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Photovoltaic effect in transition metal modified polycrystalline BiFeO$_3$ thin films

Venkata Sreenivas Puli$^{1,2,6}$, Dhiren Kumar Pradhan$^2$, Rajesh Kumar Katiyar$^2$, Indrani Coondoo$^3$, Neeraj Panwar$^4$, Pankaj Misra$^2$, Douglas B Chrisey$^1$, J F Scott$^{2,5}$ and Ram S Katiyar$^2$

$^1$: Department of Physics and Engineering Physics, Tulane University, New Orleans LA 70118, USA
$^2$: Department of Physics and Institute of Functional Nanomaterials, University of Puerto Rico, San Juan-00936, PR, USA
$^3$: Department of Ceramics and Glass Engineering and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
$^4$: Department of Physics, Central University of Rajasthan, Bandar Sindri, Rajasthan 305801, India
$^5$: Cavendish Laboratory, Dept. Physics, University of Cambridge, Cambridge CB0 3HE, UK

E-mail: pvsri123@gmail.com

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Abstract

We report photovoltaic (PV) effect in multiferroic Bi$_{0.9}$Sm$_{0.1}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BSFCO) thin films. Transition metal modified polycrystalline BiFeO$_3$ (BFO) thin films have been deposited on Pt/TiO$_2$/SiO$_2$/Si substrate successfully through pulsed laser deposition (PLD). PV response is observed under illumination both in sandwich and lateral electrode configurations. The open-circuit voltage ($V_{oc}$) and the short-circuit current density ($J_{sc}$) of the films in sandwich electrode configuration under illumination are measured to be 0.9 V and $-0.051$ $\mu$A cm$^{-2}$. Additionally, we report piezoresponse for BSFCO films, which confirms ferroelectric piezoelectric behaviour.

Keywords: ferroelectrics, photovoltaic effect, PFM, PLD, BiFeO$_3$, transition metal

(Some figures may appear in colour only in the online journal)

1. Introduction

To overcome the energy crisis for future generations, clean, renewable and low-cost potential novel candidates are needed for green energy applications. Among others, the solar energy industry is one of the fastest growing in the market. There are several major directions for solar technology development, such as the photovoltaic (PV) systems that directly convert the solar energy into electrical energy while the concentrated solar power systems first convert solar energy into thermal energy and then further convert it into electrical energy through a thermal engine.

The PV effect in ferroelectric thin films has attracted considerable interest to fulfill this requirement. Unlike the PV effect observed in a semiconductor p–n junction, the PV effect in ferroelectrics does not require an asymmetric interface and photo-voltage is not limited by the band gap of the material. Non-centrosymmetry in the unit cell might be the reason for PV effect in ferroelectric materials, which gives rise to asymmetries in electron excitation, relaxation, and scattering processes [1]. The PV effect in ferroelectric materials is relied on the polarization-induced internal electric field [2]. Although initial efforts in this direction were centred on studying PV properties in bulk and thin films of ferroelectric BaTiO$_3$, LiNbO$_3$ and Pb(Zr,Ti)O$_3$, etc [3], recently, single-phase BiFeO$_3$ (BFO) has attracted great attention due to its superior multiferroic and optical properties (band gap $\sim 2.67$–$2.74$ eV) which is highly suitable for PV applications. Compared to many other wide band gap ferroelectrics, narrow band gap BFO demonstrate higher PV quantum efficiencies ($\eta$ $\sim$ 10%) [1]. BFO is an efficient photocatalytic material in visible light region due to its narrow band gap [4]. A dramatic PV effect is observed in BFO thin films, when simulated sunlight is illuminated [5]. Recently, Ji et al [6] reported the PV effect in BFO thin films under visible light
illumination; they possess a switchable photocurrent with respect to the direction of the ferroelectric polarization. A switchable photocurrent strongly affected by the interfaces with electrodes was observed by Choi et al. [7] in a BFO bulk single crystal. It was also reported that the PV current in some BFO thin-film samples cannot be switched at all and is entirely attributed to the interface depletion layer between the BFO and electrode. Choi et al. [7] presented that diode-like rectification follows the polarization-dependent interface band bending of BFO single-crystal slabs that are electrically switchable, that is, $V_{oc}$ and $I_{sc}$ are possessed by the remanent polarization directions. Yang et al. recently demonstrated that the PV effect in BFO films that originated from the $71^\circ$ and/or $109^\circ$ domain walls owing to asymmetry in polarization [5]. Some results in the reports from Choi et al. [7] and Kundys et al. [8] showed an angular dependence of the photocurrent on the light polarization direction, although this has never been interpreted as any bulk PV effect. In BFO based PV devices both the metallic and conducting oxide top electrodes have been used, however, the oxide electrodes have shown better PV responses in ferroelectric PV devices. A recent study confirmed that narrow band gap BiFeO$_3$ ferroelectric thin films with Sn doped In$_2$O$_3$ (ITO) top electrodes played a key role in achieving larger PV properties and is about 25 times higher than Au top electrode BFO films [1, 9]. It was also reported that the PV current in some BFO thin-film samples cannot be switched at all and is entirely attributed to the interface depletion layer between the BFO and electrode [10].

Improved PV voltage and photocurrent densities were obtained when transparent indium tin oxide (ITO) was used as top electrode instead of gold electrode in bilayered (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ (NBT–BT)/BiFeO$_3$(BFO) heterostructured films [11]. Epitaxial multiferroic BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (BFO/LSMO) heterostructured films grown on LaAlO$_3$ substrate under illumination showed significantly increased photocurrent, indicating that the depolarization electric field separates the photo-generated charge carriers [12]. Additionally, when the ferroelectric polarization of the BFO layer is switched, the switched short-circuit photocurrent and open-circuit voltage were also observed suggesting that the PV effect is due to the contribution from both the ferroelectric polarization and the electrode/film interface [12]. Surface PV properties were observed in BFO microspheres which were synthesized by a facile hydrothermal method, which is related to both the ferroelectric polarization and the Schottky barrier [13].

Very recently Guo et al. [14], also reported that, reversibly switchable diode, PV effect was observed in Sr substituted BFO polycrystalline thin films (with high oxygen vacancy concentrations), whereas it is hard detect such an effect in the case of pristine BFO thin films (with lower oxygen vacancies) until the polarization flipping occurs. Co-substitution (A-site and B-site) in perovskite BFO lattice has been attempted by various researchers, to further improve the electric and magnetic properties. In general, co-substitution will suppress oxygen vacancies and reduce conductivity. Co-doping or substitution in BFO, substantially improve ferroelectric (saturation polarization ($P_s$) $\sim$ 70 $\mu$C cm$^{-2}$) and dielectric properties without losing fundamental structural and ferroelectric properties of BiFeO$_3$ and also improve ferromagnetic properties [15, 16]. Secondary phases were significantly suppressed in Pr and Sc co-substituted BFO ceramics, when compared to pure BFO [17]. PFM results also corroborated lower leakage current behaviour and enhanced magnetic properties in Pr and cobalt co-substituted BFO (BPFCO) thin films [18]. Enhanced magnetization and ferroelectric properties were observed in co-substituted BPFCO nanoparticles [19]. Cube-on-cube epitaxially grown single-phase Nb-doped BiFeO$_3$ (BFO) films on SRO/STO substrate, have shown that the piezoelectricity property is increased with varying the orientation from (0 0 1) to (1 1 1), and PFM phase images have shown ferroelectric polarization points downward due to self-poling effect [20].

In our previous studies we report, well-defined magnetic hysteretic behaviour with high magnetic moment for transition metal modified BSFCO ceramics and the origin of the strong ferromagnetic property co-substituted BFO ceramics may be due to the presence of rare earth and transition metal ions at the lattice sites of BFO at room temperature [21]. Yang et al. [5], in their experimental studies on BFO, showed that the specific arrangement of magnetic domains of a ferroelectric material lead to a new PV charge separation mechanism which produces photo voltages that are higher than band gaps of the materials. Interestingly, common ferromagnetic transition metals such as Fe, Ni and Co possess the characteristic Stoner energy band gap $\sim$ 1 eV, which can allow absorption and visible radiation from the Sun [22, 23]. These ferromagnetic transition metals convert the observed sun radiation to electrical energy which will lead to PV effect [22, 23].

Numerous studies are available on the structural, dielectric, multiferroic properties of pure BFO and co-substituted BFO bulk ceramics and thin films and few reports are made on PV behaviour of pure BFO. However, there are no reports available on PV behaviour of co-substituted BFO thin films to the best of our knowledge. In this paper we report PV behaviour for Sm and Co substituted BiFeO$_3$ thin films grown by pulse laser deposition (PLD). Our results show that Bi$_{0.95}$Sm$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BSFCO) might be an alternative material of choice for PV energy applications. Additionally, we also confirm ferroelectric behaviour in BSFCO thin films using piezoresponse force microscopy (PFM), which was found to be superior to pure BFO. Results of these studies are presented in thin paper.

2. Experimental procedure

Ceramic target of Bi$_{0.95}$Sm$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BSFCO) was synthesized by a sol–gel synthesis, as described in our previous report [21]. Polycrystalline multiferroic BSFCO thin films of thickness from 300–360 nm were grown by pulsed laser deposition on Pt/TiO$_2$/SiO$_2$/Si substrate at 700–750 $^\circ$C, under an oxygen partial pressure of 100 mTorr, annealed for 30 min, and were subsequently cooled to room temperature in 300 Torr oxygen partial pressure. An excimer laser (KrF, $\lambda$ = 248 nm) with a laser energy density of 2–5 J cm$^{-2}$, pulse repetition rate of 10 Hz with a substrate target distance of >5 cm, was used...
Pt/TiO2/SiO2/(1 0 0)Si substrate exhibited diffraction temperature.

Bi0.95Sm0.05Co0.05O3 thin films grown on (1 1 1)Pt/TiO2/SiO2/(1 0 0)Si substrate

XRD pattern of the Sm and Co co-doped BFO (BSFCO) thin films; (b) surface topography (AFM) image of Bi0.95Sm0.05Co0.05O3(BSFCO) thin films.

for film growth. Test structures were fabricated by sputtering Pt to create top electrodes with 200 µm diameter at room temperature.

3. Results and discussion

XRD pattern of the Sm and Co co-doped BFO (BSFCO) thin films grown on (1 1 1)Pt/TiO2/SiO2/(1 0 0)Si substrate is shown in figure 1(a). The BSFCO films prepared on (1 1 1)Pt/TiO2/SiO2/(1 0 0)Si substrate exhibited diffraction peaks such as BFO(0 1 2), (1 0 4), (1 1 0), (1 1 2) and (2 2 4), which indicated that the films consisted of randomly-oriented peaks corresponding to perovskite rhombohedral structure with space group R3c (JSPDS file No. 86-1518). The strong and sharp diffraction peaks suggest that BSFCO films are polycrystalline. A small amount of impurity phase corresponding to orthorhombic Bi2Fe3O9 (Fe-rich phase) was found to exist along with the desired major phase of BSFCO. The Bi2Fe3O9 phase in BFO ceramics and thin films has already been reported and corresponds to paramagnetic impurity and is marked with asterisks (figure 1(a)). The result is consistent with literature which reported that undoped and rare-earth doping cannot eliminate the impurity phase in BFO [21, 24, 25]. Impurity phases (BixSm1−xO2, BixFe21−xO4 and Bi2Fe3O9) are obvious because of its chemical kinetics of formation in meta-stable BFO [26, 27]. However Yan et al, reported that undoped, La doped BFO and La and Co co-substituted BFO thin films exhibited pure phase [28, 29].

Figure 1(b) shows the surface topography image of the co-doped thin film acquired using standard AFM technique. The film presents granular microstructure with root-mean-square (rms) roughness being 5.7 nm. It is clear that film was quite smooth to carry out the piezoresponse measurement and avoid any surface-generated artefacts. Moreover, with Sm3+ ion at Bi3+-site in BFO, we expect a good signal in PFM image as compared to that of pristine BFO film [17, 18]. This is because the bond strength of rare-earth ion with oxygen ion is much stronger than that with bismuth and oxygen ions. Therefore, less volatilization of oxygen is expected in Sm-doped BFO film leading to the more insulating film which is helpful in performing the PFM measurement (BFO films are conducting due to oxygen vacancies, which leads to the high leakage currents and early breakdown). Such behaviour we have recently reported in Pr and Co co-doped BFO [18, 30], and expect the same phenomenon to occur for the present case. The other reason for higher PFM signals in the present case is the smaller size of Sm3+ ion as compared to Bi3+. The smaller ion presence may also cause the change in bond lengths and the electron re-distribution which should help in higher piezoelectricity [31]. The idea behind using the PFM technique was to confirm the switchable polarization and hence the local ferroelectric/piezoelectric nature of the synthesized film. This is the advantage of PFM technique that it can be used to investigate the single or few grain(s), whereas the bulk technique acquires average polarization on an ensemble of grains. The other advantage is the direct visualization of the ferroelectric domains, which is not possible by any of the bulk techniques for polarization measurement.

In general, it is difficult to measure conventional (macroscopic) ferroelectric P–E loops of BFO based multiferroic materials, due to its highly leakage current behaviour and its interference significantly giving artificial large polarizations while hampering intrinsic polarization switching [32]. PFM technique helps to characterize the materials with lower resistivity (higher conductivity), which hinders macroscopic polarization measurement. Ferroelectricity/piezoelectricity in these BSFCO films was confirmed using PFM. Piezoresponse images were obtained using a conducting AFM probe and applying a local electric field bias across conductive AFM tip as top electrode and Pt/SiO2/TiO2/Si substrate as bottom electrode of the film with the bottom electrode grounded.

Further, the polarization switching was carried out by writing two square patterns of bigger area 5 × 5 µm² and the central 3 × 3 µm² area inside OPP-PFM images of 8 × 8 µm² area by applying poling (writing) on the films surface with −9 V and +9 V dc voltages, respectively.

Figure 2(a) shows the square patterns written with the application of ±9 V bias voltage. It can be clearly noticed that the polarization changes its direction with the corresponding change in bias voltage (seen as a change in phase). The local hysteresis loop further ascertains the ferroelectric nature of the film (figure 2(b)). The out-of-plane (OP) piezoresponse amplitude and phase images are shown in figure 2. The phase PFM images clearly show the
strong piezoelectric response and oppositely written square regions establishing that BSFCO films support ferroelectricity. Present Sm and cobalt co-substituted BiFeO$_3$ films have shown clear contrasts with ferroelectric switching behaviour in PFM amplitude and phase images, which might be attributed to ferroelectricity (piezoelectricity) in the films. Pr and cobalt co-substituted BiFeO$_3$ (BPFCO) thin films have not shown any PFM contrast, which might be attributed to deterioration of ferro/piezoelectricity in the BPFCO thin films owing to strong electronegativity (1.13 on the Pauling scale) of Pr$^{3+}$ substitution at Bi$^{3+}$ site in BFO lattice [18]. Clear PFM contrast was observed (figure 2(a)) in the case of Sm$^{3+}$ which may be attributed to its stronger electronegativity (1.17 on the Pauling scale). These results indicate that co-substitution of Sm–Co in BFO is helpful in improving ferroelectric/piezoelectric properties. However, it may not be the case for other substitutions [18].

Local ferroelectric switching characteristics at nanoscale level is investigated using switching spectroscopy PFM (SS-PFM) technique, which capillitates spatially resolved maps of imprint voltage, coercive bias saturation, switchable response, and nucleation bias [33]. The SS-PFM phase hysteresis loops are shown in figure 2(b). PFM hysteresis loops were obtained at fixed location on the top electrode as a function of switching pulse amplitude (pulse duration was 25 ms) superimposed on ac modulation bias with amplitude of 0.8–1V$_{pp}$ (peak to peak) at 25 kHz. The phase change in PFM loops is about 180°, which indicates complete domain switching in the BSFCO film. The local electromechanical hysteresis loop implied very little asymmetry in ferroelectric phase hysteresis loops. Negative ferroelectric coercive force was predicted to be larger than the positive coercive force, which finally might be attributed to imprint effect in material. However, both upward and downward polarizations are completely stable with about a phase angle of 70° and –85°, respectively. Imprint effect in the present films might be caused by strain gradients generated in substrate bending switches polarization in polycrystalline ferroelectric films [34]. Thus, after attesting the local ferroelectric behaviour of the film, we carried out the PV measurement on the film.

Figure 3(a) shows a $P$–$E$ hysteresis loop at 4kHz frequency using the positive-up negative-down (PUND) method at ±10 V, which uses, successively, the two positive and two negative electrical pulses, to directly measure electrical $P$–$E$ hysteresis loops, the loops clearly show the existence of a ferroelectric hysteresis and this measurement show the existence of a strong diode-like behaviour, characterized by a maximum saturation at 3 $\mu$C cm$^{-2}$ at positive directional voltages; a similar type of behaviour was also reported by Yang et al., for PV ferroelectric BFO films [1].

The PV characteristics of BSFCO film was studied in the sandwich electrode configuration. Figure 3(a) shows current density–voltage ($J$–$V$) curves of BSCFO thin films with and without illumination in sandwich electrode configuration (metal–insulator–metal (MIM)) for the polarization up state by applying a positive voltage pulse. MIM configuration is good for low voltage poling process, to avoid electrical breakdown. As can be seen, the $J$–$V$ curves taken in both the conditions of dark and with illumination revealed reversible diode-like behaviour, however, in the case of illumination, the $J$–$V$ curve exhibited higher current density both in reverse and forward bias compared to that of the dark $J$–$V$ curves. The BSFCO thin-film capacitors showed clear PV responses (e.g., photocurrent at zero bias) with and without illumination, as shown in inset of the figure 3(b), in sandwich electrode configuration for the polarization up state by applying a positive voltage pulse. The observed short-circuit current density ($J_{sc}$) is $\sim$ 0.051 $\mu$A cm$^{-2}$ and the open-circuit voltage ($V_{oc}$) is $\sim$ 0.9 V under illumination. The high $V_{oc}$ for the BSFCO film observed in our case with illumination might be due to significant piezoelectric response in the as-deposited film, indicating it is self-polarized and the observed PV effect originated from the ferroelectric polarization [6]. The resulting open-circuit voltage $V_{oc}$ of the junction solar cell is about 0.9 V, and this may be attributed to the recombination of electrons at anode and the reduced junction resistance. The higher open-circuit voltage in the present BSFCO might be due to increase in the number of domain walls and this is the reason for domain wall PV effect in BFO based ferroelectrics.
Figure 3. (a) a Polarization-electric field hysteresis loops at 4 kHz frequency using the positive-up negative-down (PUND) method at ±10 V reveal diode-like behaviour in positive direction, (b) the dark and illuminated current density–voltage (J–V) curves in sandwich electrode configuration for the polarization up state by applying a positive voltage pulse, (c) the dark and illuminated J–V curves in sandwich electrode configuration for the polarization down state by applying a negative voltage pulse for Bi$_{0.9}$Sm$_{0.1}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BSCFO) thin films.

Figure 4. Variation of current as a function of time upon turning the light on and off for Bi$_{0.9}$Sm$_{0.1}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BSCFO) thin films.

Commercial silicon based solar cells have more power conversion efficiencies (PCEs) than BFO based ferroelectric solar cells; poor PCE in ferroelectrics is due to their intrinsically low bulk conductivity of ferroelectric domains [36]. Increase in bulk conductivity is not feasible due to highly leaky ferroelectric domains, which cannot withstand strong electrical polarizations [36]. PV voltages can be turned on and off and their polarity can be switched by applying external electric field in ferroelectric PVs, which in turn controls ferroelectric domain structures and their PV output is controlled [5]. The switching (on and off state of light source) behaviour of the BSCFO film was studied in sandwich electrode configuration. For this study the incident light with intensity of ~1 kW m$^{-2}$ was exposed periodically with periods of 300 s and the photocurrent response was measured as a function of time for a fixed bias voltage of 6 V. The obtained curve is shown in figure 4. As can be seen, the photocurrent shows a rapid increase followed by a slow increase without reaching saturation upon exposing to light. When the light is turned off, the photocurrent decreases rapidly first and then decreases slowly to reach its original state. Photocurrent increases from ~0.0023 to 0.027 μA cm$^{-2}$, when light was exposed. However, it was observed that the maximum photo-current increased gradually with increasing number of exposure periods. The increase in saturation current might be due to heating of BSCFO, which in turn decreases the resistance of the capacitor.

4. Conclusions

In summary, good-quality transition metal modified BiFeO$_3$ polycrystalline thin films have been prepared on Pt/TiO$_2$/
SiO$_2$/Si substrate by PLD. XRD patterns of the films confirm rhombohedral perovskite crystalline structure. Ferroelectric $P$–$E$ hysteresis measurements show the existence of a strong diode-like behaviour. Photovoltaic behaviour was demonstrated in BSFCO films under illumination in sandwich electrode configuration for both polarizations up state and down state. Devices are characterized by large open-circuit voltage ($V_{oc}$) $\sim$ 0.9 V and with a small short-circuit current ($I_{sc}$) $\sim$ 0.051 $\mu$A cm$^{-2}$ for the polarization up state by applying a positive voltage pulse. Ferroelectric (piezoelectric) nature of the films was confirmed by FFM studies; also, photovoltaic nature cannot be ruled out as a contribution from the local ferroelectric piezoelectric polarization at nanoscale level and might also be due the presence of low-energy band gap transition metals in the BSFCO films. This discovery should encourage further exploration of transition metal modified rhombohedral structured compounds as a new class of polar, photoactive functional materials.

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