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Effect of sweeping voltage and compliance current on bipolar resistive switching and white-light controlled Schottky behavior in epitaxial $BaTiO_3$ (111) thin films

Qiong Zhang, Caihong Jia*, Weiwan Liu, Weifeng Zhang*

Key Laboratory of Photovoltaic Materials of Henan Province and School of Physics & Electronics, Henan University, Kaifeng 475001, People's Republic of China

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A B S T R A C T

Bipolar resistive switching (RS) phenomenon without required electroforming has been observed in epitaxial (111)-oriented $BaTiO_3$ (BTO) thin films deposited by PLD technique on conducting Nb-doped substrate of $SrTiO_3$ (NSTO). Negative differential resistance (NDR) is observed at about −5 V when the maximum of positive voltage exceeds 7 V and the compliance current is more than 1.5 mA. And bipolar resistive switching has also been observed. In addition, the resistance of LRS decreases with increasing compliance current or the maximum of positive voltage while that of HRS barely changes, and the resistance of HRS increases with increasing the absolute of maximum of negative voltage while that of LRS scarcely changes. A typical rectifying behavior is observed when the maximum of positive voltage is less than 4 V (such as 2 V). In this case, the reverse biased current is strongly enhanced under illumination of white-light, and vice versa. The resistance of LRS and HRS can be controlled by the applied voltage or the compliance current. The rectifying behavior can be controlled by the white-light. The transition from rectifying behavior to bipolar resistive switching can be controlled by the applied voltage. The above results were discussed by considering the oxygen vacancies that can trap or release electrons as a trapping layer at the Pt/BTO interface.

1. Introduction

Recently, resistive random access memory (RRAM) is suggested to satisfy the demands including high-speed, low power consumption, high cell density, long retention time and good compatibility with complementary metal oxide semiconductor (CMOS) process [1,2]. Resistance switching (RS) of Perovskite oxide films is in the focus of current research, such as $SrTiO_3$, $Pb(Zr,Ti)O_3$, $SrZrO_3$, etc. [3–6]. Although there have been many reports on epitaxial $BaTiO_3$ (BTO) films that makes the switching mechanism more simple, only a few reports focused on its bipolar resistive switching behavior [7–9]. As we know, the (111) plane is not a polarized axis at room temperature, so a high dielectric constant and low remanent polarization can be obtained [10], which is different from the widely investigated (001)-oriented $BaTiO_3$ films [11,12] that are promising for ferroelectric. As a result, the (111) BTO films are promising to give low dielectric relaxation in the microwave range [10,13], and then the memory devices can be used even the frequency is rather high. What is more, the photovoltaic effect has been widely studied in recent years [9,14,15]. There is no report on BTO based Schottky junctions so far, which possess multi-functions, including negative differential resistance (NDR), tunable bipolar resistive switching effect by applying different current compliances or voltages, rectifying property, photodiodes.

In this study, obvious negative differential resistance (NDR) is observed at about −5 V, which can present a new direction for high density information storage and processing [16]. A bipolar resistive switching (RS) is also observed on the Pt/$BaTiO_3$/NSTO device. The remarkable compliance current and the applied voltage controlled resistive switching has potential application for nonvolatile multistate memory devices, which can enhance the storage density [17]. Both NDR and multistate characteristics contribute to the high density information storage of resistive switching. A bipolar resistive switching appear in (111)-oriented BTO when the applied is large enough, while a typical rectifying behavior is usually observed in (001)-oriented BTO even a large voltage is applied to the device [11,12]. The reverse biased current is strongly enhanced under illumination of white-light when the maximum of positive voltage is less than 4 V (such as 2 V), which

* Corresponding authors. Fax: +86 371 2388 0659.
E-mail addresses: chjia@henu.edu.cn (C. Jia), wfzhang@henu.edu.cn, wfzhang6@163.com (W. Zhang).

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is helpful for the white-light photovoltaic effects [9,15]. The capacitance–voltage (*C*–*V*) curves and the initial decay of the low resistance state in the retention curve are supposed to support our explanation for the switching mechanism [6,18]. Furthermore, we discuss the switching mechanism in Pt/BTO/NSTO structure.

2. Experiments

The $BaTiO_3$ (BTO) film was epitaxially grown on the (111) Nb(0.7%):$SrTiO_3$ (NSTO) substrate by pulsed laser deposition (PLD) with a KrF excimer laser (λ=248 nm). The NSTO substrates are commercial single crystal conducting substrates. The (111)-oriented NSTO substrates are necessary for us to grow (111)-oriented BTO because their surface structural control is precise [13]. The lattice mismatch between BTO (cubic: $a=b=c=4.031$ Å) and NSTO (cubic: $a=b=c=3.905$ Å) is 3.23% (($a_{film}-a_{substrate})/a_{substrate}=3.23\%$), which is quite small. The simple way to grow (111)-oriented BTO is to employ optimum substrate, such as NSTO. In addition, we can grow (111)-oriented BTO through different film making methods (PLD, MBE, MOVPE, etc.). The NSTO substrate was carefully cleaned with acetone, alcohol and deionized water before deposition. During growth, the substrate temperature was kept at 700 °C, the oxygen pressure was 1 Pa and the ceramic $BaTiO_3$ target was used. The frequency of the laser beam is 5 Hz and the pulse energy density on the target is 1.5 J/cm^2. The thickness of the BTO thin film is about 200 nm and the thickness of the NSTO substrate is 0.5 mm. The crystalline structure of the film was characterized by X-ray diffraction pattern (XRD, DX-2700) with Cu Kα radiation. For the electrical device characterization, top Pt electrodes (200 × 200 μm^2) were deposited by DC sputtering and In bottom electrode (about 1 mm × 1 mm) was pressed on the back of NSTO with ohmic contact. The current–voltage (*I*–*V*) characteristics of the Pt/BTO/NSTO/In device were measured using a Keithley 2400 source meter. The capacitance–voltage (*C*–*V*) characteristics were evaluated using a Keithley 4200 semiconductor characterization system. The current from Pt to BTO was defined as a positive direction. All the characterizations and measurements were performed at room temperature.

3. Results and discussion

The XRD pattern of the BTO film deposited on NSTO is shown in Fig. 1(a). As seen from the XRD patterns of θ–2θ scans in Fig. 1(a), only (111) and (222) peaks are observed, suggesting (111) orientation growth of the film. To identify the epitaxial growth of the (111) oriented BTO film on NSTO, we performed ϕ-scans for the {100)} family of the BTO thin film and the {100} family of the (111) single crystal NSTO substrate, as shown in the inset of Fig. 1(a). The coincidence of the {100} peaks indicate the epitaxial growth of BTO on NSTO (111) substrate.

Ohmic contact forms between the In electrode and NSTO substrate, as shown in Fig. 1(b). Fig. 1(c) schematically illustrates the electrode settings in which the forward bias corresponds to application of a positive voltage of Pt. The device exhibits a rectifying behavior when a small voltage is applied, as shown in the lower inset of Fig. 1(d). The rectification ratio reaches approximately 275 at 2 V. It should be noted that a bipolar resistive switching (RS) and obvious negative differential resistance (NDR) appear when the voltage is large, which is illustrated in Fig. 1(d). During the *I*–*V* measurements, the voltage bias was scanned as 0→positive→0→negative→0 (indicated by numbered arrows). A current compliance

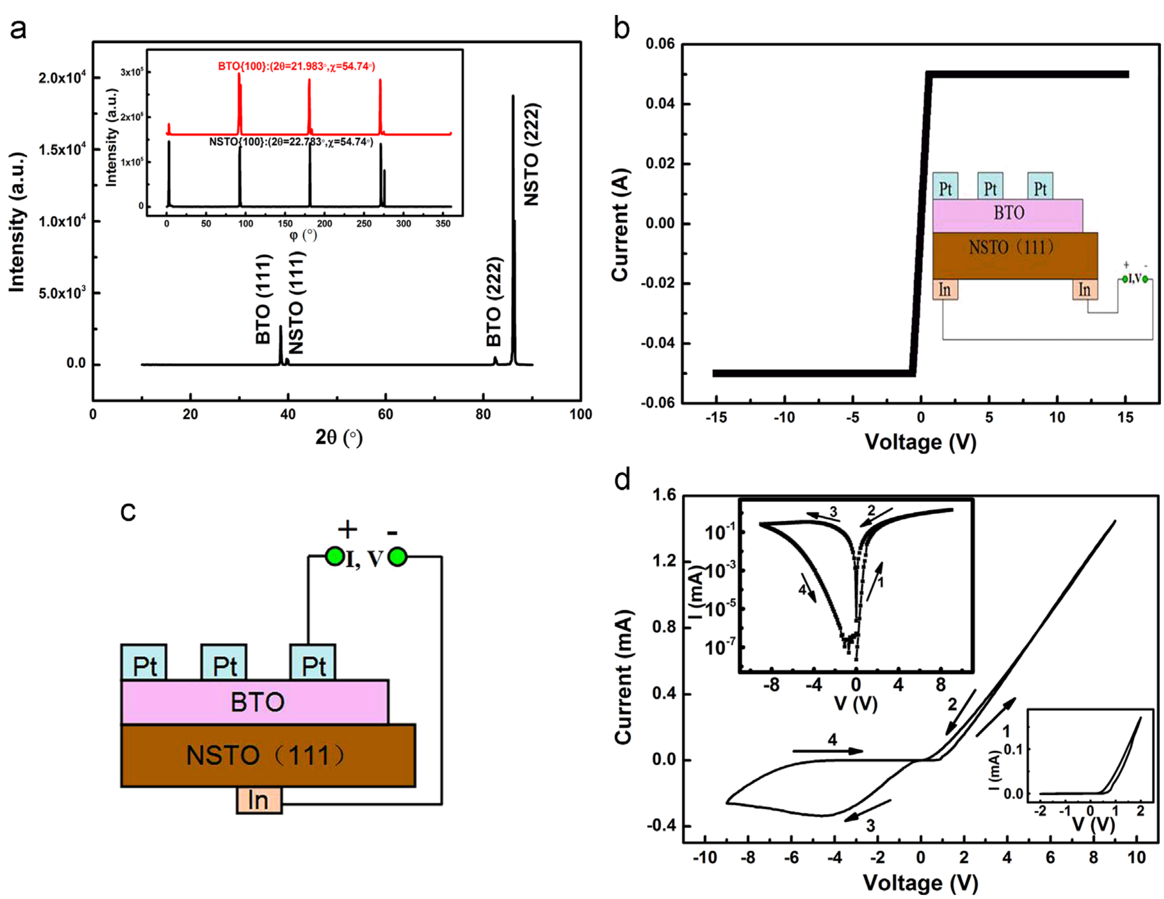

Fig. 1. (a) The XRD 2θ and ϕ scanning patterns of BTO films. The current–voltage (*I*–*V*) characteristic of In/NSTO/In structure (b) and Pt/BTO/NSTO/In system (d). (c) The measurement schematic of Pt/BTO/NSTO/In structure (not to scale).