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The study of open circuit voltage in Ag/Bi$_{0.9}$La$_{0.1}$FeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ heterojunction structure

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ABSTRACT

Bi$_{0.9}$La$_{0.1}$FeO$_3$ thin films have been grown on La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ substrates by using pulsed laser deposition with Ag as the top electrode. The intrinsic open circuit voltage (V_{oc}) (without light illumination) as large as 5.8 V was observed in this hetero-junction structure. Influences of electric pulse treatment, light illumination and measurement duration time on the V_{oc} were studied, significant V_{oc} improvements were observed after shortening the measuring duration time and/or consistent negative pulses, yet V_{oc} dropped obviously with consistent positive pulses and/or with light intensity increasing. Two stable states with high and low V_{oc} can be switched with optical switching, this may be useful in practical application. Accumulation of oxygen vacancies with positive charges near the interface is proposed to explain these results.

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1. Introduction

Multiferroic materials, which simultaneously display several types of order, such as ferroelectricity and magnetism, have recently become the focus of research because of the intriguing science behind their magnetoelectric coupling phenomenon and their exciting application potential in multiple controlled devices [1–3]. Among them, single-phase multiferroic BiFeO$_3$ (BFO) is the most extensively investigated due to its high ordering temperatures, namely, a ferroelectric Curie temperature ($T_C \sim 1100$ K) and an antiferromagnetic Néel temperature ($T_N \sim 640$ K).[3,4] Such a specific feature—that both T_C and T_N in BFO are above room temperature—is of great significance from a technological point of view. Moreover, high remnant polarization ($P_r \sim 100$ μC/cm^2), relatively smaller band gap near 2.8 eV compared to other ferroelectrics, is considered as a perspective candidate for technologically demanding applications including nonvolatile memories, solar cells and sensor [1–5]. Recently, photovoltaic effects have been observed both in BFO crystal and thin films under illumination of visible light [6–11], high external quantum efficiencies of up to 10% when illuminated with the appropriate wavelength was also reported [10,11]. The photovoltaic properties are completely different from those of conventional p–n and Schottky junctions originating from the built in field induced by space charge in depletion layers.

Remarkable photovoltaic effect can be observed under white light illumination or other lasers for the wavelengths smaller than the optical energy gap of BFO. The light-induced open circuit voltage (V_{oc}) is not limited in the band gap of BFO, and it can exceed the band gap several multiples, which can be attributed to the small optical band gap and narrow domain walls. Yang et al. [10] reported about 20 V of V_{oc} in BFO film, which is considerably larger than the band gap of BFO.

However, in previous works, V_{oc} was observed only under light illumination, and the value of V_{oc} indeed increased with light intensity and V_{oc} was negligible in dark. Herein, we report an opposite result with oxygen deficient Bi$_{0.9}$La$_{0.1}$FeO$_3$ films, several voltages of open circuit voltage (V_{oc}) without illumination is observed and V_{oc} decreases with light intensity increasing. Significant V_{oc} improvements are observed after prolonging the measuring duration time or consistent negative pulses; however, V_{oc} decreases with consistent positive pulses or light intensity increasing. Accumulation of oxygen vacancies with positive charges near the interface is proposed to explain this phenomenon.

2. The experimental process

Bi$_{0.9}$La$_{0.1}$FeO$_3$ (BLFO) thin films with 500 nm thickness were deposited epitaxially on (0 0 1) SrTiO$_3$ (STO) substrates using the pulsed laser deposition method (PLD). The deposition process was depicted elsewhere [12]. For the study of electrical properties, the conductive metallic oxide La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) layer serves as the bottom electrode. LSMO was chosen as bottom electrode

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because its lattice parameter (LSMO~0.388 nm) is very close to STO (~0.391 nm), BFO (~0.396 nm), and therefore, with small lattice parameter mismatch and stress, one expects the epitaxial growth. First, a sintered stoichiometric LSMO target was employed for deposition of LSMO thin films on STO substrates under a deposition temperature of 700 °C, and an oxygen pressure ~50 Pa. Then, the BLFO thin films were grown at 650 °C under a low oxygen pressure of 15 Pa. The other laser parameters during depositions were (i) laser source: KrF excimer laser with $\lambda = 248$ nm, (ii) repetition frequency: 5 Hz, (iii) energy density was about 1.5 J/cm^2. Typical film growth rate was around 9 nm/min. After deposition, BLFO films were slowly cooled to room temperature (2 °C/min) in the oxygen atmosphere of 100 Pa. For measuring the electrical properties of the films, a 200 nm thick Ag layer patterned with 0.2 mm diameter was deposited on BLFO as the top electrodes by PLD through a shadow mask. The thickness was controlled by deposition time after standardization. The current–voltage measurements in the dark and under illumination were performed by using a Keithley 2611 source meter. In the measurement process, Ag electrode was connected to the positive pole and LSMO as bottom electrode was connected to the negative pole of the voltage source. Green laser with wavelength of 532 nm was applied to illuminate on the Ag top electrode, the laser spot is about 5 mm^2, larger than the area of Ag electrode. In the process of applying electric pulses, Ag top electric was also connected to the positive pole of the pulse signal generator and LSMO was connected to the negative side. The pulse amplitude was 40 V with the period of 12 μs.

3. Results and discussion

Fig. 1(a) shows a typical I–V curve in dark, the measure sequence is $0 \rightarrow 6\,V \rightarrow 0\,V \rightarrow -6\,V \rightarrow 0\,V$. Fig. 1(b) is the enlargement of the rectangle area of Fig.1(a), the arrows indicate the sweep direction of the bias. It can be seen from Fig. 1(b) that the I–V curve shows a large open circuit voltage (V_{oc}) of 2.82 V rather than a negligible value in the dark reported by other authors. This big V_{oc} plays the role of cell and it may result from oxygen vacancies accumulation near Ag/BLFO interface. Therefore, V_{oc} should decrease if positive electric pulse applying to the top Ag electrode because oxygen vacancies can be repelled away from Ag/BLFO interface and injected into BLFO film. In order to study how different voltages affect V_{ov}, I–V curves with different positive pulse voltages were plotted in Fig. 1(c). To obtain the open circuit voltage directly, the I–V curve was plotted in semilog coordinate. It is found that V_{oc} decreases with the number of the pulse voltage increasing, its value decreases from 4.2 V in the original state to 3.9 V after 50 positive pulses, and 3.35 V after 2000 positive pulses, as shown in Fig. 1(c). However, consistent negative electric pulses play the opposite role, the open circuit voltage increases from 3.03 V in the original state to 4.96 V after 50 negative pulses voltage, and 5.76 V after 2000 negative pulses voltage, as shown in Fig. 1(d). It can be found from Fig.1 that the intrinsic open circuit voltage V_{oc} is always positive, no matter the voltage applied on the Ag electrode is positive or positive. However, the value of V_{oc} exhibits strong dependence of electric pulse directions, V_{oc} decrease/increase with positive/negative pulse voltages, it may be that as pulse voltages can affect the accumulation or distribution of defects, such as oxygen vacancies with positive charges, and it therefore affects the V_{oc}.

In order to analyze how the distribution or the movement of oxygen vacancies affect V_{oc}, the value of the sweeping duration time from $+6\,V$ to $0\,V$ in the I–V curve was controlled from 0.5 s to 12 s, V_{oc} as a function of sweeping duration time was shown in Fig. 2(a) and (b). It can be concluded from Fig. 2(b) that V_{oc} decreases with increasing sweeping duration time. Its value
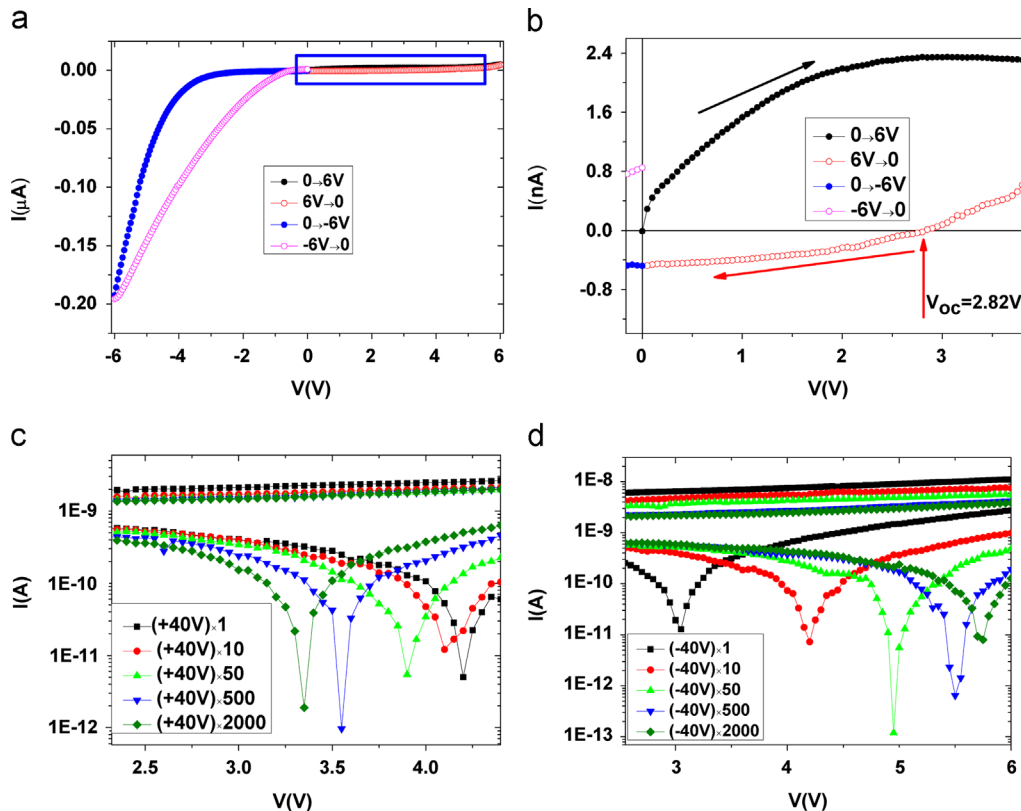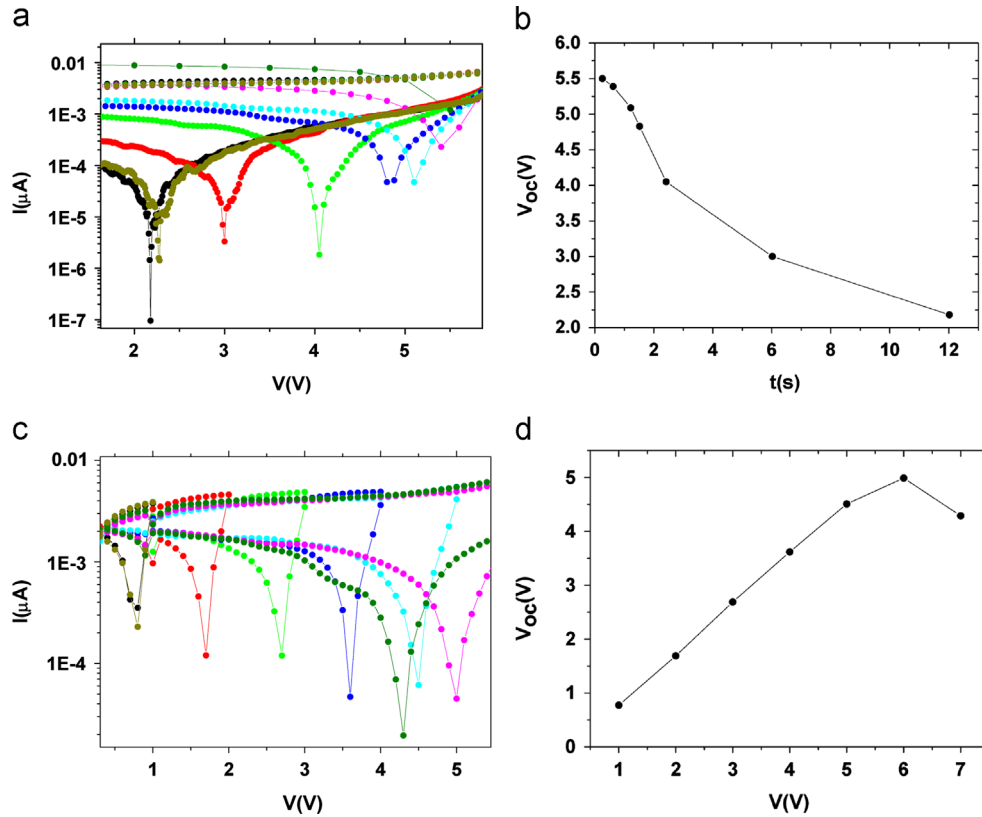

Fig. 1. (a) I–V curves of Ag/BLFO/LSMO hetero-junction in the dark, (b) enlargement of the rectangular area in (a), (c) I–V curves with different consistent positive pulse, and (d) I–V curves with different consistent negative pulse. The arrows indicate the sweep direction of the bias.

Fig. 2. (a) *I–V* curves under different times sweeping from +6 V to 0, (b) time dependence of the open circuit voltage (V_{oc}) with different sweeping time, (c) *I–V* curves under different sweeping positive voltages varying from 1 V to 7 V, and (d) sweeping voltage dependence of open circuit voltage (V_{oc}) with different sweeping positive voltages.

decreases from 5.5 V to 2.1 V when the sweeping duration time varies from 0.5 s to 12 s. This result indicates that V_{oc} depended on the accumulation of positive oxygen vacancies, with the sweeping duration time increasing, more and more positive charges will move away from Ag top electrode and ejects into LSMO bottom electrode in the discharge process. As evidenced in Fig. 2(b), after the first 2 s it looks like the beginning of exponential decay to zero. Because V_{oc} is obtained from the *I–V* sweeping curves, therefore the positive sweeping voltage also has distinct effect on V_{oc}, as shown in Fig. 2(c) and (d). It can be seen from Fig. 2(c) and (d) that V_{oc} increases from 0.77 V to 5 V as the sweeping voltage increasing from 1 V to 6 V; however, it decreases to 4.29 V when the sweeping voltage increases to 7 V. This may be that larger positive voltage can repel more positive oxygen vacancies away from Ag/BLFO interface and inject into the negative pole side, results the decrease of V_{oc}.

Different open circuit voltages induced by visible light or by ultraviolet light (UV-light) have been observed in BFO single crystal and thin films observed [13–18]. All of these results above reported indicated that the value of V_{oc} increased with light intensity. It can be seen from Fig. 3(a) that light illumination indeed obviously impacts on V_{oc}; however, the most obvious differences from other reports is that, after illumination, V_{oc} reduces rather than increasing, its value decreases from nearly 3 V to nearly zero. It is worth pointing out that two stable states with high and low V_{oc} can be switched with the light on and off, this may be useful in practical application. Fig. 3(b) shows the effect of light intensity on the V_{oc}, it can be seen form Fig. 3(b) that V_{oc} decreases with the light intensity increasing, and the variation of V_{oc} versus light intensity follows an exponentially attenuation law as shown in Fig. 3(c). Meanwhile, V_{oc} can reduce to near zero but never be negative in the downward polarization state, in contrast, in the

upward polarization state, V_{oc} can reduce from positive value to negative value under illumination, this downward-upward states dependence of positive-negative V_{oc} was observed in most cases [13–17].

The variation of V_{oc} can be understood based on the Ag/BLFO/LSMO energy band diagrams as shown in Fig. 4. To construct the band diagram, the work functions of Ag, LSMO (4.26 eV and 4.96 eV), and the electron affinity/band gap of BFO (3.3 eV/2.8 eV), [18,19] a band diagram can be depicted for the Ag/BLFO/LSMO device, here BLFO was treated as an n-type semiconductor. As shown in Fig. 4, the barrier height of the BLFO/LSMO junction is higher than that of the Ag/BLFO junction, which explains why the current level is low/high under positive/negative bias showed in Fig. 1(a). In our previous work [12], we found that all of our as-grown Ag/BLFO/LSMO thin-film capacitors exhibited a one-side diode effect. Both with the negative poling (i.e., upward polarization) and positive poling (i.e., downward polarization), the *I–V* curve clearly indicated a diode effect with negative forward bias, called a reverse diode. Similar one-side diode effects have been reported with numerous ferroelectric thin-film capacitors [20–24]. Lee et al. [24] attributed this lack of switchability to the formation of an interfacial defective layer at the Pt/BiFeO$_3$ top interface, they showed that all of their as-grown BiFeO$_3$ thin films on SrRuO$_3$ bottom electrodes were self-poled downward so that the negative polarization charge was built near the top BiFeO$_3$ surface [5,25,26]. According to PFM images, the as-grown BLFO thin films on LSMO bottom electrodes show nearly the same phase as that polarized by positive voltages, indicates self-polarized and its direction is downward, as shown in Fig. 5. Therefore, during the high-temperature film deposition, the downward self-polarization will cause the positively charged oxygen vacancies (Vo) to migrate toward the top surface to compensate for the negative polarization
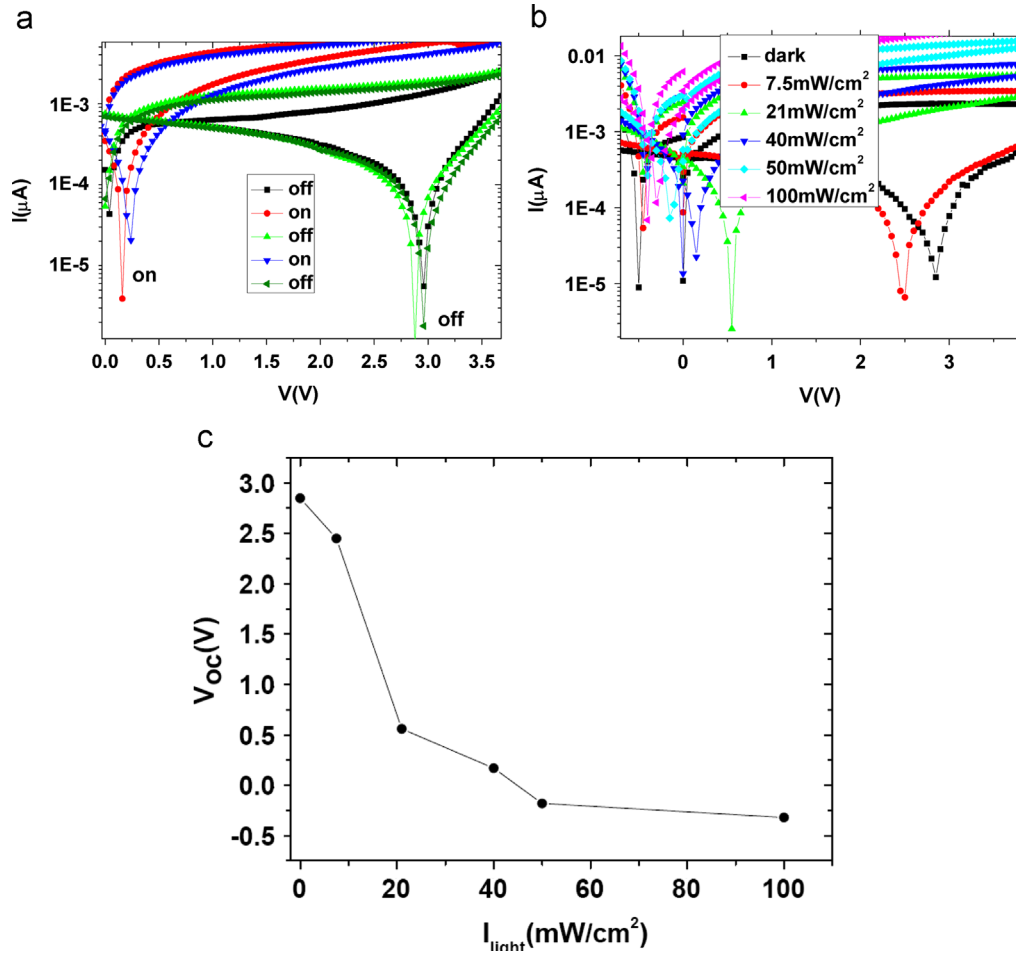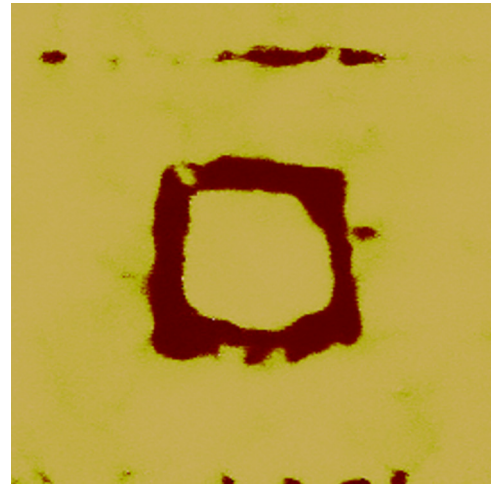
Fig. 3. (a) I–V curves in the dark and with light illumination, (b) I–V curves with illumination of different light intensities, and (c) light intensity dependence of open circuit voltage (V_{oc}).
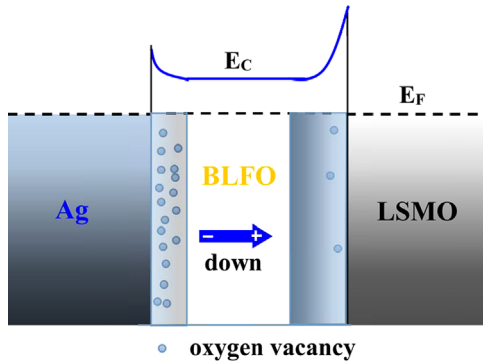
Fig. 4. Schematic energy band diagrams illustrating the distribution of oxygen vacancies (Vo) for Au/BSFO/FTO structure, the virgin BLFO samples with self-polarization at polarized down.

Fig. 5. PFM phase image of BLFO film. The film was poled through PFM tip scanning of the film surface with −10 V with a square area $1 \times 1 \ \mu m^2$. After that, the polarization in the center $0.5 \times 0.5 \ \mu m^2$ area is scanned with +10 V. Finally, the piezoelectric phase image was carried out by applying an ac voltage (frequency 6 kHz, amplitude 2 V peak-to-peak) to the PFM tip with a square area $1 \times 1 \ \mu m^2$.

charge. Hence, the migration of Vo can form a Vo-rich defective layer, which will remain between the Ag and BLFO layers in the capacitor, as shown in Fig. 4.

From our results above mentioned that, migration of oxygen vacancies is the primary factor for the observed positive V_{oc} without light illumination in the Ag/BLFO/LSMO hetero-structure. As a Vo-rich defective layer remains between the Ag and BLFO layers in the capacitor, acting as a cell with Ag as positive pole and LSMO as the negative pole, which can explain the positive V_{oc} in the I–V curve, as shown in Fig. 1(a) and (b).

In the case of consistent positive pulses applying to the Ag electrode, more and more oxygen vacancies with positive charges in BLFO are naturally attracted to, and thus accumulate, at the LSMO bottom electrode (polarization head) side when a high electric field is applied, therefore the Vo concentration near the

Ag top electrode decreases, results in a decreasing V_{oc} with increasing positive pulses, as seen in Fig. 1 (c). On the contrary, when consistent negative pulses were applied, more and more oxygen vacancies can move forward to the Ag/BLFO interface, therefore more and more positive charges accumulate near the Ag/BLFO interface, thus, V_{oc} increases with negative pulses increasing, as shown in Fig. 1(d).

In the *I–V* sweeping process, oxygen vacancies move from Ag top electrode to LSMO bottom electrode because of discharging. Therefore, with the sweeping duration time from +6 V back to 0 V increasing, i.e., as the duration of applying positive voltage increasing, more and more Vo disappeared from Ag/BLFO layer. Hence, V_{oc} decreases with the sweeping duration time increasing, as shown in Figs. 2(a) and (b). In consideration of the fact that V_{oc} was calculated from *I–V* curve, on the one hand, it was limited by the maximum sweeping voltage and it impossible exceeded the maximum sweeping voltage. On the other hand, V_{oc} should increase with the maximum sweeping voltage increasing, as shown in Fig. 2(c) and (d). Oxygen vacancies with positive charges in BLFO are naturally repelled from Ag electrode and attracted to, thus accumulate, at the LSMO bottom electrode side when a high positive electric sweeping field is applied to the Ag electrode. Therefore, the Vo concentration near the Ag top electrode decreased in high voltage (HV), which resulted in a decrease of V_{oc}. That is why V_{oc} decreases when the maximum sweeping voltage increases to 7 V as seen in Fig. 2(d).

In the case of light illumination, the most likely mechanism here is that the creation of the electron–hole pairs with the holes contributing to the conduction process while the electrons are trapped at the oxygen vacancies [27,28]. The oxygen deficiency increases meaning that the trapping mechanism for the electrons is formed, as oxygen vacancies can trap the photo induced electrons and the photo induced holes become the extra carriers that produce the increase of photo current. This model provides simple explanations for the result that the short circuit photo current (I_{short}) increased with more oxygen deficiency attracted to the Ag/BLFO interface while consistent negative pulse voltages were applied to the Ag electrode in our previous report [29]. Therefore, with the light intensity increasing, more and more photo induced electrons was trapped, and accumulated to the Ag/BLFO interface to neutralize oxygen vacancies with positive charges, which reduced the Vo concentration and confined its movement, more photo induced electrons meant more oxygen vacancies with positive charges were neutralized in the Ag/BLFO interface. As a result, the open circuit voltage decreases with light intensity, as shown in Fig. 3(b) and (c).

4. Conclusions

In conclusion, $Bi_{0.9}La_{0.1}FeO_3$ thin films have been grown on $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ substrates by using pulsed laser deposition with Ag as the top electrode. The intrinsic open circuit voltage (V_{oc}) (without light illumination) as large as 5.8 V was observed in this hetero-junction structure. Influences of electric pulse treatment, light illumination and measurement duration time on the V_{oc} were studied, significant V_{oc} improvements were observed after shortening the measuring duration time and/or consistent

negative pulses, yet V_{oc} dropped obviously with consistent positive pulses and/or with light intensity increasing. Two stable states with high and low V_{oc}.can be switched with optical switching, this may be useful in practical application. Accumulation of oxygen vacancies with positive charges near the interface is proposed to explain these results.

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