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Ferroelectric photovoltaic characteristics of pulsed laser deposited 0.5Ba$(Zr_{0.2}Ti_{0.8})O_3$-0.5$(Ba_{0.7}Ca_{0.3})TiO_3$/ZnO heterostructures

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ABSTRACT

In this work, we investigate the photovoltaic response of Pt/0.5Ba$(Zr_{0.2}Ti_{0.8})O_3$-0.5$(Ba_{0.7}Ca_{0.3})TiO_3$(0.5BZT-0.5BCT)/ITO structures through the insertion of a semiconductor ZnO layer at different positions. The values of short-circuit photocurrent density (J_{sc}) of the Pt/ZnO/0.5BZT-0.5BCT/ITO, Pt/0.5BZT-0.5BCT/ZnO/ITO and Pt/ZnO/0.5BZT-0.5BCT/ZnO/ITO capacitors are around 5.31, 0.0034 and 0.052 mA/cm^2, respectively. The enhanced photovoltaic (PV) effect is observed when ZnO layer is inserted between Pt and the 0.5BZT-0.5BCT layer. The built-in field developed at the ZnO/ferroelectric interface in the same direction of the depolarizing field, provides a favorable electric potential for the efficient separation and transportation of photo generated e-h pairs. Furthermore, the polarization-dependent interfacial coupling effect enhances PV effect, which is confirmed by investigating the role of polarization flipping on switchable photo response. This work provides an efficient pathway in tuning the PV response in ferroelectric-based solar cells.

1. Introduction

The harvesting of solar energy through the photovoltaic (PV) effect is one the most important resources for the renewable energy. PV devices have traditionally been developed by optimizing the three key steps, which are photogeneration of electron-hole (e-h) pairs, separation of e-h pairs and their transport (Liu et al., 2014). Organic and other semiconductor based solar cells essentially require a p-n junction, where the internal electric field near the junction interface is used for e-h pair separation. The main drawback of these structures is that they cannot produce the open circuit voltage (V_{oc}) above the band gap of materials and consequently causes low efficiency. Furthermore, these structures limit the material choices and also device fabrication to form a workable junction due to issues such as lattice mismatch, doping, and band alignment (Liu et al., 2014). Moreover, inevitable heavy doping processes in traditional solar cells can lead to significant levels of Auger recombination (Liu et al., 2014; Richtera et al., 2012).

Alternatively, ferroelectric materials are considered as promising candidates for photovoltaic applications due to their unique natural properties (Katiyar et al., 2015; Agarwal et al., 2015; Chen et al., 2011; Zhang et al., 2015). Due to its internal electric field, they do not need any p-n junction to produce photocurrent. The ferroelectric PV effect exhibits outstanding advantages over the conventional p-n junction based PV devices, such as high V_{oc} beyond the band gap and polarization controlled PV response (Sharma et al., 2015). However, in these materials, the short-circuit current density (J_{sc}) is low due to inefficient radiation absorption and e-h generation (Fan et al., 2014). For these reasons, PV devices based on semiconductor and ferroelectric materials alone have poor photovoltaic properties due to low V_{oc} and J_{sc}, respectively.

Therefore, the integration of semiconductor and ferroelectric materials (so called heterostructures) takes the advantage of both the semiconductor and the ferroelectric properties and may lead to high-efficiency photovoltaic effect (Fan et al., 2014). In these heterostructures, e-h pairs are created inside both the semiconductor and ferroelectric layers. The depolarizing field and the interface charge

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coupling between the ferroelectric and semiconductor are crucial for the separation and transport of photo generated e-h through the heterostructures (Fan et al., 2014; Cao et al., 2012). There are only few reports on the photovoltaic effect of heterostructures based on semiconductor-ferroelectrics (Fan et al., 2014; Cao et al., 2012; Pan et al., 2016; Chakrabartty et al., 2016). Fan et al. (2014) investigated the $BiFeO_3$ thickness dependent photovoltaic effect in an In_2O_3-SnO_2/ZnO/$BiFeO_3$/Pt heterostructure in which highest efficiency of 0.33% was achieved at a thickness of 300 nm. Cao et al. (2012) have shown that the insertion of an n-type Cu_2O cathode buffer layer into an ITO/Pb(Zr,Ti)O_3/Pt solar cell leads to the 120 times enhancement in short-circuit photocurrent. On the other hand, Pan et al. (2016) investigated the thickness (t_{ZnO}) dependence of the ZnO layer, with an intrinsic spontaneous polarization (P_s), in a ITO/Pb(Zr,Ti)O_3/ZnO/Au heterostructure. They revealed that the optimal thickness is 60 nm of ZnO in order to exhibit enhanced PV characteristics in the heterostructure due to attainment of maximum internal field in ZnO. However, very few reports have focused on interfacial coupling influence on the PV effect (Pan et al., 2016; Chakrabartty et al., 2016). Besides photovoltaic applications, interfacial charge coupling have also been investigated for other applications like resistive random access memories (RRAMs) (Silva et al., 2017b; Silva et al., 2017c).

In this work, we investigate the PV response of Pt/0.5BZT-0.5BCT/ITO structures through the insertion of a semiconductor ZnO layer at different positions. Moreover, we have further investigated the PV mechanism in a metal/semiconductor/ferroelectric/metal (MSFM) heterostructure, particularly the origin of the photocurrent enhancement and the role played by the polarization-dependent interfacial coupling effect, through systematic measurements of photovoltaic current-voltage curves at various polarization states and detailed analysis of energy band diagrams.

2. Experimental methods

Pulsed laser deposition (PLD) technique was used to deposit 0.5BZT-0.5BCT/ZnO thin film heterostructures on Pt/TiO_2/SiO_2/Si substrate. The PLD chamber is provided with a multi-target carousel system that allows the deposition of different layers without breaking the vacuum. The 0.5BZT-0.5BCT target prepared by conventional solid state reaction as described in Silva et al. (2015) and the commercially available ZnO (99.99% purity from Kurt Lesker) target were used as a source for the corresponding thin films. To grow 0.5BZT-0.5BCT/ZnO heterostructures, first a 0.5BZT-0.5BCT layer with thickness of 350 nm was deposited on a Pt/TiO_2/SiO_2/Si substrate at a temperature of 750 °C in an oxygen partial pressure (p_{oxygen}) of 0.1 mbar. A KrF excimer laser (λ = 248 nm), with a pulse energy and repetition rate of 300 mJ and 1 Hz, respectively, was used. Next, a 60 nm thick ZnO layer was grown with pulse energy of 400 mJ at a repetition rate of 10 Hz, in a p_{oxygen} of 0.01 mbar. After the deposition, the films were cooled down to room temperature in a p_{oxygen} of 5.0 mbar. Similarly, ZnO/0.5BZT-0.5BCT and ZnO/0.5BZT-0.5BCT/ZnO heterostructures were grown on Pt/TiO_2/SiO_2/Si under identical conditions.

The crystal structure of heterostructures was investigated by X-ray diffraction (XRD) using the Cu K_α radiation (λ = 0.15418 nm). TEM/STEM investigations were performed on a Cs probe-corrected JEM ARM 200F analytical electron microscope equipped with a Gatan Quantum SE Image Filter for Electron Energy Loss Spectroscopy (EELS) and EELS– Spectrum Image (EELS – SI) analysis in the STEM mode. Imaging and spectral data processing was carried out using specialized routines under Gatan Digital Micrograph. Cross-section TEM specimens were prepared from the samples by mechanical polishing down to ca. 30 µm, followed by ion milling in a Gatan PIPS machine at 4 kV accelerating voltage and 7^0 incidence angle. Low-voltage (2 kV) milling was used as final ion polishing stage in order to reduce the amorphous surface layer enveloping the specimen. For the electrical characterization, circular indium tin oxide (ITO) electrodes with the diameter of 1 mm were deposited by ion-beam sputtering deposition (IBSD) technique on the upper surface of the 0.5BZT-0.5BCT/ZnO heterostructures using a commercially available ITO target (Kurt J. Lesker, 99.99%) with the nominal composition 90 wt% In_2O_3–10 wt% SnO. During the deposition, the substrate was kept at a temperature of 100 °C and the gas pressure inside the chamber was kept constant at 3.4×10^{-4} mbar. A gas flow of 7.7 ml/min of Ar + 0.3 ml/min of O_2 was introduced into the ion beam gun where the atoms were ionized using a 50 W RF source. The photovoltaic response was investigated by performing current–voltage (I–V) measurements, both in the dark and under light illumination, with a maximum power density of 100 mW cm^{-2} (AM 1.5 G) by using a solar simulator Abet Technologies, model Sun 2000 class A. A computer controlled four-quadrant Source-Measure Unit (Model 2400 from Keithley Instruments Inc., Cleveland, OH) was used to apply an external bias and measure the current. For each poling step, the direction of the electric field was changed. The time for the poling voltage applying on the two electrodes was 1 ms, and subsequently the two electrodes were short-circuit through the Keithley 2400. After working the poling process, the transient current disappeared in the film and was ready for measuring the photocurrent (Woo et al., 2014; Zheng et al., 2008). The ferroelectric hysteresis loops (P-E) were measured with a modified Sawyer-Tower circuit using a sinusoidal signal at a frequency of 1 kHz (Silva et al., 2016b).

3. Results and discussion

Fig. 1 shows the XRD patterns of different heterostructures, where the Bragg peaks corresponding to the 0.5BZT-0.5BCT and ZnO thin layers were indexed, according to standard powder diffraction data (JCPDS Card Nos. 27-0530 (0.5BZT-0.5BCT) and 36-1451 (ZnO)).

The presence of strong ZnO (0 0 2) peak in all heterostructures suggests that ZnO grows with a preferred c-axis orientation (Sekhar et al., 2013), regardless of the ZnO layer location within the multilayer sandwich. Usually, ZnO grows along the (0 0 2) direction due to the low surface free energy of (0 0 2) plane (Singh et al., 2007). The preferred orientation in the ZnO layers corresponds to the existence of static electric dipoles along the c-axis of ZnO lattice, which causes the formation of intrinsic spontaneous polarization perpendicularly oriented to the surface (Voora et al., 2010). Furthermore, the XRD patterns of all the heterostructures show the reflections corresponding to the polycrystalline 0.5BZT-0.5BCT perovskite phase (Silva et al., 2017a). Within the resolution of the used XRD equipment, it can be concluded that the heterostructures are composed by 0.5BZT-0.5BCT and ZnO only,

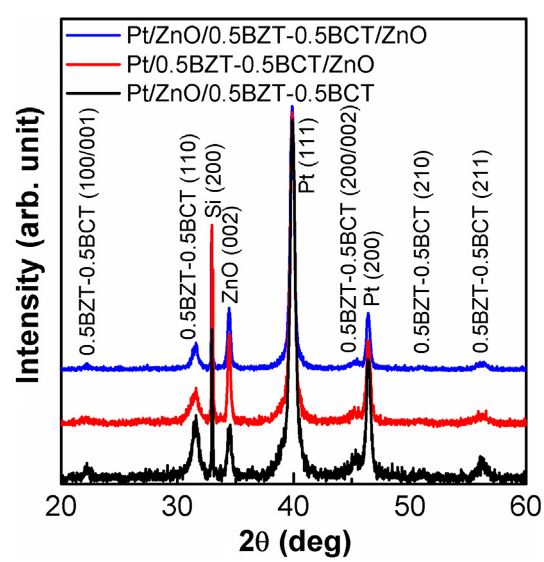

Fig. 1. XRD patterns of different heterostructures.