Chapter 8

Comprehensive Study on Piezo-Phototronic Effect: Way Forward for Ferrite Based Solar Cells

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Abstract

The wurtzite structured materials possess the inner-crystal piezopotential which comprehensively tune or control the charge carrier generation, separation, transportation, and recombination in optoelectronic devices. The piezo-phototronic effect provides a new working principle to the current traditional devices. Its effect on solar cells progresses made by the eminent scientists, and researchers in the field of piezo-phototronic modulated solar cells such as semiconductor-based, perovskite-based, multiple quantum-well (MQW) based and core/shell based. It has been described that the piezo-phototronic effect has improved the power conversion efficiency (PCE) of the solar cells, and the effect of temperature on the piezo-phototronic devices. Ferrite-based materials have emerged as a viable candidate for use in solar cells. As a result of this research, ferrite-based nanomaterials can now be used in solar cell applications, as well as the piezophototronic effect on these materials can be investigated. The piezo-phototronic effect is a novel subject that offers a new platform for material science and electronics to investigate.

Keywords

Wurtzite, Piezopotential, Piezo-Phototronic Effect, Multiple Quantum-Well, Power Conversion Efficiency

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1. Introduction

Perovskite structured materials such as Lead zirconate titanate $\text{Pb}(\text{Zr Ti})\text{O}_3$, Rochelle salt, Topaz, Tourmaline, Cane sugar, Berlinite (AlPO_4), Barium Titanate (BaTiO_3), Lead Titanate (PbTiO_3), Lithium Niobate (LiNbO_3) are of great interest in sensors, energy harvesting, and energy generation [1]. Their significant piezoelectric coefficient makes them act as an insulator. Hence, they are studied in the ceramic community [2, 3]. For electronic and photonic applications like energy harvesters, photodetectors, solar cells,

etc., Wurtzite structured materials such as ZnO, ZnS, GaN, InN CdS, etc. are gaining much attention, because of their small piezoelectric coefficient and exceptional optical, electrical and piezoelectric properties. Prof. Zhong Lin Wang introduced the concept of coupling between piezoelectric, semiconducting, optical properties of the material, and named it as a piezo-phototronic effect (Figure 1) and its applications in energy science [4, 5]. The piezo-phototronic effect explicitly supports the phenomenon of charge generation, separation, transportation, and recombination, and comprehensively modulates or tunes these processes by the induced inner crystal piezoelectric potential as a gate voltage [6-8]. This effect has propounded the concept of new technology with significant improvement in optoelectronic devices such as solar cells, photodetectors, light emitting diodes, etc. Which are called piezo-phototronic devices? The piezo-phototronic effect has shown much technological advancement for traditional devices by improving their performance. The interest of researchers in the piezo-phototronic effect is growing day by day. Figure 2 provides the data of several publications from 2010 to 2019 (March) related to this stipulated effect. The popularity of the piezo-phototronic effect is extraordinarily increasing and has paved the way to explore new technologies in the field of optoelectronics, renewable energy, electronics, etc. There are various compositions of materials on which the piezo-phototronic effect has been studied for different applications as shown in Table 1. This table gives an idea about the materials which comes under the purview of the piezo-phototronic effect, and the basic parameters that are required to study this effect. Moreover, an effort has been made to summarize almost all the materials with their applications.

This work is split into four extensive sections. First, is the recent progress made by the piezo-phototronic effect, and the different materials used so far. Second, the underlying theory, and fundamental concepts of piezo-phototronic effect. In the third section, we have focused on the fundamentals of piezo-phototronic effect modulated solar cells, the tremendous progress made by various researchers and eminent scientists on different types of solar cells. At last, a brief description to show the dependence of the piezo-phototronic effect on temperature has been conveyed.

2. Piezo-phototronic effect on ferrites

Among all the ferrites, BiFeO₃ is one of the most prominent material on which piezo-phototronic effect has been studied so far. BFO has aroused great interest in the past few decades due to its visible light photovoltaic effect, multiferroic properties at room temperature and related potential applications. BFO thin films have the advantage of low cost and accuracy to control the chemical components. As far as other ferrites are concerned, Ba-doped zinc ferrite is again an interesting candidate for photovoltaic

applications. But there is no literature available of piezo-phototronic effect on ferrites other than BFO for solar energy applications.

Figure 1: Schematic diagram showing the three-way coupling of piezoelectricity, photoexcitation and semiconducting effect which gives rise to piezo-phototronic [9].

Figure 2: Number of publications piezophototronics has produced from its commencement.

Table 1: This table signifies some of the materials on which piezo-phototronic effect has been studied.

S.No	Composition/material	Application	Reference
1.	CH ₃ NH ₃ PbI ₃ /ZnO nanowires	Perovskite solar cells	[10]
2.	GaN/ZnO naowire	The led-based pressure sensor array	[11]
3.	InGaN/GaN SQW heterostructure membrane	Direct lift off and piezo-phototronic study	[12]
4.	ZnO flexible thin film	UV photodetectors	[13]
5.	MoS ₂ single layer	NO ₂ sensor	[14]
6.	CdTe microdots	Photodetectors	[15]
7.	CdTe nanowires	Photodetectors	[16]
8.	Cu(In, Ga)Se ₂ (CIGS) heterostructure	Flexibl heterostructured photdetectors	[17]
9.	Si/ZnO/PEDOT: PSS tri-layer heterostructure	Photodetectors using both positive and negative piezo charges	[18]
10.	WSe ₂ -CdS	Flexible Photodetector	[19]
11.	TiO ₂ /BaTiO ₃ /Au heterostructure	Photodynamic bacteria killing and wound healing	[8]
12.	CH ₃ NH ₃ PbI ₃ single crystal	Photodetectors	[20]
13.	Ga ₂ O ₃ -ZnO heterojunction microwire	Deep UV light photodetectors	[21]
14.	MoS ₂ /WSe ₂	Strain tunable van der waals photdiodes	[22]
15.	ZnO based Cu(In, Ga)Se ₂ heterostructure	Flexible solar cells	[23]
16.	Si/CdS	Self-powered flexible photodetectors	[24]
17.	Ag/ZnO nanotetrapods	Piezo photocatalytic activity	[25]
18.	Si microwires/ZnO nanofilms	Flexible light emitting diodes	[26]
19.	n-ZnO/p-NiO films	Photodetectors	[27]
20.	GaN microwires	UV Light Emitting Diodes	[28]
21.	p-Si/n-ZnO	Visible NIR broadband photodiodes	[29]
22.	CdS _x Se _{1-x} nanowires	Photosensors	[30]
23.	CdS/P3HT microwires	Self-powered UV/Visible/NIR photodetectors	[31]

24. ZnO/ZnS core/shell nanowires	Electrical transport and photo sensing application	[32]
25. p-CuO/n-MoS ₂ heterostructure	Photodetector with enhanced photoresponse	[33]
26. ZnO/P3HT	Solar cells	[34]
27. CdSe nanowires	Photodetectors	[35]
28. BiFeO ₃ /ZnO	Photovoltaics	[36]
29. BiFeO ₃ /TiO ₂	Photocatalytic activity	[37]
30. Ni-(Ba,Gd)FeO ₃	Dye sensitized solar cells	[38]

Figure 3: Piezopotential in Wurtzite crystal: atomic model of ZnO crystal [42].

3. Theory of piezophotonics

To discuss the structure and piezopotential generated in Wurtzite family we have used the structure of ZnO. It is an II-VI compound semiconductor. Its ionicity resides at the borderline between the covalent and ionic semiconductors. It is non-centrosymmetric and has a hexagonal structure with a large anisotropy in c-axis or perpendicular to c-axis, which gives rise to piezoelectricity. In a single unit cell of ZnO, Zn²⁺ and O²⁻ ions are tetrahedrally co-ordinated at the corners of a tetrahedron with lattice parameters a and c in ratio $\frac{c}{a} = 1.633$, and the centre of two ions overlap with each other, due to which it is

non-polarized in stress-free condition [39]. When we apply the stress on the apex of the unit cell, the center of two charges gets separated, results in the dipole moment as shown in Figure 3. Valuable addition of all these tiny dipoles results in a potential macroscopic drop in the direction of applied stress. This is piezoelectric potential or piezopotential [40, 41]. This piezopotential in the crystal is created by the non-mobile and non-annihilative ionic charges, and its magnitude depends upon the stress applied.

Lippman theory has been used to calculate the distribution of piezopotential in deformed ZnO crystal [43]. Following formula has been used to calculate the piezopotential on the surface of the whole material, i.e. nanowire.

$$\phi_{\max}(T, C) = \pm \frac{3}{4(K_0 + K_{\perp})} [e_{33} - 2(1 + \nu)e_{15} - 2\nu e_{15}] \frac{a^3}{l^3} \nu_{\max} \quad (1)$$

Where $\nu_{\max}$ is the maximum deflection of the nanowire tip; ν is the Poisson's ratio, $K_{11} = K_{22} = K_{\perp}$, K_0 is the permittivity in a vacuum, T is the tensile side, C is the compressive side. Also, the Finite Element Analysis (FEA) has been used to investigate the piezoelectric and to depict the motion of charge carriers [44]. Two typical configurations have been used to investigate the distribution of piezopotential; transversely deflected nanowires, and the axially strained nanowires. The transversely deflected nanowires usually are utilized in energy harvesting applications [45], while axially strained nanowires are used in piezotronic applications on flexible substrates [46].

The piezophototronic effect is predominantly described by the semiconductor and piezoelectricity in the form of electrostatic equations, current density equations, continuity equations, and piezoelectric equations. The electrostatic behaviour of the charges in the piezoelectric semiconductors is described by Poisson's equation [47].

$$\nabla^2 \psi_i = \frac{\rho(r)}{\epsilon_s} \quad (2)$$

Where ψ_i is the electric potential distribution, $\rho(r)$ is the charge density distribution and ϵ_s is the permittivity of the material. The drift and diffusion current density equations that correlate the local fields charge densities and local currents are given by the following equations [47].

$$\begin{aligned} J_n &= q\mu_n nE + qD_n \nabla n \\ J_p &= q\mu_p pE - qD_p \nabla p \end{aligned} \quad (3)$$

moreover, the total current density of electrons and holes is given by,

$$J = J_n + J_p \quad (4)$$

Where, μ_n and μ_p , D_n and D_p are the charge mobility, diffusion coefficient of electrons and holes respectively. The charge transport under the driving of a field is described by the continuity equations [47],

$$\begin{aligned} \frac{\partial n}{\partial t} &= G_n - U_n + \frac{1}{q} \nabla \cdot J_n \\ \frac{\partial p}{\partial t} &= G_p - U_p - \frac{1}{q} \nabla \cdot J_p \end{aligned} \quad (5)$$

Where, G_n and G_p are the generation rates of electrons and holes. U_n and U_p are the recombination rates of electrons and holes respectively. Also, we know that the piezoelectricity is the predominant factor in piezo-phototronic, so the relationship between polarization and mechanical strain is given by [48] $(P)_i = (e)_{ijk} (S)_{jk}$ where $(e)_{ijk}$ is the third order piezoelectric tensor, and mechanical strain is given by $(S)_{jk}$. These basic equations will be used for discussing the p-n junction or Metal-semiconductor junction with applied compressive stress or tensile strain.

4. Bandgap modulation by the piezo-phototronic effect

The p-n junction within the same crystal forms the homojunction, whereas two different crystals form heterojunction [49]. This heterojunction may form p-n junction or metal-semiconductor contact. This signifies that bandgap alignment becomes more critical [50]. In the upcoming section, a brief description has been given to elaborate on how piezopotential or a piezo-phototronic effect modulates or control the band gap of p-n junction or metal-semiconductor contact.

4.1 Modulation of p-n junction

A p-type and n-type semiconductor formed a junction where the holes of p- side, and electrons of n- side, diffused across the junction and redistribute to balance the local potential. They tend to reach thermal equilibrium. The inter-diffusion and recombination of the electrons and holes formed a charge depletion zone which was carrier free [51]. This carrier free zone significantly increases the piezoelectric effect, because of the preservation of piezo charges. Let n-side is piezoelectric then local net negative piezo-charges remained preserved at the junction when the compressive strain was applied on it. The piezopotential on the piezoelectric side (n-side) tended to raise the local band and

introduced a gradual slope to the band structure (shoulder like structure) [9]. Further, the direction of the strain was reversed, the piezo charges at the interface created the downward bending in the local band. The modification of the local band at the junction introduced a significant change in the local band structure. This modification in the local band was effective for trapping the holes so that the $e^- - h^+$ separation rate was effectively enhanced. Furthermore, the slow slope tends to change the mobility of the carriers moving towards the junction [51]. For a p-n junction of two distinct materials with different band gaps, local piezo charges have affected the band profile and the transportation of charge carriers across the interface [52]. For p-n junctions, Shockley theory gave the fundamentals of I-V characteristics [53]. Schematic energy band diagram of the p-n junction has been shown in Figure 4.

Figure 4: Schematic energy band diagram of the p-n junction. The red curve shows the deformation of the energy band under strain. (a) during the compression a gradual slope can be observed, (b) during the tensile strain sharp decline in the energy band can be observed [54].

The n-type is considered piezoelectric and p-type as non-piezoelectric. Then the built-in-potential is given by the expression,

$$\psi_{bi} = q.(2\varepsilon_s)^{-1}[N_A W_{Dp}^2 + \rho_{piezo} W_{piezo}^2 + N_D W_{Dn}^2] \quad (6)$$

Where, N_D and N_A are the donor and acceptor concentration respectively W_{Dp} and W_{Dn} are the width of the depletion layer in p-side and n-side respectively, ρ_{piezo} is the density of polarization charge, W_{piezo} is the width of distribution zone of the piezo charges at the interface, ε_s is the relative dielectric constant [55]. It was observed from the above-stated equation that piezo-charges has a precise effect on built-in-potential. Thus, it can be modulated by induced strain. The total current density of p-n junction, where the n-type side has an abrupt junction with the donor concentration N_D , is given by,

$$J = J_{C0} \cdot \exp[q^2 \rho_{piezo} W_{piezo}^2 (2kT\varepsilon_s)^{-1}] \cdot \exp[qV.(kT)^{-1} - 1] \quad (7)$$

J_{C0} Is the saturation current density with the absence of piezopotential [55]. Thus, it was concluded that current transport across the p-n junction largely depends upon the exponential of piezo-charges so current transportation can be modulated by the piezopotential that is the magnitude and polarity of the strain.

4.2 Modulation of metal-semiconductor contact

For semiconductor electronics and optoelectronics, the Metal-Semiconductor contact is a basic structure [56]. When metal –semiconductor (M-S) contact takes place, redistribution of charges occurs across the interface due to the overlapping of wave functions of both the metal and the semiconductor [57, 58]. At the equilibrium, the Fermi level gets aligned on each side of the interface which results in the introduction of an energy barrier called a Schottky barrier with barrier height $e\phi_{Bn}$. This Schottky barrier between a metal electrode and semiconductor is a result of the difference between the metal-vacuum work function and the semiconductor-vacuum electron affinity [47]. For n-type semiconductor, the Schottky barrier height can be determined by $e\phi_{Bn} = e(\phi_m - \chi)$. Schottky barrier dictates the transport of charge carriers across the M-S interface. For n-type semiconductor, current can only pass through the interface if the external positive bias is higher than the threshold value ϕ_i . For semiconducting piezoelectric material, the negative piezopotential got induced at the semiconducting side with the application of external strain and increased the local Schottky band height. On the other hand, the local Schottky band height decreases with the reversal of polarity of applied strain [59, 60]. Thus, it has been observed that the piezo-charges and piezopotential present in the semiconducting side have the significant effect on the Schottky barrier height due to the crystallographic orientation of material and the polarity of applied strain [45, 59, 61-64].

Figure 5: Schematic energy band diagram of metal-semiconductor contact (a) Compressive strain increases the local Schottky barrier height, shown by raised by the blue curve. (b) Tensile strain decreases the local Schottky barrier height shown by the declining red curve [54].

During the excitation of the M-S contact with a photon having energy more significant than the band gap of the semiconductor, electron-hole pair got generated around the contact. The presence of free carriers at the interface can effectively reduce the Schottky barrier height [65].

Piezo-phototronic effect has applications in solar cells [10], photodetectors [66], LEDs [26] etc. However, solar cells are gaining most of the attraction, because of the increasing demand for energy. In the following discussion, an effort has been made to ascribe how piezo-phototronic effect has controlled the efficiency of various types of solar cells.

5. Piezo-phototronic effect modulated solar cells

One of the greatest challenges for the development is environmental pollution and to fulfil the demand of energy along with [67, 68]. To fulfil our energy needs sustainable development is the need of the hour [69]. The sources like solar, wind, biomass, etc. have attracted the scientists, and environmentalists to circumvent or to mitigate these burning issues [70-74]. As we know, the sun is a ubiquitous source of energy, and solar cells have shown a mesmerizing effect on the scientific world in order to address some of the issues. The basic working principle of the solar cells is to use the large electric field in the depletion region to assist the separation of electron-hole pair generated by the incident photon. However, the piezoelectric charges created at the junction under strain has found a significant effect on the performance of solar cells, and piezopotential significantly modifies the band structure at the interface controlling the process from charge generation to recombination. The key parameters to evaluate the performance of a solar cell: short circuit current, open circuit voltage, maximum output power, fill factor, and ideal power conversion efficiency [75-78]. The light absorption, electron-hole generation, surface interface recombination, and surface barrier are the processes that constitute the basis of power conversion efficiency (PCE) and the external quantum efficiency [79]. The EQE is the ratio of photo-generated electrons to the per incident monochromatic photon which is given by the relation,

$$EQE(\%) = \left(\frac{1240 J_{sc}}{\lambda I_0} \right) \times 100 \quad (8)$$

Where I_0 is the incident intensity of the light source, J_{sc} is the short circuit current density and λ is the radiation length [26]. The PCE is the general efficiency of the solar cell, which is defined as the ratio of generated electricity to the incoming light and given by the relation,

$$PCE = \left(\frac{J_{solar} V_{oc} FF}{P_{in}} \right) \quad (9)$$

Where P_{in} is the power and FF is the fill factor. The fill factor is defined as the ratio of the maximum output power to the product of short circuit current and open circuit voltage, and given by the relation,

$$FF = \frac{P_m}{J_{solar} V_{oc}} = \frac{J_m V_m}{J_{solar} V_{oc}} \quad (10)$$

Here J_m is the current density at maximum output power, V_m is the voltage at maximum output power and P_m is the maximum output power. These are p-n junction and M-S contact based solar cells on which we are discussing in further sections.

5.1 p-n junction based solar cells

In 2012, Zhang et al. proposed an analytical and theoretical calculations to n-type ZnO nanowire solar cell which was based on the p-n junction where n-type, i.e., ZnO was piezoelectric and p-type was non-piezoelectric [80]. Thus, under the compressive stress or tensile strain, it was observed that the induced piezopotential could modify the band structure at the interface. This ultimately increases or decreases the e^-h^+ pair separation based on the polarity of piezopotential, which resulted in the increased or decreased performance of solar cells. Further, it can be elaborated as an ideal p-n junction having two typical types of effects; one is piezo resistance, and another is piezotronic effect [9, 81]. These effects makes the output of the solar cell depends on the polarity of the crystal once it is subjected to an external strain, suggesting the key role played by the piezo-phototronic effect on solar cell output [82, 83]. To analyze the piezo-phototronic effect on solar cells, let us assume that the generation rates of e^-h^+ are constant [84],

$$G_n = G_p = J_{solar} \cdot [q(L_n + L_p)]^{-1} \quad (11)$$

Where, J_{solar} is short circuit current density, L_n and L_p represents the e^- and h^+ diffusion lengths respectively. Moreover, $U_n = U_p = 0$, which means there is no photon emission. For ideal p-n junction piezoelectric solar cells, the total current density can be written as [85],

$$J = J_{pn} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] - J_{solar} \quad (12)$$

Where, $J_{pn} = J_{pn0} \cdot \exp[q^2 \rho_{piezo} W_{piezo}^2 (2kT \epsilon_s)^{-1}]$. Therefore, the total current density is,

$$J = J_{pn0} \cdot \exp[q^2 \rho_{piezo} W_{piezo}^2 (2kT \epsilon_s)^{-1}] \cdot \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] - J_{solar} \quad (13)$$

The above equation gives that J_{pn} (saturation current density) will decrease exponentially with the generation of piezo charges at the interface. The open circuit voltage of piezoelectric solar cells could be obtained as,

$$V_{0C} = \frac{kT}{q} \cdot \ln \left[\frac{J_{solar}}{J_{pn}} + 1 \right] \text{ For } J=0 \quad (14)$$

Here, $J_{solar} \gg J_{pn}$

Therefore,

$$V_{0C} = \frac{kT}{q} \cdot \ln \left[\frac{J_{solar}}{J_{pn}} \right] = \frac{kT}{q} \cdot \ln \left[\frac{J_{solar}}{J_{pn}} \right] + q^2 \rho_{piezo} W_{piezo}^2 (2kT \epsilon_s)^{-1} \quad (15)$$

Thus, the above equation suggests that the open circuit voltage V_{0C} is not only affected by the magnitude of stress, but also the polarity of the stress applied. This effect can be applied on nanowires, thin films or bulk solar cells.

5.2 M-S contact based solar cells

For M-S structure, let the semiconducting side be n-type ZnO nanowire. Thus, the total current density across the M-S interface could be written as [85],

$$J = J_{MS} \cdot \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] - J_{solar} \quad (16)$$

Where, $J_{MS} = J_{MS0} \cdot \exp[q^2 \rho_{piezo} W_{piezo}^2 (2kT \epsilon_s)^{-1}]$ and,

$$J_{MS0} \approx q^2 D_n N_C (kT)^{-1} \cdot \sqrt{[2q N_D (\psi_{bi0} - V) \epsilon_s^{-1}] \cdot \exp[-qe \phi_{Bn0} \cdot (kT)^{-1}]} \quad (17)$$

J_{MS} represents the saturation current density in the case with piezo-charges, J_{MS0} represents the saturation current density without piezo charges ψ_{bi0} and $e\phi_{Bn0}$ is the built-in potential and Schottky barrier height without piezo charges. The open circuit voltage of an M-S contact can be expressed as,

$$V_{0C} \approx \frac{kT}{q} \left[\ln \left(\frac{J_{solar}}{J_{MS0}} \right) \right] - q^2 \rho_{piezo} W_{piezo}^2 (2kT \epsilon_s)^{-1} \quad (18)$$

This equation suggests that tensile strain induces negative piezopotential at the interface which increases the barrier height and hence decreases the saturation current J_{MS} . It increases the open circuit voltage V_{0C} . The opposite phenomenon will occur under compressive stress. These theoretical simulations using the piezo-phototronic effect not only provide a basic understanding of solar cells but also assist in designing these solar

cells [86]. Also, it was observed that light absorption and photon excitation are the two important factors for the efficiency of solar cells. To enhance these factors, the possible ways are light trapping and anti-reflective coating [87-90]. In recent studies, it was observed that the piezo-phototronic effect could provide the benefit of anti-reflective and light trapping properties in solar cells and hence eliminates the need for anti-reflective coatings [91-94].

6. Effect on solar cells

This concept has provided a clear idea about how the piezo-phototronic effect is going to modulate the solar cells based on p-n junction and metal-semiconductor contact. The following discussion will present the effect of piezo-phototronic on the power conversion efficiency (PCE) of different type of solar cells.

6.1 Heterostructure based solar cells

Zhang et al. (2020) [36] investigated the piezophototronic effect on La-doped BFO/ZnO heterojunction and observed that rise time of ZnO significantly modulated from 153.7 ms to 61.28 ms. In this study they used la-doped BFO as p-type film and ZnO as n-type film. This work not only offers a feasible and common approach for improving the heterojunction based on ferrite film by piezophototronic effect but also facilitates the development of human machine interaction systems investigated with photoexcitation.

In 2013, Wen *et. al.* [34] observed the enhancement in solar cell performance with the use of the piezo-phototronic effect. They observed that the efficiency along with the fill factor for solar cells varies with the variation in the intensity of solar radiation, because of their limited charge separation ability. Thus, to improve this, they demonstrated the piezo-phototronic effect in the ZnO/P3HT solar cell system with four groups depending upon the growth rate and mechanics. The highest current density was 0.258 mA/cm² and PCE was 0.203% under 0.32% tensile strain. However, with compressive strain results were found to decrease, which indicates that the piezo-phototronic effect is direction dependent. It was observed that the alignment of grown ZnO nanowires plays an important role to define the parameters of the piezo-phototronic effect.

Zhu. L *et al.*, [95] investigated and designed the silicon-based nano-hetero-structure (p⁺-Si/p-Si/n⁺-Si (and n-Si)/n-ZnO nanowire array) solar cell with increased PCE. Due to the enhanced light absorption efficiency through nanowire arrays, it was found that the performance of the p⁺-Si/p-Si/n⁺-Si/n-ZnO nanowire array solar cells has been enhanced significantly when subjected to 800 KPa static compressive pressure. With the vast area, it is easy for nanowires to collect the exciting photon carriers. It means the size of the electrode plays a vital role in the performance of the solar device. Larger the area, higher will be the performance of the device. Although it was observed that the nanowire array

reduces the collection ability, the increase in the light collection ability of nanowires can circumvent or tackle this problem easily.

Cu(In,Ga)Se₂ (CIGS)-based heterostructures have been considered to be the most prospective thin film solar cells as they exhibit high PCE, low price, sizeable optical absorption coefficient ($\geq 10^5 \text{cm}^{-1}$), tunable direct band gap (1.04eV-1.67eV), long term thermal and electrical stability with tremendous environmental benefits[1-3]. However, Qiao *et al.*, [23] coupled piezo-phototronic effect on CIGS solar cells. ZnO nanowires were used on CIGS as a replacement of ZnO thin film and observed that PCE quickly improved to 11.40% from 9.8%. By replacing the substrate from ITO glass to steel substrate improvement in PCE was observed from 5.43% to 5.96%. They also observed the effect of the length of nanowires on the efficiency and found that longer nanowires have less ability to transport and collect the photo-excited carriers for ZnO nanowires which suggests that moderate length nanowire sample, i.e., 850nm, have shown best PV properties.

6.2 Multiple Quantum Well (MQW) solar cells

In_xGa_{1-x}N is one of the fascinating materials for designing the multiple quantum-well solar cells, because of the wide tunable bandgap range, i.e., from 0.7eV to 3.4eV for GaN [99-101]. It has been observed that InGaN based solar cells can exhibit the efficiency of more than 50% when it has 40% of the In content [102]. Jiang *et al.*, [103] successfully analysed the piezo-phototronic effect on InGaN/GaN MQW solar cell. It was observed that the parameters of solar cells were enhanced as conversion efficiency improved from 1.12% to 1.24% and fill factor decreased slightly from 57.3% to 56.7% under external stress of 0.134%. It indicated that the piezo-phototronic modulation of solar cells is highly efficient technology to enhance the numerical power conversion efficiency of InGaN/GaN MQW solar cell. The numerical model to compare the experimental and theoretical results was also established. Both results, when compared, shown considerable enhancement is photon conversion efficiency of MQW solar cell using piezo-phototronic effect.

Jiang *et al.* presented the design of InGaN/GaN MQW solar cell coupling with Ag nanoparticles, i.e. the coupling of piezo-phototronic effect with plasmonic effect, where plasmonic nanoparticles are those whose electron density can be coupled with electromagnetic radiations of a wavelength that are far larger than the particles [104]. Power conversion efficiency increases from 0.75% to 0.98% without strain because of Ag (silver) nanoparticles as they enhance the light absorption efficiency and plasmons couples the incident light into guided modes that propagate through MQW region. When

0.152% of the strain was applied, then the PCE further improved from 0.98% to 1.25% with an overall increment of 66%.

Thus, this new coupling concept has shown effective, recoverable and straightforward method in developing the high-efficiency solar cells.

6.3 Perovskite solar cells

Perovskite materials like $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{F}, \text{I}$) have become the center of attraction in fabricating large scale commercial solar cells due to their low-cost fabrication, high absorbance and low carrier recombination rate with a high-power conversion efficiency of more than 22% [105-109]. Gu *et al.*, [110] analysed the effect of the piezo-phototronic effect on $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films based on simulation results. The PCE improved from 4.85% to 5.05% under the stress range from -1% to 1% and the fill factor improved from 78.5% to 79%. The high piezoelectric coefficient and tiny dielectric constant of perovskite material are suitable for PV application by comparing the $\text{CH}_3\text{NH}_3\text{PbI}_3$ with BaTiO_3 . BaTiO_3 has high dielectric constant, i.e., 600, which is responsible for its less use in the PV industry. Thus, the piezo-phototronic effect has significantly improved the PCE of perovskite solar cells.

Wang *et al.*, [111] successfully described the effect of the piezo-phototronic effect on perovskite/ GaN solar cell and observed that the piezo-phototronic effect has comprehensively improved the efficiency of this solar cell. The maximum efficiency was around 25.46%, and the fill factor was 84.79% under the pressure range from -1% to 1%. The performance of GaN-perovskite solar cells with different types of solar cells was also compared and found that GaN-based perovskite solar cell has gained the highest fill factor, PCE and modulation ratio, i.e., 3.66.

In another study, Sun *et al.*, [10], fabricated a perovskite solar cell with ZnO nanowires as an electron transfer layer and observed the parameters of ZnO-Perovskite Solar cell (ZPSC) using piezo-phototronic effect. A significant enhancement in PCE with the inclination from 9.3% to 12.8% under the tensile strain of 1.88% has been found. This enhancement is due to the reason that ZnO has facilitated the separation of e^- generated from $\text{CH}_3\text{NH}_3\text{PbI}_3$. It also suggests that when stress is applied on the ZPSC, the piezopotential created at the interface of ZnO, and perovskite material has significantly improved the energy level structure.

6.4 Core/Shell based solar cells

The core/shell geometry have found great attention, because of their high efficiency of charge collection by shortening the path travelled by minority carriers and high optical

quality of material [112-115]. Pan *et al.*, reported the enhanced performance of n-CdS/p-Cu₂S by a factor of 70% using the piezo-phototronic effect, which offers a new concept for improving solar energy conversion efficiency. The improved efficiency has been gained under the -0.41% applied strain, but as the strain was further increased the relative PCE decreased by a factor of 15%. This decrease in relative PCE suggests that by introducing the piezo-phototronic effect, the decrease can be made minimal.

Zhu *et al.*, [116], reported the enhanced performance of the n-ZnO/p-SnS core/shell-based PV device. SnS was used as a shell, which shows p-type conductivity and easily forms the Sn vacancy defects [117-119]. Moreover, SnS is a polycrystalline material. Piezopotential was created by ZnO only. It was observed that under no stress condition the PCE was 1.2% and the fill factor was 0.43 under AM1.5 condition. When the external strain of 320 KPa was applied, the PCE increased to 1.644% and fill factor improved to 0.48. Here the enhancement is due to the piezopotential created by ZnO which supports the charge separation and band modulation at the interface of ZnO/SnS.

In another study, Liu *et al.* [37] investigated the catalytic activity of BFO/TiO₂ core shell nanocomposite for degradation of organic dye molecule through piezophototronic effect. They observed that BFO nanoparticles can effectively reduce the recombination rate of carriers by built in electric field. It is observed that reaction rate constant (K) of piezophototronic activity is about 560% and 388% higher than that of under the sole piezo-catalytic and photocatalytic process, respectively. Now, this trend is observed when p-type BFO and n-type TiO₂ form a heterojunction structure at the interface area, which establishes the internal electric fields on both sides to enhance the separation of electron and hole pairs under the light irradiation. Without the assistance of piezoelectric polarization in the BFO/TiO₂ nanocomposite the carriers could migrate to either side.

Ni-doped (Bi,Gd)FeO₃ ceramics have been investigated and it is observed that enhanced PV effects are attributed to the reduced bandgap, polarization modulated Schottky barriers, increased O 2p-Fe 3d orbital hybridization and nucleation of domain walls to improve the transportation of charge carriers [38]. Also, Ni-doped (Bi,Gd)FeO₃ can be potential candidate for self-powered UV photodetector.

The power conversion efficiency of the solar cell is the most important parameter which represents how much incident light is being converted into sufficient output power. To improve power conversion efficiency is the most critical issue.

7. Temperature dependence of Piezo-phototronic effect

To understand the basic physics of any phenomenon, it is essential to understand its temperature dependence [120-123]. Various devices were investigated, and it was

observed that with the decrease in temperature from room temperature to low temperature, the width of the depletion region increases [124-126]. GaN nanobelts were used for investigation under 0.28% tensile strain at 77K [126].

Figure 6: Temperature dependence of piezo-phototronic effect describing how piezopotential reacts at room temperature (T) and lower temperature than room temperature (T) [126, 127].

The figure shows how piezopotential affects the photocurrent with a change in temperature. At room temperature, the compressive strain at dark condition, shown in (b1), induce the piezopotential, and causes the screening effect which decreases the current. When UV illumination takes place under the same compressive strain condition, shown in (c1) the e-h pair generated by illumination of UV are readily attracted by the negative piezoelectric polarization charges. Hence, reduction in recombination occurs which increases the photocurrent. At lower temperature than room temperature, reduction of the carrier in conduction band occurs, because free carriers got trapped in shallow donor energy state, shown in (b2). Under compressive strain with UV illumination, shown in (c2), the increase and decrease of photocurrent simultaneously take place [127]. The decrease in free mobile charges with the decrease in temperature gives the freeze out

effect [123, 128] and due to this, the free electrons get trapped in the narrow impurity centres which can be easily activated by the incident UV photon [129, 130]. Now for thermally activated transport, the conductivity can be expressed as [52],

$$G(T) = G_0 \exp \left[\frac{E_D}{k_B T} \right] \quad (19)$$

Where E_D is the thermal activation energy of the donor state. If the material can have polarization, then to check how the polarization charges change with the temperature, it is necessary to calculate the effective surface charges (M-S interface) with the expression [131, 132],

$$\rho_s = \sqrt{\left\{ 2\epsilon_r \epsilon_0 kT \left[N_D \left(\exp \frac{e\phi_{Bn}}{kT} \right) + n_{bulk} \left(\exp \frac{e\phi_0}{kT} - 1 \right) \right] \right\}} \quad (20)$$

Where ρ_s is the total surface charge, N_D is the donor dopant concentration, n_{bulk} is the temperature dependent bulk carrier density which is equal to the ionized donor dopant concentration. Here, $N_D \left(\exp \frac{e\phi_{Bn}}{kT} \right)$ represents the screening of surface charge by fixed ionized dopants and $n_{bulk} \left(\exp \frac{e\phi_0}{kT} - 1 \right)$ represents the screening by free electrons. Thus, the above numerical methods show how the temperature variation effectively compensates the piezopotential induced charges [129].

Conclusion

In this chapter, we have outlined the fundamentals of the piezo-phototronic effect, fundamentals of solar cells and recent progress made by the piezophototronic effect on solar cells. This chapter also explores the growth of the piezo-phototronic effect in terms of publications. It also describes the various materials or compositions used so far to study this effect.

As the piezo-phototronic effect is the three-way coupling and predominantly modulates or controls the free charge carrier generation, separation, transportation, and separation at the interface or junction in optoelectronic processes. These controllable or tuning characteristics make it a very powerful concept to introduce in the widespread traditional devices with new working principle.

Ferrite based materials have come up as a potential candidate for solar cell application. Thus, study paves a way for the ferrite-based nanomaterials for the use of solar cell applications as well to investigate the piezophototronic effect on these materials. The piezo-phototronic effect is an emerging field and provides a new platform for material

science and electronics and explore the new area to work upon. This concept needs a multidisciplinary contribution so that every field of society could be benefitted.

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