Theoretical investigation of the effect of Ga content on the power conversion efficiency in ZnO/CdS/Cu(In,Ga)Se₂ cells

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Power conversion efficiency of solar cells is theoretically expected to have its maximum at an absorber energy band gap of \( E_g = 1.4 \) eV, but experimentally it is found at \( E_g = 1.18 \) eV for ZnO/CdS/Cu(In,Ga)Se₂ cells. In the present work, the explanation of this shift is sought in terms of optical losses through the window layer and interface recombination. The calculated results are compared with theoretical and experimental findings as reported in the literature.

Keywords: Cu(In,Ga)Se₂ solar cells, Ga content, Photovoltaic parameters, Interface recombination, Solar cells

1 Introduction

Theoretically, the highest power conversion efficiency of a solar cell should be obtained using an absorber with an energy band gap of approximately \( E_g = 1.4 \) eV. The chalcopyrite compound system Cu(In,Ga)Se₂ provides an absorber material with a continuously adjustable energy band gap between \( E_g = 1.02 \) eV (for CuInSe₂) and \( E_g = 1.68 \) eV (for CuGaSe₂), and therefore, it is suitable and has been often used to verify this prediction. Adjusting absorber energy band gap is performed through the variation of Ga content \( x = |\text{Ga}|/(|\text{Ga}|+|\text{In}|) \) in the absorber system. In the first approximation, a simple linear relation between \( E_g \) and \( x \) is assumed 

\[
E_g(x) = E_{CuInSe_2} + x(E_{CuGaSe_2} - E_{CuInSe_2})
\]

Solar cells based on this system exhibited a record power conversion efficiency of \( \eta = 20.3\% \) for a cell with an energy band gap of \( E_g = 1.18 \) eV (a Ga content of approximately 20-30\%), in disagreement with the theoretically expected statement mentioned above and also with theoretical studies made for ZnO/CdS/Cu(In,Ga)Se₂ solar cells without consideration of interface recombination.3,5

In an effort to explain this discrepancy a large number of investigations have been performed. Some groups attributed efficiency limitation at higher Ga content to a limited value of open-circuit voltage \( V_{oc} \) despite higher absorber energy band gaps.5-12 However, other works reported an increase in \( V_{oc} \) over the energy band gap range between \( E_g = 1.16 \) eV and \( E_g = 1.54 \) eV; they attributed the decrease in device efficiency with higher Ga content primarily to a lower fill factor.13,14 Limitation mechanisms are related to negative band offset between absorber and window layer,5,6 energy band gap inhomogeneity,7-10 or to higher density bulk defects in the absorber.11-15 Still, another group found a sharp drop down in the built-in potential at grain boundaries in the range of \( x = 28\% -38\% \), a fact that might explain the lower efficiency for \( x > 38\% \).

The explanation sought in the present paper for the discrepancy is based on two factors: on the one hand the window layer (including buffer) which obviously cuts a part of the solar spectrum, and on the other hand the interface recombination that always plays a considerable role in hetero-junctions as has been demonstrated for ZnO/CdS/CuGaSe₂ solar cells,18-20 meanwhile other researchers have considered recombination at grain boundaries.21 Hence, a detailed and comprehensive illustration of cell photovoltaic parameters as functions of Ga content is presented and discussed in terms of the effect of optical losses through the window layer and the effect of interface recombination.

2 Theory

The value of the light-generated current density \( j_{L0} \) can be calculated through the following integration:

\[
j_{L0} = q \int_{\lambda_{AM1.5}} Q(\lambda) \cdot \Phi(\lambda) \cdot d\lambda
\]

where \( q \) represents the electron charge, \( \lambda \) the wavelength and \( \Phi(\lambda) \) the AM1.5 solar spectrum, \( Q(\lambda) \) is the solar cell spectral quantum efficiency.
In the first stage, the effect of losses through the window layer on cell efficiency is considered, where \( j_{sc} = j_{L0} \) since there is no current loss of any type in the junction. Photovoltaic parameters are estimated for the ideal case (with no window layer) and for a realistic case (with a window layer composed of a thick ZnO film and a 50 nm CdS thin film) in the whole range of \( x \) between 0% and 100% in steps of 10%.

The ideal case is defined as the case without any optical losses. Here, \( Q(\lambda) \) is set equal to 1 for \( \lambda < \lambda_g \) where \( \lambda_g \) represents the wavelength equivalent to the energy band gap \( (\lambda_g = \hbar c/E_g) \), with \( E_g \) the energy band gap of Cu(In,Ga)Se\(_2\).

The minimum saturation current density \( j_0 \) is estimated\(^1\) as follows:

\[
    j_0 = 1.5 \times 10^6 \exp \left( \frac{E_g}{k_B T} \right) \quad \ldots(2)
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature.

The open-circuit voltage\(^1\) can be calculated through:

\[
    V_{oc} = \frac{k_B T}{q} \ln \left( \frac{j_{L0}}{j_0} + 1 \right) \quad \ldots(3)
\]

The maximum fill factor \( ff \) is given through the expression:\(^1\)

\[
    ff = \frac{V_{oc} - \ln \left( V_{oc} + 0.72 \right)}{V_{oc} + 1} \quad \ldots(4)
\]

where \( V_{oc} \) is a normalized voltage \( \left( V_{oc} = \frac{qV_{oc}}{k_B T} \right) \).

The power conversion efficiency \( \eta \) is defined as:

\[
    \eta = \frac{j_{sc} V_{oc,ff}}{P_{in}} \quad \ldots(5)
\]

where \( P_{in} \) is the total solar light power density incident on the cell.

The realistic case accounts for a reasonable window layer composed of a thick ZnO film that absorbs 100% of the incident light with \( \lambda < \lambda_g^{(ZnO)} \), and a 50 nm CdS thin film that absorbs ~40% of the incident light with \( \lambda < \lambda_g^{(CdS)} \). The calculation is performed by setting \( Q(\lambda) \) equal to 1 between \( \lambda_g^{(absorber)} \) and \( \lambda_g^{(CdS)} \) and equal to 0.6 between \( \lambda_g^{(CdS)} \) and \( \lambda_g^{(ZnO)} \) and to zero elsewhere. This leads to changes in the values of \( j_{L0}, V_{oc}, ff \) and \( \eta \) according to Eqs (1, 3-5).

In the next stage, in addition to the losses through the window layer (as defined in the realistic case) the effect of interface recombination will be considered. Hereby, the values of \( j_{L0} \) are set the same as in the realistic case. All other parameters will be calculated according to the interface recombination model described earlier.\(^5\) In the model, the saturation current density \( j_0 \) and the diode ideality factor \( n \) relate to the interface state density \( N_s \) as follows:

\[
    j_0 = q v_m \sigma_p N_s N_n \exp \left[ -\frac{qV_{d}}{n k_B T} \right] \quad \ldots(6)
\]

\[
    N_s = \sqrt{\frac{2 e_1 e_0 N_p V_{d} (n-1)}{q n}} - \sqrt{\frac{2 e_2 e_0 N_p V_{d}}{q n}} \quad \ldots(7)
\]

and the short-circuit current density can be calculated through the following equations:

\[
    j_{sc} = \frac{j_{L0}}{1 + \frac{\sigma_p v_m N_s e_0 e_1}{q \mu_{CdS} N_p W_t}} \quad \ldots(8)
\]

\[
    W_t = \sqrt{\frac{2 e_2 e_0 V_{d} (n-1)}{q N_p n}} \quad \ldots(9)
\]

where \( v_m \) is the thermal velocity, \( \sigma_p \) the capture cross-section for holes at the interface, \( N_p \) the donor concentration, \( N_n \) the acceptor concentration, \( e_1, e_2 \) are the relative dielectric constant of CdS and Cu(In,Ga)Se\(_2\), respectively, \( e_0 \) is the dielectric constant of free space and \( V_{d} \) is the diffusion voltage. \( W_t \) represents the depletion layer width in the window layer and \( \mu_{CdS} \) the mobility of electrons in CdS. The short-circuit current density \( j_{sc} \) can be calculated using Eq.(8), and then the open-circuit voltage \( V_{oc} \) can be determined using the following equation:

\[
    V_{oc} = \frac{n k_B T}{q} \ln \left( \frac{j_{sc}}{j_0} + 1 \right) \quad \ldots(10)
\]

The illuminated \( j-V \) characteristic can then be drawn and the fill factor \( ff \) can be calculated through:
where $P_m = j_m V_m$ is the value of maximum power of the cell. $j_m$ the current density value and $V_m$ is the voltage value at the maximum power point.

The cell efficiency can be calculated through Eq. (5). By changing the Ga content, other parameters also change.

The diffusion voltage $V_d$ is related to the energy band gap by:

$$V_d = \frac{E_g - \delta_n - \delta_p - \Delta E_C}{q}$$

where $\delta_n = E_C - E_F$ and $\delta_p = E_p - E_V$. The quantities $E_C$, $E_F$ and $E_V$ represent the conduction band energy, Fermi-level energy and valence band energy, respectively. The Fermi levels can be calculated using the Eqs (13 and 14):

$$E_F - E_C = k_B T \ln \frac{N_i}{N_c} \quad \text{(for n-type semiconductor)}$$

and

$$E_V - E_F = k_B T \ln \frac{N_d}{N_v}$$

(for p-type semiconductor)

The conduction band effective density of states can be written as:

$$N_C = 2.5 m_{eff.,C}^2/3 \times 10^{19} / \text{cm}^3$$

and for the valance band of CdS the following equation is valid:

$$N_V = 2.5 m_{eff.,V}^2/3 \times 10^{19} / \text{cm}^3$$

The conduction band offset $\Delta E_C$ is defined as:

$$\Delta E_C = q (\chi_{CdS} - \chi_{Cu(In,Ga)Se_2})$$

where $\chi_{CdS}$ and $\chi_{Cu(In,Ga)Se_2}$ are the electron affinity of CdS and Cu(In,Ga)Se$_2$, respectively. Due to inter-diffusion at the hetero-junction, it is reasonable to assume a reduced $\Delta E_C$ as compared to its expected value taking the affinity data for bulk materials. Based on this assumption and following the literature data that indicate that the electron affinity of CdS is higher than that of CuInSe$_2$, and the last one is also higher$^{27-29}$ than that of CuGaSe$_2$, the conduction band offset for the junction CdS/CuInSe$_2$ can be set to $\Delta E_C = 0.1$ and for CdS/CuGaSe$_2$ to $\Delta E_C = 0.2$. This is justified through the estimation of the diffusion voltage for a CdS/CuGaSe$_2$ cell to $V_d = 1.26$ V according to Eq. (12) with $E_g = 1.68$ eV, $\delta_n \sim 0.02$ eV and $\delta_p \sim 0.2$ eV. Otherwise, the expected value of the diffusion voltage for this cell using the bulk-affinity data would be $V_d = 0.86$ V. This value is lower than the experimentally achieved open-circuit voltage$^{30}$ of $V_{oc} = 0.946$ V, in contradiction to the fact that the diffusion voltage represents the highest achievable open-circuit voltage value. The conduction band offset $\Delta E_C$ changes linearly with Ga content $x$ according to the following relation:

$$\Delta E_C = 0.1 + 0.1 x$$

The effective mass of holes is assumed to change as:

$$m_{eff.,h} = 0.73 m_0 + x (m_{eff.,h2} - m_{eff.,h1})$$

where $m_{eff.,h1}$, $m_{eff.,h2}$ are the effective mass of holes in CuInSe$_2$ and CuGaSe$_2$, respectively. In the literature $m_{eff.,h1}$ has a value of $m_{eff.,h1} = 0.73 m_0$ (Ref. 30), and $m_{eff.,h2}$ has a value of $m_{eff.,h2} = 1.2 m_0$ (Ref. 31). For CdS, the value of the effective mass of electrons is $m_{eff.,e} = 0.21 m_0$ (Refs 32, 33).

The carrier’s thermal velocity $v_{th}$ is given by:

$$v_{th} = \frac{kT}{\sqrt{m_{eff.}}}$$

The relative dielectric constant was set $\varepsilon_r = 11.6$ for CdS, $\varepsilon_r = 10$ for CuInSe$_2$, and $\varepsilon_r = 13.6$ for CuGaSe$_2$ (Ref. 31). The value of $\varepsilon_r$ was assumed to change linearly with increasing Ga content between $\varepsilon_r(CuInSe_2)$ and $\varepsilon_r(CuGaSe_2)$.

Based on these relations, photovoltaic parameters are calculated depending on $N_i$ in the whole range of $x$ between 0% and 100% in steps of 10%. The calculation was performed taking the following reasonable material parameters:
Donor concentration in the window layer $N_1 = 1 \times 10^{18}$ cm$^{-3}$, acceptor concentration in the absorber $N_2 = 1 \times 10^{16}$ cm$^{-3}$, mobility of electrons in CdS $\mu_{\text{CdS}} = 0.005$ cm$^2$/Vs, and capture cross-section for holes at the interface $\sigma_p = 5 \times 10^{-17}$ cm$^2$.

3 Results and Discussion

Figure 1 shows the calculation results of the photovoltaic parameters ($j_{\text{sc}}, V_{\text{oc}}, ff, \eta$) for the ideal case and the realistic case mentioned above depending on Ga content without any recombination losses. Starting from the ideal case, whose results agree well with Ref. (1), Fig. 1 clearly shows that optical losses due to absorption in the window lead mainly to a parallel shift in the short-circuit current density towards lower values, whereas there is no noticeable change in open-circuit voltage and fill factor. The overall effect on solar cell efficiency is a larger shift towards lower values with increasing Ga content; for example, the window layer leads to a reduction in efficiency of approximately 2% at $x = 0\%$ (CuInSe$_2$), whereas this reduction exceeds 4% for $x = 100\%$ (CuGaSe$_2$). For both cases the power conversion efficiency reaches its maximum at $x = 50\%$ ($E_g = 1.35$ eV), although that maximum is less pronounced for the realistic case with optical losses. This was a first indication of how a change in only one parameter (short-circuit current density) has caused an overall change in the power conversion efficiency dependence on Ga content. Additionally, interface recombination affects all other parameters, as shown in Fig. 2.

Concerning the influence of $N_{ir}$ on $j_{\text{sc}}$, it is clear that very low values of $N_{ir}$ lead to a rapid reduction in $j_{\text{sc}}$ and that a further significant increase in $N_{ir}$ does not lead to a further decrease in $j_{\text{sc}}$. Concerning the open-circuit voltage, Fig. 2 shows that the curves $V_{\text{oc}}(N_{ir})$ for different $x$ values cannot be reproduced from each other through a pure shift in y-axis. By changing $x$ between $x = 0\%$ (CuInSe$_2$) and $x = 100\%$ (CuGaSe$_2$), $V_{\text{oc}}$ changes from $V_{\text{oc}} = 0.62$ V to $V_{\text{oc}} = 1.16$ V for a low $N_{ir}$ value ($N_{ir} = 1 \times 10^{12}$ cm$^{-2}$), while for a moderate $N_{ir}$ value ($N_{ir} = 2.5 \times 10^{12}$ cm$^{-2}$) $V_{\text{oc}}$ changes from $V_{\text{oc}} = 0.30$ V to $V_{\text{oc}} = 1.04$ V. The behaviour of the fill factor $ff$ is similar to that of $V_{\text{oc}}$, however, more pronounced: while it exhibits only a small change from $ff = 0.82$ to $ff = 0.89$ for $N_{ir} = 1 \times 10^{12}$ cm$^{-2}$, it shows a significant increase from $ff = 0.44$ to $ff = 0.82$ for $N_{ir} = 2.5 \times 10^{12}$ cm$^{-2}$. Solar cell efficiency $\eta$ as a product of $j_{\text{sc}}, V_{\text{oc}}$ and $ff$ behaves in a more complex manner.
manner; unlike other parameters, the curves of $\eta$ intersect, resulting in a maximum of $\eta$ at a certain value of $x$ for each $N_{ir}$.

In Fig. 2, both $N_{ir}$ and $x$ are dealt with as independent parameters. However, in order to gain statements about photovoltaic parameters as functions of Ga content $x$, it is reasonable to define a relation between $N_{ir}$ and $x$. Often interface state density is represented through another parameter $N^*_ir$, which is the interface state density per energy unit of the energy band gap in units of cm$^{-2}$ eV$^{-1}$, unlike $N_{ir}$ which is given in units of cm$^{-2}$ meaning the amount of interface state density in the whole band gap. The total amount of interface state density $N_{ir}$ is a direct product of $N^*_ir$ and the band gap $E_g$. Photovoltaic parameters ($j_{sc}$, $V_{oc}$, $ff$, $\eta$) can now be calculated as functions of Ga content for a certain value of $N^*_ir$. Figure 3 shows these parameters depending on Ga content $x$ between $x = 0\%$ (CuInSe$_2$) and $x = 100\%$ (CuGaSe$_2$) for 4 different values of $N^*_ir$ representing a wide range of interface state densities. Additionally, in Fig. 2, the parameters calculated for the ideal case

Fig. 2 — Calculation results of the photovoltaic parameters depending on the interface state density $N_{ir}$ depending on Ga content. Two lines are drawn for guidance at $N_{ir} = 1\times10^{12}$ cm$^{-2}$ and $N_{ir} = 2.5\times10^{12}$ cm$^{-2}$ in the graphs for open circuit voltage and fill factor.
and realistic case are also presented for comparison. While the influence of the window layer is a simple parallel shift of all current densities towards lower values, the shift caused by $N^*_ir$ depends on the value of $j_{sc}$ itself. The effect of interface states on $j_{sc}$ seems to be approximately the same for all 4 $N^*_ir$ values: they cause a reduction in $j_{sc}$ of approximately 3 mA/cm² for $x = 0\%$ and of approximately 1 mA/cm² for $x = 100\%$ compared to the realistic case with $N^*_ir = 0$. Concerning the open-circuit voltage, Fig. 3 shows that while the effect of window layer on $V_{oc}$ is almost negligible for all $x$ values, the reduction of $V_{oc}$ caused by interface states is proportional to both parameters $x$ and $N^*_ir$, so that for $N^*_ir = 2 \times 10^{12}$ cm⁻² eV⁻¹ the value of $V_{oc}$ reaches a saturation at $x = 60\%$. The same statements are valid for the fill factor, with the difference that for high $N^*_ir$ the values of $ff$ start to decrease with increasing $x$. In comparison to the effect of window layer on solar cell conversion efficiency which keeps the maximum of $\eta$ at about $x = 50\%$, the effect of interface states further reduces $\eta$ and shifts its maximum towards
\( x = 20\% \). This effect is more pronounced for higher \( N_{ir}^* \) values. These results agree well with experimental findings\(^{2,11-14} \), meanwhile they disagree with theoretical studies that do not take interface recombination into account\(^{3,4} \). Those studies expect \( \eta \) to have its maximum at about \( x = 50\% \) assuming a mid-gap recombination center and neglecting interface recombination. In the present investigation, however, the maximum of \( \eta \) is shifted to about \( x = 20\% \) even for very low values of \( N_{ir}^* \). This investigation clearly demonstrates that taking the effect of window layer and interface recombination into consideration provides an evident explanation for the disagreement between theoretically expected statement and experimentally observed results concerning the Ga content value at which power conversion efficiency of ZnO/CdS/Cu(In,Ga)Se\(_2\) solar cells reaches its maximum.

### 4 Conclusions

Our calculations revealed that the effect of window layer on ZnO/CdS/Cu(In,Ga)Se\(_2\) solar cell performance is mainly restricted to a simple parallel shift of the current density curve towards lower values, with no considerable effect on open circuit voltage nor on fill factor. The overall effect of window layer on cell efficiency is a higher reduction of \( \eta \) at higher Ga content \( x \) leading to the maximum of \( \eta \) at \( x = 50\% \) to become less pronounced.

The application of the interface recombination model resulted in a further decrease in efficiency values and in a shift in its maximum position from \( x = 50\% \) towards \( x = 20\% \). Furthermore, the application of the interface recombination model allows the simulation of a saturation behaviour of the open circuit voltage and even a fall down in the fill factor with higher \( x \) at sufficiently high \( N_{ir}^* \) values. These results agree well with experimental findings, meanwhile they disagree with theoretical studies that do not take interface recombination into account. Taking the effect of window layer and interface recombination into consideration, provides an evident explanation for the discrepancy between the absorber band gap at which efficiency maximum is theoretically expected and that gap at which the maximum is experimentally found.

### References