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Switchable photovoltaic effect in Au/$Bi_{0.9}La_{0.1}FeO_3$/$La_{0.7}Sr_{0.3}MnO_3$ heterostructures

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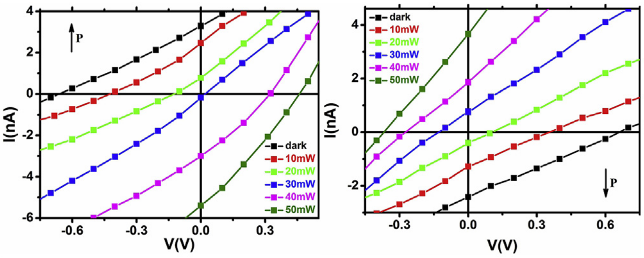
HIGHLIGHTS

- Pure phase $Bi_{0.9}La_{0.1}FeO_3$ thin films were grown using pulsed laser deposition.
- The as grown films were self poled and the polarization direction is downward.
- The switchable photovoltaic effect depend on ferroelectric polarization directions.
- Photovoltaic effect can be switched by changing the intensity of incident radiation.
- Depolarization field and oxygen vacancies together induce the photovoltaic effect.

GRAPHICAL ABSTRACT



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ABSTRACT

$Bi_{0.9}La_{0.1}FeO_3$ (BLFO) films were fabricated on $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/$SrTiO_3$(STO)(001) substrates by pulsed laser deposition. The ferroelectric photovoltaic characteristics of Au/BLFO/LSMO heterostructures were studied under green light illumination. The open circuit voltage and short circuit current were observed to be positive and negative values under weak light illumination in the as-grown self-poled downward BLFO thin films, while they changed the signs when the light intensity is strong. On the contrary, this photovoltaic properties can be switched when the BLFO films were in poled up state. The photovoltaic effect was also strongly dependent on the polarization direction, incident light intensity and the distribution of oxygen vacancies. As a result, the sign of open circuit voltage and short circuit current could be independent of the direction of polarization. We believe that the switchable diode and photovoltaic effects can be explained well using the concepts of Schottky barrier modulation by polarization flipping and of oxygen vacancies and the distribution of oxygen vacancies at Au/BLFO or BLFO/LSMO interface. Our work provides deep insights into the nature of diode and photovoltaic effects in ferroelectric films, implying an effective approach to improve photovoltaic effect by tuning oxygen vacancies in ferroelectric materials.

1. Introduction

Owing to their anomalous photovoltaic effect and potential

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application in photovoltaic cells, ferroelectric materials have been gained extensive attention since it has been discovered one century ago [1–3]. Among them, $BiFeO_3$ (BFO) is considered as a perspective candidate for demanding applications in nonvolatile memories, solar cells and sensor not only due to its high remnant polarization, relatively smaller band gap but also because of its multiferroic properties at room temperature [3–5]. Apart from the fundamental research on its ferroelectric and magnetic properties, the photovoltaic (PV) effect of BFO has been observed both in BFO crystal and thin films under illumination of visible light [6–11]. Although ferroelectric PV effect has been extensively studied in the past few years and considerable progress has been made, many results are seemingly contradictory and the mechanism is still in debate, including domain walls theory, depolarization field, defects, and interface barriers [9–12]. Yi et al. [13] observed switchable FPV effect and the short-circuit current (I_{sc}) direction is always opposite to the forward bias direction, and the I_{sc} after downward poling was negative, whereas the I_{sc} after upward poling was positive. For a period of the reported photovoltaic effect accompanying polarization flipping, polarization direction is thought to be an essential role in the switchable photovoltaic effect. Although Guo et at[14] observed switchable photovoltaic effect accompanying polarization flipping, their results indicate that I_{sc} is negative for the polarization up state and positive for the polarization down state. However, some researchers recently observed that the polarization direction is not as important as it has been deemed in the switchable photovoltaic effect, the signs of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) are independent of the polarization direction. Yang et al. [15] found that switching the ferroelectric state of the BFO layer did not change the photovoltaic response. Guo et al. [16] suggested that 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, whereas the oxygen vacancies act as shunts and trapping center due to their positively charged and higher mobility. Therefore, clearly more detailed studies are necessary to elaborate on the role of ferroelectricity and oxygen vacancies in enabling the photovoltaic effect and the switchable phenomenon.

It is suggested that besides polarization direction, oxygen vacancies, domains, depolarization field and interface barriers are responsible for the switchable photovoltaic effect in ferroelectric thin films [15–20]. We note that most of the previous reports focus on the polarization-induced surface charge combined with the migration of oxygen vacancies as well as the conductive ferroelectric domain wall on the photovoltaic effect. Although it was reported that light intensity has apparent effect on the phtovoltaic effect because increasing light intensity can generate more electron-hole pairs which lead to larger V_{oc} and I_{sc} [14,21], light illumination induce switchable photovoltaic effect has never been reported before. In this paper, we report a switchable PV effect in $Au/Bi_{0.9}La_{0.1}FeO_3/La_{0.7}Sr_{0.3}MnO_3$ sandwiched capacitors by changing the intensity of incident light. The accumulation of oxygen vacancies at the $Au/Bi_{0.9}La_{0.1}FeO_3$ interface induced by polarization charges are believed to responsible for this result.

2. Experimental process

Epitaxial $Bi_{0.9}La_{0.1}FeO_3$(BLFO) films with the thickness of 500 nm were fabricated by pulsed laser deposition (PLD) technique on (001)-oriented $SrTiO_3$ substrate with 10 nm $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) as buffer layer. The doping of 10% La was used to decrease the leakage current of BFO. The target was prepared by mixing Bi_2O_3, La_2O_3 and Fe_2O_3 in a 1.1: 0.1: 1 stoichiometric ratio and sintering at 800 °C in air. The larger amount of Bi_2O_3 was used compensated for 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. Typical film growth rate was around 8 nm per minute. The conductive metallic oxide LSMO was chosen as bottom electrode because the pseudo-cubic crystal lattice is ~0.3878 nm for LSMO thick film, ~0.3905 nm for STO crystal substrate and ~0.3965 nm for BFO crystal [4,7,8]. Therefore, with small lattice parameter mismatch and stress, one can expect epitaxial growth. The detailed deposition process were depicted elsewhere [13]. Following the growth, these films were cooled to room temperature at 5 °C/min with an oxygen pressure of 500 Pa. Structural characterization was performed using X-ray diffraction (XRD) using a Cu Kα source operating at a scan rate of 1°/min over the 2θ range of 20–80°. The polarization switching was studied by Piezoresponse Force Microscopy (PFM). In order to measure the electrical properties of the films, a 200 nm thick Au layer patterned with circles of 200 μm diameter was deposited on BLFO as the top electrodes by PLD through a shadow mask. The polarization–electric field (P–E) hysteresis loops were measured at room temperature using a ferroelectric test system (Radiant, Premier II). In this paper, applying a positive (negative) voltage on the top electrode is defined as positive (negative) direction. The photovoltaic characteristics were measured in top-bottom configuration through current-voltage (I-V) measurements using a Keithley 2611 electrometer. Green laser with the wavelength of 532 nm (100 mW/cm^2) was used as excitation light source for the PV measurement.

3. Results and discussion

Fig. 1(a) shows the structural properties of the as grown BLFO thin films studied using X-ray diffraction, which reveals high quality, epitaxial films that appear to be single phase. The diffraction peaks of the LSMO thin film are not observed because of its thin deposition and the peaks of STO (001)/LSMO (001) and STO (002)/LSMO (002) might overlap in XRD pattern. Atomic force microscope analysis shows the grain size of ~300 nm and the surface root mean square roughness of ~2 nm, as shown in Fig. 1(b). The out-of-plane piezoresponse phase images of the as grown BLFO film is shown in Fig. 1(c) wherein a clear contrast in phase and amplitude is observed, and the dark and bright areas correspond to upward and downward poled domains, respectively. It should be pointed out that according to the PFM images, the as-grown BLFO thin films show distinct contrast in phase of that polarized by −10 V, indicating downward self-polarized direction of the untreated films, this self-polarized phenomenon is common and the direction can be controlled by choosing proper bottom electrodes [22–24]. Fig. 1(d) shows P–E hysteresis loops for BLFO thin films measured at a frequency of 5 kHz, showing good rectangular shape. The remnant polarization ($\boldsymbol{P_r}$) of the samples is ~80 $\mu C/cm^2$, which is slightly larger than previous values reported in BFO film [25–28].

The I-V characteristics of the as grown downward self-polarization Au/BLFO/LSMO heterostructures in dark and under illumination with different light intensity are shown in Fig. 2(a). It is worth mentioning that although without illumination, the I-V curve shows large open circuit voltage (V_{oc}) of and short circuit current (I_{sc}) values, the V_{oc} is 0.64 V and I_{sc} is −2.4 nA. However, in contrast with conventional ferroelectric PV effect reported before, the values of both V_{oc} and I_{sc} decrease firstly and then increase with increasing the light intensity, and even changes the signs. When the light intensity is increased to 50 mW, the V_{oc} is −0.3 V and I_{sc} is 3.2 nA, respectively. These results show that V_{oc} can be switched from positive to negative value and I_{sc} can be switched from negative to positive under illumination, exhibiting strong dependence of light intensity. This anomalous phenomenon may be