INTERNATIONAL RESEARCH JOURNAL ON ADVANCED SCIENCE HUB
e-ISSN : 2582 - 4376
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Recent Developments on Ferroelectric PZT-Photovoltaics

Vivek Kumar[1], E. Bhawani[2], T. Babu[3], Balgovind Tiwari[4], R.N.P. Choudhary[5]
[1]*Assistant Professor, Dept. of Chemical Engineering, IIIT-RKValley, RGUKT, A.P., India*
[2]*Mentor, Dept. of Physics, IIIT-RKValley, RGUKT, A.P., India*
[3]*Teacher, Dept. of Physics, Sri Chaitanya High School, Vempalli, Kadapa, A.P., India*
[4]*Assistant Professor, Dept. of Physics, IIIT-RKValley, RGUKT, A.P., India*
[5]*Professor, Dept. of Physics, ITER-SOA University, Bhubaneswar, Orissa, India*
balgovindtiwari@gmail.com[4]

Abstract

The silicon based solar cells are expensive, and also said to have limited power conversion efficiency. Though a lot of organic, inorganic and organic-inorganic hybrid solar cells were developed, they could not sustain in long run. This has open doors for the development the ferroelectric based solar cells/photovoltaics. Because the ferroelectric based photovoltaics show high open circuit voltage, short circuit current/current density, unlimited power conversion efficiency, tunable bandgap, high polarization properties, etc. The main reason to shift the focus from semiconductor solar cells is,the ferroelectrics are said to be stable under changing environmental conditions. In addition, such materials help to develop thinner solar cells devices with low cost. Hence, an attempt has been made to understand the photovoltaic response of ferroelectric lead zirconate titanate (PZT). In this paper, we report the review on the photovoltaic properties of PZT films. The literature was collected from various internet sources.

Keywords: **PZT; Photovoltaic; open circuit voltage; short circuit current;**

1. Introduction

Among the sources of renewable energy, sunlight/solar energy is one of the significant and prominent renewable energy source. Since the consumption of electricity is increasing continuously, it is worth to use the renewable energy sources (specifically solar energy) to produce the electricity. For the conversion of solar energy into electrical energy, several solar cells and photovoltaic devices have been developed. They are semiconductor solar cells (e.g. Si/Ge/GaAs, etc.), perovskite solar cells, halide perovskite solar cells, organic solar cells, hybrid solar cells (inorganic-organic), ferroelectric photovoltaics, etc. To understand the photovoltaic response of ferroelectric materials, it is good to understand the basic terminology related to photovoltaics [1-3].

1.1 Basic Terminology

***Ferroelectrics*:** A class of materials that show the presence of polarization when the applied ac electric field is reduced to zero. Examples include PZT, PLZT, $BiFeO_3$, $CaTiO_3$, $BaTiO_3$, etc.

***Photovoltaics*:** Devices that is capable of converting the light (photons) into electricity (electrons). Examples include silicon/ germanium/ gallium arsenide solar cells, etc.

***Photo-ferroelectrics*:** Ferroelectrics that is capable of converting the light (photons) into electricity (electrons). For instance, PZT in thin film form.

***Photocurrent/short circuit current*:** The amount of current generated by a material when light falls on it i.e. the flow of photon induced negative charge carriers and holes, towards the respective electrodes is known as photocurrent (J_p) or short circuit current (I_{sc}).

***Open Circuit Voltage*:** It is the voltage developed across a solar cell when there is no flow of current

i.e. the terminals of a solar cell are open. It is denoted by V_{oc}.

***Photo-conversion efficiency (PCE)*:** It is the ratio of output power (P_{out}) to the input power (P_i), where P_{out} is the product of V_{oc} and J_p. Therefore,

$$PCE = \frac{V_{oc} \times J_p \times \text{fill factor}}{P_i}.$$

1.2 Understanding the Photovoltaic Response of Ferroelectrics

Photoferroelectrics are the materials with the combined property of ferroelectricity and photovoltaicity. Ferroelectrics contain domain walls based on the directions of polarizations. Hence, the photovoltaic effect is due to the possible separation of electrons and holes at domain walls. When external field is applied to the ferroelectric, all the dipoles start orienting in the direction of field and hence the net dipole moment is produced. The regions across the crystal contain different dipoles oriented in different directions, called domains. These domains are assumed to be separated by domain walls. When an ac electric field is applied externally, the domain polarize in the direction of applied field. When all the domain are polarized in the direction of field, material shows maximum polarization i.e. saturated polarization. When the field is reduced to zero, there will be still some polarization within the material. This kind of polarization, in the absence of field, is called remanant polarization (P_r).

Photovoltaicity can be described in two different mechanisms. One is the generation of electrons and holes, in semiconductors/dyes, with the absorption of light (photons). Other is the separation of electron and hole pairs, by the built in electric field (also called as the depolarization field). Basically, the operation/functioning/performance of photoferroelectrics can be assessed/judged by the ability of light absorption, P_r, V_{oc}, I_{sc}, depolarization field, type of poling, etc. The intense interest in ferroelectric based photovoltaics is due to the fact that the semiconductor based photovoltaics show limited V_{oc} [4].This could be easily overcome by the photoferroelectrics.

The photo-ferroelectric structure can be visualized, as shown in figure 1. The ABO3 strucutre of PZT can be found in one of or report [5]. The structure is as follows: electrode-Ferroelectric layer-electrode, where one will be the top electrode and other will be the bottom electrode. Poling can be done in two ways. One is applying the voltage to bottom electrode, usually known as positive poling. Other is applying the voltage to top electrode, usually known as negative poling [4].

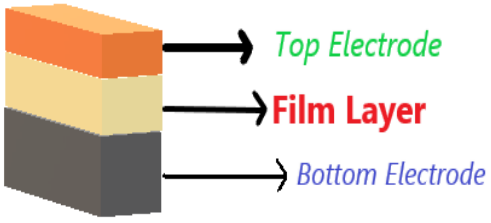

Fig. 1. Normal structure of Photo-Ferroelectric

In the structure, ferroelectric layer is responsible for the generation of electrons and holes. Also, it could produce an internal electric field (also called as depolarization field) which will be helpful in the separation of electrons and holes. Though they generate high open circuit voltages, the current induced by photons is observed to be very small. So, the performance of photoferroelectric devices should be enhanced to make them efficient and effective [4].

In this report, we report the review on photovoltaic performance of ferroelectric PZT based photovoltaics. The photovoltaic properties such as V_{oc}, and I_{sc} are summarized in numerous tables, for PZT of different compositions, and different structures. Because the structure can be changed with change in metal electrode, and hence altering the photovoltaic response. The metal electrodes, used mostly, are gold, platinum, silver, etc. One of the most used bottom electrode is In_2O_3 (ITO) substrate. The main reason of choosing the PZT is, it is one of the most widely used and investigated ferroelectric material.

2. Discussion and Analysis

One of the prominent source of electricity is found to be the conversion of solar light/energy [6]. The conversion is commercially employed with silicon solar cells. But later, photovoltaic effect has been discovered. This has open new doors for the development of stable solar cells. Especially, the perovskite compounds such as barium titanate ($BaTiO_3$), lithium niobate ($LiNbO_3$), bismuth ferrite ($BiFeO_3$), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), bismuth neodymium titanate, etc [6-7]. Even, solar cells based on thin films were fabricated, by depositing

ferroelectrics on semiconductors. Silicon (Si), silicon oxide (SiO_2) and gallium arsenide (GaAs), etc. layers were used for the deposition purpose. Hence, the solar cells based on heterojunctions i.e. ferroelectric/semiconductor junction, were successfully fabricated [6]. As compared to Si deposition layers, GaAs layers are quite good in terms of bandgap (i.e. narrow), optical transparency, high mobility, etc [6]. The solar cell efficiency can be defined with the amount of power conversion efficiency (PCE). Hence, several attempts were made to enhance the PCE of ferroelectric/semiconductor heterojunctions.

In one of the work [6], a famous ferroelectric, PZT of 52/48 ratio has been deposited on GaAs substrate through laser molecular beam epitaxy. The buffer layer used is strontium titanate ($SrTiO_3$). The electrical characteristics (i.e. polarization properties) were investigated for the as prepared compound. Generally, PZT of 52/48 composition shows large values of polarization. In this work, also large value of remanant polarization (P_r) is achieved i.e. 46 $\mu C/cm^2$. This may be due to the method of preparation. Before recording the photovoltaic response, the samples were poled. It has been observed that the magnitude of short circuit current (I_{sc}) is 3.8 mA/cm^2 and 52 mA/cm^2, when sample is poled positively and negatively respectively. The magnitude of PCE is around 20%.

In another work [7], PZT was prepared by sol-gel method, and it has been deposited on In_2O_3:Sn (ITO) glass substrate. Then on PZT, a film made up of amorphous silicon was deposited. The whole sample can be thougjt of as an amorphous silicon/PZT/ITO glass sample (as shown in figure 2). The magnitude of I_{sc} of the sample is observed to be 2.56 mA/cm^2. The low magnitude of I_{sc} is may be due to its large bandgap that is approximately 3.6 eV. Hence, PZT solar cells can absorb only the ultraviolet radiation of light.

A work, on PZT in 2013, revealed the ferroelectric, current density, and photovoltaic properties [8-15]. PZT was first prepared through a standard sol-gel method. Through sputtering, metals such as platinum, gold, copper and silver were deposited on PZT film. ITO quartz substrate has been used as the bottom electrode (refer figure 3).

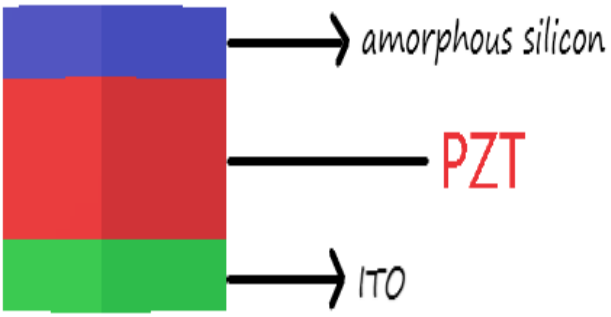

Fig. 2. Illustration of amorphous silicon /PZT /ITO glass sample

Fig. 3. Illustration of Metal/PZT/ITO quartz sample (X = Platinum/Gold/Copper/Silver)

In these kind of structures, photocurrent (J_p) is induced mostly between the interface of ITO-quartz and PZT. Because, under the illumination of light, the holes tend to move towards the bottom electrode and the electrons tend to move towards the top electrode. So the J_p of PZT is limited because the light induced electrons will be forced to leave the top electrode, and hence the electrons will be expelled to PZT film. The nanoparticles such as gold and silver, introduced in a semiconductor, are referred as surface Plasmon structures. Because they can enhance the photovoltaic properties of materials. So the surface Plasmon structure actually refer to the excitement of free electrons between the interface of a metal and dielectric. Hence, an attempt has been made in the work addressed above, to investigate the photovoltaic properties of ITO-quartz/PZT film/surface Plasmon. The ferroelectric properties are summarized in table 1.

Table.1. Ferroelectric Properties of ITO-quartz/PZT film/surface Plasmon

S.No.	Sample	P_r ($\mu C/cm^2$)	Ref.
1.	ITO-PZT-platinum	54.6	8
2.	ITO-PZT-gold	51.8	
3.	ITO-PZT-copper	48.0	
4.	ITO-PZT-silver	42.3	

The low value of P_r of ITO-PZT-silver is due to its low work function i.e. 4.26 eV. The PV properties are shown in table 2.

Table.2. Photovoltaic Properties of ITO-quartz/PZT film/surface Plasmon

S.No.	Sample	I_{sc} (mA/cm^2)	V_{oc} (V)	Ref.
1.	ITO-PZT-platinum	0.09	0.63	8
2.	ITO-PZT-gold	0.26	0.69	
3.	ITO-PZT-copper	0.14	0.82	
4.	ITO-PZT-silver	1.22	0.78	

One can infer from the table that, ITO-PZT-copper structure shown high V_{oc} whereas ITO-PZT-silver structure has shown high I_{sc}. Due to increasing requirement of electrical energy, solar energy conversion can be one of the key process. Hence various researchers and scientists, across the world, are inventing and investigating the novel materials for photovoltaic devices. Among those novel materials, ferroelectrics are also a part. Numerous studies have been done to investigate the ferroelectric photovoltaic properties, as we have presented in the aforementioned discussion. A material, PLZT, has been synthesized by depositing on ITO substrate [4-10]. Metals such as magnesium, silver and platinum have been used as the top electrodes. The device can be visualized as shown in figure 4. The ferroelectric properties are given in table 3 (values were estimated from the polarization hysteresis loop).

ITO-PLZT-Magnesium sample has been characterized photovoltaically, by radiating UV light on ITO and magnesium in one and the other case respectively. The V_{oc} and J_{sc} are 8.34 V and 3.25 nA/cm^2 respectively, when ITO electrode was radiated. When light was illuminated on magnesium electrode, the V_{oc} and J_{sc} are 3.58 V and 1.08 nA/cm^2 respectively.

Fig. 4. Illustration of Metal/PLZT/ITO sample (X = Magnesium/Platinum/Silver)

Table.3. Ferroelectric Properties of Metal/PLZT/ITO sample (X = Magnesium/Platinum/Silver)

S.No.	Sample	P_r ($\mu C/cm^2$)	Coercive field (kV/cm)	Ref.
1.	ITO-PLZT-Magnesium	42	20	4
2.	ITO-PLZT-Silver	40	20	
3.	ITO-PLZT-Platinum	50	22	

Summary of photovoltaic properties of similar PZT photovoltaic (FEPV) materials are summarized in table 4.

Recently in 2018 [18], PZT based composites were prepared in the form of films. The composite prepared is PZT/CuO film. The device structure is as shown in figure 5.

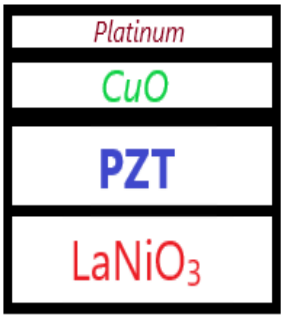

Fig. 5. Illustration of $LaNiO_3$/PZT/CuO/ Platinum (a composite film)

Table.4. Photovoltaic Properties of PZT based Photovoltaics

S.No.	FEPV	I_{sc} ($\mu A/cm^2$)	V_{oc} (V)	Ref.
1.	Platinum-PZT-Platinum (52/48)	0.03	0.8	9
2.	ITO-PLZT-Platinum	0.86	1700	10
3.	Gold-PL(Tungsten)ZT-gold	7.0	-	11
4.	Gold-PL(Tungsten)ZT-gold	0.6	-	12
5.	Niobium: strontium titanate-PLZT-LSM	0.7	0.8	13
6.	Platinum-PZT-Platinum (20/80)	-	8	14
7.	ITO-PZT/copper II oxide-Platinum	0.6	4800	15
8.	ITO-PZT-ITO (53/47)	0.45	0.006	16
9.	ITO-PLZT-Magnesium (52/48)	8.34	3.25	4
10.	PZT (52/48) thin film	-0.7	2	17

The properties of the composite are shown in table 5.

Table.5. Ferroelectric and Photovoltaic Properties of $LaNiO_3$/PZT/CuO/Platinum (a composite film)

S.No.	Property	Value	Ref.
1.	Pr ($\mu C/cm^2$) ($LaNiO_3$/PZT/Pt)	53.21	18
2.	Pr ($\mu C/cm^2$) ($LaNiO_3$/PZT/CuO/Pt)	72.48	
3.	Coercive voltage (V) ($LaNiO_3$/PZT/Pt)	7.79	
4.	Coercive voltage (V) ($LaNiO_3$/PZT/CuO/Pt)	5.20	
5.	V_{oc} (V) ($LaNiO_3$/PZT/Pt)	0.248	
6.	V_{oc} (V) ($LaNiO_3$/PZT/CuO/Pt)	0.27	
7.	I_{sc} (mA/cm^2) ($LaNiO_3$/PZT/Pt)	-0.0045	
8.	I_{sc} (mA/cm^2) ($LaNiO_3$/PZT/CuO/Pt)	-0.027	
9.	PCE ($LaNiO_3$/PZT/Pt)	2.79×10^{-6}	
10.	PCE ($LaNiO_3$/PZT/CuO/Pt)	1.82×10^{-5}	

In another work [16-19], PZT was also used as an electron extraction material for stable halide perovskite solar cells. Generally, halide perovskite solar cells use semiconducting oxides as electron extraction/transport materials. So the stability of solar cell gets reduced over the time, because of the defects. But the usage of PZT, as an electron extraction material, helps in the creation of dipole defects. These defects result in the separation of photon charge carriers, providing the stability to halide perovskite solar cells [19]. The halide perovskite solar cells are said to have the PCE of around 22.7%.

The photovoltaic response of 20/80 PZT films were prepared through radio frequency (RF) sputtering [20]. The as prepared films were deposited on ITO glass substrate. The diameter of

the sample is around 50 mm. The structure of the device is as follows: gold-PZT-ITO glass (refer figure 6).

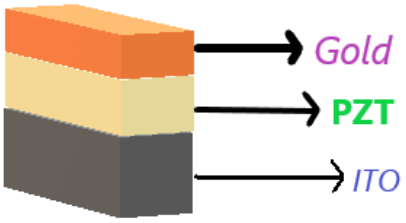

Fig. 6. Illustration of Gold/PZT/ITO glass

The sunshine was illuminated on the bottom electrode i.e. ITO glass. In this work, an attempt has been made to correlate the photovoltaic response with ferroelectric response. The photocurrent shows hysteresis behavior, with respect to the poling electric field [20].

A capacitor structure, Sn: ITO/PZT/Platinum, has been developed for transparent solar device [21,22]. The preparation has been done through solution process, because it is one of the cost effective method. The thickness of the platinum and PZT layers are around 5 nanometers and 100 nanometers respectively. The P_r of the materials is nearly 40 $\mu C/cm^2$. It very high compared to polycrystalline PZT films whose P_r is between 15-30 $\mu C/cm^2$. The coercive voltage of the as prepared capacitor is nearly 3 volts. The photovoltaic properties of as prepared capacitor structure, and other capacitor strucutres are given in table 6.

Table.6. Photovoltaic Properties of PZT based Capacitor Structures

S.No.	Structure	V_{oc} (V)	Isc ($\mu A/cm^2$)	Ref.
1.	ITO-PZT-Pt-ITO	-0.62	0.6	21
2.	Pt-PLZT-Pt	0.17	0.64	22
3.	Al-PLZT-Pt	0.37	3.6	22
4.	ITO-PZT-ITO	-0.45	0.6 (pA)	16

Conclusions

Based on the review that has been done in this work, the following conclusions and recommendations have been made:

- The photovoltaic response of PZT depends on top metal electrode, bottom electrode, and composition of PZT.
- The output response of PZT photovoltaics is dependent on the illumination of light on bottom electrode also, not just top metal electrode.
- It has been identified that, PZT which shows high polarization exhibit good photovoltaic properties.
- The giant open circuit voltage (1700 V) has been observed for ITO/PLZT/Pt structure.
- It recommended to prepare and characterize the PZT on different substrates, and with different other metal electrodes.

Acknowledgement

We thank the partial financial support of DST-SERB.

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