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The effect of polarization fatigue process and light illumination on the transport behavior of $Bi_{0.9}La_{0.1}FeO_3$ sandwiched capacitor

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In this paper, Ag/$Bi_{0.9}La_{0.1}FeO_3$ (BLFO)/$La_{0.7}Sr_{0.3}MnO_3$ sandwich structure was grown epitaxially on $SrTiO_3$ substrates using pulsed laser deposition. Short-circuit photocurrent (I_{short}) and frequency dependence of the capacitance were investigated. It reveals that this heterostructure exhibits strong photocurrent responses, the orientation of I_{short} depends strongly on the polarization orientations, and it varies monotonically from one orientation to the other as the polarization orientation switching gradually from upward (downward) to downward (upward), the I_{short} value becomes zero when the film is in zero polarization states. The intensity of the I_{short} can be strengthened by several times after thousands of bipolar electric pulses. Moreover, after polarization fatigue process of bipolar electric pulses or under light illumination, the capacitance of this sandwich structure is always bigger than the original state. However, the magnifying ratio of the capacitance after and before polarization fatigue process or under light illumination decrease with increasing the frequency in the C-*f* curves. These results suggest that polarization induced surface charge combined with migration of oxygen vacancies is the primary driving force for the varying of interfacial barriers and the oxygen vacancies density near the interface, which in turn leads to different orientations and values of I_{short} as well as the differential interfacial capacitance. Our results indicate that the photovoltaic response in ferroelectric BLFO thin films could be further explored for solar light photovoltaic and other capacitor devices applications. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4804308]

I. INTRODUCTION

Multiferroic materials, which simultaneously show magnetic and ferroelectric orders, have attracted considerable interest recently because of the intriguing fundamental physics and wide range of potential applications.[1–6] Among them, $BiFeO_3$ (BFO) is few known show single phase multiferroic materials at room temperature. Robust ferroelectricity ($P_r \sim 100\,\mu C/cm^2$), relatively smaller band gap near 2.8 eV compared to other ferroelectrics and lead-free nature, makes BFO a prime candidate for next-generation devices including nonvolatile memories, solar cells, and lead-free piezoelectric.[7,8]

Photovoltaic effects have been observed in BFO crystal and thin films under illumination of visible light.[9–12] It was found that the orientation of photocurrent was strongly depended on the polarization switching, changes of Schottky barrier at the metal/BFO interface accompanying the polarization reversion and oxygen vacancies movement were proposed as the origin of this phenomenon.[13–15] However, some authors reported that the orientation of photovoltaic current in their BFO thin films cannot be switched accompanying polarization switching at all, they attributed this results to the interface depletion layer between BFO and the electrode.[16] Yang *et al.* demonstrated that the photovoltaic effect in BFO thin films arises from domain walls.[14] Some results in the reports from Kundys *et al.*[17] and Choi *et al.*[9] showed an angular dependence of the photocurrent on the light polarization direction. Though the photovoltaic effect of BFO crystal and thin films have been studied extensively and explored recently for applications of solar cell and optical sensors, the mechanism of the photovoltaic effect is not very clear and needed for further research. It is very possible that many factors can affect the photovoltaic effect, the photovoltaic effect can originate from a variety of mechanisms, such as a gradient in a chemical potential,[18] the built-in electric field in a p-n junction,[19] or spin polarization.[20] Another mechanism was discovered in noncentrosymmetric materials, such as ferroelectrics and is called the bulk photovoltaic effect (BPVE).[21] In the previous work, the sandwiched structures were considered only in fully upward states (UPS, i.e., the states of polarization with upward orientation) or fully downward states (DPS, i.e., the states of polarization with downward orientation), which make it difficult to separate the effect of polarization, interfacial barriers, domain walls, and oxygen vacancies density form the photovoltaic effect. In order to answer these questions, it necessary to investigate the relations between polarization and photocurrent characteristic for intermediately polarized states. Our prior work shows that the polarization fatigue process has strong effect on the interface characteristics and domain structures, which indicated that the fatigue process might has some effects on the photocurrent and other transport behaviors.[22] However, there were few reports about how the photocurrent varied with intermediately polarized states and how the polarization fatigue process and light illumination affect the transport behavior. In order to analyze the role of every factor that affects the photocurrent, we have systematically investigated the effects of

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polarization fatigue process, polarization states, and light illumination on the transport behaviors and their correlations.

II. EXPERIMENTAL PROCESS

In this work, $Ag/Bi_{0.9}La_{0.1}FeO_3/La_{0.7}Sr_{0.3}MnO_3$ (Ag/BLFO/LSMO) hetero-junctions were deposited on (001) oriented $SrTiO_3$ (STO) substrates by using pulsed laser deposition (PLD). The deposition process were depicted elsewhere.[22] LSMO with the thickness of 30 nm was deposited as the bottom electrode and 500 nm BLFO was deposited on LSMO, finally, Ag with the diameter of 200 μm was deposited as top electrode. Similar to reported results,[23] only the (00l) ($l = 1, 2, 3$) reflections of BLFO and STO were detected in the 2θ range from 10° to 80° by x-ray diffraction (the diffraction peaks of the LSMO film cannot be observed because of the thick BLFO over-layer), as shown in Fig. 1(a). The full width at half maximum of the rocking curve of (002) peak is ~0.6°, which is slightly narrower than reported values.[24] These results indicate that the BLFO film was epitaxially growth. In order to investigate the relations between polarization and photocurrent characteristic for intermediately polarized states, we measure the voltage dependence of polarization, the so called positive–up-negative-down (PUND) method was adopted.[24,25] In this paper, applying a positive (negative) voltage on the top electrode is defined as downward (upward) poling. The measurement circles were shown in Fig. 1(b), +40 V pulse with the width of 12 μs was first applied to pole the polarization downward, and then different negative pulse was applied to pole the polarization upward. From the step by step increase in V of the above pulse, we can obtain the curve of time dependence of the switching current I with varied negative V_{pulse}, as Fig. 1(c) shown. The remanent polarization (P_r) was quantified by the area below the I-t curves, divided by electrode area. Fig. 1(d) presents poling voltages dependence of the polarization of BLFO. A zero polarization state (ZPS), in which half domains are upwards poled and half domains are downwards poled, is obtained around the coercive voltage (~20 V). The shorted photocurrent (I_{short}) was measured by SourceMeter (Keithley 2611) under illuminations with the light on/off for 50 s. The green laser with wavelength of 532 nm was used to illuminate on the top Ag electrode when measuring.

III. RESULTS AND DISCUSSION

Fig. 2(a) shows the short-circuit photocurrent (I_{short}) as a function of time after the BLFO film poled by −40 V and +40 V. It can be seen that I_{short} is about 15 nA and −7 nA after poled by −40 V (UPS) and +40 V (DPS), respectively. These results show that I_{short} exhibits strong dependence of polarization orientation and the orientations of I_{short} and polarization are opposite. In order to check the photocurrent properties and how it evolves with polarization, the BLFO film was first driven to the fully UPS by a negative pulse of −40 V (with pulse width of 12 μs) then to an intermediate

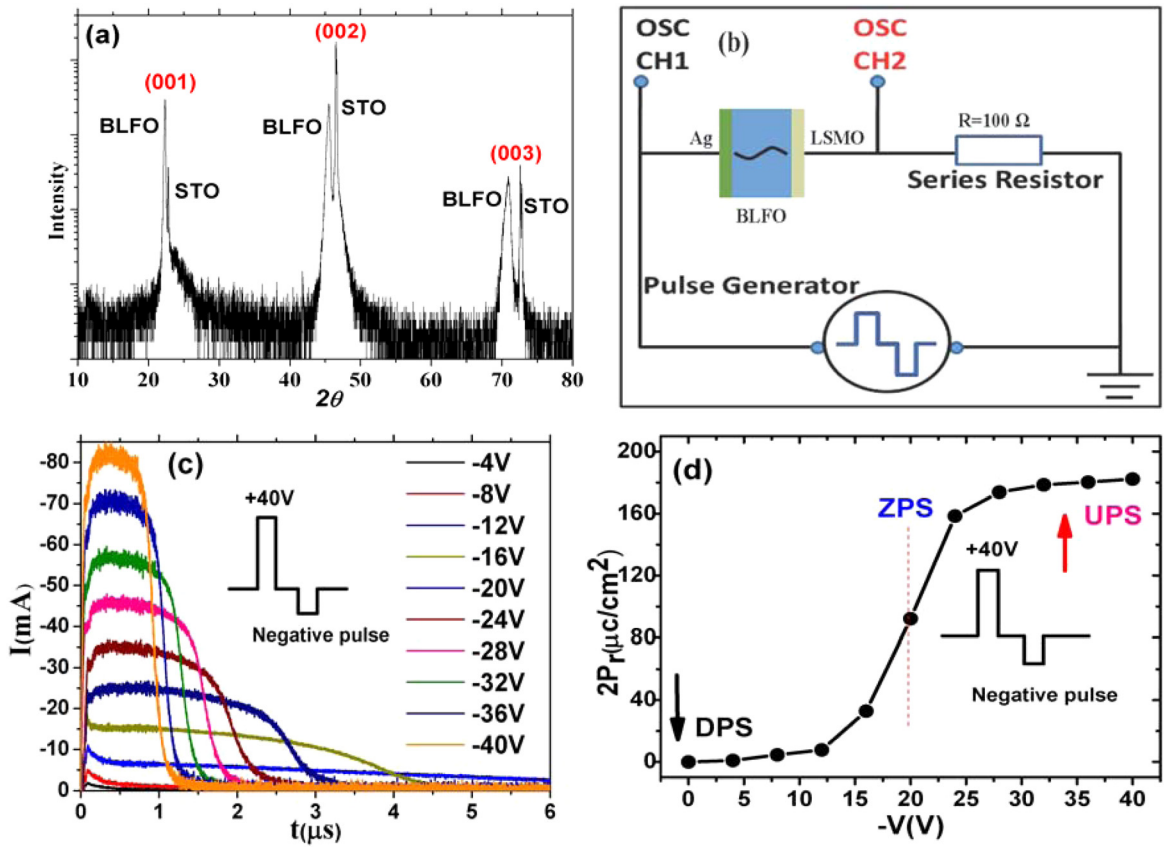

FIG. 1. (a) X-ray $\theta \sim 2\theta$ scans of BLFO film with 30 nm LSMO buffer grown on STO substrate. The peaks of BLFO and STO are labeled. (b) Experiment setup for the polarization switching by electric pulses with $R_0 = 100\ \Omega$. (c) Time dependence of the switching current with varied negative V_{pulse} from −4 V to −40 V. (d) 2Pr-V_{pulse} curve derived from the transient current. DPS, UPS, and ZPS are the state of polarizations orientation are fully downward, upward, and half domains are upwards poled and half domains are downwards poled, respectively.

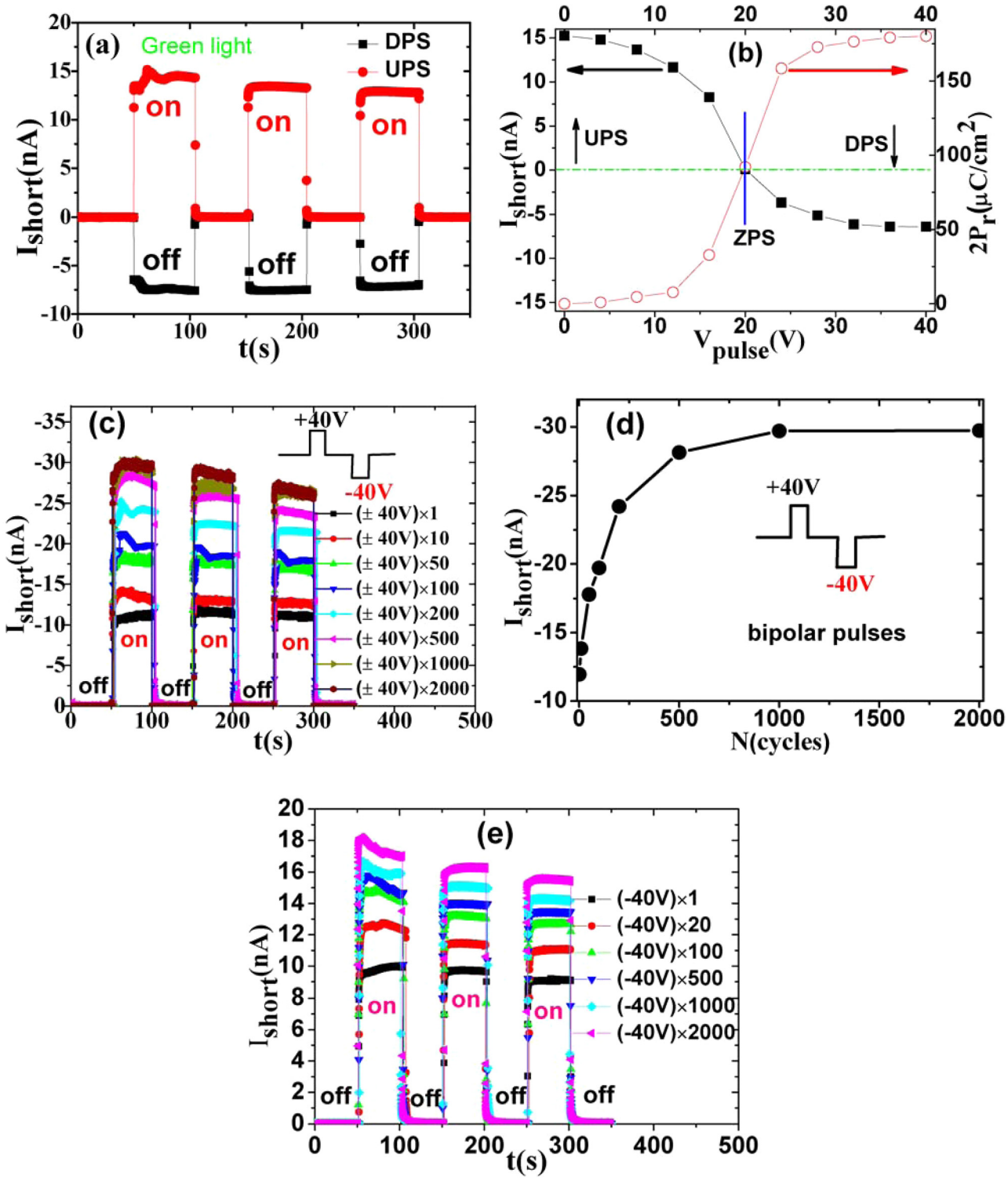

FIG. 2. (a) Time dependence of the short photocurrent (I_{short}) under light illumination with upward and downward states, the time of light illumination is 50 s. (b) V_{pulse} dependence of Short photocurrent (I_{short}) and remanent polarization 2Pr with the domains poled from DPS (poled by +40 V pulse) to UPS (poled by −40 V pulse). (c) Time dependence of I_{short} with different number of alternative pulses (bipolar pulses). (d) I_{short} as a function of the number of bipolar pulses. (e) Time dependence of I_{short} with different number of identical pulses (unipolar pulses).

state by a positive pulse with the amplitude between 0 and 40 V, after each pulse, I_{short} was measured. From the step by step increase in V of the above pulse, we can get a curve of I_{short} dependence of polarization. As expected, the value of I_{short} changes from positive to negative monotonically as the polarization orientation varies gradually from UPS (poled by −40 V pulse) to DPS (poled by +40 V pulse), as shown in Fig. 2(b). I_{short} is zero when BLFO film is in the ZPS. On the contrary, when the polarization orientation varies from DPS to UPS, I_{short} changes accordingly from negative value to positive value monotonically and also becomes zero in ZPS. These results indicate that I_{short} is entirely decided by the polarization. However, as defect migration and redistribution usually occur simultaneously with domain flipping, which in

turn could affect photocurrent. Therefore, it is difficult to distinguish whether the polarization or the defect affect the photocurrent, or to say, which is the main factor. In order to understand and make clear this mechanism, fatigue process was tested. I_{short} was plotted as a function of alternative electric pulse (bipolar pulses) numbers and it is found that alternative electric pulses have great impact on I_{short}. As shown in Figs. 2(c) and 2(d), the I_{short}-N (N is the number of alternative electric pulses) curve displays an increasing curve bending with the number of bipolar pulses N. I_{short} increases from the initial value ~7.5 nA to ~20 nA after 100 cycles, −28 nA after 1000 cycles, and ~28.5 nA after 2000 cycles. Analogous results can be concluded when consistent electric pulses were applied, as shown in Fig. 2(e).

Generally, the direction of the photocurrent can be switched by polarization-related asymmetry of impurity potentials. Our results suggest that polarization induced surface charge combined with migration of oxygen vacancies is the primary driving force for the switchable Schottky-to-Ohmic contacts, which in turn decide the directions and values of I_{short} in the heterostructure. In general, the photocurrent has two contributions: diffusion current ($I_{diffusion}$) and drift current (I_{drift}) as shown in Figs. 3(a) and 3(b). $I_{diffusion}$ 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 the drift current (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 and then drift current can be formed. Based on the work functions of Ag, LSMO and the electron affinity/band gap of BFO that the barrier height of the BLFO/LSMO junction is higher than that of the Ag/BLFO junction.[16] The reduction of the Schottky barrier height induced by the positive surface charge in the polarization head side and the further reduction driven by the accumulation of oxygen vacancies in the polarization head side are visualized in Figs. 3(a) and 3(b). Oxygen vacancies with positive charges in BLFO are naturally attracted to, and thus accumulate at, the positive electrode (polarization head) side when a high electric field is applied. The accumulation of oxygen vacancies induces a heavily doped n^+ layer. $I_{diffusion}$ and I_{drift} can be sketched as shown in Figs. 3(a) and 3(b). After upward poling, a relatively large amount of electrons are generated due to more oxygen vacancies accumulate in Ag/BLFO interface.

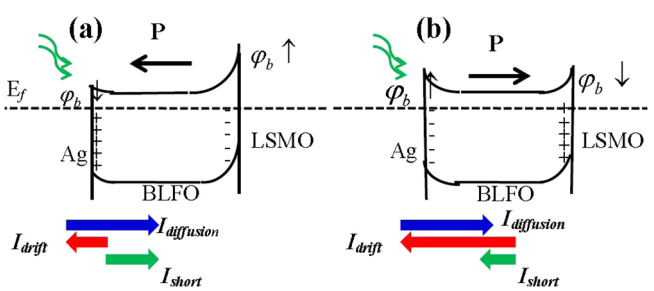

FIG. 3. Band diagram and the variation of diffusion current ($I_{diffusion}$), drift current (I_{drift}), and short current (I_{short}) of Ag/BLFO/LSMO device with (a) upward and (b) downward polarization under light illumination on the top electrode.

Therefore, a large $I_{diffusion}$ flows to the downward direction (BLFO/LSMO interface) because photo-generated electrons diffuse effectively to the top electrode due to short traveling distance and thus a low probability of electro-hole recombination, whereas a tiny I_{drift} flows to the upward direction due to the relatively small barrier height induced by the positive surface charge in the polarization head side and the further reduction driven by the accumulation of oxygen vacancies in the polarization head side. If $I_{diffusion}$ is bigger than I_{drift}, I_{short} ($I_{short} = I_{diffusion} - I_{drift}$,) flows downward ($I_{short}$ is positive). After downward poling, i.e., in the DPS, a relatively small amount of electrons are generated due to the absence or relatively small amount of oxygen vacancies, but I_{drift} increase originating from the relatively large barrier height compared with UPS. In the evolution of the polarization flipping, $I_{diffusion}$ is bigger than I_{drift} initially in UPS, finally $I_{diffusion}$ is smaller than I_{drift} in DPS, and $I_{diffusion}$ is equal to I_{drift} in ZPS. As a result, in the case of UPS, ZPS, and DPS, I_{short} is negative, zero, and positive, respectively.

In the case of fatigue process, there are two situations: the bipolar electric pulses and consistent electric pulses. In the case of bipolar pulses (±40 V), domain walls, which are beneficial to the movement of electrons, increase with alternative pulses number. Therefore, photocurrent will increase exponentially after bipolar pulses. When consistent electric pulses (−40 V) were applied, more and more oxygen vacancies move forward to the top electrode; as the pulses increase, the Ag/BLFO barrier height will be further reduced. Therefore, $I_{diffusion}$ increases and I_{drift} decreases, with an increase in I_{short}. If more and more oxygen vacancies move forward to the Ag/BLFO interface, the interfacial properties would be changed, such as the capacitance. In order to verify our scenario, frequency dependence of the capacitance was measured, as Fig. 4(a) shown. It can be seen that with increasing pulse numbers, the capacitance increased, but the magnifying ratio, which equal to (C_{1000}-C_1)/C_1 (C_1 is the capacitance with only one alternative pulse, and C_{1000} is the capacitance after 1000 alternative pulses) decrease from 125% (at 100 Hz) to 8% (at 200 kHz) with frequency increasing after 1000 alternative electronic pulses, i.e., ±40 V. This result indicates that after repeating pulse numbers, more and more oxygen vacancies move to the interface, which in turn affects the interfacial capacitance. More over, it was found that the interfacial capacitance can increase after light illumination, as indicated by Fig. 4(b), and the magnifying ratio, which equal to (C_{on}-C_{off})/C_{off} (C_{on} and C_{off} is the capacitance with light is turned on and off, respectively) decrease from 45% (at 100 Hz) to 5% (at 200 kHz) with frequency increasing. In order to make clear this phenomenon, the impedance spectra of the sample were further studied by Precision impedance analyzer (Agilent 4294 A). The imaginary part of the frequency-dependent modulus (M″) calculated from the impedance Z*, which is measured under −6 V is shown in Fig. 4(c). According to $M^* = j\varpi C_0 Z^*$, where Z^* is the impedance, for a parallel RC circuit, the M″ should be $M'' = \frac{C_0}{C}\left(\frac{\omega RC}{1+(\omega RC)^2}\right)$, where $\omega = 2\pi f$ is the angular frequency and C_0 is the vacuum capacitance. According to this formula, the peak maximum position is at $\omega = 1/RC$ with a peak height equal to C0/2C,

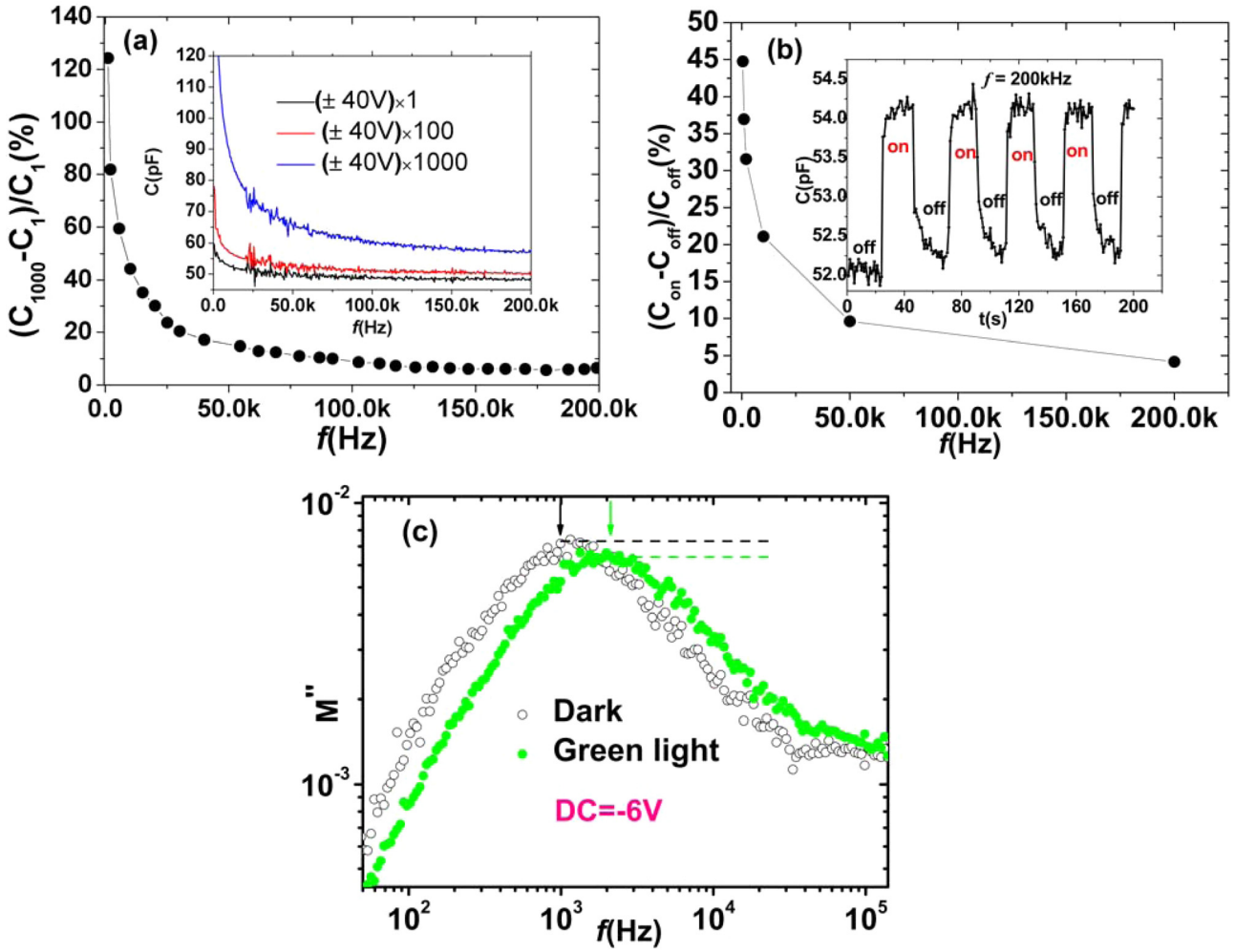

FIG. 4. (a) Frequency dependence of the magnifying ratio $(C_{1000}\text{-}C_1)/C_1$ after one and 1000 bipolar pulses (±40 V). Inset is the capacitance as a function of frequency with different bipolar pulses. (b) Frequency dependence of the magnifying ratio $(C_{on}\text{-}C_{off})/C_{off}$ with light illumination on and off. Inset is the capacitance as a function of frequency under light illumination. (c) Frequency dependence of the electric modulus M″ (imaginary part) before and after green light illumination with DC = −6 V. The imaginary lines are guide for the eye and the downward arrows indicate the moves of the peak of M″ after light illumination.

respectively.[17] Considering the fact that the band bending of BLFO near the BLFO/LSMO interface will be flattened by the negative bias (−6 V), the impedance may be mainly contributed by the Ag/BLFO junction. The most remarkable observation is that the peak height is only a tiny decrease, whereas the peak position changes obviously after illumination. This result implies only a little capacitance increase (which is consistent with the result from Fig. 4(b)) and a varied resistance. It is possible that after illumination, the photo-induced electro-hole pairs will affect the oxygen vacancies or deficiency accumulation in interface, which will further affect the depletion layer, and thus, modify the transport property.

IV. CONCLUSIONS

In conclusion, the orientation of I_{short} depends strongly on the polarization orientations, and it varies monotonically from one orientation to the other as the polarization orientation switching gradually from upward (downward) to downward (upward), the I_{short} value becomes zero when the film is in ZPSs. The intensity of the I_{short} can be strengthened by several times after thousands of bipolar electric pulses. Moreover, after polarization fatigue process of bipolar electric pulses or under light illumination, the capacitance of this sandwich structure is always bigger than the original state. However, the magnifying ratio of the capacitance after and before polarization fatigue process or under light illumination decrease with increasing the frequency in the C-*f* curves. These results suggest that polarization induced surface charge combined with migration of oxygen vacancies is the primary driving force for the varying interfacial barriers and the oxygen vacancies density near the interface, which in turn leads to different orientations and values of I_{short} as well as the differential interfacial capacitance. Our results indicate that the photovoltaic response in ferroelectric BLFO thin films could be further explored for solar light photovoltaic and other capacitor devices applications.

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