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Advances in Photovoltaic Behavior of Ferroelectric $BiFeO_3$

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ABSTRACT

Bismuth ferrite (BFO) is perhaps the only material that is multiferroic (ferroelectric, antiferromagnetic) at room temperature. In this review, its use in photovoltaic applications has been investigated. A low band gap (Eg ~ 2.2-2.7 eV) within the visible light range makes BFO a potential candidate for such application. We review recent progress in the observance of photovoltaic effect in BFO addressing the role of heterostructures, effect of doping and the role of domain and electrode in the photoresponse of BFO. Recent studies reveal the perovskite ferroelectrics are the promising materials for photovoltaic application. In the last few years, a considerable rise has been witnessed in the study of ferroelectric thin films. This can be attributed to the high open circuit voltages in these thin films. It has been observed that the physical mechanism of photovoltaic effect in ferroelectrics is still under observation /advancement as compared to the semiconductor conventional photovoltaic.

1. Introduction

Driven by the energy crisis in the world, research efforts have been directed towards efficient solar harvesting in order to generate electricity and thereby contributing to environmental conservation. Ferroelectrics and multiferroics have received a lot of attention for their breakthrough in photovoltaic application. Multiferroic is a class of materials, with two or more ferroic properties coupled to each other. Harvesting of energy from ferroelectrics and multiferroic is an extensive research area. A revolution has been brought by the coupling of ferroic and optical properties in photovoltaics. Global recognition has already been given to the harvesting of solar energy through Photovoltaic (PV) solar cell (as shown in Fig. 1) which has emerged as the most promising alternative of traditional energy sources depending on the mechanisms, materials and conversion efficiencies. The first generation silicon based single p-n junction device conventional solar cells are commercially available in the market. Today solar cell production is largely dominated by crystalline silicon modules. The relatively high efficiencies and matured fabrication techniques are the factors that make it popular. But still there is major issue of power harvesting from photovoltaics compared to existing fossil fuel technologies because cost of silicon wafers used in solar cell is very high. Although the second and third generation solar cells are cost effective but efficiencies are compromised with cost.

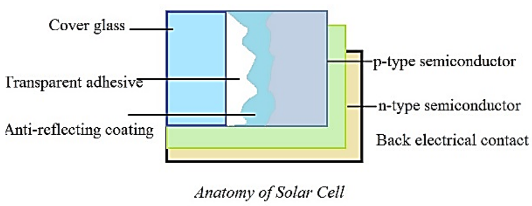

Fig. 1 Anatomy of solar cell

The PV technologies are different on the basis of type of material used, which determines current-voltage (I-V) characteristics and device `s efficiency. Photovoltaic cells, based on silicon and II-IV semiconductor compounds have high conversion efficiencies and charge transportation is often limited by diffusion in the junction based solar cell. In conventional junction based cells, the open circuit voltage cannot exceed the energy barriers height of the junction, which is usually lower than 1V [1-3]. The highest conversion efficiencies are reported for single junction and multi junction derivatives of the PV cells materials and it originate from a variety of other mechanisms such as gradient in a chemical potential [3] or spin polarization [4]. Research and development efforts in the last 30 years, solar cells have achieved an efficiency of ~46 % [3]. There is an ongoing quest to improve the efficiency of the PV cells further, and to reduce the fabrication cost. The factor that drives the PV research is the generation of maximum power per dollar. For this reason, exploring other alternatives has gained momentum in last recent years. Ferroelectric materials are one of the latest additions among these and this research area is generally referred to as ferroelectric photovoltaic (FEPV).

As per the recent National Renewable Energy Laboratory (NREL) reports, perovskites solar cells are exhibiting efficiency of 20.1%. A new manufacturing method has been proposed by the scientists in South Korea who broke the efficiency record for a perovskite solar cell earlier this year. The technique producing solar absorbers are capable of breaking the efficiency record of 20.1%. There has been a significant rise in the perovskite device efficiency – from 14% to 20% between 2012 and 2014. Silicon solar cells have been used since decades but the perovskites`s performance is still doubting as some research groups are still inquiring their stability issues in the long run. An efficient and cost-effective strategy to manufacture perovskite solar cells has been devised by the group from the Korea Research Institute of Chemical Technology. This solar cell exhibited a maximum efficiency of 20.2% which is one of the best performances in perovskite solar cells. Low band gap (in visible spectrum) ferroelectric materials are promising in their potential application in novel solar energy devices. Low band gap $BiFeO_3$ (BFO) with multiferroic properties at room temperature has attracted much attention in future solar cell applications [5].

2. Mechanism of Ferroelectric Photovoltaic (FEPV)

The interesting feature in ferroelectric materials is their spontaneous polarization which is essential for device applications [6-7]. Moreover, they show an intrinsic photovoltaic (PV) response. It arises from a strong coupling between light, photocurrents and atomic scale degrees of freedom that cause a modulation (driven by the current) of the internal field [8].

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When a ferroelectric material is illuminated with light of wavelength corresponding to the energy band gap (Eg) of the material, charge carriers (electron-hole pairs) are generated. These photogenerated carriers are separated and driven to the electrodes by the internal electric field induced by polarization, causing a photovoltaic output. For a junction-based semiconductor photovoltaic device, the electric field, existing at the depletion layer at the interface (p-n junction) (Fig. 2) separates the charge carriers. Thus, photovoltaic effect in ferroelectrics is a bulk-based effect. It differs from the junction-based semiconductor photovoltaic effect. In view of the fact that the internal electric field is not limited to an interfacial region in a ferroelectric, PV responses can be generated without forming complex junction structures [9].

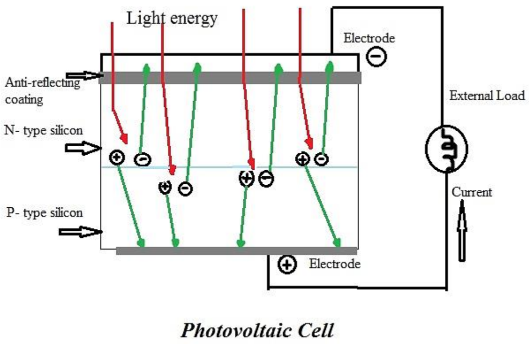

Fig. 2 Mechanism of PV cell

The following four mechanisms can be stated for the charge separation in Ferroelectric Photovoltaic (FEPV) devices: (1) depolarization field or the domain walls [10, 11], (2) presence of the hetero-junction or p–n junction at the interfaces [12, 13], (3) ferroelectric material's non-centro symmetry [14], and (4) Granular interface i.e. poorly controlled [15]. The photo-voltage in ferroelectric PV devices is not limited by the band gap of the material as the photovoltaic effect observed in a semiconductor p–n junction. Since the ferroelectric materials have large bandgap, the energy conversion efficiency and short circuit current (Isc) are found to be low when observed under sunlight, however with the help of domain engineering, high open circuit voltage (Voc) can be obtained [16].

Investigation of ferroelectric photovoltaic effect was originally explored in several perovkite oxides such as $BaTiO_3$ [17, 15], $PbTiO_3$ [18], $Pb(Zr,Ti)O_3$ [19, 20-22], PLZT [23] and $LiNbO_3$ [24]. Oxide materials are cheap, abundant, stable, highly light absorbing and their properties such as band gap and its conductivity can be tuned through chemical substitution making them a suitable candidate for thin film ferroelectric photovoltaic [25]. An excitement was generated due to its large open circuit voltage > 10^2 V, when crystal was subjected to illumination [26]. Bulk ferroelectric photovoltaic effect (BFPVE) is a fascinating phenomenon with many unique features, where a photocurrent is proportional to the polarization magnitude and charge carriers separation in homogeneous media [9]. The remnant polarization and the polarization induced internal field exist over the whole bulk region of the ferroelectric in bulk ferroelectric photovoltaic effect rather than a thin interfacial depletion layer. The small current densities of the order of nA/cm^2 limit the photovoltaic efficiency in ferroelectric because of their large band gaps. In case of BFPVE, the charge transportation is not limited by diffusion and energy barriers (energy band gap) doesn't restrict open circuit voltage (Voc) [9, 27]. The intrinsically low bulk conductivity of ferroelectric domains is one major drawback in achieving high conversion efficiency as it is proven weak conversion in ferroelectric materials, because leaky domains cannot withstand a strong electric polarization. Moreover, the large band gap of the ferroelectric materials allow strong absorption of light in UV region, It was also shown that the photo voltage could be reversed or enhanced, by controlling the ferroelectric polarization, which was in turn controlled by electrical poling on lead based thin films [23]. The process of applying an electric voltage higher than the coercive field, to a ferroelectric material, while cooling it from transition temperature to room temperature is known as Poling. To achieve maximum polarization, poling helps to orient ferroelectric domains in one particular direction.

Recently, ferroelectric and multiferroic photovoltaic have again vitalized the third generation solar cells through the discovery of very large photo responses in a few ferroelectric and multiferroic compounds like Pb $(Zr,Ti)O_3$ (PZT), $BiFeO_3$ (BFO) and Bi_2FeCrO_6 (BFCO). PV effect in ferroelectric (FE) has been discovered about five decades back, though it came to limelight through the discovery of large photovoltage (15 V) in BFO thin films [28, 29]. The inherent electric field due to non centrosymmetricity is responsible for causing PV effects in ferroelectrics as it maintains the charge separation through spontaneous polarization. The developed photovoltage is found to be proportional to the magnitude of electric polarization and separation between electrodes i.e. the thickness of the material [30]. Although, it is possible to generate very large photovoltage in ferroelectrics though the photocurrent is low. But, the recent reports say, low photocurrent is no more a limit for this dielectric class as the new ideas such as 'above bandgap large photovoltages' [28],'role of domain walls' [31], 'effect of thin films' [32] 'tip enhanced PV effects' [33] etc., are developed [34].

Reviews of the general study of magnetoelectricity exists by Schmid [35] followed by Fiebig [36] and then Eerenstein [37] et al. The current interest in the bismuth ferrite was augmented by a 2003 paper by Ramesh`s group [38]. They showed an unexpected large remnant polarization that was 15 times larger than the previous value as seen in the bulk, together with a large ferromagnetism of ca. 1.0 Bohr magnetron. Single crystals grown in France confirmed this large value of polarization in films and showing it to be intrinsic. This paper proved to be stimulating which further inspired others to research in the field of BFO.

In recent years, $BiFeO_3$, one of the most actively studied multiferroic material [39-41], is a multiferroic pervoskite compound with multiferroic properties exhibiting at room temperature has attracted a considerable attention since it has high ferroelectric Curie temperature (Tc ~830 °C) and also the antiferromagnetic Neel temperature (T_N~370 °C). The Bi^{3+} and Fe^{3+} ions are responsible for the ferroelectricity and magnetism. Ferroelectricity is produced due to Bi^{3+} and antiferromagnetism is due to Fe^{3+} ions [42]. The ferroelectric photovoltaic effect has opened possibilities in potential applications including energy harvesting and photovoltaic applications. BFO is popular as it is a lead-free multiferroic with relatively narrow bandgap, thus making it environmentally friendly. FEPV (Ferroelectric photovoltaic) has also been observed in other materials such as $BaTiO_3$, $LiNbO_3$, PZT. These materials have large optical bandgap and small current density. The efficient functional devices appears to be realized due to the exceptional benefits of FEPV over conventional PV including high output voltage and PV response controlled by polarization.

Even though initial efforts were centered on studying the photovoltaic properties in bulk and thin films of ferroelectric $BaTiO_3$, $LiNbO_3$and $Pb(Zr,Ti)O_3$ etc [29], however recently single phase multiferroic $BiFeO_3$(BFO) has received great attention due to its lower band gap in the range of ~2.2–2.7 eV [43, 44] and high polarization [45, 46]. Further, the presence of multiple degrees of freedom due to multiferroic properties in BFO are beneficial to further control the photovoltaic properties which may provide further functionality to next generation solar cells. Recently, several groups have reported photovoltaic response in high quality BFO thin films grown on different substrates which include oxides and metals.

Here in this review we try to summarize the photoelectric effect observed in thin films of BFO. The role of heterostructures, doping, electrode and domain walls has been reviewed. Appreciable photoconductivity has been shown in BFO under visible light illumination due to the presence of other mechanical, electrical and magnetic functionality [25, 47, 48].

3. Factors Affecting Photoconductivity

3.1 Role of Heterostructure

The ability to grow high quality films with controlled interfaces, atomic arrangement and composition has led to the creation of new functional materials and in fact seems promising for the rational design of new multiferroics. Here we review the progress in the formation of multilayer heterostructures for enhanced photoresponse.

Recently, Sharma et al [49] reported a multilayered heterostructure with five alternating layers of single phase BFO and BTO thin films that were deposited using PLD technique. A remarkable increase in photocurrent and improved ferroelectric properties was observed. The two factors that resulted in good ferroelectric photovoltaic response were the low optical band gap (~2.6 eV) and high ferroelectric polarization (~60 μC/cm^2) in BFO multilayered structure. The light-to-electricity power conversion efficiency calculated at 405 nm was relatively high (0.067%). This response was attributed to the strong depolarization field due to higher remnant polarization and lower band gap. BFO multilayered system showed a potential for energy harvesting and other photovoltaic applications. Tiwari et al [50] examined the BFO/ZnO heterojunction. It was observed that the films when deposited by metal organic precursor solution followed by annealing resulted in a photoconversion efficiency of 3.98%. Hence different heterojunction has also been prominent for photovoltaic effects. Qu et al [12] fabricated the BFO/NSTO heterojunctions with room-temperature resistance switching (RS) and white-light photovoltaic (PV) effects on PLD grown with a KrF excimer laser =248 nm. The frequency of the laser beam was 5 Hz and the pulse energy density on the target was 1.2 J/cm^2. The power of white-light illumination source is 285 mWcm^{-2}. The open-circuit voltage was about 40 mV. The PV efficiency of the heterojunction is about ~3 x 10^{-2}%. Chang et al [51] investigated the photovoltaic properties of $BiFeO_3$ thin films grown on Pt/Ti/SiO_2/Si (100) substrate by RF sputtering. An increase in photocurrent density was observed on increasing the intensity of laser with 405 nm wavelength used for illumination. However, the open circuit voltage (Voc) was not reported. Recently diode-like behavior and photovoltaic effect in $La_{0.67}Sr_{0.33}CoO_3$/BFO/ZnO:Al structure was reported with short-circuit current of ~4 μA/cm^2 and open-circuit voltage of ~0.22 V, obtained under white light illumination [52].

In another work Fang et al [53] reported large switchable photovoltaic response in Pt/BFO/$La_{0.7}Sr_{0.3}MnO_3$ heterostructure. The reported values of Voc and Isc were ~0.20 V, 1.0 pA and ~0.18 V and 1.44 pA for downward and upward polarization respectively. Puli et al synthesized transition metal modified polycrystalline BFO thin films grown on Pt/Ti/SiO_2/Si substrates and reported photovoltaic response with Voc and short-circuit current density (Jsc) as ~0.9 V and ~0.051 μAcm^{-2} in sandwich electrode configuration using Pt top electrode [54].

3.2 Effect of Doping

The most successful approach in reducing the leakage current density has been observed using doping (substitution of small amount of impurity A-/B- site cation) in BFO unit cell which further improves the ferroelectric photovoltaic properties [29, 32, 55]. Doping can stimulate the controlled and significant distortion in the structure of pervoskite that leads to improved as well as new functional properties [9, 28, 56, 57]. The site engineering approach can be well applied to the existing thin film deposition methods including RF magnetron sputtering, MOCVD, chemical solution deposition, pulse laser ablation. Still reports are needed to be available.

Fu et al [58] studied the effect of doping on BFO thin films for corresponding changes in photovoltaic effects. It was shown that when the bismuth ferrite and Nd-doped barium titanate thin films were prepared via sol-gel spin coating, the effect of substitution of Nd^{3+} ions for Ba^{2+} on A sides was observed. A decrease in band gap was observed and the subsequent increase in the power conversion efficiency, open circuit photovoltage and short circuit photocurrent density of Nd-doped barium titanate thin films reaching their maximum followed by the decrease due to the increase in the content of Nd. Observation of the variation of annealing temperature was also performed. As the annealing temperature increased, a decrease in short circuit photocurrent density was seen whereas the open circuit photovoltage and the power conversion efficiency of thin films annealed at lower temperature were higher than the higher annealing temperature. Gobinda et al [59] studied the photovoltaic effects and switchable photovoltage generation in pure and Pr–Cr codoped $BiFeO_3$ (BFO) nanotubes (NTs). The investigation of influence of metal doping on open circuit voltage, fill factor, short circuit current and also on the power conversion efficiency were done. It was seen that the power conversion efficiency of pure BFO NTs was found to be enhanced (almost ~0.207%) in comparison with the reported bulk effect. The highest value of power conversion efficiency (~ 0.5%) was found for Pr-doped NTs. These were characterized by highest η ~ 0.5%Voc ~ 0.21 V and Isc ~ 0.89 nA values among the NTs under illumination. The PV property of the Cr-doped BFO NTs is the weakest among the NT samples.

It is evident that the photovoltaic properties are completely different from the conventional p-n as well as the Schottky junctions since here it is originating from the built-in-field induced by space charge in depletion layers. Several research groups have reported that in order to suppress the leakage current in BFO films, a site-engineering technique using various elements is indeed effective [28, 60-63]. BFO has large polarization and a rather small energy gap Eg of 2.67 eV with the direct transition type, among the ferroelectrics [64]. The latter feature is expected to have in the visible light regime, a large optical absorption coefficients providing promising photovoltaic material with a novel mechanism [54]. In contrast to the ferroelectric applications, the disadvantages of a large leakage current and a large Ec can be turned into be advantages for photovoltaic applications with excellent and stable properties. Recently, Sharma et al [65] reported improved photovoltaic properties in (0.9) $BiFeO_3$(0.1)-$YCrO_3$ composite thin films as compared to pure BFO films [65]. To overcome the leakage current effect on photovoltaic properties of FEPVs, one of the possible ways is the doping of foreign atoms into BFO and/or fabricating a composite film with other single phase ferroelectric materials.

3.3 Role of Domain Walls and Domains

Research on domain and domain walls has intensified due to the 1) behavior of domain is directly responsible for switching characteristics (switching of polarization takes place through nucleation and growth of domains) and 2) domain size scales with sample size, so thin films can have very small domains and hence a high volume density of domain walls. BFO exhibits a new domain wall related phenomenon which makes it fascinating. Domain walls have their own properties owing to their local symmetry. In case of BFO, it includes enhanced local conductivity.

Generally domain walls exist in many materials that possess certain order parameters such as ferroelectric and ferromagnetic materials, superconductors and liquid crystals. The reason for their formation are when the symmetry of a single crystalline region is changed or reduced in the process of a phase transition and separate regions with different orientation of the order parameter form. The static and dynamic property of the domain walls defines the response to the applied fields. It is important in numerous technological applications, such as nonvolatile ferromagnetic, ferroelectric memories etc. [66].

Domain wall represents a special type of inhomogeneity. On comparison with domain bulk, its symmetry is lowered. Large structural gradients in domain walls result in new effects that do not exist in the domain bulk [67, 68]. The detailed structure and formation energy of domain wall in conventional ferroelectrics are now well established [69-71]. On the contrary, research on the domain walls in multiferroics is scarce. Lajzerowicz predicted that in systems with two coupled order parameters, domain walls could result in the emergence of one order inside the domain wall of the other [72]. For multiferroic materials, it means a net electric or magnetic moment could in principle exist in the center of domain walls while the domain themselves were non-electric or non-magnetic. Later, Privratska and Janovec [67, 68] using group-theory argument, generalized this analysis to show what crystal symmetries might exhibit such behavior, Multiferroic $YMnO_3$ was studied and the results showed that the antiferromagnetic walls have a strong interaction with ferroelectric walls [66]. Recently, several groups reported domain wall conductivity [73] and magnetoelectricity [74-76] in BFO thin films.

BFO has a narrow band gap (2.7 eV) [77] lies within the visible light range. The visible-light photovoltaic effect makes BFO a promising candidate for novel photovoltaic cells and optoelectronic devices. In 2003, Choi et al [57] reported a switchable visible-light photovoltaic effect in single domain BFO crystals which generated interest in researchers on the study of the photovoltaic effect in BFO. It was observed that normal ferroelectric photovoltaic effect was caused by the incomplete screening of polarization charge in a single crystal single domain BFO, which gives rise to the depolarization field in the sample. This depolarization field direction depends on the direction of the polarization, and is therefore switchable [43, 78, 79]. On top of the depolarization field, the band bending in the film may be induced by the the schottky barriers at the electrode/film interface and the different work functions of the electrodes, but these are independent of the polarization direction [32]. In 2010, Yang et al [28] reported a very large photovoltage in BFO films with well aligned 71° domains. It was proposed that the effect arises from the structurally driven electrostatic potential steps at the nanometer-scale domain walls. Driven by the periodic potential steps at ferroelectric domain walls, this new photovoltaic mechanism was later further explained by them in details [80]. Ferroelectric domain walls function as nanoscale generators of photovoltaic current and the accumulative effect of all the domain walls is large output photovoltage. Consequently they proposed that photovoltaic effect should arise in any system with a periodic potential structure similar to BFO. In fact, there is an extensive literature unfolding anomalous ferroelectric photovoltaic effect in ceramic ferroelectrics which is explained as the result of series addition of smaller-than-band-gap photovoltages [15, 27, 81]. To conclude, when there are grains (as in polycrystals) or domains in the sample, each grain or domain generates its own photovoltaic response. The overall response of the sample is thus a set of small "batteries" in series, thus leading to large photovoltage.

For the domain wall contribution, it was reported that potential steps at different domain walls were different, and the potential step at 109° domain walls was much larger than that at 71° domain walls [73]. It is thus expected that BFO films with well aligned 109° domain walls will generate a significantly larger photovoltage. However, macroscopic photovoltaic measurement of BFO films with 109° domain walls is restricted due to the presence of domains with in-plane polarizations and pointing in opposite directions, thus canceling the effect.

Recently Yang et al [28] investigated the photovoltaic response of BFO thin films when it was illuminated with white light. Current voltage (I-V) measurement was carried out parallel to domain wall to observe PV effect which became prominent when measured perpendicular to domain wall. The band gap open circuit voltage (Voc) was shown to be proportional to the number of domains and hence can be altered by tailoring domains and domain walls. Hence, it was observed that the photovoltaic properties could be controlled by controlling the domain structure of the films.

Ramesh et al [73] reported that certain domain walls in BFO were more conductive than the domain themselves [73]. It was seen that the wall conductivity was directly related to the domain they separate. Therefore, 180° walls were most conductive followed by 109° walls and then 70° walls. The two reasons for this effect of enhanced conductivity were attributed to the depolarization field that attracts charge carriers, was found to be formed, when the polarization normal to the domain wall was not constant across it and reduced bandgap for 180° walls and 109° domain walls. An explanation for a decrease in band gap was related to the local distortion of Fe-O-Fe bond angle which controls the orbital overlap. Noheda [82] recently demonstrated the PV effect in BFO films. It was shown that the PV effect originating from the 71° and/or 109° domain walls was due to the asymmetry in polarization. Further, two mechanisms were also proposed for the separation of photo-excited charge carriers, one taking place at the interfaces and the other was due to intrinsic polarization [60]. Domain structure has significant effect on the properties of multiferroic BFO. It is thus important to control the domain structure for different applications. There has been much research in the factors affecting domain structure in BFO.

In a study, Zhang et al [83] suggested the important roles played by the elastic energy and depolarization energy in determining the equilibrium domain structure in BFO. Different results were observed on varying film orientation and strain states. It has been demonstrated that the thicker films favor the formation of regular domain structures [84, 85]. Chu et al [86] has reported that for BFO films grown on $DyScO_3$ (DSO) with $SrRuO_3$ bottom electrode, it was observed that the growth mechanism of the underlying $SrRuO_3$ layer determined the final domain structure of BFO. Chu et al [87] successfully obtained BFO films with only 71° domain walls located on (101) type planes and 109º domain walls located on (100) type planes. It was possible by the careful control of the boundary conditions.

3.4. Role of Electrode

Recently, several groups have reported photovoltaic response in high quality BFO thin films grown on different substrates including oxides and metals. Yang et al [32] studied the PV effects in BFO films deposited on $SrRuO_3$ using transparent conducting indium tin oxide as top electrode. A high quantum efficiency of ~10% with open-circuit voltages ~0.8- 0.9 V was reported. Further, Chang et al [51] investigated the photovoltaic properties of $BiFeO_3$ thin films grown on Pt/Ti/SiO2/Si (100) substrate by RF sputtering. An increase in photocurrent density was observed by increasing the intensity of laser with 405 nm wavelength used for illumination. However, the open circuit voltage (Voc) was not reported. Moreover, Lee et al [78] reported that epitaxial single-crystal BFO films grown on $SrRuO_3$ as the substrate and Pt as the top electrode showed a "below band gap" photovoltage. Further, it was concluded that the photoexcited electrons and holes were separated by macroscopic depolarization over the entire film. Although studies exist on the photovoltaic effect based on polycrystalline ferroelectric films, the observed phenomena have been inconsistent.

In another study, Ding et al [88] studied the FEPV effect based on polycrystalline BFO films with extremely large remnant polarization that were successfully deposited on glass substrates coated with ITO using a modified RF magnetron sputtering method. To understand the relationship between polarization and photovoltaic response, symmetric and asymmetric cells were constructed. The FEPV is highly dependent on the material used for the top electrode and the thickness of the polycrystalline film. It was observed that the short circuit current density of as-prepared capacitors with ITO as the top electrode was higher than that of capacitors with Ag as the top electrode. Capacitors with 105 nm thick BFO films sandwiched between the top and bottom electrodes also showed significant improvement in photovoltaic output relative to those with 150 or 200 nm thick BFO film. Chen et al [89] investigated the electrode effect on photovoltaic properties for the poly-BFO film based capacitor. The photovoltaic efficiency in ITO/poly-BFO/Pt capacitors, was almost 25 times larger than that in Au/poly-BFO/Pt capacitors. The efficiency approached to 0.125%. These experimental results revealed that a combined system of narrow-band-gap ferroelectric BFO and oxide ITO electrodes could give a considerably high photovoltaic response. It suggested that the narrow-band-gap poly-BFO films would be a promising material for the photo-related applications. Guo et al [90] investigated the diode and photovoltaic effects of $BiFeO_3$ and $Bi_{0.9}Sr_{0.1}FeO_3$ polycrystalline thin films. This was done by poling the films with alternating direction and increased magnitude. It was found that both electromigration of oxygen vacancies and flipping of polarization were able to induce switchable diode and photovoltaic effects. Choi et al [57] found the diode effect on BFO. The electronic transport properties of three thin plates like BFO crystals placed between symmetric electrodes like Au/BFO crystal/Au, Ag/BFO-crystal/Ag were studied. The incident wavelength was 532-nm green light and 630 nm red light, with the total power density being less than 20 mW/cm^2. The Jsc values and efficiency was found to be J_{SC} (green) = 735 μAcm^{-2}, J_{SC}(red) = 2.6 nAcm^{-2}, η = 0.001%. Basu et al [25] reported the photoconductivity in $BiFeO_3$ films under illumination from a 100 mW/cm^2 white light source. The wavelength was 550 nm. The J_{SC} value of 13.4 μAcm^{-2} was reported. PLD was used to deposit film of BFO on thick film of bottom electrode SRO (111) and DSO (110). Films were deposited at 700 °C in 100 mTorr partial pressure of oxygen and also cooled to tune the oxygen stoichiometry.

Further, Zhou et al [91] studied the effects of film thickness on photovoltaic outputs, lattice parameters and direct band gap in the sol-gel derived $BiFeO_3$ thin films. With the change of the film thickness, the great transitions took place in the preferred orientation and lattice parameters. Also, the photovoltaic outputs are found to be significantly dependent on the film thickness. The results showed that with the increase of film thickness, the open circuit voltage increases in a gradual manner and the short circuit current decreases reciprocally. Hung et al [32] investigated the short-circuit photocurrent and open-circuit photovoltage in $BiFeO_3$ (BFO) ceramics as functions of laser wavelength (373 nm and 532 nm), illumination intensity, and sample thickness. Under near-ultraviolet illumination of 373 nm,BFO ceramics exhibit significant photovoltaic responses. The reported value for Jsc is JSC = 1.2 μAcm^{-2}..

4. Conclusion

We hope that this review has captured some of the exciting new development in the field of multiferroics especially from a perspective on thin film. Also, new developments are occurring at the rapid rate throwing light onto the intricacies of this material. One of the biggest challenges in the field of multiferroic is the need for the room temperature functionality. Despite the consistent effort by a number of researchers this still remains a difficult problem. The role of thin film heterostructures domain wall or domain and the effect of doping in the photo response of Bismuth ferrite have been reviewed in an attempt to bring the recent advances in the field of photovoltaic effect in BFO. Various parameters play a role in the enhancement of photo response of perovskite solar cells.

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