Theoretical Performance Study of n-TiO_2/p-$CuInSe_2$ Solar Cell and Its Modification for Improved Efficiency

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A theoretical study of a proposed *n*-TiO_2/*p*-$CuInSe_2$ heterojunction solar cell is made in order to find out its feasibility as a photovoltaic energy converter. A theoretical efficiency limit of only 1.51% has been found under ideal condition. The high barrier height ΔE_c at the conduction band edge shows a deleterious effect on the cell performance. However, the cell can be modified by introducing a new oxide semiconductor $Pb_xTi_{1-x}O_2$ instead of TiO_2. The band gap and the conduction band discontinuity of $Pb_xTi_{1-x}O_2$ both can be lowered by varying x. The theoretical efficiency limit of such a solar cell has also been calculated assuming $\Delta E_c=0$.

1. Introduction

Extensive research work has been carried out in the field of Si and GaAs solar cells and an efficiency of as high as 35% has been obtained[1]. But the mass generation of electricity using these devices for common consumer applications, which costs almost ten times more than the conventional methods, is still unrealistic[2]. In a quest for low cost, high efficiency solar cell, Gratzel and coworkers developed a photoelectrochemical cell(PECC), where the titanium dioxide film is coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting and an efficiency of about 13% has currently been obtained in recent years[3]. The titanium dioxide film which is easy to prepare, is probably the cheapest available semiconductor. The cell, though efficient in charge transfer and free from electron-hole recombination loss, suffers a lack of stability and the dye sensitizer, which can be considered as the weakest point in the cell, is prone to chemical degradation. So, apart from this, we propose a thin film heterojunction solid state solar cell using the low-cost film of TiO_2 which, we believe, will be much more stable than the dye-sensitized PEC cells. TiO_2 is a high band gap (3.2 eV) semiconductor material. So it will act as a window material for our proposed cell. $CuInSe_2$ has been chosen as the base material for the cell which has a low band gap (1.04 eV), high absorption coefficient and stable electro-optical characteristics.

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2. Model Development

2.1. Assumptions

Certain assumptions are made in the model development for the performance study of our proposed *n*-TiO_2/*p*-$CuInSe_2$ solar cell.

(1) The device is a true n-p heterojunction with a band diagram under illumination as shown in Fig.1

(2) Because of wide band gap(3.2 eV) of TiO_2, photocurrent is generated mostly in $CuInSe_2$ film and those in TiO_2 can be neglected.

(3) Because of the high barrier height ($\Delta E_c=0.48$ eV) at the junction, transmission of photogenerated carriers are limited by quantum tunneling probability.

(4) Dark currents are mainly due to thermoionic emission and tunneling current through the barrier. At low junction voltage, tunneling current dominates, while at sufficiently high junction voltage thermoionic emission takes over.

(5) Any loss of photogenerated carriers due to recombination is negleted.

(6) There is also no reflection loss in the cell.

(7) All the calculations are carried out considering an illumination level of 1 SUN at AM 1.5 condition.

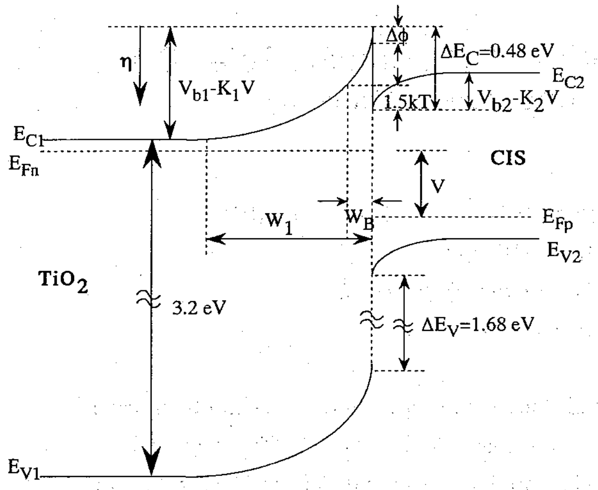

Fig. 1. Band diagram of n-TiO_2/p-$CuInSe_2$ cell under illumination.

2.2. Computational Strategy

With the assumptions stated above, following equation is proposed to calculate the IV-characteristics of n-TiO_2/p-$CuInSe_2$ solar cell under illumination,

$$J=A^*T^2\exp\left(-\frac{V_{bi}}{V_T}\right)\exp\left(\frac{V}{V_T}\right)+\frac{A^*T}{k}\int_0^{\eta_f}F_1(\eta)T(\eta)\{1-F_2(\eta)\}d\eta-P_T(V)I_L \quad (1)$$

The first and the second terms represent thermoionic emission current over and tunneling current through the barrier from TiO_2 to $CuInSe_2$ respectively[4]. $P_T(V)$ is the quantum tunneling probability of photogenerated electrons from $CuInSe_2$ to TiO_2 and I_L is the photogenerated current. A^* is the Richardson constant, V_{bi} is the built-in voltage in TiO_2. η is measured downward from the potential maximum (Fig.1), $F_1(\eta)$ and $F_2(\eta)$ are the Fermi-Dirac distribution functions for TiO_2 and $CuInSe_2$ respectively. $T(\eta)$ is the quantum transmission probability of electrons from TiO_2 to $CuInSe_2$.

The occupation probability $F_1(\eta)$ in TiO_2 is given by

$$F_1(\eta)=\frac{1}{1+\exp\{(E-E_{F_1})/kT\}} \quad (2)$$

where $E-E_{F1}=qV_{b1}-qK_1V+E_{F1}-E_{C1}-\eta$.

$1-F_2(\eta)$ is the unoccupied probability of states in $CuInSe_2$ and for $\eta>\Delta E_C$, no state is available for an electron in $CuInSe_2$ at the junction. So we approximate $1-F_2(\eta)$ as

$$1-F_2(\eta)\approx 1, \quad \text{for } 0<\eta<\Delta E_C-\Delta\phi$$
$$=0, \quad \text{for } \eta>\Delta E_C-\Delta\phi \quad (3)$$

Transmission probability is derived as (see Appendix I)

$$T(\eta)=\left[\exp\left\{\frac{W_BE}{h}\left(\frac{2m^*}{H_B}\right)^{\frac{1}{2}}\left(\frac{1}{2}\sinh 2u-u\right)\right\}+\frac{1}{4}\exp\left\{-\frac{W_BE}{h}\left(\frac{2m^*}{H_B}\right)^{\frac{1}{2}}\left(\frac{1}{2}\sinh 2u-u\right)\right\}\right]^{-2} \quad (4)$$

where $u=\cosh^{-1}\left(\sqrt{\frac{H_B}{E}}\right)$.

Here W_B is the effective barrier width and is derived as (see Appendix II)

$$W_B=W_1\left\{1-\left[\frac{V_{b1}-K_1V-H_B}{V_{bi}-K_1V}\right]\right\} \quad (5)$$

where $K_1=\frac{\varepsilon_2N_A}{\varepsilon_1N_D+\varepsilon_2N_A}$,

$H_B=\Delta E_C-E-\Delta\phi$, is the effective barrier height where $\Delta\phi$ is the barrier height lowering due to Schottky effect and is given by

$$\Delta\phi=\frac{q}{2\varepsilon_s}\left(\frac{N_DW_1}{\pi}\right)^{\frac{1}{2}}.$$

And E is the energy of an electron as measured from the bottom of the barrier and is given by $E=\Delta E_C-\eta-\Delta\phi$.

Transmission probability $P_T(V)$ for photogenerated electrons in $CuInSe_2$ is the same as that given by eqn.4 except that here E instead of being continuously varying energy from $\Delta E_C-\Delta\phi$ to 0, it is the average thermal energy of photogenerated electrons in $CuInSe_2$ which is equal to $3kT/2$.

3. Calculated Results and Discussion

3.1. n-TiO_2/p-$CuInSe_2$ Solar Cell

The I-V-characteristics of n-TiO_2/p-$CuInSe_2$ in ideal case i.e., not considering the recombination losses, is evaluated according to eqn.1 at 1 SUN AM 1.5 condition and is shown in Fig.2. All the parameters for efficiency calculation are taken from literature[5]. An open circuit voltage $V_{OC}=0.68$ V, short circuit current $I_{SC}=4.27$ mA/cm^2, fill factor=0.44 and efficiency $\eta=1.51\%$ have been obtained. Transport of photogenerated carriers in $CuInSe_2$ film is limited by the quantum tunneling probability of the carriers through high barrier at the conduction band edge of $TiO_2/CuInSe_2$ interface. The work functions of TiO_2 and $CuInSe_2$ are 4 eV and 4.48 eV respectively which give a conduction band discontinuity of 0.48 eV[6]. Even after taking into account the barrier height lowering due to Schottky effect, which is found to be around 0.08 eV, the barrier height is (0.48−0.08=)0.4 eV which is still too high and limits the quantum tunneling probability to only 15%. Fill factor of this cell is also low. As the junction voltage increases, the effective barrier width W_B, which is shown in Fig.1, also increases. This in turn decreases the tunneling probability and consequently the output current. This increase in effective base width W_B and decrease in tunneling probability $P_T(V)$ with voltage is shown in

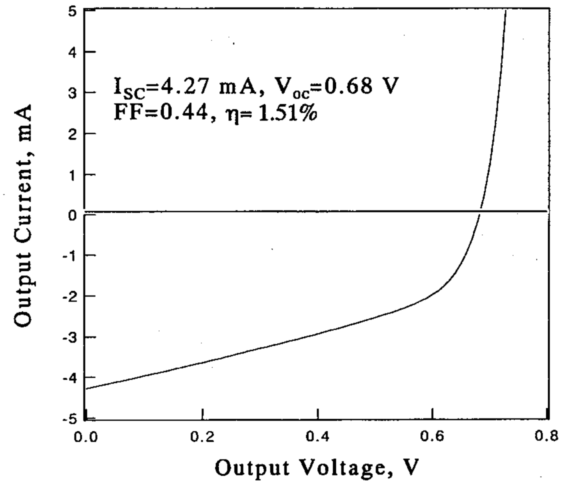

Fig. 2. I-V Characteristics of n-TiO_2/p-$CuInSe_2$ solar cell at 1 SUN AM 1.5 condition.

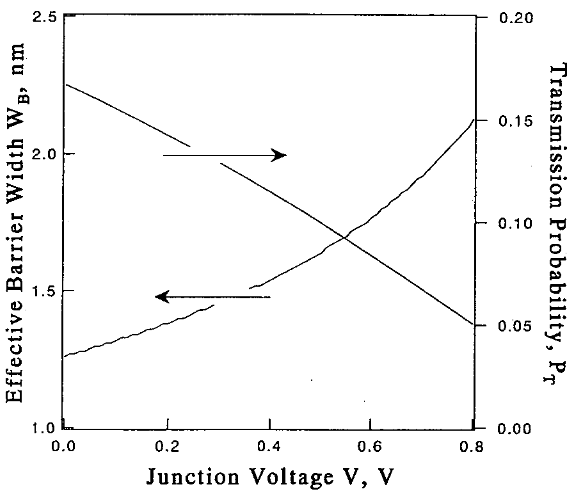

Fig. 3. Variation of effective base width W_B and transmission probability P_T as a function of junction voltage V.

Fig.3. This phenomenon leads to a low fill factor. One might be tempted to increase the tunneling probability by increasing the doping density and thereby decreasing the depletion width. But in our model calculation a donor doping density $N_D=10^{20}$ cm^{-3} has been assumed which is already too high to be achieved practically.

3.2. Modification of $TiO_2/CuInSe_2$ Solar Cell

Because of high barrier at the junction of n-TiO_2/p-$CuInSe_2$ cell, the cell efficiency is very low. So in order to reduce or eliminate this barrier from the junction of the cell, we propose $Pb_xTi_{1-x}O_2$ as the window material instead of TiO_2. It has been shown by Krishna et. al.[7] in a theoretical work that the band gap of TiO_2 can be varied by mixing it with PbO_2 at different proportions. With the decrease of band gap there is an increase in work function and consequently the difference between the work functions of the two materials $Pb_xTi_{1-x}O_2$ and $CuInSe_2$ decreases. In our calculation of IV characteristics of n-$Pb_xTi_{1-x}O_2$/p-$CuInSe_2$, it is assumed that the work functions of the two semiconductors are perfectly matched and that the band gap of $Pb_xTi_{1-x}O_2$ is 2.58 eV. These assumptions are in consistent with the calculated results of Krishna et. al.[7] when PbO_2 and TiO_2 are mixed at a ratio of 1:3.

The calculated IV-characteristics of our proposed n-$Pb_xTi_{1-x}O_2$/p-$CuInSe_2$ solar cell is shown in Fig.4. All the parameters for $Pb_xTi_{1-x}O_2$ are chosen the same as

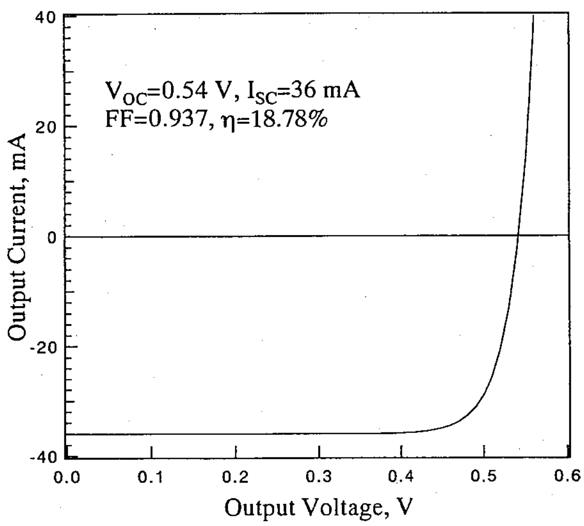

Fig. 4. IV Characteristics of n-$Pb_xTi_{1-x}O_2$/p-$CuInSe_2$ solar cell at 1 SUN AM 1.5 condition assuming $\Delta E_C=0$.

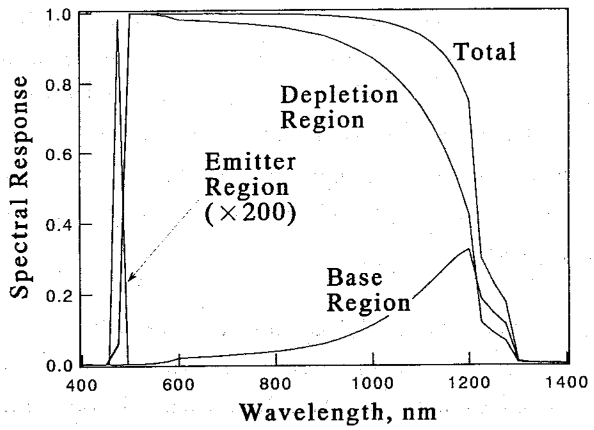

Fig. 5. Spectral Response of n-$Pb_xTi_{1-x}O_2$/p-$CuInSe_2$ solar cell at 1 SUN AM 1.5 condition.

that of TiO_2. An open circuit voltage $V_{oc}=0.54$ V, short circuit current I_{sc} mA/cm^2, fill factor$=0.937$ and efficiency $\eta=18.78\%$ have been obtained. Efficiency can be further increased if we make some optimization with respect to carrier doping density. The calculated spectral response curve is shown in Fig.5. The spectral response from the emitter region is shown on a much exaggerated scale. This shows that the spectral response from emitter region is very small and has negligibly small effect on the total spectral response. This is because both the minority carrier diffusion length $L_p(3\times10^{-7}$cm) and mobility μ_p (0.1 cm^2/V.s) are very small.

4. Concluding Remarks

Theoretical performance study of n-TiO_2/p-$CuInSe_2$ has been made. A theoretical efficiency limit of only 1.51% has been obtained. The high barrier height at the conduction band edge of $TiO_2/CuInSe_2$ interface limits the quantum transmission probability of photogenerated electrons from $CuInSe_2$ to TiO_2 to only 15%. This further decreases with increase in the junction voltage. To reduce the high barrier at the junction, the ternary oxide semiconductor $Pb_xTi_{1-x}O_2$ has been proposed as the top material of the cell instead of TiO_2. The efficiency of n-$Pb_xTi_{1-x}O_2$/p-$CuInSe_2$ solar cell has been calculated assuming $\Delta E_C=0$ and an efficiency of 18.78% has been obtained at 1 SUN AM 1.5 condition. The efficiency can be further increased by making some optimization with respect to the carrier doping density.

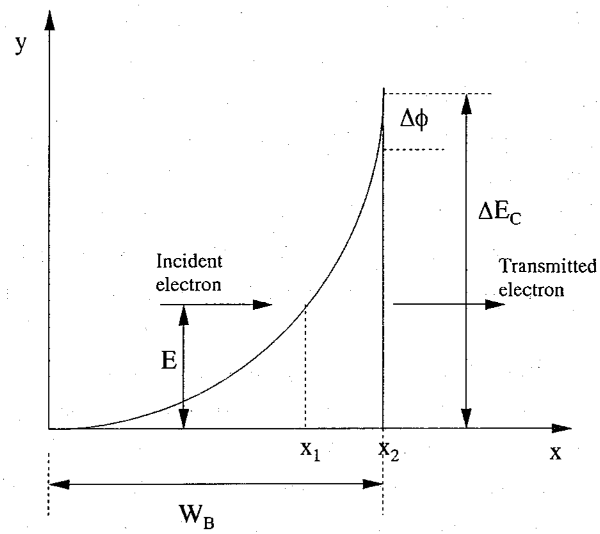

Fig. 6. Plot of Energy Barrier at the conduction band edge of n-TiO_2/p-$CuInSe_2$ junction.

Appendix I: Derivation of Quantum-Mechanical Transmission Probability T

The plot of energy barrier at the conduction-band edge between TiO_2 and $CuInSe_2$ is shown in Fig.6 it is assumed that the barrier is parabolic so that it can be described by the equation $y=ax^2$ where a is a constant of proportionality. H_B is the effective barrier height and is given by the difference between conduction band discontinuity ΔE_C and barrier height lowering $\Delta\phi$ due to Schottky effect. E is the energy of the electrons in the conduction band of TiO_2 and is measured from the bottom of the barrier.

The probability of quantum-mechanical tunneling for a particle with energy E, using the WKB approximation, is given by [8]

$$T=\left[\exp\left(\frac{2\pi}{h}\int_{x_1}^{x_r}dx|p(x)|\right)+\frac{1}{4}\exp\left(-\frac{2\pi}{h}\int_{x_1}^{x_r}dx|p(x)|\right)\right]^{-2} \tag{6}$$

where $p(x)=\sqrt{2m^*(E-V(x))}$ (7)

and $V(x)=y=ax^2$ (8)

Hence, $p(x)=\sqrt{2m^*(E-ax^2)}$ (9)

From Fig.6, at $x=W_B$, $y=H_B$. Hence, from eqn.(8), $a=H_B/W_B^2$.

Substituting this into eqn.(9), we get

$y=(H_B/W_B^2)x^2$ and (10)

$$p(x)=\sqrt{2m^*\left(E-\frac{H_B}{W_B^2}x^2\right)} \tag{11}$$

Now we will first evaluate the integral $\int_{x_1}^{x_r} dx|p(x)|$ of eqn.(6).

$$\int_{x_1}^{x_r} dx|p(x)| = (2m^*)^{\frac{1}{2}} \int_{x_1}^{x_2} \left(\frac{H_B}{W_B^2} x^2 - E\right)^{\frac{1}{2}} dx$$

$$= (2m^*)^{\frac{1}{2}} \frac{W_B E}{\sqrt{H_B}} \int_{x=x_1}^{x=x_2} \sinh^2 u du \quad (11)$$

$$= (2m^*)^{\frac{1}{2}} \frac{W_B E}{\sqrt{H_B}} \left[\frac{1}{2}\sinh 2u - u\right]_{x=x_1}^{x=x_2}$$

here we have put $x = W_B\sqrt{\frac{E}{H_B}} \cosh u.$ (12)

Hence, $u = \cosh^{-1} \frac{x}{W_B}\sqrt{\frac{H_B}{E}}.$ (13)

At $x=x_1$, $y=E$ and from eqn.(10),

$$x_1 = W_B\sqrt{\frac{E}{H_B}}. \quad (14)$$

Hence, $u = \cosh^{-1} \frac{x_1}{W_B}\sqrt{\frac{H_B}{E}} = \cosh^{-1} 1 = 0.$ (15)

At $x=x_2, u_2 = \cosh^{-1} \frac{x_2}{W_B}\sqrt{\frac{H_B}{E}} = \cosh^{-1}\sqrt{\frac{H_B}{E}},$

since $x_2 = W_B$. (16)

From eqns.(11),(15) and (16) we get

$$\int_{x_1}^{x_r} dx|p(x)| = (2m^*)^{\frac{1}{2}} \frac{W_B E}{\sqrt{H_B}} \left[\frac{1}{2}\sinh 2u_2 - u_2\right] \quad (17)$$

Replacing u_2 by u, we get

$$\int_{x_1}^{x_2} dx|p(x)| = (2m^*)^{\frac{1}{2}} \frac{W_B E}{\sqrt{H_B}} \left[\frac{1}{2}\sinh 2u - u\right]$$

$$= \left(\frac{2m^*}{H_B}\right)^{\frac{1}{2}} W_B E \left[\frac{1}{2}\sinh 2u - u\right] \quad (18)$$

Hence the quantum transmission probability T is given by

$$T = \left[\exp\left\{\frac{W_B E}{h}\left(\frac{2m^*}{H_B}\right)^{\frac{1}{2}}\left(\frac{1}{2}\sinh 2u - u\right)\right\} + \frac{1}{4}\exp\left\{-\frac{W_B E}{h}\left(\frac{2m^*}{H_B}\right)^{\frac{1}{2}}\left(\frac{1}{2}\sinh 2u - u\right)\right\}\right]^{-2} \quad (4)$$

Appendix II: Derivation of Effective Barrier Width W_B

The conduction band diagram in the depletion region of TiO_2 is shown in Fig.7. The band is assumed to be parabolic and can be described by the equation $y = ax_2$. The two points x_1 and x_2 mark the starting and the end of the barrier and their difference $(x_2 - x_1 =) W_B$ is defined as the effective Barrier width. From the equation $y = ax^2$, we can write the following

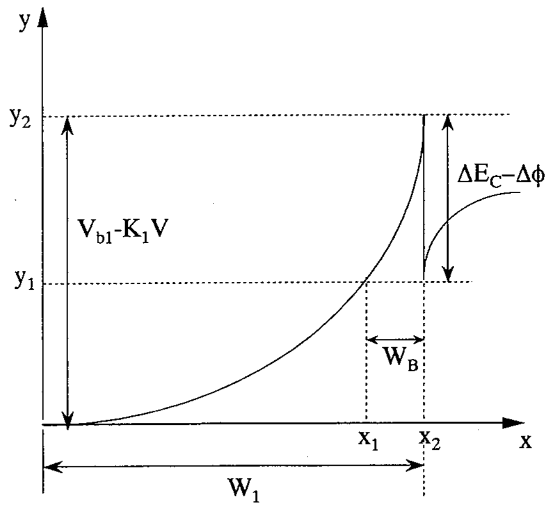

Fig. 7. Conduction band diagram in the depletion region of TiO_2.

relation

$$\frac{y_1}{y_2} = \frac{x_1^2}{x_2^2} \quad (19)$$

Here $x_2 = W_1$, the depletion width in TiO_2, $y_2 = V_{b1} - K_1V$, the junction voltage in TiO_2 depletion region under illumination, and $y_1 = V_{b1} - K_1V - H_B$.

Hence, $x_1 = \sqrt{\frac{y_1}{y_2}} x_2 = \sqrt{\frac{V_{b1} - K_1V - H_B}{V_{b1} - K_1V}} W_1.$ (20)

So the effective base width is given by

$$W_B = x_2 - x_1 = W_1\left\{1 - \sqrt{\frac{V_{b1} - K_1V - H_B}{V_{b1} - K_1V}}\right\} \quad (5)$$

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