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Ultraviolet photovoltaic effect in BiFeO₃/Nb-SrTiO₃ heterostructure

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We report on ultraviolet photovoltaic effects in a BiFeO₃/Nb-doped SrTiO₃ heterostructure prepared by a pulsed laser deposition method. The heterostructure exhibits rectifying behaviors in the temperature range from 80 K to 300 K. The photovoltage of heterostructure is about 0.33 V at $T=80$ K when it is illuminated by a KrF excimer laser with a wavelength of 248 nm. The peak photovoltages decrease with increasing the temperature because of the accumulation of photogenerated carriers. Moreover, the peak photovoltages of heterostructure almost linearly increase with an increase of the power density of laser at $T=300$ K. The results reveal some properties that may be useful for possible applications in multiferroic photoelectric devices. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4759049>]

I. INTRODUCTION

During the past few years, multiferroics have attracted much attention because of *simultaneous* existence of (anti)ferroelectricity and (anti)ferromagnetism.^{1–10} Moreover, multiferroic heterostructures have been the subject of intensive theoretical and experimental studies. Among all the multiferroic materials studied so far, BiFeO₃ (BFO) with a perovskite structure is a known room temperature single-phase magneto-electric material. Thus, BFO in both polycrystalline and epitaxial films has been extensively studied owing to potential applications in storage and electron spin devices. There are some reports on a wide variety of properties in BFO, such as the dielectric property,¹¹ magnetic property,¹² nonvolatile bipolar resistance switching effect,¹³ spontaneous polarization,¹⁴ photostrictive properties under the illumination of visible light,¹⁵ and electrical properties.¹⁶ The photovoltaic effect is another important characteristic of BFO. Generally, two kinds of photovoltaic effects are considered. The first one is attributed to the electron-hole separation at ferroelectric domain walls in BFO films or crystals.¹⁷ Choi *et al.* observed the large photocurrent effect in BFO films under a green light illumination with the steady-state photocurrent density of about 7.35 mA/cm² and indicated that the photoexcited charge carriers across the bulk optical gap contributed to the photovoltaic effect.¹⁸ Yang *et al.* showed that the white light photovoltaic effect arose from the ferroelectricity of BFO films.¹⁹ Ji *et al.* studied bulk photovoltaic effect at visible wavelength in epitaxial ferroelectric BFO thin films and found the open-circuit photovoltage up to 0.3 V.²⁰ Yang *et al.* observed the photovoltaic effect with the value of about 16 V in BFO films.²¹ Ferroelectric photovoltaic effects also were observed in single-ferroelectric-domain BFO crystals.²² The second one

originates from the heterostructures comprised of BFO. Qu *et al.* studied the white-light photovoltaic effect of BFO/Nb-SrTiO₃ (NSTO) heterostructure with the open-circuit voltage of about 40 mV at room temperature.²³ Wang *et al.* investigated the photovoltage of BFO/NSTO heterostructures under the excitation of a pulsed Nd:YAG laser at room temperature.²⁴ In this letter, the heterostructure composed of BFO and NSTO has been prepared by a pulsed laser deposition method. The rectifying characteristics and nanosecond photovoltaic effects under ultraviolet laser irradiation (248 nm) have been investigated over a temperature range of 80–300 K. The experimental results are possibly applied in multiferroic ultraviolet photoelectric devices.

II. EXPERIMENT

BFO film was deposited on a 0.7 wt. %Nb-SrTiO₃ (001) substrate by a pulsed laser deposition method. During the deposition process, a substrate temperature and an oxygen pressure were kept at 650 °C and 10 Pa, respectively. The frequency of a KrF excimer laser with a wavelength of 248 nm was maintained at 2 Hz. The deposited film was annealed at 650 °C in the oxygen atmosphere for 2 h and then cooled to the room temperature. The thickness for the BFO sample was about 50 nm estimated by SPECEI-2000-VIS ellipsometer. The x-ray diffraction (XRD) of the sample was performed on a RigakuD X-ray diffractometer (RigakuD/max-2400, Cu K α radiation). The ferroelectric characterization was illustrated by piezoelectric force microscopy (PFM, Asylum Research MFP-3D™, USA) and with the Pt/Ir coated tips (Al reflex coated, 70 kHz resonant frequency, ~320 kHz contact resonance frequency). In measurement, the heterostructure was placed in a Janis VPF 475 closed-circuit liquid nitrogen cryostat with quartz glass windows and the current versus voltage characteristics were measured in the temperature ranging from 80 K to 300 K. Indium electrodes were pressed on the surfaces of BFO film and NSTO

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FIG. 1. (a) XRD diffraction pattern of the heterostructure. (b) Out-of-plane PFM image of the BFO film.

substrate to obtain Ohmic contacts, respectively. The electrical properties of BFO/NSTO heterostructure have been measured using a Keithley 2182 A nanovoltmeter and a 6485 picoammeter. The light source used in the photovoltaic experiment was a pulsed laser with a wavelength of 248 nm. The photovoltaic signals were gathered with a Tektronix digitizing oscilloscope (MSO4054) with a 500 MHz bandwidth and an input impedance of 1 MΩ.²⁵ A 50 Ω load resistance was connected in parallel with two electrodes in order to reduce RC effect in the photoresponsive signal and the influence of circuit in the measurement.

III. RESULTS AND DISCUSSION

A. Structures and PFM images

X-ray diffraction pattern of BFO/NSTO heterostructure is shown in Fig. 1(a). X-ray diffraction pattern reveals that BFO film is *c*-axis oriented and no impurity phases are detected. Figure 1(b) displays an out-of-plane PFM image for the $1 \times 1 \mu\text{m}^2$ region, illustrating the ferroelectric domain structure of BFO film grown on a NSTO substrate. The BFO film has two polarization directions. The bright regions represent the domains with the polarization direction oriented upward; on the contrary, the dark regions represent the polarization direction oriented toward NSTO.

B. Current-voltage characteristics

The current-voltage characteristics of BFO/NSTO heterostructure at different temperatures are shown in the Fig. 2. The inset shows the schematic circuit of the heterostructure. The positive bias applied the heterostructure is defined as the current flowing from BFO film to NSTO substrate. The heterostructure exhibits rectifying behaviors at the measuring temperature range. Due to the volatility of bismuth in the process of deposition, Bi vacancies appear in BFO film. Considering that cation vacancies are shallow, Bi vacancies are assumed as acceptors and therefore BFO film can be considered *p*-type semiconductors with high resistivity.^{26,27} Therefore, the *p*-*n* heterostructure is formed. The threshold voltages remarkably become smaller and the slope of *I*-*V* curves becomes steeper with increasing the temperature. This is similar to that of conventional semiconductor *p*-*n* junctions. This is attributed to the wider depletion region and the higher potential barrier with decreasing the temperatures. The current-voltage characteristics at the positive bias are fitted by the formula,²⁶ which is expressed as

$$I \propto \exp(qV/nkT), \quad (1)$$

where *q* is the electron charge, *n* is the ideality factor, *k* is the Boltzmann constant, and *T* is the temperature. The fit curves are coincident with the experimental data. The ideality factor *n* is evaluated by the experimental data. The values of *n* change from 51.0 to 7.1 as temperatures increase from 80 K to 300 K. These ideality factors deviate significantly from the traditional diode ideal factor 1–2 due to the lattice mismatch at the interface state.

C. Ultraviolet photovoltaic effect

For better understanding of the heterostructure, we further investigate the ultraviolet photovoltaic effect irradiated by a KrF laser with a wavelength of 248 nm at different temperatures. Figure 3 presents the photovoltaic values as a function of time in BFO/NSTO heterostructure under the laser irradiation with power density of 0.35 mJ/mm^2 at different temperatures. The photovoltages increase to the peak values and then decrease with increasing the time. The peak photovoltage of the heterostructure is about 0.33 V and the rise time is about 37 ns at *T* = 80 K. The oscillation behavior of the tail traces may be caused by the impedance mismatch in measurement circuit, the external environment (strepitus), and the change of domain structure in BFO film. The peak photovoltages of BFO/NSTO heterostructure at a function of temperatures are shown in the inset of Fig. 3. We can see that the peak photovoltages (*U_p*) decrease with increasing

FIG. 2. Current-voltage curves of the heterostructure at different temperatures (80 K–300 K). Solid lines are fitting curves, which is described by the exponential relation $I \propto \exp(qV/nkT)$. The inset shows the schematic circuit of the heterostructure.

FIG. 3. The time dependence of photovoltages in the heterostructure at different temperatures. The inset displays the relationship between the peak photovoltages and temperatures.

temperatures. The time dependence of photovoltages at different power densities at $T = 300$ K is shown in Fig. 4. It can be seen that the photovoltages of heterostructure increase with the increasing power density. The peak photovoltage is about 0.23 V at the power energy of about 0.86 mJ/mm^2 . At the negative bias, the photovoltage also increases with the power density due to depolarizing electric field which is the main driving force of charge separation and ferroelectric domain. The dependence of the peak photovoltages U_p on the power density at $T = 300$ K is presented in the inset of Fig. 4. When the power density of the laser increases, the U_p almost linearly increases. The solid line is the fitting curve fitted by the formula,²⁸

$$U_p = K_B T / e \ln(1 + \alpha P), \quad (2)$$

where k_B is the Boltzmann constant, e the electron charge and $T = 300$ K. The value of α is about 0.48 estimated from a fit to the experimental data. This is in agreement with the semiconductor theory for a standard p - n junction.

Figure 5 shows the energy band diagram of the heterostructure. In our previous works,²⁹ the absorption spectrum measurement for BFO film indicated that the absorption edge was about 457 nm. We got its optical band gap about 2.72 eV from the curve of $(\alpha h\nu)^2$ versus $h\nu$. Therefore, the photogenerated carriers could be emerged under the light

FIG. 4. The photovoltages of the heterostructures under the excitation of a laser with different power density at $T = 300$ K. The inset shows the peak photovoltages as a function of the power density.

FIG. 5. The energy band diagram of the heterostructure under the irradiations.

irradiation with the photon energy larger than 2.72 eV. The electron affinity of BFO is about 3.3 eV.³⁰ For NSTO, the electron affinity and band gap are taken as 4.0 eV and 3.2 eV, respectively.³¹ The energy band structure for the heterostructure is plotted to understand the observed phenomena. The electrons in NSTO flow into BFO film and meanwhile the holes in BFO film inject NSTO owing to the diffusion. In this process, the recombination of electrons and holes produces the depletion layer and builds up the diffusion barrier at the interface. When the heterostructure is irradiated by the laser with the photon energy of about 248 nm (5.1 eV) larger than the band gaps of BFO and NSTO, electrons in the valence band of BFO are excited to the conduction band. The electrons in BFO film flow to NSTO layer with lower potential. At the same time, holes in NSTO layer flow to BFO film due to the built-in electric field in the heterostructure. Finally, the photovoltage appears in the sample. The photovoltage values are related with the accumulation of photogenerated carriers and depletion layer width.³² When the temperature increases, the accumulation of photogenerated carriers is reduced due to strong thermal fluctuation, leading to a decrease in the peak photovoltages. We found no photovoltaic signals of the heterostructure irradiated by a 532 nm (2.3 eV) laser. As the photon energy of 248 nm (5.1 eV) laser is larger than the band gaps of BFO and NSTO, the electrons and holes in BFO and NSTO can be created in the heterostructure. For a 532 nm laser, the photon energies are lower than the band gaps of either BFO or NSTO. This result reveals that the production of photogenerated carriers plays a crucial role in the process of the nanosecond photovoltaic effect.

IV. SUMMARY AND CONCLUSIONS

In summary, the BFO/NSTO heterostructure exhibits a rectifying behavior in the temperature range from 80 K to 300 K. Under ultraviolet irradiations, the heterostructure shows the nanosecond photovoltaic effect. It is observed that the photovoltages increase with decreasing temperatures and increasing power densities, respectively. With increasing the temperature from 80 K to 300 K, the photovoltage of heterostructure becomes smaller due to the accumulation of photogenerated carriers. The peak photovoltages of the sample

almost linearly increases with the increase of power density. We hope that our results add more to the performances of multiferroic heterostructures and open another door for applications in photoelectric devices.

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