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Efficiency of Heterojunction Solar Cells Based on Optical Band Gap

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Abstract

Electric energy production by fuel burning produces dangerous pollutants. The photovoltaic solar cell is a suitable alternative. For thin film solar cells, efficiency improvement should be carried out through continued development of their characteristics. The homojunction solar cell has reached its optimum. In the present work, a relationship between optical band gap and solar cell efficiency of heterojunctions has been established. Suitable band gaps of a pair of heterojunctions are required to get maximum efficiency for an appropriate frequency of solar radiation. The efficiency of a couple of extrinsic semiconductors can be calculated theoretically. An optimum band gap of a pair of heterojunctions with the highest efficiency may be found by this process. The efficiency of a few heterojunctions has been calculated using reported data. The results show that efficiency is increased with optical band gaps, and type-I is more efficient than type-II heterojunctions. The work may help to improve the solar cell efficiency.

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Solar Cells, Band Gap, Heterojunction, Efficiency, Fermi Level.

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1. Introduction

Energy production by fuel burning produces dangerous pollutants, such as sulfur and nitrogen oxides, carbon monoxide, carbon dioxide, and hydrocarbons [1]. For this reason, a search is going on over the world for alternative energy sources such as solar energy, wind power [2, 3], hydroelectric power [4], tidal power [5], sea wave power [6], thermoelectric power [7, 8], nuclear power [9] and photovoltaic power [10, 11]. Clean energy from the sun can replace a power source and keeps a pollution-less environment. Solar energy generates our present capital energy resources [12]. The wide use of solar cells that absorbs solar energy may reduce global warming. Therefore, solar energy is perhaps the most popular choice. Essentially, there are many approaches to the utilization of solar energy. Until now solar cells are costly and inefficient. Recently, researchers have been working with heterojunction solar cells to achieve more electric power. In heterojunction solar cell, the p type and n-type parts are made by distinct semiconducting materials. The solar cells' efficiency depends on many parameters of the semiconductors, such as absorption coefficient, matching of p and n-type layers, photosensitivity, optical band gap, etc. The values of optical band gaps play a vital role in increasing photo voltage. To generate photo voltage, the solar cells absorb solar energy by its absorbing quality. Some part of the solar radiation whose energy is lower than the band gap (E_g) of the solar cell semiconductor passes through. Another part (E) is absorbed by solar cell, but some part of that (excess of band-gap ($E - E_g$) is wasted as

heat. Research is being performed on energy levels and their effects on solar cell performance [13-22]. Many have calculated the solar cells' efficiency based on the traditional equation [13-16]. Few researchers have doped semiconductors to make intermediate band gaps, which help to absorb more spectrum of the solar radiation [17, 18]. Brown et al. [19] limited the efficiency of the multiband solar cells containing three and four bands to improve the solar cell efficiency. Zdanowicz et al. [20] theoretical analyzed the optimum energy band gap for the fabrication of solar cells. Schockley and Queisser [21] have estimated the efficiency of semiconductors with energy band gap by considering the detailed balance limit of efficiency of solar cells. They emphasized the carriers' movement and temperature effect on the movement and impedance of the semiconductors. Bremner et al. [22] have used a new efficiency equation associated with photon absorption rate, solar cell voltage, and electronic charge. De Vos et al. [23] showed that open-circuit operation is a reversible process and leads to Carnot efficiency using thermodynamic concepts.

In this work, an efficiency relation with optical band gap, considering Fermi energies, was established. The established efficiency equations (Eqs. (10) and (18)) are associated with band gap and electron affinity, which is totally different from other reported studies. The theoretical efficiency of the heterojunction solar cells can be estimated using the efficiency equation based on the experimentally observed optical band gaps of the solar cell materials. By calculating the theoretical efficiency beforehand, a researcher can determine whether the materials will be used effectively in their experiment.

2. Basic Principle

Depending on the band gaps of the semiconductors and their relation to each other, heterojunctions are of three types based on different band alignments (i) type-I, where either the band gap of the p-type semiconductor (E_{gp}) is totally within the band gap of the n-type semiconductor($E_{gn} > E_{gp}$), or the band gap of the n-type semiconductor (E_{gn}) is totally within the p-type semiconductor ($E_{gn} < E_{gp}$), as shown in Fig. 1(a) and (b), (ii) type-II where both band gaps of n and p-types overlap partially with each other, the electron affinity of n-type part is smaller than that of the p-type part, i.e. $E_{an} < E_{ap}$, as shown infig.1(c) or the electron affinity of the p-type part is smaller than that of the n-type part, i.e. $E_{an} > E_{ap}$, as shown in Fig. 1(d), and (iii) type-III, in this type, there is no band gaps overlapping with each other. So, the summation of the electron affinity and band gap of n-type is smaller than the electron affinity of p-type, i.e., $E_{ap} > (E_{an} + E_{gn})$, as shown in Fig. 1(e) or the electron affinity of n-type part is bigger than the summation of the electron affinity and band gap of p-type, i.e., $E_{an} > (E_{ap} + E_{gp})$, as shown in Fig. 1 (f).

In solar cells, the generated electrons (by sunlight) pass through the depletion region from the p-type side to the n-type side by the force of static electric field and the static electric potential [24]. Thus, a photo-voltage is generated with opposite polarity of static potential. The value of the photo-voltage (V_{pt}) can be between zero and static voltage (V_{st}) depending on the power of the solar radiation strength. For sufficient energetic solar radiation, the photo-voltage can be equal to the static potential (i.e., $V_{pt} = V_{st}$), and equilibrium is established. The value of V_{pt} cannot exceed the value of V_{st} because V_{st} is the source of V_{pt} [25]. It is necessary to increase the static voltage V_{st} to increase the efficiency of a solar cell. However, only particular range of solar radiation can produce carriers. In semiconductors with a bigger band gap, the solar radiation passes through the solar cell materials. So, the semiconductor with high band gap energy (but smaller than the sunlight energy) can produce photo-voltage and so can be used as photovoltaic devices. Before the equilibrium of a pn junction, electrons from the

n-type go to the valence band of the p-type, and thus, the Fermi energy difference is reduced. Therefore, the Fermi energy difference becomes zero at equilibrium. The value of the Fermi energy difference is the main feature to determine efficiency because the produced electric energy of the solar cells can be up to the value of Fermi energy difference ($E_{Fn} - E_{Fp}$).

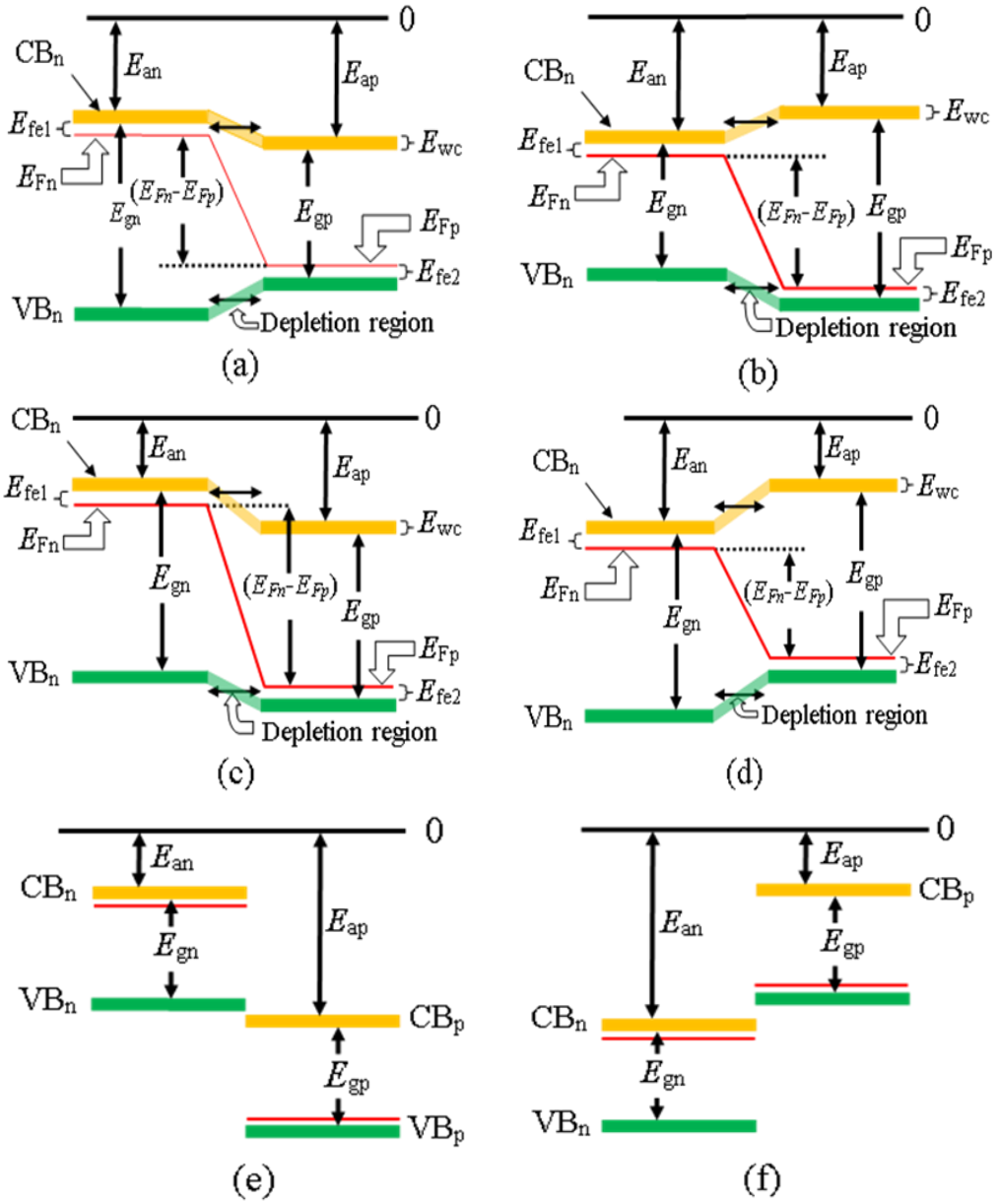

Figure 1: Three types of heterojunction solar cells: (a) and (b): Type-I, (c)and (d): Type-II, (e)and (f) Type-III:

Symbols prefacing: The symbols of different parameters have been used to describe the Fig. 1 and the description of all symbols are given in "Basic Principle" section. For the readers' convenience, a description of the symbols has been summarized here.

E_{Fn} → Fermi energy level for n-type semiconductor
E_{Fp} → Fermi energy level for p-type semiconductor
CB_n → Conduction band energy level for n-type semiconductor
CB_p → Conduction band energy level for p-type semiconductor
V_{st} → Static electric potential in the depletion region

E_{an} → Electron affinity for n-type semiconductor
E_{ap} → Electron affinity for p-type semiconductor
E_{gn} → Band gap energy of n-type semiconductor
E_{gp} → Band gap energy of p-type semiconductor
E_{fe1} → Energy difference between Fermi energy E_{Fn} and band edge of the conduction band
E_{fe2} → Energy difference between Fermi energy E_{Fp} and band edge of the valence band
E_{wc} → Energy width of the conduction band.

Let us consider the three types (six categories) of heterojunctions with different optical band gaps and different electron affinities under equilibrium, as shown in Figs. 1(a) to 1(f). Since the static electrical energy is equal to the Fermi energy difference, the equation of the energy can be written as [25]:

$$eV_{st} = E_{Fn} - E_{Fp} \quad (\mathbf{1})$$

The static electrical energy can be measured using the values of the optical band gap and electron affinity. Fig. 1(a) and Fig. 1(b) represent type-I, and Fig. 1(c) and Fig. 1(d) represent type-II heterojunction solar cells. From the figures, a relation of the static electrical energy of the heterojunction solar cells can be found easily as:

$$eV_{st} = \left(E_{ap} + E_{gp} + E_{wc} - E_{fe2}\right) - (E_{an} + E_{wc} + E_{fe1}).$$

or,

$$eV_{st} = \left(E_{ap} - E_{an}\right) + E_{gp} - (E_{fe2} + E_{fe1}) \quad (\mathbf{2})$$

here, E_{wc} is the width of the energy of the conduction band. The energy difference between the Fermi energy and conduction band edge is E_{fe1}, and the energy difference between the Fermi energy and valence band edge is E_{fe2}. Consider the summation of the energy differences E_{fe1} and E_{fe2} as:

$$E_{fe} = E_{fe1} + E_{fe2} \quad (\mathbf{3})$$

If the solar cell produces maximum photo-voltage (i.e $V_{st} = V_{pt}$) then from Eq. (2) and Eq. (3) the maximum photo-voltaic energy can be written as:

$$eV_{pt} = \left(E_{ap} - E_{an}\right) + E_{gp} - E_{fe} \quad (\mathbf{4})$$

The photo-voltage can be found using Eq. (4) after knowing the electron affinities, band gaps, and E_{fe}. The generation of photo-voltage depends on the static potential of the pn junction; the static potential depends on the Fermi energy difference of the n-type and p-type sides of the junction. If the electron affinity of the n-type and p-type sides are the same or almost the same value, then the Fermi energy difference of the n-type and p-type sides depends on the band gaps of both sides of the heterojunction. Usually, the energy difference E_{fe} is very small compared to the values of band gaps and electron affinities. Considering the donor concentration N_d in the n-type semiconductor, and the acceptor concentration N_a in the p-type semiconductor, which is substantially larger than the intrinsic concentration, then the total band edge energy E_{fe} [26] can be written as:

$$E_{fe} = E_{fe1} + E_{fe2} = kT\ln\frac{N_c}{N_d} + kT\ln\frac{N_v}{N_a} \quad (5)$$

where: N_c and N_v are the effective density of states in the conduction and valence bands, respectively, k is the Boltzmann constant, and T is the temperature. If $N_c \approx N_d$ and $N_v \approx N_a$ then E_{fe} will be almost zero.

Considering (type-III solar cells), Fig. 1(e), the electrons of the conduction band of the n-type side transmit to the valence band region of the p-type side via two intermediate energy levels. The first one is the valence band of the n-type side, and the second is the conduction band of the p-type side. In the ideal case, the valence band of the n-type semiconductor is completely full. So, forming a pn junction is not possible. For the case of the other structure, as in Fig. 1(f), the energy of the electrons of the conduction band of the n-type side is lower than the energy of the valence band of the p-type side. So, type-III solar cells should not generate any static potential in the ideal case. Therefore, no photo-voltage from type-III solar cells can be obtained.

The conventional efficiency equation of a solar cell is [27]:

$$\eta = \frac{\text{Produced energy by solarcell}}{\text{Solar energy}} \quad (6)$$

From Eq. (4) the maximum efficiency is:

$$\eta = \frac{eV_{pt}}{\text{Solar energy}} \quad (7)$$

or,

$$\eta = \left(\frac{(E_{ap} - E_{an}) + E_{gp} - E_{fe}}{\text{Solar energy}}\right) \quad (8)$$

The value of the energy difference between the Fermi energy and the band edges E_{fe} is around the fraction of an eV. Despite that the value of E_{fe} may not be ignored for the lower band-gaps' semiconductor. If a particular solar spectrum (a single photon) with energy hν interacts with a single electron, then the maximum efficiency of the solar cells can be written as:

$$\eta = \left(\frac{(E_{ap} - E_{an}) + E_{gp} - E_{fe}}{h\nu}\right) \quad (9)$$

In some cases, the value of the E_{fe} is ignored when the optical band gap is large enough or when $N_c \approx N_d$ and $N_v \approx N_a$. If E_{fe} is ignored, the maximum efficiency of the solar cells, Eq. (9), can be written as:

$$\eta = \left(\frac{E_{ap} - E_{an} + E_{gp}}{h\nu}\right) \quad (10)$$

and Eq. (4) should be:

$$eV_{pt} = (E_{ap} - E_{an}) + E_{gp} \quad (11)$$

In some cases of type-I and type-II solar cells, the electrons move from the conduction band of the n-type side to the valence band of the p-type side via the energy offset region of heterojunction. The energy offset is a barrier to electron transmission due to the energy differences between the conduction bands (and valence bands also for some solar cells) of the n-type and p-type semiconductors. Then, it is possible that the solar cell with an energy offset creates static electric potential with less value than that expected from Eq. (10). If the electron does not face any barrier during transmission from p-type to n-type semiconductor of heterojunction, then the static electric potential will be maximum, and the efficiency will be the same as of Eq. (10).

Eq. (10) has been established considering the energies of the solar cells and the solar radiation. The solar cell's energy is associated with the band gap of the semiconductor materials. The photo-voltage (V_{pt}) is associated with the band gap. The same band gap of several materials should build the same photo-voltage as Eq. (10). However, the photocurrent can be different for different photo-sensitive materials, although their band gap is the same. In this case, the interaction of the multiple photons with multiple electrons should be considered. Let us consider that the n is the number of photons falling on a unit area (1 m^2) in a second, and then n' is the number of electrons generated to make the photovoltaic power from the unit area of the solar cells for a second. The unit of both n and n' is $s^{-1}m^{-2}$. The efficiency equation can then be written as:

$$\eta = \frac{n'\left(E_{ap} - E_{an} + E_{gp}\right)}{nhv} \qquad (\mathbf{12})$$

The value of n' depends on the photo-sensitivities of the solar cell materials. Usually, a photon interacts with an electron and breaks a bond. Some photons are unable to break the chemical bonding due to their low energy. So, n' could be smaller than the n. For highly sensitive materials, n' equals n (i.e., n' = n). Then, Eq. (12) becomes equal to Eq. (10). The photovoltage depends on the band gap, and the photocurrent depends on the value of n'. Therefore, two solar cells with the same band gap of their materials have not the same efficiency as Eq. (12).

The intensity (I) of the solar radiation can be written as:

$$I = nhv \quad Wm^{-2} \qquad (\mathbf{13})$$

Eq. (13) indicates that the falling rate of the photon per unit area (n) is inversely proportional to the frequency (ν) of the photon. The value of n is measurable for a frequency of solar radiation after measuring its intensity. From Eqs. (13) and (12), the efficiency (where n' < n) of the solar cell can be written as:

$$\eta = \frac{n'\left(E_{ap} - E_{an} + E_{gp}\right)}{I} \qquad (\mathbf{14})$$

Using Eq. (11), Eq. (14) can be written as:

$$\eta = \frac{n'eV_{pt}}{I} \qquad (\mathbf{15})$$

If all induced electrons form the current of the outer circuit into the load, then the current density can be written as:

$$J = n'e \quad (Am^{-2}) \qquad (\mathbf{16})$$

From Eqs. (15) and (16), the efficiency of the solar cell can be written as:

$$\eta = \frac{JV_{pt}}{I} \quad (\mathbf{17})$$

For highly sensitive materials, *n'* equals *n*. Then Eq. (14) will be:

$$\eta = \frac{n\left(E_{ap} - E_{an} + E_{gp}\right)}{I} \quad (\mathbf{18})$$

3. Efficiency Calculation

Solar cell efficiency was theoretically calculated using Eqs. (10) and (18). The data needed for the calculations, such as optical band gaps of the individual materials of a heterojunction and electron affinities, were obtained from various published papers [28-33]. The solar spectrum shows that solar energy with the value of 2.486 eV (of equivalent wavelength of 500 nm) is the highest intensity [25]. To calculate solar cell efficiency of a heterojunction, the 2.486 eV energetic solar spectrum was chosen. This energy, the band gap energy values and electron affinity were used in Equation (10). The efficiency versus solar energy graphs plotted for cadmium sulfide-cadmium telluride (CdS-CdTe) gallium and nitride-gallium arsenide (GaN-GaAs) solar cells are shown in Fig. 2. Table 1 displays the band gap energies and electron affinities of various semiconductors, which are used to calculate the efficiency. Equation (18) was used to calculate the efficiency several heterojunction solar cells are tabulated in Table 1, for light intensity of 1361.8 Wm^{-2}, as calculated using Equation (13) for light wavelength of 500 nm and induced electrons number $n = 3.42\times10^{21}$ $s^{-1}m^{-2}$. The band gap energy values, electron affinity and the intensity of the solar spectra were used in this case.

4. Results and Discussion

The practical result of a solar cell's output is from the interaction of a single photon and a single electron. In the case of single photon interaction with an electron, the receiving energy of the solar cells depends on the frequency (energy) of the solar radiation; thus, the efficiency is frequency dependent (see Eq. (9)). The theoretical efficiency versus solar energy graph was plotted for two heterojunctions solar cells, CdS-CdTe and GaN-GaAs, using Eq. (10), as shown in Fig. 2. The figure shows that for particular energy of the solar cell, the efficiency was almost 100%. After that, the efficiency decreases with frequency. Solar radiation ($h\upsilon$) with low energy ($< E_g$) passes through the solar cell materials. These energies are not able to generate photo-voltage. The lower energy limit that can produce photo-voltage equals the band gap energy. Higher energy ($> E_g$) of the solar radiation ($h\upsilon$) can generate photo-voltage with maximum value (eV_{pt}) of solar cell ability. The rest ($h\upsilon - eV_{pt}$) of the solar energy is lost as heat, so the net generated energy remains unchanged; thus, the efficiency decreases with increased frequency. The figure indicates that the GaN-GaAs heterojunction solar cell is more efficient than the CdS-CdTe heterojunction solar cell. The generation of photo-voltage depends on the Fermi energy difference of the n-type and p-type sides of the junction. If the values of the electron affinity of the n-type and p-type sides are almost the same, then the Fermi energy difference (as well as the photo-voltage) of the pn junction depends on the band gaps of the pair of the heterojunction. The band gaps of the GaN-GaAs heterojunction solar cell are larger than those of the CdS-CdTe heterojunction. So, the heterojunction solar cell with the higher band gap results in higher efficiency. However, solar energy with a value lower than the band gap cannot

create photo-voltage. This is a major issue for photovoltaic systems, as many researchers have reported low efficiency values for solar cells [21-24].

The band edge energy E_{fe} depends on the donor (N_d) and acceptor (N_a) densities. Collecting information on E_{fe} of solar cell materials is a difficult task. If the band gap of a semiconductor is large enough compared with the value of E_{fe} or when $N_c \approx N_d$ and $N_v \approx N_a$, then the band edge energy E_{fe} can be ignored. In this condition, Eqs. (12), (14) and (18) are derived when multiple photons interact with multiple electrons.

To produce photo-voltage, the frequency (as well as energy) of solar radiation is associated with the band gap of the semiconductor materials, so it is difficult to find the efficiency of a heterojunction for all the frequencies of the solar spectrum. There is no energy equation to measure the energy of solar radiation considering all frequencies at the same time. The energy equation ($h\upsilon$) is related to a single frequency only. As an alternative, the light intensity (I), which is measured by an intensity measurement instrument, was considered for Equation (18) to calculate the efficiency of solar cell. To compare the efficiency of different semiconductors, Eq. 18 was used, and the results are tabulated in Table 2, where I is equal to 1361.8 Wm^{-2}, which was obtained from the study of Meftah et al. [34]. It is not possible to get the absolute values of band gaps and electron affinities as perfect for a heterojunction solar cell. Different studies [20-23, 35] gave different efficiency values according to the method and instruments used. To overcome this problem, the values of the band gaps and electron affinities for each of the heterojunctions were chosen from previous studies. The values for GaN-GaAs heterojunction were taken from the study of Hara [36], for TiO_2-CuO from the study of Enebe et al. [28], and for CdS-CdTe from Chen et al. [29]. It can be noted from Table 2 that the efficiency of Si is 49 %, whereas Green et al. reported a value of around 25% [32]. They calculated the efficiency on the basis of the global AM1.5 spectrums (1000 Wm^{-2}). A power conversion efficiency of 31% was achieved with numerical simulation for the crystalline silicon solar cell [33]. S. Rühle [35] tabulated the electric power conversion efficiency (η) as a function of the light absorbers' band gap energy for single junction solar cells. They calculated the efficiency of a silicon solar cell to be 32.23%.

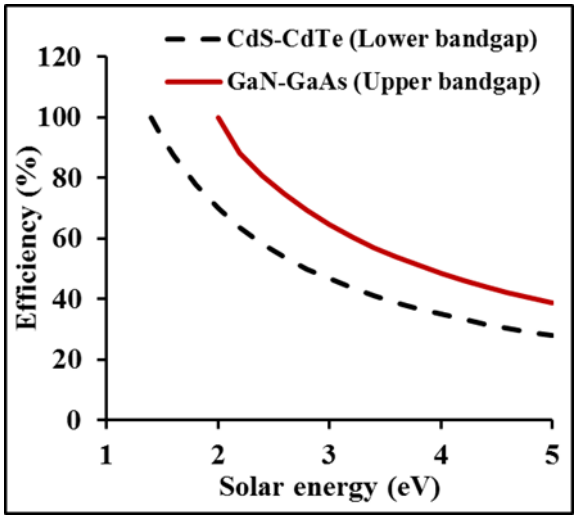

Figure 2: Efficiency according to solar energy for cadmium sulfide-cadmium telluride (*CdS-CdTe*) and gallium nitride - gallium arsenide (*GaN-GaAs*) heterojunctions solar cells.

In this work, since solar cell efficiency depends on the frequency of the solar radiation, it was calculated due to the solar radiation frequency of 6×10^{14} Hz equivalent to 2.486 eV solar energy, considering a band edge energy E_{fe} to be zero (i.e., $N_c \approx N_d$ and $N_v \approx N_a$). The heterojunctions efficiency was calculated for several heterojunction

solar cells as shown in Table 2, the values were larger than those reported in previous studies [32, 33, 36]. They have considered single junctions, but compound semiconductor materials are available such as GaAs (28.8 %) [36], CdTe (21.5 %) [29], etc. Typically, a compound semiconductor is either an n-type or a p-type, but not both simultaneously; as for an example the CdS is only available as n-type semiconductor. So, considering it as a single junction is unsuitable. Table 2 indicates that the efficiency has increased with band gaps for a particular type of heterojunction solar cell. Type-I solar cells have higher efficiency than type-II for constant band gaps due to a large amount of energy difference between the conduction band of the n-type level and the valence band of the p-type. The static potential is bigger for the large Fermi energy difference. As for example: the maximum efficiency of the TiO_2-CdTe heterojunction (Type-I) is higher than that of the TiO_2-CuO heterojunction (Type-II), although the band gaps of both are the same. The efficiencies (Table 2) of the ZnO-GaAs, TiO_2-CuO and CdS-CdTe heterojunctions (Type-II) are higher than some Type-I hetero and homojunctions due to the sufficiently larger band gaps (Table 1) of the semiconductors involved. If different energies of solar radiation were selected for calculating efficiency, the basic characteristics of the efficiency would remain unchanged (efficiency increased with larger band gaps). However, the value of the efficiency would vary.

Table 1: Band gap energies and electron affinities of some semiconductors* at *1361.8 Wm^{-2} solar radiation with the value of $n = 3.42\times10^{21}$ $s^{-1}m^{-2}$.

n-type semiconductor			**p-type semiconductor**		
Name	E_{gn} **(eV)**	E_{an} **(eV)**	**Name**	E_{gp} **(eV)**	E_{ap} **(eV)**
Ge	0.62 [31]	4.31 [31]	Ge	0.62 [31]	4.31 [31]
Si	1.22 [31]	4.12 [31]	Ge	0.62 [31]	4.31 [31]
Ge	0.62 [31]	4.31 [31]	Si	1.22 [31]	4.12 [31]
Si	1.22 [31]	4.12 [31]	Si	1.22 [31]	4.12 [31]
TiO_2	2.26 [32]	4.20 [32]	CdTe	1.50 [33]	4.40 [33]
GaN	3.05 [31]	3.34 [31]	GaAs	1.23 [31]	4.05 [31]
SnS_2	2.28 [34]	4.16 [34]	SnO	0.70 [35]	3.70 [35]
ZnO	2.62 [31]	4.34 [31]	GaAs	1.23 [31]	4.05 [31]
TiO_2	2.26 [32]	4.20 [32]	CuO	1.50 [32]	4.07 [32]
CdS	2.42 [33]	4.50 [33]	CdTe	1.50 [33]	4.40 [33]

Table 2: Calculated efficiency of some heterojunctions.

Heterojunction	**Produced energy (eV)**	**η (%)**	**Type**
Ge- Ge	0.62	24.91	I
Si- Ge	0.81	32.55	I
Ge- Si	1.03	41.39	I
Si- Si	1.22	49.02	I
TiO_2- CdTe	1.70	68.31	I
GaN- GaAs	1.94	77.95	I
SnS_2- SnO	0.24	9.64	II
ZnO- GaAs	0.94	37.77	II
TiO_2- CuO	1.37	55.05	II
CdS- CdTe	1.40	56.26	II

5. Conclusions

Solar cell efficiency based on Fermi energy levels was studied. A relation between band gap and solar cell efficiency was established. The equation helps to calculate the efficiency of a couple of extrinsic semiconductors theoretically. To compare between different heterojunctions, their efficiencies were calculated with respect to the standard intensity (1000 Wm^{-2}). The theoretical results show that the increased band gaps (up to a limit) of a pair of heterojunctions increase the efficiency. The efficiency equation can find efficient semiconducting materials with an appropriate band gap. The concept may help to determine the theoretical efficiency of solar cells correctly.

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Conflict of interest

Authors declare that they have no conflict of interest.

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