Light regulated I-V hysteresis loop of Ag/BiFeO₃/FTO thin film

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ABSTRACT

A hysteresis loop of current–voltage characteristics based multiferroic BiFeO₃ nanoribbons memory device is observed. Moreover, the white-light can greatly regulate both the current–voltage hysteresis loop and the ferroelectric hysteresis loop. The stored space charges within the electrodes/BiFeO₃ interface can lead to hysteresis-type I-V characteristics of Ag/BiFeO₃/FTO devices. The white-light controlled I-V loop and ferroelectric loop result from photon-generated carries. Since the I-V hysteresis loop and ferroelectric hysteresis loop have a potential application prospect to the memory devices, these two white-light controlled the hysteresis loops curves are likely to provide promising opportunity for developing the multi-functional memory devices.

Keywords BiFeO₃ nanoribbons; Ag/BiFeO₃/FTO; hysteresis loop; current–voltage characteristics;

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1. Introduction

To store information, memory devices make use of a physical property that displays hysteresis in response to an applied electric field or magnetic field. The stored information is retrieved by measuring the actual state of the hysteretic property. Many different physical phenomena can be used to obtain a memory effect. Today's computer memories, for example, are based on the hysteresis of charging and discharging capacitors. A downside of this technology is that the stored charge tends to leak away and needs to be restored at regular time intervals. Volatile memories such as this are unsuitable for many applications.

BiFeO_3 is one of the most extensively investigated perovskite oxide materials because of its remarkable multiferroic and optical properties at room temperature and potential applications in memory and logic devices [1–7]. Much work has been done on the fabrications and rich properties of BiFeO_3 single crystals and thin films [8–11]. These reports demonstrated that BiFeO_3 possesses various interesting properties, which provide an opportunity of making multifunctional devices based on BiFeO_3 .

To the best of our knowledge, no paper has been published so far concerning the study of the hysteresis loop of current–voltage characteristics based multiferroic BiFeO_3 . In this work, a white-light controlled hysteresis loop of current–voltage characteristics based the BiFeO_3 nanoribbons at room temperature is observed.

2. Experimental procedure

2.1 Preparation of BiFeO_3 Nanoribbons

BiFeO_3 nanoribbons were prepared using an improved hydrothermal process. Firstly, a little $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.475 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.352 g) were dissolved in 50 ml acetone (99.8%) with

stirring until completely dissolved. Secondly, distilled water and concentrated ammonia were added and stirred until the pH value of the mixed solution reached 13~14. After stirring continuously for 2 hours, the sediment is centrifuged out and washed with distilled water several times until the pH value is about 7.0. Thirdly, the co-precipitate was dispersed in 40 ml of distilled water, and 8.0 g of NaOH was added under vigorous stirring for 30 min. Then the solution was transferred to a sealed, Teflon-lined steel autoclave and heated at 120 °C for 144 hours. The black powder obtained was washed with distilled water and ethanol and dried at 70 °C for 12 hours.

2.2 Preparation of the Ag/BiFeO₃/FTO Devices

The Ag/BiFeO₃/FTO devices were prepared by spin-coating method. Firstly, fluorine-doped tin oxide (FTO) substrates were cleaned by acetone, ethanol, and deionized water, and subsequently dried on the spin coater. Secondly, BiFeO₃ films were prepared on FTO substrate by spin-coating method. The detail preparation process of BiFeO₃ films is as follows: Firstly, we grinded the as-prepared BiFeO₃ nanoribbons powder for 2 hours. Next, we dissolved the powder in polyvinylidene fluoride (PVDF) solution to prepare precursor gel. Then the precursor gel is spin-coated on the FTO substrate. The spin-coating process at 1,000 rpm for 20 s was used to prepare BiFeO₃ films with thickness of about 500 nm. Then these samples were subsequently dried at 120 °C for 12 hours. The thickness of the BiFeO₃ film was detected by the step profiler. The Ag electrode with thickness of 100 nm and diameter of 0.5 mm was deposited by magnetron sputtering equipment on top of the BiFeO₃ films by shadow mask at room temperature. A schematic drawing of the structures is shown in the inset of Fig. 1(a).

2.3 Characterizations

The crystal structures of BiFeO₃ nanoribbons were characterized at room-temperature by X-ray

diffraction (XRD, Shimadzu XRD-7000 X-ray diffractometer) with Cu K α radiation. Surface morphology of BiFeO₃ nanoribbons was characterized using scanning electron microscopy (SEM, JSM-6510). The size and structure of the BiFeO₃ nanoribbons were observed by transmission electron microscopy (JEM-2100). The current–voltage characteristics of the device were measured with a Keithley model-2400 system. The measurements of ferroelectric hysteresis loops (P–E) were performed using a Precision Premier Workstation ferroelectric test system (Radiant Technology, USA). The inset of Fig. 1(a) shows a schematic diagram of the test circuit.

3. Results and discussion

Fig. 1(a) displays the results of X-ray diffraction (XRD) of the BiFeO₃ nanoribbons, which shows that the pure phase of the BiFeO₃ nanoribbons is prepared successfully. All the diffraction peaks can be assigned to the pure phase of the BiFeO₃ nanoribbons (JCPDS No. 20-0169). The sharp peaks demonstrate good crystallinity of the nanoribbons, indicating a rhombohedrally distorted perovskite structure in a space group of R3c, which is consistent with the literature [12]. The EDX data of the BiFeO₃ nanoribbons in Fig. 1(b) confirms that composition of the BiFeO₃ nanoribbons are only Bi, Fe and O without any other impurities, which indicates that we have not mixed any impurity element in preparation process. The Al peaks are due to the substrate used for dispersing the sample. Fig. 1(c) shows the SEM image of the BiFeO₃ nanoribbons. The as-prepared sample consists of BiFeO₃ nanoribbons, which have several microns length. The TEM image shows that the individual BiFeO₃ nanoribbon present 50 nm width (in inset of Fig. 1(c)). Fig. 1(d) shows the P-E hysteresis loops of the single-crystalline BiFeO₃ nanoribbons at 20 Hz in the dark and under illumination (white light) at room temperature. The ferroelectric hysteresis loop greatly changes when subjected to light irradiation. The saturated ferroelectric polarization and the remanent

ferroelectric polarization increase quickly with power density of white light increasing. The saturated ferroelectric polarization and the remanent ferroelectric polarization increase about 150 % and 70 % respectively when subjected to light irradiation with power density 60 mW/cm^2 , which indicates strong coupling between optical property and ferroelectricity in the single-phase BiFeO_3 nanoribbons. Therefore, a large photo-ferroelectric effect is observed in the BiFeO_3 nanoribbons at room temperature. The observed remarkable improvement in the ferroelectric polarization of the single-crystalline BiFeO_3 nanoribbons should be attributed to the photo-generated charge at domain boundaries [13–14]. The devices provide the possibility to study their light-controlled ferroelectric random access memory devices.

Fig. 2(a) and Fig. 2(b) show the hysteresis loops of the current–voltage characteristics of $\text{Ag/BiFeO}_3/\text{FTO}$ structure in the different voltage range in dark and under white light illumination. The hysteresis curves show asymmetry. A different V_{OC} (open circuit voltage, where a non-zero voltage is observed at zero current) and I_{SC} (short circuit current, where a non-zero current is observed at zero voltage) value of the hysteresis curves are observed. Similar hysteresis behavior has been observed on several conjugated polymers [15–17]. Lebeugle et al. reported similar $I - V$ hysteresis loop, but its mechanism is not adapt to our devices [18]. The origin of the hysteresis loop lies in the presence of a displacement current I_d adding to the conductive part I_r . The I_d is represented by

$$I_d = \frac{d(CV)}{dt} = C \frac{d(V)}{dt} + V \frac{d(C)}{dt}. \quad (1)$$

The $I_d = d(CV)/dt$ is due to both voltage variation (CdV/dt) and capacitance variation $V(dC/dt)$. The first contribution is typically due to voltage sweep speed (dV/dt), which results in the change of I - V hysteresis loop of $\text{Ag/BiFeO}_3/\text{FTO}$ device corresponding to various voltage sweep speed

as shown in the Fig. 3(a). Whereas the second one $V(dC/dt)$ is due to stored space charges [15, 17]. In Ag/BiFeO₃/FTO devices, the space charges are stored in the two interface (Ag/BiFeO₃ interface and BiFeO₃/FTO interface). Therefore, The I-V hysteresis curves are asymmetry. The total current (I) is represented by

$$I = I_d + I_r \quad (2)$$

The magnitude of these contributions determine the total value of the detected current. The hysteresis I-V loop has been repeated more than 100 cycles, and the endurance performance of the device cell is present in Fig. 3(b). It is clearly noticed that I-V loops have a high degree overlap, hardly show any degradation after 100 cycles, indicating the high stability of the device.

The BiFeO₃ thin films can be regarded as an n-type semiconductor due to the naturally produced oxygen vacancies that act as donor impurities [8]. Hence, when the initial sweep from 0 to a positive voltage, a space charge layer of electrons is accumulated in the BiFeO₃ film near the FTO electrode and a space charge layer of holes is accumulated in the BiFeO₃ film near the Ag electrode (Fig. 2(a) and Fig. 2(b)). With the increase in voltage, space charges are stored in the device and spatial distribution of such charges occurs. When the sweep direction was reversed (from positive voltage to 0 V), the device retained its spatial distribution of charge carriers. A small positive voltage, open circuit voltage (V_{+OC}), is required to balance the effect of the space charges and to maintain zero current. At zero voltage, the flow of stored charges through the external circuit could give rise to a negative short circuit current (I_{SC}). At the same time, charge storage occurs when the voltage is swept from 0 V to negative voltage. In the subsequent forward sweep direction (i.e. from negative to 0 V), an open circuit voltage (V_{-OC}) and a short circuit current (I_{+SC}) are again observed. The magnitudes of I_{SC} and V_{OC} during the two sweep directions are different (in inset of Fig. 3(b)).

Under forward bias, the open circuit voltage (V_{+OC}) and short circuit current (I_{SC}) increase with increasing of applied voltage amplitude (V_L). Under reverse bias, the open circuit voltage (V_{-OC}) and short circuit current (I_{+SC}) decrease with increasing of applied voltage amplitude (V_L). This might represent asymmetric density of stored space charges in the forward and reverse sweep, and suggest more stored charges in the device with increasing of applied voltage amplitude (V_L) [15]. This is because the amounts of stored charges are different in the FTO/BiFeO₃ interface and the Ag/BiFeO₃ interface due to the different electrodes (FTO and Ag) work functions.

Fig. 4(a) shows time variation of the device current after application of a positive voltage pulse (from 0 to 20 V). The current is a negative value due to the flowing of stored charges. The absolute value of current decrease with the time increasing (in inset of Fig. 4(a)), because the stored space charges are slow recombined. Fig. 4(b) shows reversible switching of the Ag/BiFeO₃/FTO device between low and high-conductivity states when the white-light lamp was turned on and off. The results showed fast-switching behaviors and also good reproducibility, which suggest that our simple photo device can also be used as an optoelectronic switching device.

The hysteresis loops can be influenced by white light irradiation (Fig. 2(a) and Fig. 2(b), which show that the open circuit voltage (V_{+OC}) and short circuit current (I_{SC}) of the hysteresis loop decrease with light power density increasing under forward bias. The open circuit voltage (V_{-OC}) and short circuit current (I_{+SC}) of the hysteresis loop increase with light power density increasing under reverse bias (Fig. 2(a)). The hysteresis loop area values increase with light power density at 1 V loop amplitude in the inset of Fig. 2(a). The large enlargement of the hysteresis curve areas indicates the presence of a displacement current adding to that measured under dark together with a DC photocurrent effect producing the rotation of the hysteresis axis [15]. This conversely explains

also the observed V_{OC} values lower than those seen under dark. The hysteresis loop of current–voltage characteristics could be applied to the memory devices [15, 19]. A white-light controlled hysteresis loop of current–voltage characteristics is likely to provide promising opportunity for developing the multistate memory devices.

In previous reports, the device just presents one of the two storage effect: I-V hysteresis loop and ferroelectric hysteresis loop. Our device shows both of these two storage effect. In addition, the white light can greatly regulate these two storage effect in our device. Hence, it is likely to provide promising opportunity for developing the multi-functional memory device.

4. Conclusions

In conclusion, this work study the I-V hysteresis loop and P-E hysteresis loop in Ag/BiFeO₃/FTO device, which are caused by charge storage. In addition, the white-light can control these two loops due to photon-generated carriers.

Acknowledgments

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Figure Captions:

Fig. 1 (a) X-Ray diffraction pattern of BiFeO₃ nanoribbons. The structure diagram of the device and the experimental test circuit shown in the inset. (b) The EDX spectrum of BiFeO₃ nanoribbons. (c) SEM image of BiFeO₃ nanoribbons. The inset shows TEM image of the individual BiFeO₃ nanoribbons. (d) Ferroelectric hysteresis loop of the Ag/BiFeO₃/FTO devices measured at 20 Hz under ordinary filament lamp with various power density at room temperature.

Fig. 2 (a) and (b) Hysteresis-type current–voltage characteristics collected of BiFeO₃ at a same voltage sweep speed at different power density for 1.0 V and 2.0 V. The inset of Fig. 2 (a) shows the hysteresis loop area values increase with light power density at 1 V loop amplitude.

Fig. 3 (a) Hysteresis-type current–voltage characteristics collected of the Ag/BiFeO₃/FTO devices at different voltage speed rate for 6 V loop amplitude at a voltage speed rate of 0.06 V/s, 0.1 V/s, 0.2 V/s, 0.4 V/s and 0.6 V/s. (b) I-V curves with 100 consecutive cycles of the device at a voltage speed rate 0.2 V/s and 0.6 V/s, respectively. The inset of Fig. 3(b): Hysteresis-type short circuit current (I_{SC}) – voltage loop amplitude (V_L) characteristics and hysteresis-type open circuit current (V_{OC}) – voltage loop amplitude (V_L) characteristics in dark at a same voltage sweep speed.

Fig. 4 (a) Time variation of the device current after application of a 20 V voltage pulse. The time was measured from the end of the 20 V voltage pulse. The inset shows variation of the device current within 500 seconds. (b) Reversible switching of the Ag/BiFeO₃/FTO device between low and high conductivity states when the white-light lamp (60 mW/cm²) was turned on and off at 2.0

V.

Fig. 1

Fig. 2

Fig. 3

Fig. 4