ferroelectric films during UV illumination. They found that the polarization direction has back switched from up to down.

Considering that the photo-currents detected in the virgin samples are very stable, therefore, the related physical mechanism underlying the stability of the PV effect for poled samples needs to be clarified. To detect the polarization direction has been changed or not during illumination, the so called positive-up-negative-down (PUND) method was adopted [25,26]. However, our results indicate that the polarization state under illumination is stable. Thus, the polarization flipping can be excluded for the observed switchable PV effect as seen in Fig. 6(c). The absence of the switchable PV effect in the as-grown BLFO samples and with 500 Pa Po₂ cooling films demonstrates that V_0 s is important in acquiring a switchable PV effect.

In order to fully understand the different characteristics of switchable PV effects in the BLFO samples and the unstable nature of photo-current in the poled BLFO samples, schematic energy band diagrams should be established for the virgin and poled samples. Because V_0 s always exist in perovskite oxides, it is reasonable

to regard BLFO based thin films as a n-type semiconductor [15,27]. The work functions of Ag and LSMO are 4.26 eV and 4.96 eV, respectively, and the electron affinity/band gap of BLFO is 3.3 eV/ 2.8 eV [28]. Because of the high resistivity of BLFO films, we presume that its Fermi level locates approximately in the middle of the energy band gap. Then the work function of BLFO films is supposed to be approximately 4.7 eV. Besides the different work functions of Ag, BLFO and LSMO, ferroelectric polarization can affect interfacial barrier [29], therefore, band diagram can be depicted for the Ag/LBFO/LSMO device, as shown in Fig. 7(a) and (b). Fig. 7(a) and (b) shows an ideal schematic energy band diagram for the Ag/BLFO/LSMO structures before and after contact, respectively, for downward and upward polarization. Fig. 7(c) shows the schematic energy band diagram for the as-grown and with upward self-polarized Ag/BLFO/LSMO structure. At the two interfaces, the band bending behavior will change. In the n-type BLFO films, the barrier height can be reduced by introducing a high concentration $V_{\rm o}$ s layer to the interface. For the negatively (positively) poled BLFO samples, the barrier height at the Ag/BLFO (BLFO/LSMO) interface will reduce (Fig. 7(d)–(g)). With occurrence of the polarization flipping, the polarization becomes the main driving force to modulate energy band for the BLFO samples with a low V_0 s concentration.

The modulation of the energy band induced by the migration of V_{os} can also satisfactorily explain the direction of the photocurrent. It is known that the photocurrent has two contributions: diffusion current ($I_{diffusion}$) and drift current (I_{drift}) [7,14]. $I_{diffusion}$ is related to the gradient of photo-induced electron–hole pair density. Electrons always diffuse from high density areas to low density regions, which form the so called diffusion current. While I_{drift} is affected by the internal electric field of the depletion layer, electrons moves as a result of the drift force of the electric field. On one hand, the



Fig. 7. Schematic energy band diagrams of Ag, BLFO and LSMO, (a) before contact and (b) after contact. Schematic energy band diagrams illustrate the variations of photocurrent and Schottky barriers for Ag/BLFO/STO structure for (c) the as-grown BLFO films with upward polarization, (d) the samples poled at -30 V before oxygen vacancies diffusion, (e) the samples poled at -30 V after oxygen vacancies diffusion, (f) the samples poled at +30 V before oxygen vacancies diffusion and (g) the samples poled at +30 V after oxygen vacancies diffusion.

photo generated electron–hole pairs can drift toward/against the surface under the field E_{A-B} and E_{L-B} (Here, E_{A-B} and E_{L-B} indicates the electric field between A-BLFO and BLFO-LSMO, respectively). On the other hand, the electrons can be generated more effectively in the region with a low band gap of defect states induced by V_{os} . $I_{diffusion}$ and I_{drift} for the virgin and poled BLFO samples are sketched in Fig. 7(c)–(g). The value of $I_{diffusion}$ could be large if the V_{os}

concentration is high enough, because photo-generated electrons can diffuse effectively to the negative electrode due to the short traveling distance, thus gives a low possibility of recombination of electron–hole. Furthermore, the V_{os} in the oxygen deficient film can trap the photo induced electrons and the photo induced holes become the extra carriers. Therefore, more V_{os} mean lower recombination of electron–hole.

Table 1

The parameters and the estimated values of the out-of-plane lattice strains, diffraction peak maximum, oxygen vacancy deficient and the characteristic time of J_{sc} etc., for investigated samples.

Cooling oxygen pressure (Pa)	500	20	0.5
Diffraction peak maximum (2 theta, degrees)	45.75	45.67	45.52
Out-of-plane strain in the film, ε_{001} (%)	-0.082	-0.248	-0.561
Oxygen vacancy deficient (%)	4.2	11.3	21.6
Measured J_{sc} (virgin films) (μ A/cm ²)	2.25	22	80
V _{schottky} at Ag/BLFO interface (virgin films) (eV)	0.16	0.17	0.17
V _{schottky} at BLFO/LSMO (virgin films) (eV)	0.87	0.85	0.86
Characteristic time of J _{sc} change (virgin films)	1.03	1.11	1.06
Measured J_{sc} (films poled by +30 V) (μ A/cm ²)	-28	-31	15
V_{schottky} at Ag/BLFO interface (films poled by +30 V) (eV)	0.81	0.83	0.89
V _{schottky} at BLFO/LSMO (films poled by +30 V) (eV)	0.19	0.12	0.07
Characteristic time of J_{sc} change (films poled by +30 V)(s)	1.25	3.44	8.98
Measured J_{sc} (films poled by -30 V) (μ A/cm ²)	43	52	90
V_{schottky} at Ag/BLFO interface (films poled by -30 V) (eV)	~ 0	~ 0	~0
V_{schottky} at BLFO/LSMO (films poled by -30 V) (eV)	0.97	0.98	1.03
Characteristic time of J_{sc} change (films poled by -30 V) (s)	1.02	2.36	4.05

For the as-grown and with upward self-polarized Ag/BLFO/ LSMO structure (Fig. 7(c)), the barrier height between Ag/BLFO is low so that $I_{diffusion}$ is bigger than I_{drift} , therefore the direction of $J_{\rm sc}$ is the same as $I_{\rm diffusion}$, and thus a positive current (from top to bottom in the BLFO film) can be detected. For the sample poled with -30 V, more V_0 s are repelled to the Ag/BLFO interface, for on hand, I_{drift} is small because of the low barrier height between Ag/ BLFO interface. For another hand, more V_0 s accumulate at the Ag/ BLFO interface which induces lower recombination of electronhole and larger $I_{diffusion}$, therefore the direction of I_{sc} is the same as that of $I_{diffusion}$ and a large J_{sc} can be detected. When the electric field is removed, V_0 s with positive charge will diffuse from top to bottom because of the concentration gradient and the repulsive force from the polarization head side with positive charge. As a result, Idrift increase because of the increase of Ag/BLFO barrier height, and I_{diffusion} decrease because of lower oxygen vacancies near the top sides. Therefore, Isc decrease compared with the original state (Fig. 7(d) and (e)).

When the BLFO samples are poled with +30 V, the direction of $I_{\text{diffusion}}$ is opposite to that of I_{drift} , and thus the PV effect can be reversed when $I_{\text{diffusion}}$ is smaller than (the same as) I_{drift} . Therefore, $I_{\rm sc}$ is negative, and the direction of $I_{\rm sc}$ is the same as that of $I_{\rm drift}$ as shown in Fig. 7(f). When the electric field is removed, oxygen vacancies with positive charge will diffuse from bottom side to the top side because of the different concentration gradient and the repulsive force from the polarization head side with positive charge. As a result, Idrift decrease due to the decrease of Ag/BLFO barrier height resulted by more oxygen vacancies accumulation. For another hand, I_{diffusion} increases because of higher concentration of V_0 s near the top side. Therefore, the sign of photocurrent could be independent of the direction of polarization when the modulation of the energy band induced by V_0 s is large enough to offset that induced by polarization, as shown in Fig. 7(g). For the samples with low oxygen vacancy concentration (such as cooled by 500 Pa cooling films), the $I_{diffusion}$ is very small and its effect on photocurrent is negligible. Thus, the sign of photocurrent is always opposite to the direction of polarization, and a switchable PV effect can only be observed when the polarization flipping occurs (Fig. 6(a) and (b)).

According to the model proposed above, we list the estimated parameters, by which significant increase of short-circuit current may be resulted. The estimated values of the out-of-plane lattice strains, diffraction peak maximum, oxygen vacancy deficient, characteristic time of J_{sc} and the Schottky barrier, etc., for the investigated samples are summarized in Table 1. It can be seen from Table 1 that different cooling Po₂ can induces different strain and oxygen deficient, the characteristic time of J_{sc} change and the

variation of short circuit current in the films indicate the diffusion and redistribution of $V_{o}s$. Besides, the barrier height between Ag/ BLFO and BLFO/LSMO can be effectively affected by V_os , which will in turn impact photovoltaic effect in Ag/BLFO/LSMO structures. The diffusion and redistribution of V_os proposed in this model can explain the switchable photovoltaic effect without changing the polarization direction very well.

4. Conclusions

In summary, epitaxial (001)-oriented 500 nm Bi_{0.9}La_{0.1}FeO₃ films were deposited on SrTiO₃ substrates with 30 nm La_{0.7}Sr_{0.3-} MnO₃ as buffer layers. It is found that the photovoltaic effects in Ag/BLFO/LSMO heterostructures are strongly dependent on the Vos concentration oxygen vacancies. Switchable photovoltaic effects can be observed without an electric field applied in high oxygen vacancy concentration, however, the switchable photovoltaic effect is hard to be detected with lower oxygen vacancy concentration until the occurrence of polarization flipping by applied electric field. The switchable photovoltaic effects can be explained well by the variation of the Schottky barrier at the metal-semiconductor interface resulting from the combination of oxygen vacancies and polarization. The sign of photocurrent could be independent of the direction of polarization when the modulation of the energy band induced by oxygen vacancies is large enough to offset that induced by polarization. The photovoltaic effect induced by the electro migration of oxygen vacancies is unstable due to the diffusion and redistribution of oxygen vacancies or the recombination of oxygen vacancies with hopping electrons. Our work provides new ideas for tuning the photovoltaic effect in ferroelectric materials.

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