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Optically Modulated Resistance Switching Polarities in $BaTiO_3$ Thin Film

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Abstract

The light response and resistance switching behavior in $BaTiO_3$ (BTO) films are studied for a symmetric Pt/BTO/Pt structure. The resistance of films as a function of time with and without ultraviolet light has been studied. Furthermore, resistance switching behavior was clearly observed based on the application of 365 nm wavelength ultraviolet light. Consequently, the polarities of resistance switching can be controlled by ultraviolet light when the energy is larger than the band excitation energy. It is proposed that the polarity of the resistance switching is dictated by the competition of the ferroelectricity and oxygen vacancy migration. This provides a new mechanism for modulating the state of ferroelectric resistive memory devices.

Keywords: resistance switching; ferroelectric polarization; oxygen vacancies; thin films; phontoresponse

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Recently, resistive random access memory (RRAM) devices possessing many advantages such as simple structure, low cost, and a nonvolatile characteristic, have been suggested as promising candidates for next generation nonvolatile memory applications[1-3]. Perovskite oxides are fundamental materials for applications in RRAM, with particular interest being paid to materials such as $SrTiO_3$[2], $BaTiO_3$(BTO)[4-6] and $BiFeO_3$[7-9]. Furthermore, a number of studies have been focused on the functional tunable effect, the electroresistance effect induced by ferroelectric polarization[10], the photoresistance effect induced by an ultraviolet laser[7], giant tunneling electroresiatance in ferroelectric tunnel hunctions[11] and the resistive switching (RS) of polarities controlled by different deposition conditions[12]. Correspondingly, various microscopic mechanisms such as ferroelectric polarization[4,13], conductive filaments mechanisms and Schottky barriers[14,15] at the interfaces have been proposed to explain the resistive switching effects. In spite of the excellent work in the field the ferroelectric resistive switching mechanisms are still controversial and in need of additional exploration. In the work of W. J. Ma et al.[16], conductive filaments mechanisms are considered to explain the resistive switching. And in the work of Li et al.[12], they observed two completely opposite RS polarities for the BTO films deposited in different oxygen pressures. They showed that ferroelectric polarization is the main cause of the RS effect when lower oxygen pressures is used during the film deposition while vacancy migration is the primary source of the RS effect when higher oxygen pressures is used.

In this work, we present a resistive switching behavior in a symmetric structure Pt/BTO/Pt, which combines the light induced resistance change and the polarities of

resistance switching. It is found that not only can the high and low resistance states of the film be switched by applying ultraviolet 365nm wavelength light but also that the polarities of resistance switching can be controlled under an opportune oxygen condition. The two mechanisms of RS, the ferroelectric polarization and oxygen vacancies, can coexist and compete with each other. Neutral oxygen vacancies can easily releases electrons to the conduction band under stimulation from certain wavelength of light[17]. So, we designed a film where the two mechanisms coexisted and then modulated the oxygen vacancy transition by light above the bandgap to demonstrate the change of the RS mechanisms.

Results and discussions

As illustrated in Figure 1 we estimate the direct bandgap of the thin BTO layer to be ~3.18eV. We used a modified square law based bandgap calculation using the $(\alpha hv)^2$ vs hv plots, by extrapolating the linear portion of the absorption to the X-axis where the absorption coefficient becomes zero. This optical gap is consistent with the reported value of 3.20eV for bulk BTO[18].

In order to confirm the stability and repeatability of the Pt/BTO/Pt device, we studied the ultraviolet (UV) periodic response. For this study, we periodically shone 365 nm UV light for 600 s. The UV response of BTO film is shown in Figure 2(a). It can be seen that current decreases rapidly when the sample is exposed to UV, followed by a gradual decrease in current until saturating at a value of 3.2 nA. When the light is turned off, the current increases gradually over 120 s to reach its original value of 0.09 nA. The behavior is observed to be periodic with the periodic illumination. To further understand the mechanism of the repetition state, we investigated the relaxation process during the UV response due to the switching of

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the illumination. The carriers excited by the photo-induced effect can accumulate in the conduction band reducing the resistance of the film. They then release their energy through the emission of longitudinal optical phonons when the light is off. Figure 2(b) illustrates the resistance relaxation when the UV light is on and off with the pink and blue regions respectively. These can be fitted by an exponential function.

$$R = R_0 + A\exp(-(t/\tau)),$$

where R_0 represents the initial resistance, A is a prefactor standing for the difference of resistance between the on and off conditions, τ is the time constant of relaxation. The fitting curve is in good agreement with the experimental values. Here the time constants obtained by simulations are 3.81 s and 34.46 s as shown in Figure 2(c) and (d), respectively. The transient photoresponse is dictated by the generation and recombination rates of photocarriers, typically in the ms range[19]. Oxygen vacancies serve as charge traps increasing the time constant to the seconds range. Due to the time of carrier drift being extremely short and the thermal excitation being slow the light on and light off processes are limited by the rate of photoexcitation and the rate of thermal excitation, respectively. The ratio 9.0 between the resistance for the light being on and off is consistent with previously reported values 6.1[20].

The resistive switching properties of the Pt/BTO/Pt device structures under dark conditions and 365 nm UV light exposure were investigated. The observed I – V hysteresis loops, shown in Figure 3, were measured by four continuous voltage scanning cycles of 0→+2→0→−2→0V. For the dark condition it demonstrates an almost symmetric behavior where during the positive voltage scanning cycle (0→+2→0V) and the negative voltage

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scanning cycle (0→−2→0V), the sample changes from a high resistance state (HRS) to a low resistance state (LRS). As shown in Figure 3 when we illuminated the film under the UV light the hysteresis direction is completely opposite to that of the dark condition behavior, the sample changes from a LRS to a HRS during the 0→+2→0V cycle and the 0→−2→0V cycle.

The two resistance states exhibit opposite hysteresis directions and different resistance magnitudes, indicating a significant change of the mechanisms. We propose the following microscope RS mechanisms, shown in Figure 4, to explain behaviors of film. We ascribe the change of the hysteresis direction to the switch to an oxygen vacancy migration mediated RS effect in the case of no light as compared to the more typical ferroelectric case occurring under the UV light. In the virgin state, shown in Figure 4(a), the distribution of oxygen vacancies is homogenous. When a 0→2 V process is applied to the top interface in the dark condition, the oxygen vacancies will be forced away from the Pt/BTO interface, as shown in Figure 4(b), increasing the width and height of the Schottky barrier. When the voltage is swept back from 2 V, the oxygen vacancies concentration at the top interface will experience a continuous positive voltage as shown in Figure 4(c), further increasing the width and height of the Schottky barrier. Consequently, the BTO film will change from a LRS to a HRS due to the increased barrier at the interface. A similar interpretation also applies when a negative sweeping voltage is applied.

Under UV light, the films RS behavior is completely different from that in the dark condition. Figure 4(d) shows the virgin state of the energy band diagrams. When a UV light beam with an energy bigger than that of the gap of the single crystal illuminates the film,

electrons from oxygen vacancies or in the valence band (VB) can be promoted to the conduction band (CB)[17], thus the resistivity inside the semiconductor decreases and the depletion region becomes thinner. In this case oxygen vacancies are no longer the primary effect producing the RS behaviors. The charge transport across the Pt/BTO/Pt device is controlled by the ferroelectric polarization switching inducing a Schottky barrier at the interface. In order to further demonstrate that the larger polarization remnant plays a more important role under UV light, we tested the change of the P-V loops when the light is on/off in supplemental materials Figure s3. For the same positive voltage as applied to the dark sample the film will now have the down polarization continuously increasing, resulting in the polarization and energy band changes shown in Figure 4(e) and Figure 4(f), leading to the final resistance from voltage scans 2→0V being lower than that for 0→2V. The negative voltage scans have a similar effect due to the symmetry.

It should be noted that both the oxygen vacancy mechanism and the ferroelectric polarization mechanism are present in all of the charge transport processes. Although the effect of the ferroelectric polarization is small it is still present when oxygen vacancies are playing an important role, and vice versa. There is a competition between oxygen vacancy mechanism and ferroelectric polarization but their inclusion would not change the physics picture presented.

Conclusions

In summary, we have fabricated a symmetric metal/ferroelectric/metal device to study the distinct RS effects on normal state and UV light illuminations. We find that the UV light can modulate the resistive state from a HRS to a LRS. More importantly, the polarity of the

resistance switching can be changed by illumination of UV light. We have demonstrated that the oxygen vacancy mechanism and ferroelectric polarization have a competitive relationship in controlling the RS behaviors of our films. In the normal state, the oxygen vacancy mechanism plays dominant role in inducing the RS effect, while under UV light, the ferroelectric polarization is the major mechanism for controlling the charge transport. The present work presents a microscopic mechanism for Pt/BTO/Pt device RS behaviors under UV light, and provides insight for the accurate design and control of high quality ReRAM devices.

Methods

High quality BTO films were grown on fused silica substrates to test the bandgap and on conducting Pt/TiO_2/SiO_2/Si using pulsed laser deposition (PLD) with a laser energy of 140 mJ/pulse on the target. The film growth was carried out at a 5 Pa oxygen pressure and a 750 ^{o}C substrate temperature using a 2 Hz pulse repetition rate during about 30 minutes. The top Pt electrodes were sputtered using a sputtering system with a shadow mask. The structure of the films was determined by X-ray diffraction (XRD), performed on a BRUKE D8 using a Cu Kα source, as shown in Figure s1. The optical transmission spectra of the films were measured by UV spectroscopy. The electrical properties were examined using an electrometer, Keithley model 2400 and 6487. Ferroelectric properties of the films were measured by a Piezo Force Microscope (PFM) operated in contact mode and a Radiant Technology precision workstation in Figure s2 and s3. Illumination tests were performed with a 365 nm ultraviolet light with a power density of 150mW/cm^2 in order to characterize photovoltaic properties.

Supplementary material

See supplementary material for the XRD diffracts, PFM, and P-V hysteresis loops at different conditions, including normal hysteresis loop and under UV light.

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Author contributions

J. Wang contributed to thin film growth and structural characterization by XRD. J. Wang and B. Luo carried out measurements of physical properties for BTO films. C. Chen, L. Miao, J. Wang and B. Luo were involved in the discussions regarding the data interpretation. J. Wang and B. K. Bedford wrote the manuscript. This project was supervised by B. Luo.

Competing financial interests

The authors declare no competing financial interests.

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Figure Captions

Figure 1. Modified Tauc's plot for the BTO sample for the determination of energy bandgap. Optical transmittance spectrum of the film is displayed in the inset.

Figure 2. (a) The current of BTO film illuminated with a 365nm UV light as a function of time. (b) Zoom in one period of illumination on and off. The fitting curve of resistance relaxation in figure (b) pink and blue region were shown in (c) and (d), respectively.

Figure 3. Typical of I-V characteristic of film under normal and UV light. The direction of scans was shown as arrows.

Figure 4. The schematic energy band and V_O migration under different conditions. (a) virgin state (b) positive circle 2→0V, (c) positive circle 0→2V, (d) virgin state under UV light, (e) 0→2V circle under UV, (f) 2→0V circle under UV.

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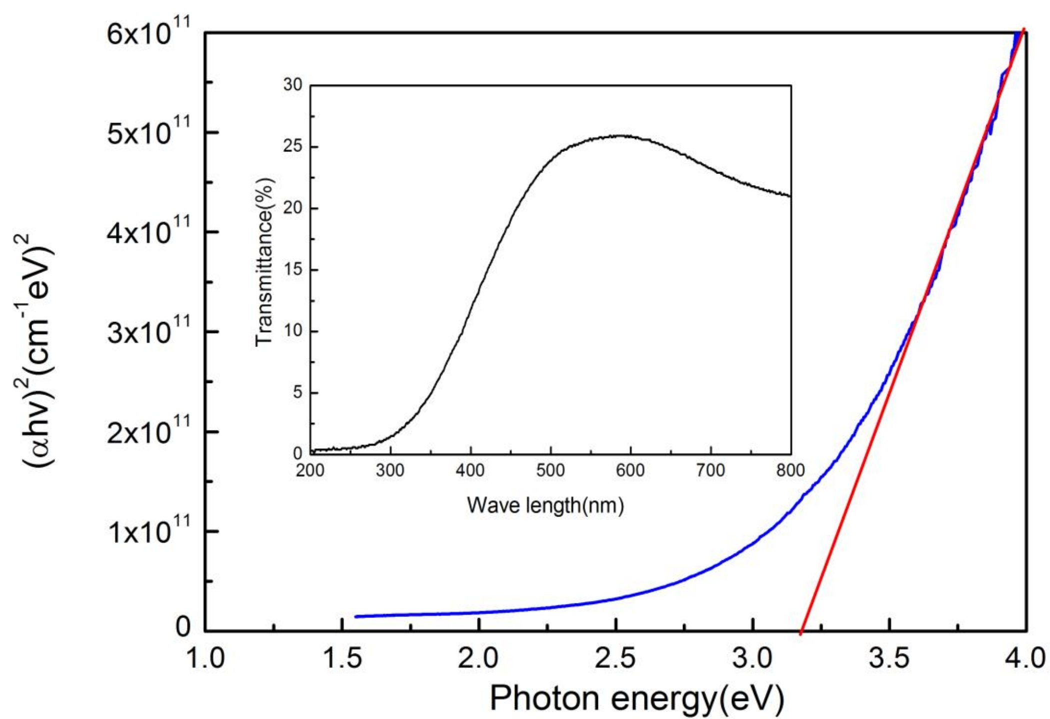

Figure 1, Jing *et al.*

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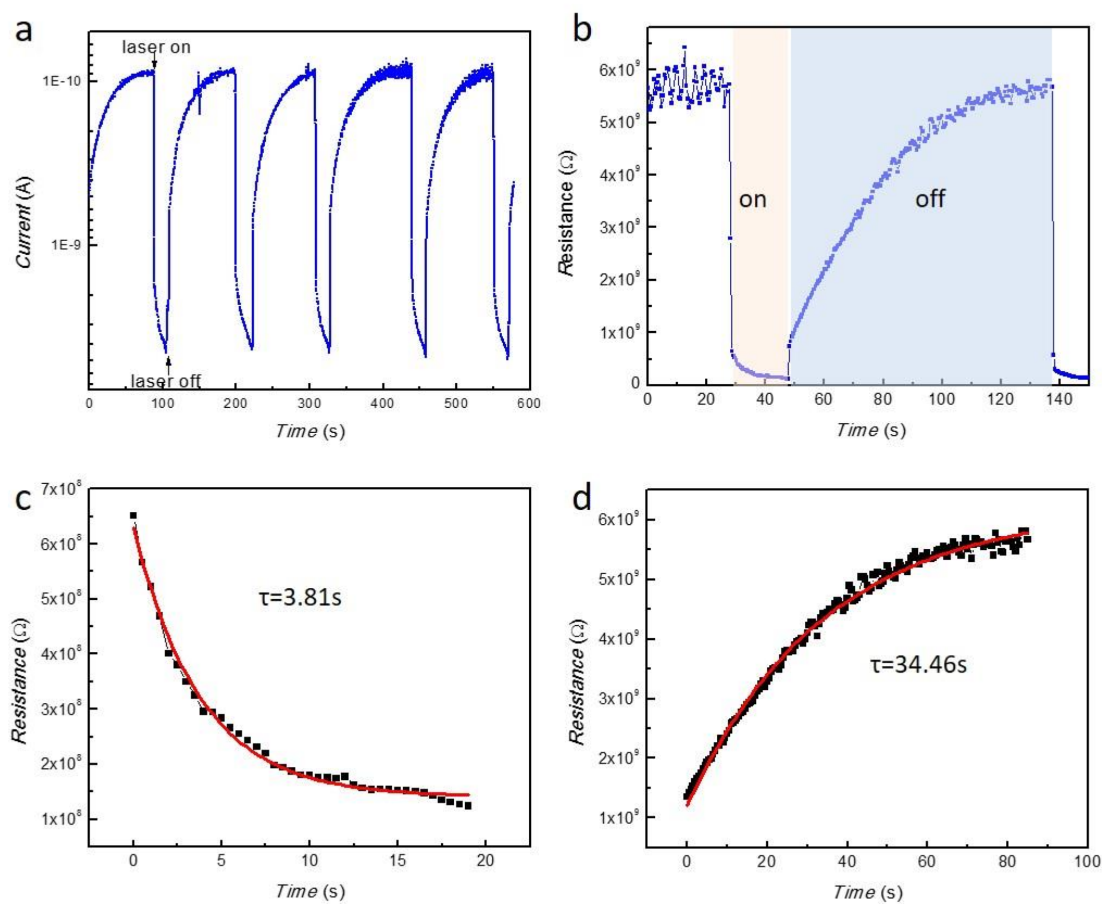

Figure 2, Jing *et al.*

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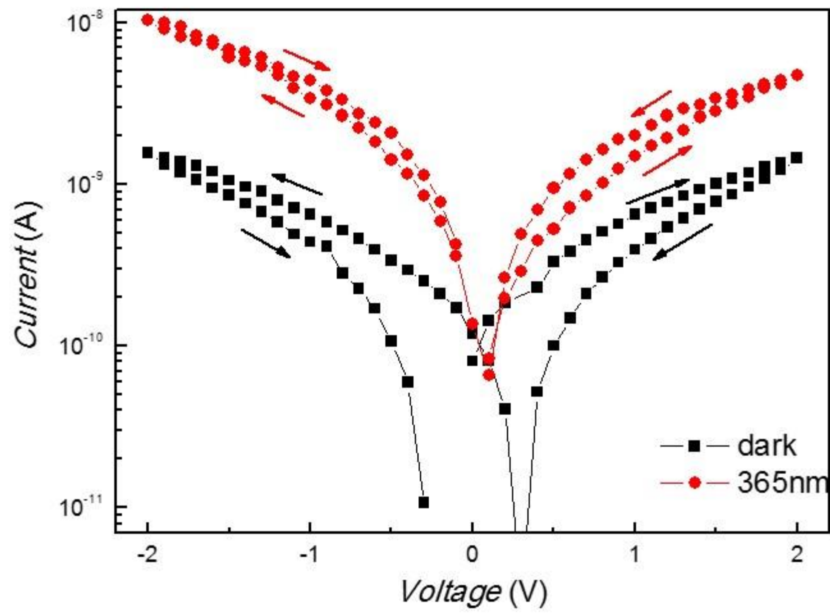

Figure 3, Jing *et al.*

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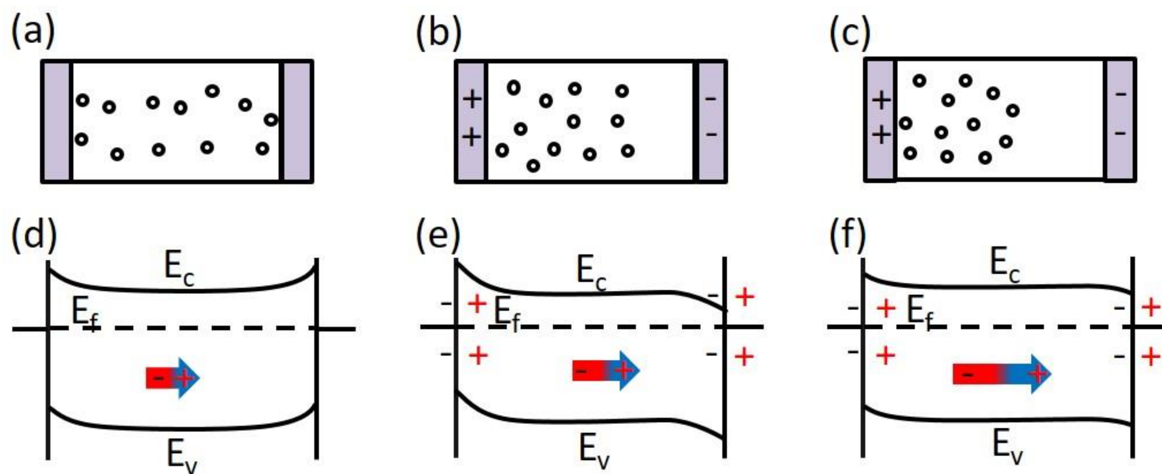

Figure 4, Jing *et al.*