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Effect of top electrodes and light sources on photovoltaic properties of polycrystalline $Bi_4Ti_3O_{12}$ film

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ABSTRACT

Polycrystalline $Bi_4Ti_3O_{12}$ (BTO) film was deposited by a sol-gel method. Piezoelectric force microscopy measurement confirmed the local ferroelectricity of the BTO film. The band gap of the BTO film is estimated to be 3.45 eV and the absorption intensity of Ag/BTO/FTO is larger than that of Pt/BTO/FTO. The photovoltaic (PV) properties of the two structures were measured under the illumination of white light and purple light of 405 nm, respectively. It was found that the PV responses of the devices strongly depended on the excitation light sources and top electrodes. The devices show large ON/OFF photocurrent ratio with good stability and repeatability. The PV responses are briefly explained combined with Schottky barrier and surface plasmon effect.

1. Introduction

Recently, photovoltaic (PV) effects of ferroelectric films are attracting tremendous attention due to their great potential in photodetectors and optical sensors [1,2]. Among ferroelectric films, $Bi_4Ti_3O_{12}$ (BTO) has been widely concerned due to their high Curie temperature and excellent chemical stability. At present, the photovoltaic effect of ferroelectrics has remained an academic curiosity due to low power conversion efficiency (PCE) caused by the wide band gap of ferroelectrics [3]. To enhance the PCE of ferroelectric films, some methods including element doping and incorporation of narrow band gap semiconductors have been adopted [4,5]. So far, researchers have engaged in investigating the PV properties of BTO film [6,7]. However, the measures to improve the PV output of BTO are still relatively limited. In order to fill in this gap, we investigate the influence of metal top electrode and light source on the PCE of BTO film and the mechanism of enhancement of PCE is briefly discussed combined with Schottky barrier and surface plasmon effect.

2. Experimental

BTO films were prepared on fluorine-doped tin oxide (FTO) conductive glass substrate by a sol-gel method. The X-ray diffraction (XRD) pattern was collected on a DX-2700 X-ray diffractometer. Piezoelectric force microscopy was performed by commercial Atomic Force Microscope (Bruker multimode 8). The optical absorption spectrum was measured by a UV–vis–NIR spectrophotometer (UV-2550). The Pt and Ag dots arrays were fabricated as top electrodes. The current density-voltage (*J-V*) behaviors of the Pt/BTO/FTO and Ag/BTO/FTO devices were recorded by a Keithley 2400 by a low noise probe station in dark and under the illuminations of white light (AM 1.5) and purple light (405 nm, 100 mW/cm^2), respectively. All measurements were conducted at room temperature.

3. Results and discussion

As seen from Fig. 1(a), BTO film is well crystallized (JCPDS No. 65–2527) with polycrystalline nature. From the inset of Fig. 1(a), the thickness and the root mean square surface roughness of the film are approximately 400 nm and 8.54 nm, respectively. Fig. 1 (b) shows the out-of-plane (OP) phase, the $3 \times 3\ \mu m^2$ and $1 \times 1\ \mu m^2$ regions were polarized with -19.8 V and 19.8 V sample biases upon FTO bottom electrode, respectively, and then the PFM phases were scanned with an ac probing voltage immediately. The

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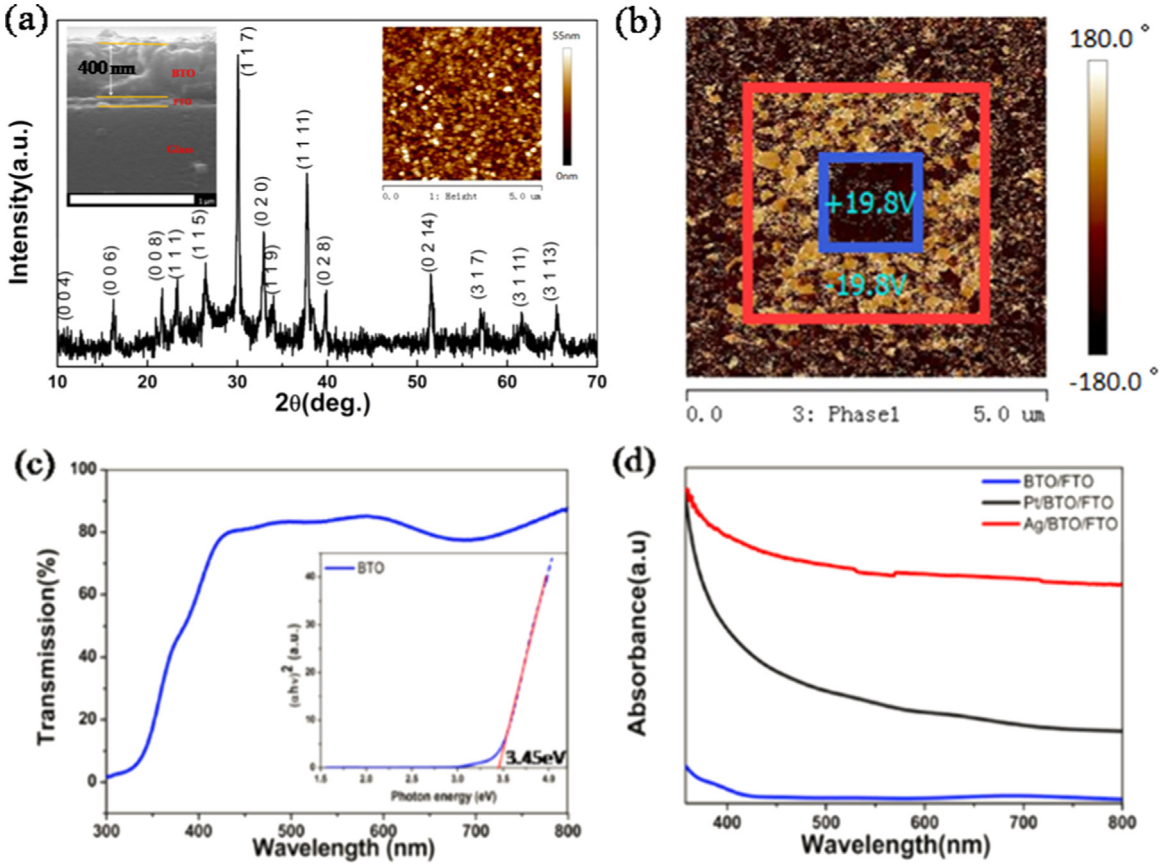

Fig. 1. (a) The XRD pattern, the inset shows SEM and AFM images; (b) the OP phase, where the $3 \times 3\ \mu m^2$ and $1 \times 1\ \mu m^2$ regions are polarized with -19.8 V and $+19.8$ V biases and marked with solid red/blue squares, respectively; (c) UV–vis transmittance spectrum, the inset shows the plot of $(\alpha h\nu)^2$ as a function of hν around the absorption edge; (d) UV–vis absorption spectra of BTO without and with top electrodes.

square patterns of two opposite polarization domains can be seen from the distinct color contrasting areas. The domain switching behavior verifies local ferroelectric and electrically writable properties of the BTO film [8,9]. Moreover, the as-grown BTO film outside the poled area exhibits almost the same color as that of the $+19.8$ V poled area, suggesting the film have upward self-polarization, which has been reported elsewhere [10–12].

The optical transmission spectrum of the film is displayed in Fig. 1(c). The direct optical bandgap (E_g), estimated to be 3.45 eV, is calculated from modified square law based bandgap calculations by the $(\alpha h\nu)^2$ vs $h\nu$ plot, by extrapolating the linear portion of the absorption to the X-axis, where absorption coefficient becomes zero is shown in inset of Fig. 1(c) [13]. Fig. 1(d) indicates the UV–vis absorption spectra of BTO/FTO, Ag/BTO/FTO and Pt/BTO/FTO structures. The absorption intensity of Ag/BTO/FTO is significantly larger than that of Pt/BTO/FTO, especially in the visible region. It is suggested that this may be due to the surface plasmon (SP) effect of Ag/BTO/FTO structure which can couple and trap the light into the film and therefore enhance optical absorption. Usually, Ag has large electrical conductivity and minimal loss, making it an extensively used metal in semiconductor SP enhanced PV effect [14]. As a consequence, Ag/BTO interface is more easily to form SP than that of Pt/BTO. It is noteworthy that although no synthetic nanostructures such as periodic metallic nanoparticles are purposely introduced, the natural random roughness of BTO-metal interface could provide a possibility of the coupling between the SPs and the incident photons at the Ag surface. A similar experimental phenomenon has also been reported elsewhere [15].

Seen from Fig. 2(a), the Pt/BTO/FTO structure shows a PV performance with short circuit current density (J_{SC}) of 35 μA/cm^2, open voltage (V_{OC}) of 0.016 V and PCE of 0.00016%, under white light. Under purple light irradiation, a better PV performance is achieved with $V_{OC}=255$ μA/cm^2, $J_{SC}=0.1$ V, PCE=0.0068%. It is readily understood that illumination of purple light could induce more photo-excited carriers because the absorption edge of BTO locates in UV region, which is responsible for the increase of PV performance. In addition, the PCE of the device with purple light illumination (0.0068%) is 42 times larger than that under white light irradiation (0.00016%), suggesting illuminating source plays an important part in determining the PV output of BTO film.

The J-V curves of the Ag/BTO/FTO device were also measured, as shown in Fig. 2(b). The J_{SC}, V_{OC} and PCE under white light are 55 μA/cm^2, 0.15 V and 0.0021%, respectively; while the corresponding PV parameters with purple light illumination are 400 μA/cm^2, 0.45 V and 0.0485%, respectively. It is noticed that the PV performance of Ag/BTO/FTO is larger than that of the Pt/BTO/FTO under either white or purple light. To our knowledge, it is the first time to study the PV performance of BTO films with different top electrodes.

Fig. 2(c) and (d) shows time-dependent J_{SC} curves of the two devices. The J_{SC} increases dramatically at the beginning and finally reaches to saturated value. It is obvious that no decay of photocurrent was observed during 5 cycles of on-off the illumination light. Moreover, the photocurrent density keeps almost constant with the extension of time and no spikes were found in the curves [16], demonstrating the Joule heating effect on the photocurrent is inappreciable. A steady and large ON/OFF photocurrent density ratio illustrates the feasibility for a potential in a photodetector and photosensitive resistor.

To explain the experimental results, a simple and possible model combining the energy band diagram with the SP effect was constructed, as shown in Fig. 3(a) and (b). In a normal structure of