Mechanism of switchable and nonswitchable short-circuit photocurrent accompanying polarization switching in Bi$_{0.9}$La$_{0.1}$FeO$_3$ thin films

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 EPL 105 37008
(http://iopscience.iop.org/0295-5075/105/3/37008)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 159.226.35.189
This content was downloaded on 22/12/2014 at 04:17

Please note that terms and conditions apply.
Mechanism of switchable and nonswitchable short-circuit photocurrent accompanying polarization switching in Bi$_{0.9}$La$_{0.1}$FeO$_3$ thin films

R. L. Gao$^{1,2}$, H. W. Yang$^2$, Y. S. Chen$^2$, J. R. Sun$^2$, Y. G. Zhao$^3$ and B. G. Shen$^2$

$^1$ School of Metallurgy and Materials Engineering, Chongqing University of Science and Technology
Chongqing, 401331, China
$^2$ Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences
Beijing 100190, China
$^3$ Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University
Beijing 100084, China

received 17 September 2013; accepted in final form 27 January 2014
published online 21 February 2014

PACS 73.40.Ei – Rectification
PACS 81.15.Fg – Pulsed laser ablation deposition

Abstract – The short-circuit photocurrent ($I_{sc}$) of Bi$_{0.9}$La$_{0.1}$FeO$_3$ epitaxial thin films has been investigated. Switchable and nonswitchable $I_{sc}$ accompanying polarization switching was observed and it can be explained well using the concepts of drift current and diffusion current controlled by the combination of oxygen vacancies, polarization and conductive domain wall. The sign of photocurrent is independent of the polarization direction when the modulation of photocurrent induced by oxygen vacancies or conductive domain walls is large enough to offset that induced by polarization. Our work provides a deep insight into the nature of photovoltaic effects in ferroelectric films, and will facilitate the advanced design of switchable devices combining spintronic, electronic, and optical functionalities.

Copyright © EPLA, 2014

Introduction. – Multiferroic materials, which simultaneously show ferroelectric and magnetic orders, have recently attracted considerable interest due to their wide range of potential applications and intriguing fundamental physics [1–5]. At room temperature, however, the number of candidate materials for multifunctional applications is very limited [6], because most of the currently known materials exhibit a low magnetic-transition temperature (<273 K) in contrast to a high ferroelectric transition temperature ($T_C > 350$ K) [7–10]. The large difference between the magnetic and ferroelectric transition temperatures is clearly one of the obstacles to the exploitation of multiferroics in real applications at room temperature. From this point of view, BiFeO$_3$ (BFO) is a well-known single phase multiferroic material at room temperature and it is the best candidate because it has both high antiferromagnetic ($T_N = 640$ K) and ferroelectric ($T_C = 1100$ K) transition temperatures [6,11–13]. Robust ferroelectricity ($P_r \sim 100 \mu$C/cm$^2$), a relatively smaller band gap near 2.8 eV compared to other ferroelectrics and its lead-free nature make BFO a prime candidate for next-generation devices including nonvolatile memories and sensor [13–16].

Recently, photovoltaic (PV) effects have been observed both in BFO crystal and thin films under illumination of visible light [17–20]. The photovoltaic effect has received increasing interest due to its small band gap, large open-circuit voltage ($V_{oc}$) and switchable PV effects [20–22]. PV effects can be reversibly switched by applying an alternating electric field, and the sign of photocurrent is opposite to the polarization direction [21–23]. It is believed that polarization flipping plays an essential role in the observed PV switching effects. However, several sensitive experiments show that the migration of oxygen vacancies with positive charge under an external electric field is as essential as the polarization flipping to produce the switchable PV effects [21], and even the critical parameter for defining such phenomenon in BFO-based thin films [24]. It was 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 [24]. Some authors reported that the orientation of photocurrents in their BFO thin films cannot be switched accompanying polarization switching at all, and they attributed this result to the interface depletion layer between BFO and the electrode [24,25]. 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 make a contribution to the PV effect [21,26–29]. Harshan et al. [27] and Zhang et al. [28] observed an enhanced PV effect in PZT-based ferroelectric films by introducing an asymmetric metal electrode structure. Yang et al. [30] gained control over the photoproperties by controlling the domain structure in the BFO film. Therefore, it would be of great value to disentangle how oxygen vacancies, polarization, and domain wall density modulate PV effects of ferroelectric films.

Experimental process. – Epitaxial Bi$_{0.7}$La$_{0.3}$FeO$_3$ (BLFO) films with the thickness of 500 nm were grown on La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) buffered SrTiO$_3$ (001) substrates using pulsed-laser deposition (PLD). The doping of 10% La was used to decrease the leakage current of BFO. The target was prepared by mixing Bi$_2$O$_3$, La$_2$O$_3$ and Fe$_2$O$_3$ in a 1.1 : 0.1 : 1 stoichiometric ratio and sintering at 800°C in air. The larger amount of Bi$_2$O$_3$ was used compensating the easy volatilization of Bi. The films were grown at 650°C under a low oxygen pressure of 15 Pa. The laser output was about 1.5 J/cm$^2$ with a repetition rate of 5 Hz. The typical film growth rate was around 8 nm per minute. In order to ensure oxygen equilibrium, the films were slowly cooled to room temperature (2°C/min) in the oxygen atmosphere of 500 Pa. For the ferroelectric and photovoltaic measurements, a 100 nm thick Ag layer patterned with circles of 200 µm diameter was deposited on BLFO as top electrodes and LSMO served as bottom electrode. In this paper, applying positive (negative) voltage on the top Ag electrode is defined as downward (upward) poling. A green laser with wavelength of 532 nm (100 mW/cm$^2$) was used as excitation light source for the PV measurement. Pulse generator with an amplifier was used to pole the samples and a Keithley 2611 source meter was used to measure I-V curves.

Results and discussion. – Figure 1(a) shows I-V curves of BLFO films with downward polarized state (DPS: polarized by +40 V pulse voltage) in the dark and under illumination. A distinct PV response is observed under illumination, which is quite usual in ferroelectric films. The open-circuit voltage ($V_{oc}$) and short-circuit current ($I_{sc}$) can reach up to −0.1 V and −10 nA, respectively. The sign of $V_{oc}$ and the direction of $I_{sc}$ can be switched with the polarization direction switched from downward to upward (UPS: polarized by −40 V pulse voltage), as shown in fig. 1(b). Figure 2(a) shows $I_{sc}$ as a function of time, in upward and downward polarized states. $I_{sc}$ is 7 nA and −6 nA after BFLO films poled by −44 V and +44 V, respectively. These results show that the direction of $I_{sc}$ can be switched accompanying polarization switching. On the other hand, we found that the photocurrents of the polarized BLFO samples decrease slowly over multiple cycles. This unstable PV effect has also been observed in other ferroelectric films [24,31,32]. For ferroelectrics with a higher oxygen vacancy concentration, the state after removing the poling field is unstable, in which the hopping electrons will recombine with the oxygen vacancies. Meanwhile, the diffusion of oxygen vacancies may also have a large influence on this instability. Figure 2(b) shows $I_{sc}$ as a function of pulse voltages ($V_{pulse}$); for comparison, the voltage dependence of remanent polarization has also been showed (voltage dependence of polarization can be seen in ref. [33]). $I_{sc}$ changes from positive to negative.
monotonically with the polarization orientation varying gradually from UPS to DPS, $I_{sc}$ is zero when the BLFO film is in the zero polarization state (ZPS), indicating a switchable PV effect accompanying polarization flipping in BLFO films.

However, besides the polarization states, domain structure and oxygen vacancies distribution are also affected by voltage training [30,33,34], which in turn affects the PV effect. Herein, we reported a very simple method to disentangle the contribution of domain walls, oxygen vacancies and polarization to the PV effect. In order to understand and make clear how the domain wall density affect the properties of materials. In general, the electron-hole pair density, the recombination rate and the internal electric field of the depletion layer, which depends on the barrier height. Based on the work functions of Ag, LSMO and the electron affinity/band gap of BFO, the electric field, they cannot be neglected especially in the pulse training process. In order to further probe the impact of migration and redistribution of oxygen vacancies, unipolar pulses were applied. It can be divided into two situations according to the oxygen vacancies accumulation at either the Ag/BLFO or BLFO/LSMO interface. In the situation of oxygen vacancies accumulation at the Ag/BLFO interface, $I_{sc}$ increases ($\delta I_{sc}$ is positive) with negative pulse numbers in UPS, as shown in fig. 3(c). In DPS (the final pulse is positive, +40 V), $I_{sc}$ decreases (however, $\delta I_{sc}$ is also positive) with negative pulse numbers at first, finally, $I_{sc}$ changes the sign, i.e., from negative value to positive value, as shown in fig. 3(d), which is similar to that of fig. 3(b). This means that by changing the distribution of oxygen vacancies, the direction of $I_{sc}$ can be switched without changing the polarization direction. In the other situation, i.e., oxygen vacancies accumulation at the BLFO/LSMO interface, $I_{sc}$ increases ($\delta I_{sc}$ is negative) with positive consistent pulse numbers, as shown in fig. 3(e). Nevertheless, $I_{sc}$ decreases (but $\delta I_{sc}$ is also negative) with the pulse numbers, in the UPS (the final voltage is −40 V), as shown in fig. 3(f). It can be concluded that after consistent negative pulses, the increment of $I_{sc}$ ($\delta I_{sc}$) is always positive, while $\delta I_{sc}$ is negative after consistent positive pulses, independently of the polarization states.

From the above-mentioned results we may conclude that the polarization direction, distribution of oxygen vacancies and domain wall are the primary driving force for $I_{sc}$ in the Ag/BLFO/LSMO heterostructure. In general, the photocurrent has two contributions: diffusion current and drift current. And $I_{sc}$ can be described as

$$I_{sc} = I_{\text{diffusion}} - I_{\text{drift}},$$

where $I_{\text{diffusion}}$ and $I_{\text{drift}}$ are the diffusion current and drift current, respectively. $I_{\text{diffusion}}$ is related to the gradient of the electron-hole pair density, the recombination rate and the properties of materials. $I_{\text{drift}}$ is originated from the internal electric field of the depletion layer, which depends on the barrier height. Based on the work functions of Ag, LSMO and the electron affinity/band gap of BFO, the
sc as a function of time after different electric pulses. (a) with different alternative positive-negative pulses (±40 V); (b) with different alternative negative-positive pulses (±40 V); (c) with different consistent negative pulses (−40 V); (d) with different consistent negative pulses (−40 V) and finally applying a positive pulse (+40 V); (e) with different consistent positive pulses (+40 V); (f) with different consistent positive pulses (+40 V) and finally applying a negative pulse (−40 V).

schematic of energy band of Ag/BLFO/LSMO structure and the variations of $I_{\text{diff}}$, $I_{\text{drift}}$ and $I_{sc}$ in different situations are shown in fig. 4(a) and (b).

In the case of upward poling, oxygen vacancies in the oxygen-deficient film can trap the photo-induced electrons and the photo-induced holes become the extra carriers [35,36]. Therefore, a large $I_{\text{diff}}$ flows in the downward direction because of a low probability of electro-hole recombination, whereas a tiny $I_{\text{drift}}$ flows to the upward direction due to the relatively small barrier height induced by polarization and oxygen vacancies with positive charge. From formula (1) we can speculate that if $I_{\text{diff}}$ is bigger than $I_{\text{drift}}$, $I_{sc}$ should flow downward ($I_{sc}$ is positive). After downward poling, i.e., in the DPS, on the one hand, a relatively small amount of electrons is trapped by oxygen vacancies due to a relatively small amount of oxygen vacancies accumulated at the Ag/BLFO interface; therefore the recombination rate of electron-holes increases which, in turn, result in small $I_{\text{diff}}$. On the other hand, $I_{\text{drift}}$ increases originating from the relatively large barrier height compared with UPS because of the negative charge of polarization head side and a relatively small amount of oxygen vacancies in the Ag/BLFO interface. Therefore, if $I_{\text{diff}}$ is smaller than $I_{\text{drift}}$, $I_{sc}$ flows upward ($I_{sc}$ is negative). Consequently, the direction of $I_{sc}$ can be switched accompanying polarization switching, and $I_{sc}$ is zero in certain intermediate polarization states, as depicted in fig. 1 and fig. 2.
When applying alternative pulses, as the domain wall density increases with increasing alternative pulse number [33], the domain wall can decrease the recombination of photo-induced electron-hole pairs [30]; therefore, $I_{\text{diff}}$ increases with alternative pulse number. In view of the process of the application of alternative pulses, as the final pulse voltage is the same every time, the final polarization direction does not change and the distribution of oxygen vacancies does not change significantly. Hence, the variation of the Ag/BLFO interfacial barrier height can be neglected. Therefore, $I_{\text{drift}}$ might have minor changes because it is primarily decided by the barrier height and the density of electron-hole pairs. Thus, in the UPS, $I_{\text{sc}}$ is positive and it increases with an alternative positive-negative pulse and $\delta I_{\text{sc}}$ is always positive (it points downward), as shown in fig. 3(a). On the other hand, in the DPS, $I_{\text{sc}}$ is initially negative and it decreases with alternative negative-positive pulse while $\delta I_{\text{sc}}$ is always positive (points downward). When the number of alternative pulses further increase, $I_{\text{diff}}$ can be larger than $I_{\text{drift}}$, thus, $I_{\text{sc}}$ is always positive, except in DPS, as shown in fig. 3(b). The orientation of $I_{\text{sc}}$ can be switched according to the change of the domain wall density, which in turn affects $I_{\text{diff}}$, without changing the polarization direction.

When consistent negative pulses are applied, as more and more oxygen vacancies can move forward to the Ag/BLFO interface, the barrier height of Ag/BLFO further reduces, and more electrons are trapped by oxygen vacancies due to a relatively big amount of oxygen vacancies; therefore $I_{\text{diff}}$ increases but $I_{\text{drift}}$ decreases due to a relatively lower barrier of the Ag/BLFO interface. Finally, in the UPS, $I_{\text{sc}}$ is positive and it increases with consistent negative pulses and $\delta I_{\text{sc}}$ is positive, as shown in fig. 3(c). On the other hand, in the DPS (the final pulse is +40 V), as $I_{\text{diff}}$ is smaller than $I_{\text{drift}}$, $I_{\text{sc}}$ is initially negative, and it decreases with consistent negative pulses while $\delta I_{\text{sc}}$ is also positive. If the number of negative pulses further increase, $I_{\text{diff}}$ can be greater than $I_{\text{drift}}$, thus, $I_{\text{sc}}$ is always positive, although the BLFO film is in DPS, as shown in fig. 3(d). The orientation of $I_{\text{sc}}$ can be switched according to the change of the distribution of oxygen vacancies, without changing the polarization direction. This result is similar to that of fig. 3(b).

On the contrary, when applying consistent positive pulses, as more and more oxygen vacancies can move forward to the BLFO/LSMO interface, the barrier height of Ag/BLFO increases. Besides, a small number of electrons are trapped by oxygen vacancies due to a relatively small amount of oxygen vacancies in the Ag/BLFO interface. Therefore, $I_{\text{diff}}$ decreases while $I_{\text{drift}}$ increases due to a relatively higher barrier of the Ag/BLFO interface. Finally, in the DPS, $I_{\text{sc}}$ is negative and it increases with consistent positive pulses and $\delta I_{\text{sc}}$ is negative, as shown in fig. 3(e). In the UPS (the final pulse is −40 V), as $I_{\text{diff}}$ is bigger than $I_{\text{drift}}$, $I_{\text{sc}}$ is positive and it decreases with consistent positive pulses while $\delta I_{\text{sc}}$ is also negative, as shown in fig. 3(f).

Conclusions. — In conclusion, the short-circuit photocurrent in Ag/Bi$_{0.9}$La$_{0.1}$FeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ sandwich structure has been investigated by poling the films with magnitude increased pulse voltages, alternative pulse voltages and consistent pulse voltage training. Both switchable and nonswitchable $I_{\text{sc}}$ accompanying polarization switching can be obtained; moreover, the direction of $I_{\text{sc}}$ can be switched without changing the polarization direction by choosing a proper electric pulse. Bipolar electric pulses and unipolar electric pulses have different effects on the photocurrent in different polarization states. Our results indicate that electromigration of oxygen vacancies, polarization flipping and domain wall density are able to induce switchable photovoltaic effects. This switchable or nonswitchable $I_{\text{sc}}$ can be explained well using the concepts of drift current and diffusion current controlled by the combination of oxygen vacancies, polarization and conductive domain wall. The sign of
photocurrent is independent of the polarization direction when the modulation of photocurrent induced by oxygen vacancies or conductive domain walls is large enough to offset that induced by polarization. Our work provides a deep insight into the nature of photovoltaic effects in ferroelectric films, and will facilitate the advanced design of switchable devices combining spintronic, electronic, and optical functionalities.

***

The present work has been supported by the National Basic Research of China, the National Natural Science Foundation of China, the Knowledge Innovation Project of the Chinese Academy of Sciences, and the Beijing Municipal Natural Science Foundation.

REFERENCES