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EPL, **96** (2011) 17008

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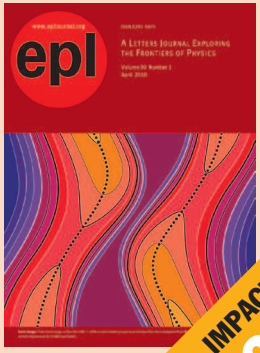

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October 2011

EPL, **96** (2011) 17008
doi: 10.1209/0295-5075/96/17008

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Photo-resistance and photo-voltage in epitaxial $BiFeO_3$ thin films

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received 23 May 2011; accepted in final form 18 August 2011
published online 16 September 2011

PACS 73.50.Pz – Photoconduction and photovoltaic effects
PACS 73.40.Ei – Rectification
PACS 81.15.Fg – Pulsed laser ablation deposition

Abstract – The photo-resistance and photo-voltage of the heterostructures of $BiFeO_3$ (BFO) films grown on Nb-doped $SrTiO_3$ (SNTO) substrates by laser molecular-beam epitaxy irradiated by UV light are systematically studied. The *I-V* measurements on the Au/$BiFeO_3$/Nb-doped-$SrTiO_3$ heterostructures show a good rectifying property with the maximum rectifying ratio of 3.5×10^3. It was observed that the photo-resistance and photo-voltage change with the intensity of laser and the thickness of BFO films, respectively. We conclude that the potential barrier at the BFO/SNTO interface and that at the Au/BFO interface are both responsible for the rectification and photo-electric characteristics.

Multiferroic materials, which exhibit ferroelectric and ferromagnetic behaviors simultaneously, have attracted much attention due to their interesting physics and immense potential for multifunctional applications [1–4]. As to one of those materials, $BiFeO_3$ (BFO) has been widely studied since it exhibits a high Curie temperature ($T_C \approx 1100\,K$), a high Néel temperature ($T_N \approx 643\,K$) and a large remnant polarization over $50\,\mu C/cm^2$ [5]. In addition to the great efforts devoted to the structure and properties of the bulk single crystal, the investigations on the electric and magnetic properties of BFO films have attracted much attention in recent years [6–8]. The photoelectric effect, as one of the most important characteristics of BFO films and their heterostructure, was observed by Choi *et al.* in BFO diode structures under the irradiation of visible light [9]. Then, Yang *et al.* reported the photo-voltaic effects with large open-circuit voltages ($V_{OC} \sim 16$–$18\,kV/cm$) for BFO films thicker than 200 nm with a structure as that of ITO/BFO/$SrRuO_3$ (SRO) heterostructures [10]. The study on the meaningful photoelectric effect of BFO thin films and heterostructure provides us with the opportunity to fully understand the underlying nature and to further develop the multifunctional devices based on BFO combined with photoelectric applications. In our previous works, the dielectric property, current-voltage hysteresis, and switchable rectifying characteristics were observed in epitaxial multiferroic BFO thin films and heterostructures [11–13]. In this letter, the photo-resistance and photo-voltage of Au/BFO/Nb-doped $SrTiO_3$ (Au/BFO/SNTO) heterostructures with various thicknesses of BFO films were systematically investigated. The results demonstrate that the potential barrier at the BFO/SNTO interface and that at the Au/BFO interface are both responsible for the rectification and photo-electric characteristics.

BFO thin films were grown on (001) $SrTiO_3$ (0.8 wt% Nb-doped) substrates by a laser molecular-beam epitaxy system (L-MBE) [14], using a XeCl 308 nm excimer laser with an energy density of $\sim 2\,J/cm^2$. A $Bi_{1.5}FeO_3$ ceramic was used as target and the excess bismuth was used to compensate the volatilization during deposition. The substrate temperature was kept around 560 °C and an oxygen pressure of 1.0 Pa was maintained during the deposition process. After deposition, the samples were *in situ* annealed for 30 min under the deposition condition before cooling down to the room temperature. Three BFO samples with different thicknesses were fabricated under the same experimental conditions and marked as S1 (100 nm), S2 (200 nm) and S3 (300 nm), respectively. The film thicknesses were confirmed by an *ex situ* surface profile measuring system. Au electrodes with a diameter of 200 μm and a thickness of 50 nm were deposited on the surface of the BFO films. The structures of the BFO/SNTO heterostructures were characterized by X-ray

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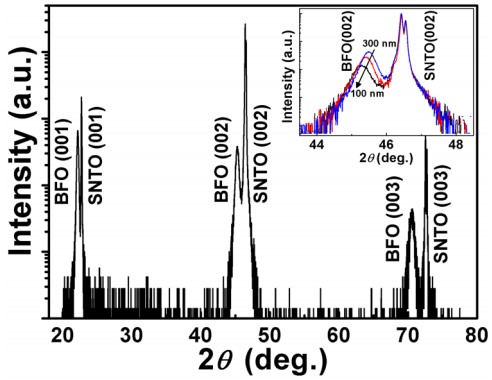

Fig. 1: (Color online) XRD diffraction pattern for the 100 nm BFO thin film. The inset shows the expanded area of (002) peaks from both films and substrates, indicating the effect of the epitaxial strain on the BFO films with different film thicknesses.

diffraction (XRD), as shown in fig. 1. The current-voltage (I-V) properties of Au/BFO/SNTO heterostructures were measured by a Keithley 2400 sourcemeter at room temperature. The optical transmittance spectrum measurement indicated that the absorption edges of our BFO films were around 560 nm, corresponding to a band gap of ~ 2.2 eV, identical with that reported by previous works [9,15]. The photo-electric properties of the Au/BFO/SNTO heterostructures were investigated under the irradiation of a continuous HeCd laser (wavelength of 325 nm) and a pulsed Nd:YAG laser (wavelength of 355 nm).

Figure 1 shows the XRD pattern of the BFO/SNTO heterostructure with film thickness of 100 nm, from which single-phase BFO films with c-axis orientation can be deduced. The (002) diffraction peaks of the three BFO samples were presented in the inset of fig. 1. The systematical shift towards the higher 2θ value indicates that the out-of-plane lattice constant of BFO decreases from 4.001 Å to 3.985 Å, while the film thickness increases from 100 to 300 nm.

Figure 2(a) displays the I-V behaviors of the sample S1 in the dark and under the irradiation of the HeCd laser with various power densities. The schematic measuring circuit was shown in the inset of fig. 2(a). It is notable that the Au/BFO/SNTO heterostructure exhibits a good rectifying feature without any light irradiation. However, with the increase of the power density of the laser, the leakage current at the reverse bias increased dramatically due to the generation of photo-induced carriers. The dependence of photo-resistance of sample S1 on the power density of the laser at different reverse biases was shown in fig. 2(b). The photo-resistance is defined as $(R_d - R_l)/R_d$, where R_d and R_l are the junction resistances in the dark and under irradiation of laser, respectively. It was found that the photo-resistance shows a sharp increase at low power density of the laser and gradually saturates when the power density of the laser increases to a certain value. Moreover, the photo-resistance decreased with the increase

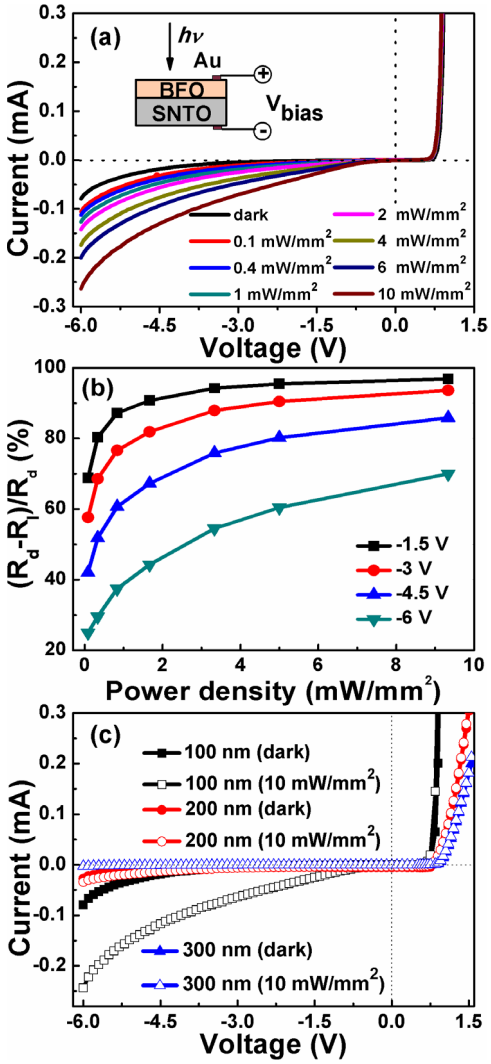

Fig. 2: (Color online) (a) I-V curves measured on a 100 nm BFO thin film in the dark and under the irradiation of a 325 nm laser. The inset shows the schematic circuit of measurement. (b) The photo-resistance of sample S1 changes with the power density of the laser at different reverse bias values. (c) Variation of I-V curves of samples S1, S2, S3 measured in the dark (solid symbols) and under the irradiation (open symbols) of a 325 nm laser.

of the applied bias. Figure 2(c) displays the comparison of the transport with the photo-electric properties of samples S1, S2, S3, respectively. As the film thickness increased, the rectifying property of the heterostructure became weak. The rectifying ratios, defined as the ratio of forward-to-reverse currents at the bias of ± 1 V, were about 3.5×10^3, 1.1×10^3, and 4.8×10^2 for samples S1, S2, and S3, respectively. From fig. 2(c), we can also see that the photo-current decreased dramatically with increasing film thickness. For example, the photo-current of sample S1 at -6 V is about 1.64×10^{-4} A, while that of sample S3 is merely about 1.51×10^{-6} A.

In order to confirm our results, we also measured the photo-electric properties of the Au/BFO/SNTO

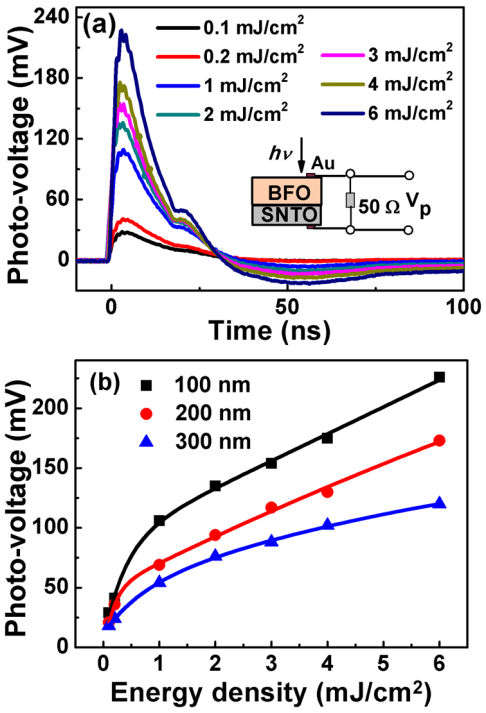

Fig. 3: (Color online) (a) Variation of photo-voltages of sample S1 with different energy density under the excitation of a pulsed Nd:YAG laser. The inset displays the schematic circuit of measurement. (b) The photo-voltages of samples S1, S2, S3 under the excitation of a pulsed Nd:YAG laser.

heterostructure by using a pulsed laser. Figure 3(a) shows the photo-voltaic responses of sample S1 measured under the excitation of a Nd:YAG pulsed laser. The photo-voltaic signals were recorded by an oscilloscope with a 500 MHz bandwidth and an input impedance of 50 Ω. Figure 3(b) shows the photo-voltages of samples S1, S2, and S3 under the same irradiation conditions. From fig. 3(b), it can be seen that the photo-voltages increases with increasing energy density of the laser and decreases with increasing thickness of the BFO thin film. The peak values of the photo-voltages of samples S1, S2, and S3 were 136, 94, and 79 mV, respectively, when the BFO thin film was irradiated by the laser with an energy density of 2 mJ/cm^2. Moreover, we did not observe any photo-electric effect when the Au/BFO/SNTO heterostructure was irradiated by a 632.8 nm HeNe laser, as the photon energy is smaller than the band gaps of BFO and SNTO.

To understand the above results of samples S1, S2 and S3, we plot the schematic energy band structure for the Au/BFO/SNTO structure in fig. 4. For SNTO, the electron affinity and band gap were taken as 4.05 eV and 2.8 eV, respectively [16]. Our Hall measurement showed that the carrier density of the n-type SNTO is around 2×10^{20} cm^{-3}, and our calculations indicated that its Fermi level is close to the bottom of the conduction band and the difference is merely 0.01 eV. For BFO, the electron affinity and band gap were taken as 3.3 eV [17,18] and

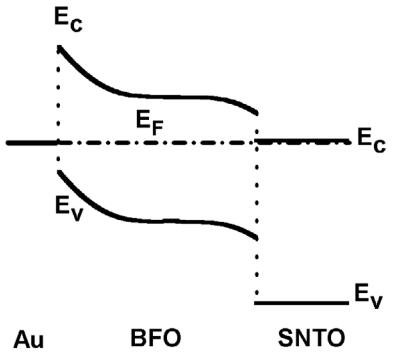

Fig. 4: Schematic band structure for the Au/BFO/SNTO structure at thermal equilibrium.

2.2 eV [9]. The BFO thin films can be treated as an n-type semiconductor due to the naturally emerged oxygen vacancies [19]. We suppose that its Fermi level is just a little above the middle of the energy band gap. Thus, a heterojunction is formed at the interface between SNTO and BFO as shown in fig. 4. By taking into account the Schottky barrier at the Au/BFO interface, we can conclude that the potential barrier at the BFO/SNTO interface and that at the Au/BFO interface are both responsible for the rectification effect in the system.

The photo-voltage increased with increasing energy density of the laser as expected, but decreased with increasing thickness of the BFO film. We show that the increase of the BFO film thickness will elongate the path photo-generated electrons passing through, and increase the recombination of photo-generated electrons. In order to further confirm the dominant mechanism for the enhancement, we have measured the photo-voltage using a pulsed laser of wavelength 532 nm. The photon energy of the laser with a wavelength of 532 nm is larger than the band gap of BFO but smaller than that of SNTO. Then the photo-generated electron-hole pairs can only be produced in BFO thin films. Similar results were obtained for the same samples, compared with the results using a laser with wavelength of 355 nm. This indicates that the enhancement of the photo-voltage in Au/BFO/SNTO structures with a thinner BFO film mainly comes from the BFO. The defect in the surface layers of BFO films may also affect the photo-voltaic results [20]. It has been known that the photo-voltage would reduce the barrier height, and the junction's resistance contributes to the major part of the resistance of this structure, so a smaller resistance can be obtained with a larger energy density of laser. This can well explain the photo-resistance phonomenon we observed, *i.e.*, the photo-resistance $(R_d - R_l)/R_d$ increases with increasing power density of the laser as shown in fig. 2(b).

In conclusion, we have shown that the Au/BFO/SNTO heterostructures exhibited good rectifying behaviors at room temperature. It was observed that the photo-resistance and photo-voltage vary with the intensity of the

laser and the thickness of BFO films, respectively. With the thickness of BFO films varying from 100 nm to 300 nm, the photo-voltage of Au/BFO/SNTO heterostructure becomes smaller. We conclude that the potential barrier at the BFO/SNTO interface and that at the Au/BFO interface are both responsible for the rectification and photo-electric characteristics in the system.

* * *

This work was supported by the National Natural Science Foundation of China and the National Basic Research Program of China.

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