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2011 Nanotechnology 22 195201

(http://iopscience.iop.org/0957-4484/22/19/195201)

Nanotechnology **22** (2011) 195201 (5pp) doi:10.1088/0957-4484/22/19/195201

Effect of top electrodes on photovoltaic properties of polycrystalline $BiFeO_3$ based thin film capacitors

Bin Chen, Mi Li, Yiwei Liu, Zhenghu Zuo, Fei Zhuge, Qing-Feng Zhan and Run-Wei Li[1]

Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences (CAS), Ningbo, Zhejiang 315201, People's Republic of China

E-mail: runweili@nimte.ac.cn

Received 11 October 2010, in final form 21 February 2011
Published 23 March 2011
Online at stacks.iop.org/Nano/22/195201

Abstract

We investigated capacitors based on polycrystalline narrow-band-gap $BiFeO_3$ (BFO) thin films with different top electrodes. The photovoltaic response for the capacitor with a Sn-doped In_2O_3 (ITO) top electrode is about 25 times higher than that with a Au top electrode, which indicates that the electrode plays a key role in determining the photovoltaic response of ferroelectric thin film capacitors, as simulated by Qin *et al* (2009 *Appl. Phys. Lett.* **95** 22912). The light-to-electricity photovoltaic efficiency for the ITO/polycrystalline BFO/Pt capacitor can reach 0.125%. Furthermore, under incident light of 450 μW cm^{-2} and zero bias, the corresponding photocurrent varies from 0.2 to 200 pA, that is, almost a 1000-fold photoconductivity enhancement. Our experiments suggest that polycrystalline BFO films are promising materials for application in photo-sensitive and energy-related devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Driven by the worldwide energy crisis and ever increasing concern for clean and renewable energy, researchers are continuously exploring novel candidate materials for thin film photovoltaic cells in pursuit of low cost and high light-to-electricity power conversion efficiency [1–4]. The photovoltaic properties of numerous ferroelectric oxide materials, including $BaTiO_3$ (BTO) and $Pb(Zr, Ti)O_3$ (PZT), have been extensively investigated [5–8]. However, these materials have not been considered for applications in photovoltaic devices due to their small photovoltaic efficiencies resulting from the relatively wide band gap of ferroelectric materials [4]. Utilization of narrow-band-gap ferroelectrics is therefore a promising route towards their application in both the novel optoelectronic and the solar energy devices [4]. Multiferroic material $BiFeO_3$ (BFO), which possesses rather a narrow band gap (~2.2 eV) and a higher saturation polarization (~90 μC cm^{-2}), offers an exciting opportunity for such applications [4, 9]. A significant photovoltaic effect has already been observed in single crystalline BFO in both bulk and thin film forms [4, 10–12]. Moreover, as a typical single phase multiferroic material, the coupling between various ferroic orderings in BFO films provides multiple degrees of freedom for controlling the photovoltaic effect, which may endow the next generation solar cells with additional functionality.

Recently, a high light-to-electricity power conversion efficiency (10% for 340 nm wavelength light) has been experimentally obtained in epitaxial BFO thin films [11]. However, due to their low cost and simple fabrication process, polycrystalline BFO (poly-BFO) films seem more suitable for practical applications rather than epitaxial films would be. It should be noted that the photovoltaic efficiency of the polycrystalline films is usually smaller than that of epitaxial films [13]. In this regard, it is necessary to study and improve the photovoltaic effect in polycrystalline ferroelectric films. However, the photovoltaic properties in poly-BFO thin films have not been reported before. On the other hand, Qin *et al* [14] recently established a general physical model by considering

[1] Author to whom any correspondence should be addressed.

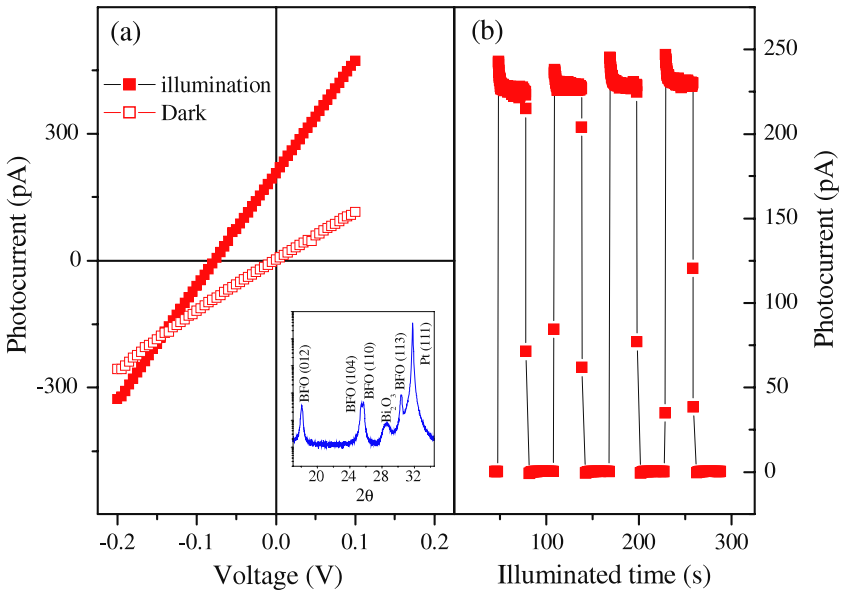

Figure 1. (a) I–V curves of poly-BFO films under dark and illumination. (b) Time dependence of photocurrent under a zero bias and an incident light intensity of 450 μW cm^{-2}. Inset, XRD profile of the poly-BFO films.

both ferroelectric materials and their electrodes as a whole system to study the mechanism of the photovoltaic effect in ferroelectrics, and suggested that the oxide electrodes could provide a larger photovoltaic response. In this paper, we have prepared poly-BFO thin films on Pt/Ti/SiO_2/Si substrates by the sol–gel method, and studied the effect of the top electrodes on the photovoltaic response. It is found that a Sn-doped In_2O_3 (ITO)/poly-BFO/Pt capacitor has almost 25 times larger photovoltaic response than that of a Au/Poly-BFO/Pt capacitor. Moreover, an almost 1000-fold photoconductivity enhancement is obtained in a ITO/poly-BFO/Pt capacitor at an incident light intensity of 450 μW cm^{-2} and zero bias.

2. Experimental details

Poly-BFO ferroelectric thin films were grown by means of the conventional sol–gel method. Bismuth nitrate [$Bi(NO_3)_3{\cdot}H_2O$] and iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] were used to prepare the BFO solution with a concentration of 0.2 mol l^{-1}. An excess of 5% bismuth nitrate was added to compensate the expected loss of volatile Bi during the following heat treatment. The BFO solution was spin coated on commercial Pt/Ti/SiO_2/Si substrates, and then annealed at 550 °C for 10 min. The structure of poly-BFO films was confirmed by checking the x-ray diffraction data (XRD), which was obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.24 Å. The size of the focus spot is about 0.3 mm × 0.3 mm and the end station is equipped with a Huber 5021 diffractometer. The surface morphology and the local conductance were measured by an atomic force microscope (AFM, dimension V, Veeco) equipped with a conductive cantilever. Au and ITO top electrodes of 100 μm in diameter were deposited on the poly-BFO films at room temperature using electron-beam evaporation and magnetron sputtering, respectively. The current–voltage (I–V) behavior of the films was characterized using a Keithley 4200 semiconductor characterization system. For the photovoltaic measurements, the samples were illuminated from the top electrodes with the light source.

3. Results and discussion

The quality of the poly-BFO films was confirmed by XRD measurement (figure 1 inset). XRD data indicates that poly-BFO without a preferred orientation has been successfully grown on the substrates, except for a small amount of the Bi_2O_3 phase. The dark and illuminated I–V curves for the ITO/poly-BFO/Pt capacitor show a typical photovoltaic effect, as revealed in figure 1(a) [10, 11]. The photocurrent is significantly increased under illumination, and remains positive at zero bias. In principle, the photocurrent at zero bias is determined by the difference in work function between the top and bottom electrodes, which will be discussed below. Figure 1(b) presents the time dependence of the photocurrent for the poly-BFO films at an incident light intensity of 450 μW cm^{-2} and zero bias. It shows an instantaneous response of the photocurrent to the light illumination, as demonstrated by the on/off property of the photocurrent. The value of photocurrent is increased from 0.20 to 200 pA when turning on the light, that is, a 1000-fold photoconductivity enhancement in response. The high sensitivity makes it possible for the poly-BFO films to be applied in a photo-sensitive resistor.

Illuminated I–V curves at different incident light intensities for a 300 nm-thick poly-BFO film are shown in figure 2(a). It can be seen that the short circuit photocurrent I_{SC} (the intersection point of the I-axis and the I–V curve) is proportional to the incident light intensity, as shown in figure 2(b). Since the photovoltaic effect in ferroelectric materials is related to the light-induced carriers and carrier separation under an internal electric field [10, 15], this linear

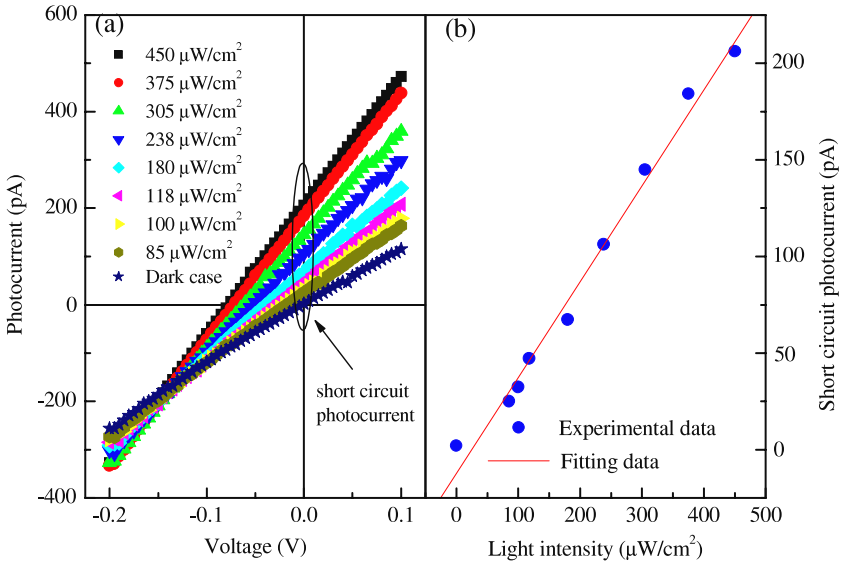

Figure 2. (a) I–V curves of poly-BFO films under various incident light intensities, and the short circuit photocurrent corresponding to the intersection point of I-axis and I–V curve. (b) Light-intensity dependence of the short circuit photocurrents.

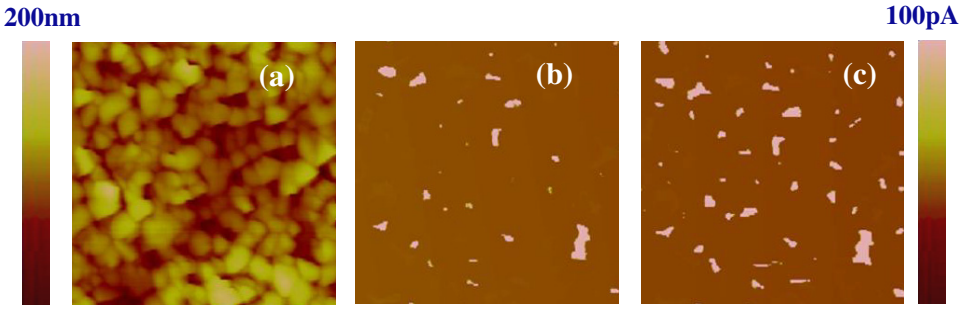

Figure 3. (a) The surface image (1×1 μm^2) measured by AFM and the corresponding current images obtained by CAFM with a tip bias of 500 mV for the poly-BFO film under (b) dark and (c) illuminated conditions.

relationship between I_{SC} and the light intensity indicates that the carrier concentration in poly-BFO film is determined by the incident light intensity.

Conductive AFM (CAFM) measurements were carried out to simultaneously examine the surface morphology and the local current behavior for the as-grown poly-BFO films without the top electrode. The AFM image in figure 3(a) reveals that the surface of the poly-BFO films consists of grains with a root mean square (rms) roughness of 10 nm. The AFM image scan size is 1×1 μm^2 and a tip bias of 500 mV is applied for CAFM current image measurement. Comparing the current images under dark and illumination, shown in figures 3(b) and (c), respectively, one can observe that the charge transport paths are clearly increased under illumination. This photocurrent variation measured by CAFM is consistent with the above macroscopic I–V measurements (see figure 1(a)). Since there is no Schottky barrier variation in the CAFM measurements under dark or illuminated conditions, the light-induced carriers in the poly-BFO films plays a key role in the increased photocurrent.

The ferroelectric contribution on the photovoltaic effect was examined by applying an electric field to switch the polarization state of ferroelectric films. For epitaxial and polycrystalline PZT films, both the poling direction and the poling magnitude have been observed to give some contribution to the photovoltaic behavior [13, 16]. In our case, however, the poling effect only has weak influence on the photovoltaic behavior of the poly-BFO films, as clearly shown in figure 4. This small effect on the photovoltaic response in poly-BFO films may be due to the small ferroelectric polarization or the small poling contribution in these poly-BFO films, since there are several conflicting experimental reports about the poling effect on the photovoltaic properties in epitaxial BFO films. Yang *et al* [12] found that there was no observable change in the light I–V curve upon applying an electric field to switch the polarization, while Ji *et al* [10] suggested that the poling effect played a key role in influencing the photovoltaic properties of epitaxial BFO films.

In order to examine the ferroelectric–electrode interface effect on the photovoltaic properties, both Au/BFO/Pt and ITO/BFO/Pt capacitors were prepared in the same poly-BFO films. Figure 5 presents the I–V curves under dark and illumination, and the terminal voltage dependence of the photovoltaic efficiency for poly-BFO thin film based capacitors with Au and ITO top electrodes. For the capacitor with the ITO top electrode, the open circuit voltage V_{OC} (the intersection

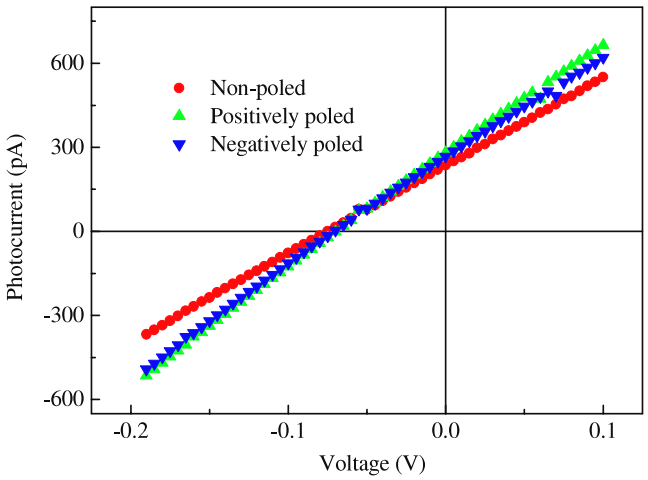

Figure 4. I–V characteristics for poly-BFO films in different polarization states.

point of V-axis and I–V curve) is negative and the short circuit photocurrent I_{SC} is positive, while for the capacitor with Au top electrode, V_{OC} is positive and I_{SC} is negative. This is because of the different work functions between the electrodes and ferroelectric materials. A similar phenomenon has also been observed in PZT capacitors [13]. In our samples, this behavior can be understood by considering the variation of the internal net potential $\Delta\varphi_B$, which can be calculated as $\Delta\varphi_{B\_Au/BFO/Pt} = -0.6$ eV for the Au/BFO/Pt capacitor and $\Delta\varphi_{B\_ITO/BFO/Pt} = +0.2$ eV for the ITO/BFO/Pt capacitor, respectively[2]. Figures 5(b) and (d) show the terminal voltage dependent power conversion efficiencies η for Au/BFO/Pt and ITO/BFO/Pt capacitors, respectively, where η is the ratio of the output electric power P_{out} to the input optical power P_{in}, i.e., $\eta = P_{out}/P_{in}$. The input power P_{in} (W) is termed as the incident light intensity, and the photovoltaic output power density is $P_{out} = JV$ (mW cm^{-2}) [13]. As shown in figures 5(b) and (d), the maximum η for Au/BFO/Pt and ITO/BFO/Pt capacitors are about 0.005% and 0.125%, respectively. The magnitude of photovoltaic output of the capacitor with the ITO top electrode is about 25 times larger than that with the Au electrode. Since the photovoltaic effect in ferroelectric materials is related to the light-induced carriers and their separation under an electric field, the higher photovoltaic output of the ITO/BFO/Pt capacitor can be understood in two respects. On one hand, when using a transparent ITO top electrode, more incident light can penetrate into the poly-BFO films than that using a semitransparent Au top electrode. In the visible region, the transmittance of the ITO layer is about 80%. However, the difference in the light penetration is not enough to induce such a large variation in the photovoltaic response of the capacitors. On the other hand, the high photovoltaic output is related to the carrier movement and the carrier separation driven by the larger internal electric field. This internal electric field in ferroelectric capacitors can be classified as two independent components and written as: $E = E_{bi} + E_p$, where E_{bi} is the built-in field and E_p is the depolarization field. The built-in field E_{bi} in ferroelectric capacitors originates from various factors [18, 19]. The depolarization field E_p is proportional to the strength of polarization: $E_p = -\frac{P}{\varepsilon_0\varepsilon_F}\left(\frac{2\varepsilon_F/d}{2\varepsilon_F/d+\varepsilon_e/\lambda}\right)$, where ε_F the relative dielectric constant of the ferroelectric thin film, ε_e the relative dielectric constant of the electrode layer, λ the screening length, P the polarization value, and d the ferroelectric film thickness. Both Kim *et al* and Qin *et al* have theoretically predicted that oxide top electrodes combined with ferroelectric capacitors could provide a larger depolarization and induce a higher photovoltaic output than that of metal electrode capacitors [14, 20]. Thus, an ITO oxide electrode and ITO/BFO interface play a key role on the photovoltaic effect in our poly-BFO films by providing a higher depolarization field as a driving force to separate the light electron–hole

[2] The work functions of Au, Pt and ITO are 4.7, 5.3 and 5.5 eV, respectively. The electron affinity of BFO is 3.3 eV, also see [17].

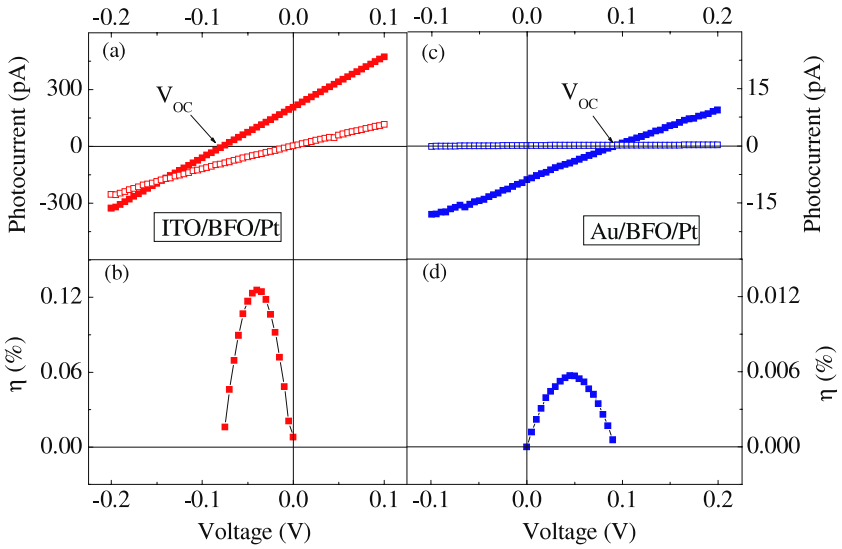

Figure 5. I–V curves and the corresponding terminal voltage V_{oc} dependence of light-to-electricity power conversion efficiency η for ITO/BFO/Pt ((a) and (b)) and Au/BFO/Pt ((c) and (d)) capacitors, respectively.

carriers. Furthermore, the maximum power conversion efficiency of 0.125% in ITO/poly-BFO/Pt capacitors is much higher than the previously reported efficiency of 0.005% obtained in polycrystalline La-doped PZT based photovoltaic capacitors [11, 15]. This higher photovoltaic efficiency in our samples likely results from the smaller band gap of BFO (∼2.2 eV) [4] as compared to conventional wide-band-gap ferroelectric material, such as PZT (∼3.5 eV) [11].

4. Summary

In summary, the electrode effect on photovoltaic properties for the poly-BFO film based capacitor has been investigated. The photovoltaic efficiency in ITO/poly-BFO/Pt capacitors, approaching to 0.125%, is almost 25 times larger than that in Au/poly-BFO/Pt capacitors. These experimental results reveal that a combined system of narrow-band-gap ferroelectric BFO and oxide ITO electrodes can give a considerably high photovoltaic response. Our experiments suggest that the narrow-band-gap poly-BFO films would be a promising material for the photo-related applications.

Acknowledgments

The authors gratefully thank Dr Xiao Long Li of SSRF for XRD measurements, and acknowledge the financial support from the Chinese Academy of Sciences (CAS), the National Natural Science Foundation of China, and the Zhejiang and Ningbo Natural Science Foundations.

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