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Enhanced ferroelectric photovoltaic effect based on converging depolarization field

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ABSTRACT

We report a photovoltaic effect in ferroelectric $Bi_{0.9}La_{0.1}FeO_3$ ferroelectric films grown on $SrTiO_3$ substrates with tubular $La_{0.7}Sr_{0.3}MnO_3$ films as buffer layers. The photovoltaic effect can be enhanced by increasing the tubular radius of $La_{0.7}Sr_{0.3}MnO_3$ bottom electrode, the open circuit voltage, short circuit current and power conversion efficiency are 2.05 V, 0.31 mA/cm^2 and 0.82%, respectively. Remarkably, the efficiency is about 250- fold of magnitude larger than that of ordinary sandwich structure for visible wavelengths. The role of converging electric field formed by asymmetric top and bottom electrodes is similar to that of an electrostatic lens, and it is suggested to be the reason of such significant photovoltaic effect. Our results imply that the conversion efficiency of ferroelectric photovoltaic can be strengthen effectively by converging electric field, suggesting that the photovoltaic effect in ferroelectric thin films could be further explored for solar light photovoltaic applications.

1. Introduction

The photovoltaic effect in ferroelectric thin films has received considerable attentions due to its promising application in conventional photonic and photovoltaic devices since it was discovered one century ago [1–3]. In recent years, researches on the photoelectric properties of $BiFeO_3$(BFO) become a popular field and enterprise spring up like bamboo shoots after a spring rain not only due to its large polarization and its possible coupling with the magnetic moment but mostly because of its low band-gap (~2.7 eV) is in the visible range [4–10]. Recently, anomalous photo-voltages in BFO films exceed a few times the band-gap have been reported [11–13], which makes it attractive for applications in photovoltaic devices. However, long after its discovery, there has not any realistic application because of the extremely low power conversion efficiency (10^{-4} or less) [14–17], mainly due to the very small output photocurrent in the order of nA/cm^2. Although many efforts have been made to enhance the photocurrent density, such as inserting layer between the top electrode and ferroelectric films, adopting transparent film as the top electrode, the effect is not very obvious (at best ~μA/cm^2 order), or at the cost of reducing the open circuit photo-voltages, which is usually less than one volt [18–22].

Here we report an enhanced photovoltaic effect in the ferroelectric BFO thin films by using converging electric field formed by tubular $La_{0.7}Sr_{0.3}MnO_3$(LSMO) films bottom electrode.

We believe that for one hand the non-equilibrium photoexcited carriers(electron hole pairs) do not massively recombine in the extensive diverging depolarization field region, for another hand, the electrostatic lens-like converging depolarization field results in the effective volume from which the carriers will be driven to the top electrode to be significantly larger than its contact area with BFO films, unlike in the case of a parallel field (traditional sandwiched structures). We also present, besides the high photocurrent (~mA/cm^2) and photovoltage (~2 V), the diverging depolarization field enables an effective collection of the photoinduced carriers, thus enhancing the power conversion efficiency by up to 50 times of magnitude. This ferroelectric lens enhanced photovoltaic effect opens a viable alternative for the ferroelectrics in photoelectric applications.

2. Experimental process

In this study, $Bi_{0.9}La_{0.1}FeO_3$ (BLFO)/LSMO heterostructures were fabricated using pulsed laser deposition (KrF excimer laser,

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λ = 248 nm) on (001)-oriented $SrTiO_3$ (STO) single-crystal substrates, as described in our previous report [23]. By using conventional mask technique, tube-like LSMO bottom electrodes with the thickness of 20 nm and different pipe radius (0, 1, 2, 3, and 4 mm) were deposited at 700 °C in 50 Pa flowing oxygen using Ar as a carrier gas with the total air pressure of 60 Pa, and were subsequently cooled to room temperature at the same pressure. The laser energy density and repetition rate were 2 J/cm^2 and 2 Hz, respectively. Following the deposition of the LSMO bottom electrode, epitaxial BLFO film of around 500 nm was grown at 650 °C and oxygen partial pressure of 15 Pa, Ar was used as carrier gas and the total air pressure is 20 Pa. The laser energy density and repetition rate were 1.8 J/cm^2 and 5 Hz, respectively. For the electric and photovoltaic measurements, transparent conducting oxide tin doped indium oxide (ITO, 10 wt% SnO_2 −doped In_2O_3) with the thickness of 80 nm and the diameter of 100 μm (~8×10^{-5} cm^2) were patterned using standard photolithography process at room temperature to form the top electrodes. The crystal structure of the samples was studied using X-ray diffraction (XRD, DX-2700 model, with the Cu Kα radiation, a characteristic wavelength of 1.5406 Å). The surface morphology was measured by scanning electronic microscopy (SEM, S-4800, Japan), a commercially available atomic force microscope (AFM, NTEGRA Prima, NT-MDT, Russia) working in the contact mode was used to perform the piezoelectric force microscopy (PFM) measurement. Polarization-electric (P-E) field hysteresis measurements were performed using a ferroelectric test system (TF2000e, aixACCT, Germany) at the frequency of 10 kHz. The transmission characteristics were measured using a double beam ultraviolet–visible (UV–vis) spectrophotometer (TU1810, Persee, China) in the wavelength range of 200–1100 nm. The photoelectric effect was measured by illuminating the ITO electrodes with a λ ≈ 480 nm ($E \approx 2.6$ eV) laser (Newport LQA405-85E) and the incident light power density on the sample surface was controlled 25 mW/cm^2 and simultaneously measuring the photocurrent using a high-input impedance electrometer (Keithley 6517).

3. Results and discussion

Fig. 1(a) shows the results of the x-ray diffraction θ-2θ scans of BLFO thin films deposited on LSMO coated STO substrate. Only the (00*l*) peaks from the substrate and the film are evident, indicating that BLFO films are epitaxially grown on the substrates. The diffraction peaks of LSMO films cannot be observed because it is

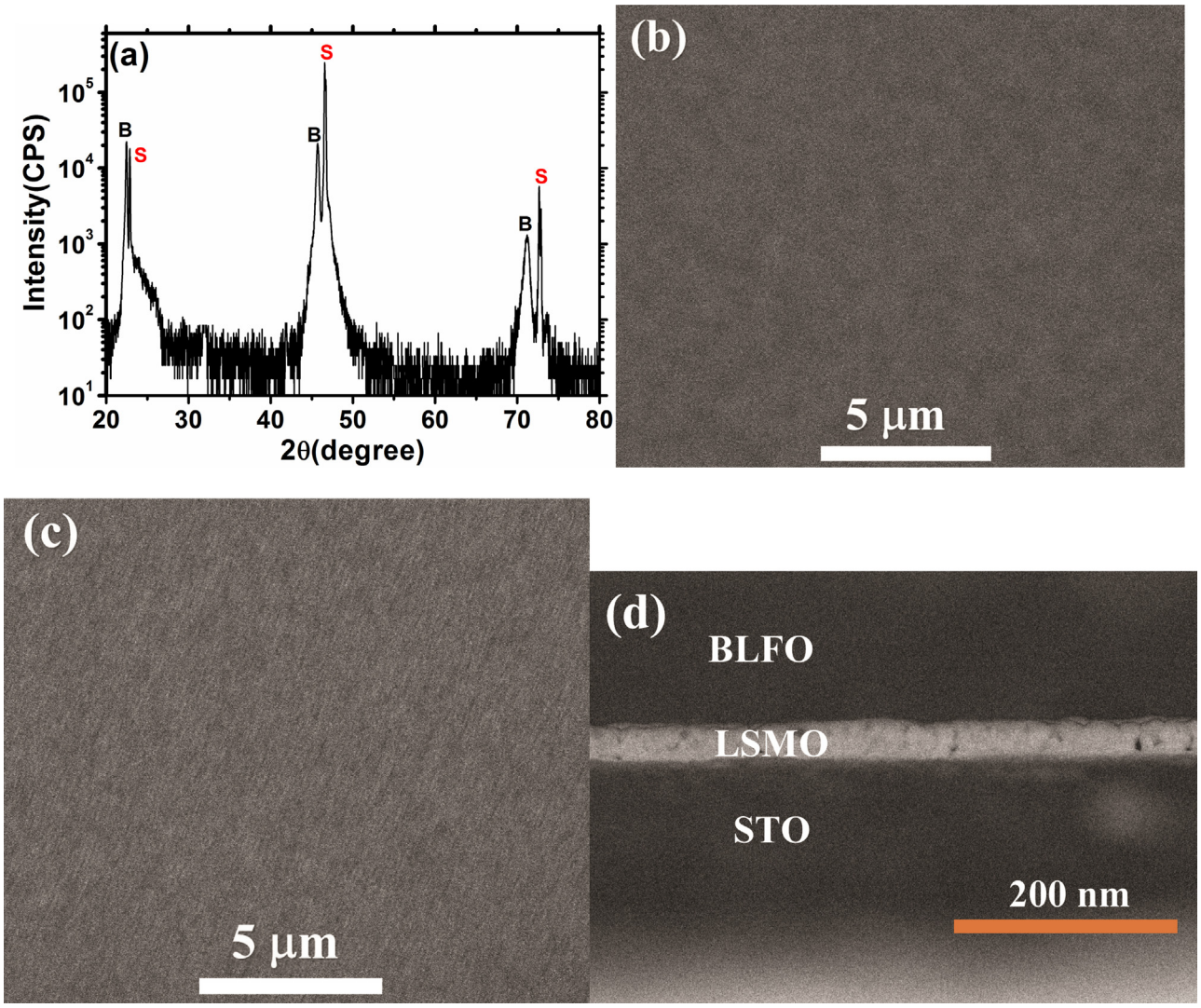

Fig. 1. (a)XRD patterns of BLFO thin films, S denotes STO substrate and B represents BLFO films. (b) SEM images of LSMO thin films. (c) SEM images of BLFO thin films. (d)The cross section scanning electron microscopy (SEM) image of BLFO/LSMO/STO sandwiched structure.