Ferroelectric Photovoltaic effect

Introduction

Researchers worldwide are working very hard to open different corridors for the production of renewable energy to meet the evolving demands of the inexhaustible energy and clean fuel sources. Harnessing solar energy as an alternative to compensate the depleting non renewable energy resources is a technological field with great potential. Photovoltaic (PV) materials and devices, commonly known as solar cells, convert sunlight into electrical energy. Generation of electricity in a clean, quiet and reliable way is one of the major attractions of PV technology. On illumination of a conventional semiconductor-based PV cell, generation of charge carriers (electron–hole pairs) takes place at the depletion region (p-n junction) of the semiconductor. The carriers thus produced are responsible for the generation of photo current, which can be harvested in a useful manner. The electronic band gap of the semiconductor determines the photovoltage produced by the PV cell.

1. Conventional Solar Cells

The PV technologies can be classified on the basis of the material used, which in turn is responsible for the determination of the current voltage (I-V) characteristics and the efficiency of photovoltaic device. High conversion efficiencies have been demonstrated by photovoltaic cells based on silicon and III-V semiconductor compounds. The highest conversion efficiencies are shown by single and multi junction derivatives of these materials and find applications in space and terrestrial technologies. Inorganic, organic and quantum dot cells are some emerging PV cell technologies. Though the efficiencies of ferroelectric PV cells are lower as compared to their semiconductor counterparts but they have found place in figure 1 due to their cost effectiveness.

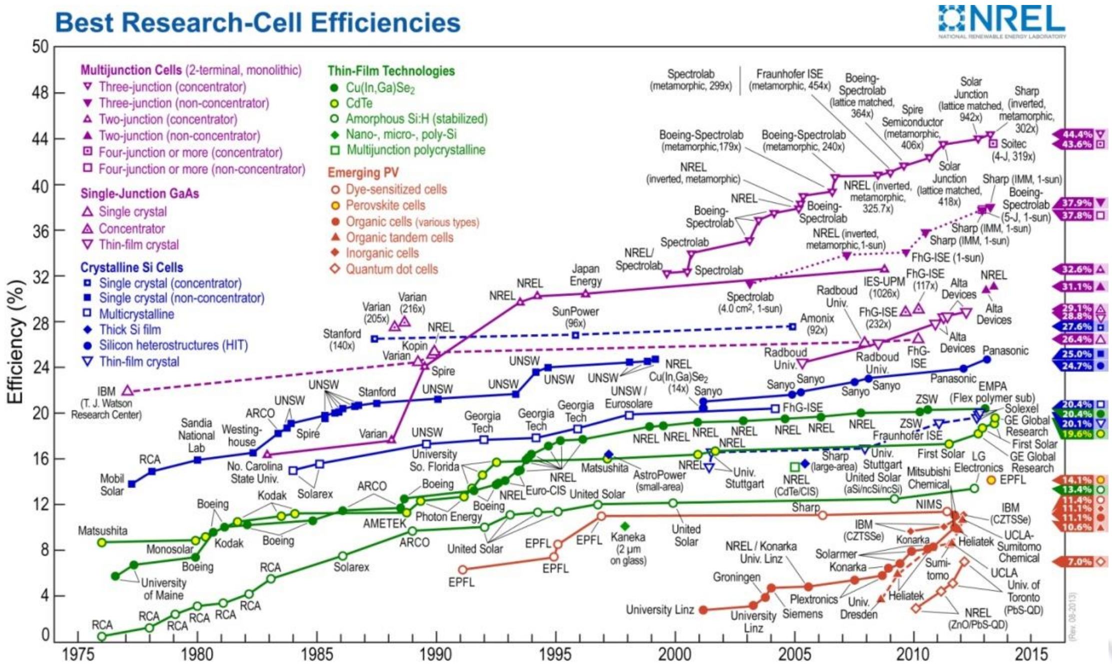

Figure 1: *Review chart showing the work done on solar cells [Website 2].*

Figure 1 shows the review of various companies, universities and research institutes behind the advancements of solar cells based on silicon. It's impressive to see how National Renewable Energy Limited (**NREL)** has been heavily involved in many technological advancements since the 90s. Other heavyweights have been research-labs like **Fraunhofer** and **(Boeing)-Spectrolab**. Focusing on the corporate giants, we notice that **Sharp** , but also **Panasonic** , **Sanyo** and **Siemens** have contributed to the field with their own R&D departments (figure 1). There is an ongoing pursuit for further improvement of the PV cell efficiency along with reduction in the fabrication cost. The PV industry and research is driven by the quest of maximizing the power generated per rupee. The past decade has seen the momentum in exploring the viability of alternate materials to increase the efficiency of PV cells. Lately, ferroelectric materials have been used for PV technology and this research area is generally referred to as ferroelectric photovoltaic.

Silicon-based photovoltaic (PV) technology has dominated the solar cell Industry over the past many years and continues to foster till date. Typically PV effect involves two processes, creation of electron-hole pairs as the electrical charge carriers, and formation of electric current due to the motion of separated electrons and holes. In the junction-based photovoltaic effect, the internal electric field only exists in a very thin space charge region of a p-n junction or Schottky barrier which separates the charge carrier as shown in Figure 2. Without the internal field in the bulk material region, the photo-generated charge carriers swept out of the depletion region have to diffuse to the cathode or anode. Thus, the charge transportation is often limited by diffusion in the junction-based photovoltaics. The open circuit photo voltage (V_{oc}) cannot exceed the energy barrier height of the junction, which is usually lower than 1 V for Si. Moreover, a p-n junction is not a prerequisite for the photovoltaic effect. The photovoltaic effect can originate from a variety of other mechanisms such as gradient in a chemical potential or spin polarization.

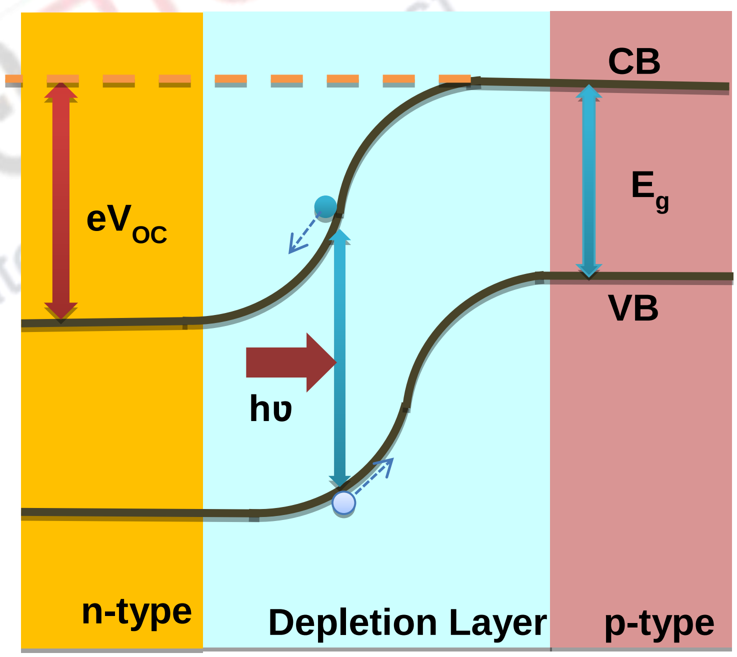

Figure 2: Band diagram of conventional p–n junction, showing the conduction band (CB), valence band (VB), band gap (E_g) and open-circuit voltage (V_{OC}). Here, hν is the incident photon energy and e is the elementary electric charge.

2. Mechanism of ferroelectric photovoltaics

Another mechanism was discovered in non-centro-symmetric materials, such as ferroelectrics and is called the bulk photovoltaic effect (BPVE), which differs from the conventional junction-based interfacial photovoltaic effect in semiconductors, such as p-n junction or Schottky junction. Ferroelectrics have shown potential as promising material for future photovoltaic applications. Observance of high open circuit voltages in ferroelectric thin films, have generated considerable interest in the field of ferroelectric photovoltaic in recent years. The field of ferroelectric photovoltaic is evolving and not yet completely understood compared to the semiconductor based photovoltaic technology.

Bulk ferroelectric photovoltaic effect (BFPVE) is a fascinating phenomenon with many unique features such as extremely large photo-voltage, where a photocurrent is proportional to the polarization magnitude and charge carrier separation in homogeneous media. In bulk BFPVE, the remnant polarization and the polarization-induced internal electric field exist over the whole bulk region of the ferroelectric rather than a thin interfacial depletion layer. In case of BFPVE, the charge transportation is not limited by diffusion, and V_{OC} is not restricted to the energy barrier (energy band gap). As a result, the photo voltage observed here is significantly higher than the electronic band gap and proportional to the inter electrode distance in the polarization direction, which is found to be originated from the engineered domain walls of the ferroelectric material.

Ferroelectric photovoltaic effect was originally investigated in several ferroelectric perovskite oxides, such as in $BaTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, PLZT and $LiNbO_3$.

Oxide materials are cheap, abundant, stable, highly light absorbing and their properties such as band gap and conductivity can be systematically tuned through chemical substitutions, making them promising candidate for thin film ferroelectric photovoltaics. Much excitement was generated due to the anomalously large open circuit photo voltage (in some case $V_{oc} > 102$ V), which is produced when crystal was subjected to illumination. However, the light-to-electricity conversion efficiency (power conversion efficiency) of the bulk PV effect in ferroelectric thin film based solar cell is reported to be significantly lower ($< 10^{-4}$) than that of commercially available silicon based solar cell. One major obstacle in achieving high conversion efficiency is the intrinsically low bulk conductivity of ferroelectric domains. Indeed, any effort to increase the bulk conductivity of ferroelectric domains has proved to be ineffective, because leaky domains cannot withstand strong electric polarization as charge density associated with ( ) across a domain wall will therefore be reduced for a leaky ferroelectric material, resulting in a low open circuit voltage. Moreover, the large energy band gap of ferroelectric materials allows strong absorption of light in UV region only.

A simple possible explanation of ferroelectric photovoltaic (FE-PV) is schematically illustrated in Figure 2. When a light of source wavelength corresponding to the energy band gap of the ferroelectric material is incident, photons are absorbed with the generation of charge carriers-electrons and holes. The photo-generated electrons and holes are driven by the polarization induced internal electric field in opposite directions, and thus contribute to the photovoltaic output. In other words, this effect is associated with the loss of inversion symmetry in the distribution of defects, impurities, space charges and polarizations in ferroelectric materials.

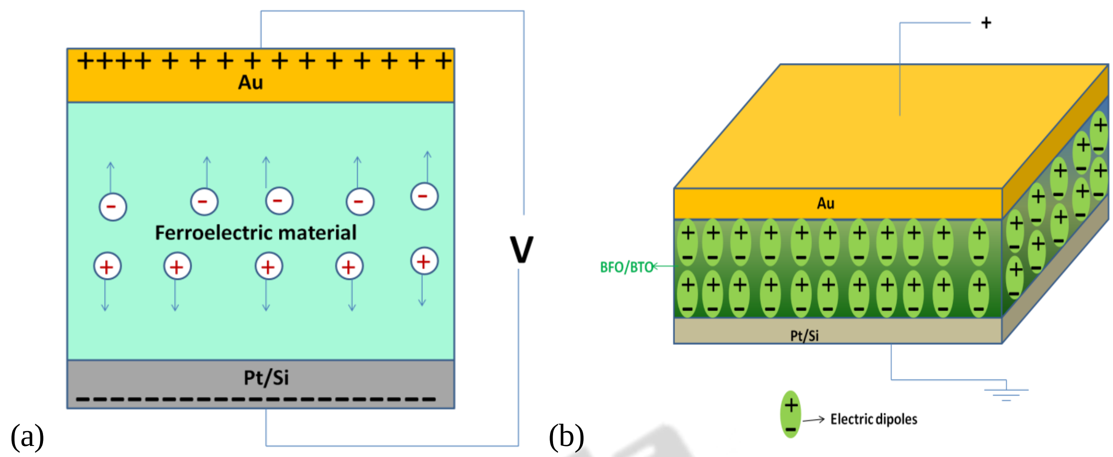

Figure 2: Schematic illustration of mechanism of photovoltaic effect in ferroelectric thin film.

The output signal of solar cell made up of ferroelectric material can be tuned by various other means including mechanical, electrical and magnetic functionality. Designing of materials having enhanced magnetoelectric (ME) properties can be achieved using the principle of strain engineering employed to multiplayer structures and superlattices (SLs). In this regard, recent study of a number of multilayer heterostructures containing alternating ferroelectric and multiferroic layers, such as $Pb(Zr,Ti)O_3/CoFe_2O_4$, $BiFeO_3/BaTiO_3$, $(Bi,Nd)FeO_3/(Ba,Sr)TiO_3$ etc. has been useful in observing the enhanced ME properties.

3. Conventional p-n junction based photovoltaics Vs. Ferroelectric Photovoltaics

Charge carriers (electron-hole pairs) are generated when a ferroelectric material is illuminated with a light of wavelength corresponding to its energy band gap (E_g). A photovoltaic output is generated when the photo generated carriers are separated and driven to the electrodes by the polarization induced by the internal electric field (Fig. 3). On the other hand, for a junction-based semiconductor photovoltaic device, the charge carriers are separated by the electric field which exists in the depletion layer at the p-n junction interface (Fig. 3). Thus, in ferroelectrics the photovoltaic effect is a bulk-based effect, which is different from the junction-based semiconductor photovoltaic effect. In ferroelectric photovoltaic, the PV responses can be generated without forming complex p-n junction structures since the internal electric field is not limited to an interfacial region. A simplified schematic of this mechanism in conventional semiconductor p-n junction and ferroelectrics photovoltaic is shown in figure 3 (a and b).

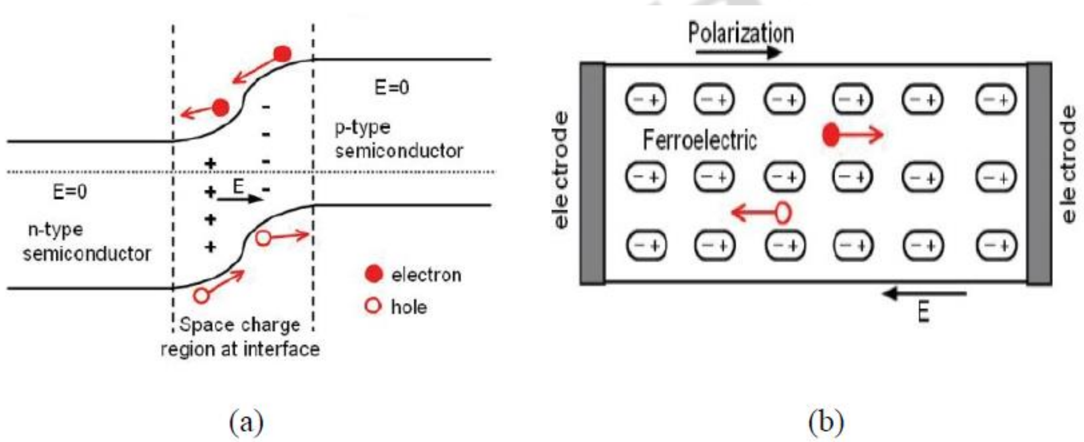

Figure 3: *Simplified schematics of PV mechanism in (a) semiconductor p-n junction and (b) ferroelectric thin film.*

4. History and current status of ferroelectric PV

The photovoltaic effect in ferroelectric ceramics (bulk) and single crystals such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $LiNbO_3$ were observed earlier. The non-centrosymmetric nature of the unit cell gives rise to this effect. However, owing to small current densities of the order of nano-amperes/cm^2 due to large band gaps in the ferroelectric materials, the photovoltaic efficiency was limited. Observation of photo voltage larger than the band gap in thin films of Bismuth ferrite ($BiFeO_3$) lead to a renaissance of research in photovoltaic ferroelectric materials (FE-PV). An open circuit voltage (V_{oc}) of ~20V was reported for $BiFeO_3$ thin film, which have a band gap (E_g) of 2.67 eV. It was further shown that the photo voltage could be enhanced or reversed by controlling the ferroelectric polarization which in turn is controlled by electrical poling in lead based thin films. Poling is 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. Poling results in orienting the ferroelectric domains in one particular direction, leading to maximum polarization. The internal polarization (PS) is not uniform throughout a ferroelectric. For instance, at the surfaces the crystal terminates and polarization becomes zero and, in the neighborhood of defects, the value of PS may differ from that of the perfect crystal. This variation in PS gives rise to depolarizing field. This field can be compensated by the flow of free charge in the crystal or by the free charge in the surrounding medium at the crystal surface. The depolarization field energy (WE) is zero for a totally compensated crystal in equilibrium. However, for insulators this is not readily attained.

Ferroelectric materials, which exhibit strong bulk photovoltaic effect, have been widely explored since 1956 for harvesting light energy. Compared to other ferroelectric materials like $BaTiO_3$, $LiNbO_3$, $PbTiO_3$, $(PbLa)(ZrTi)O_3$ with a wide energy band gap, the smaller band gap of $BiFeO_3$ (2.2 - 2.8 eV) can generate a significant current in response to the interaction with visible light photons coming from sun, as an abundant renewable clean energy. The above mentioned discussion clearly point towards the advantages of ferroelectric materials which crystallizes in the perovskite structure and are compatible with many other functional compounds such that their ferroic property and electric behaviour can be tailored for the desired photovoltaic applications.

5. Advantages of Ferroelectric Photovoltaic effect

1. In ferroelectric photovoltaic, the PV responses can be generated without forming complex p-n junction structures since the internal electric field is not limited to an interfacial region.
2. Extremely large photo-voltage. V_{OC} is not restricted to the energy barrier (energy band gap). As a result, the photo voltage observed here is significantly higher than the electronic band gap.
3. The output signal of solar cell made up of ferroelectric material can be tuned by various other means including mechanical, electrical and magnetic functionality.
4. Oxide materials are cheap, abundant, stable, highly light absorbing and their properties such as band gap and conductivity can be systematically tuned through chemical substitutions, making them promising candidate for thin film ferroelectric photovoltaics.
5. The photo-voltage can be enhanced or reversed by controlling the ferroelectric polarization which in turn is controlled by electrical poling in lead based thin films.
6. Ferroelectric materials are compatible with many other functional compounds such that their ferroic property and electric behaviour can be tailored easily for the desired photovoltaic application.
7. The composite/ multilayers of multiferroic materials exhibit larger ME effect as compared to single phase materials, and thus can be exploited for magnetic field controlled photovoltaics with added functionality.
8. By using suitable ferromagnetic electrodes and clever design of the device structure, it may also be possible to control the spin polarization of the output photocurrent favoring device

miniaturization with novel applications such as optical micro-sensing, light controlled elastic micro-motion and micro-actuation in micro-electro-mechanical systems.

9. Exploitation of suitable ferroelectric materials having narrow-band gap useful for visible region are promising for their potential application in both the novel optoelectronic and the solar energy devices making them multifunctional.

Disadvantages of Ferroelectric Photovoltaic effect

1. The main limitation of using ferroelectric thin films for photovoltaic applications is its leakage current that degrades its multiferroic and hence PV properties.
2. One major obstacle in achieving high conversion efficiency in ferroelectric phtotovoltaics is the intrinsically low bulk conductivity of ferroelectric domains.
3. The large energy band gap of ferroelectric materials allows strong absorption of light in UV region only.
4. The internal polarization (PS) is not uniform throughout a ferroelectric. This variation in PS gives rise to depolarizing field.