Indian Journal of Pure & Applied Physics
Vol. 53, April 2015, pp. 263-270

Theoretical investigation of the effect of Ga content on the power conversion efficiency in ZnO/CdS/Cu(In,Ga)Se_2 cells

A Kassis & M Saad

Atomic Energy Commission of Syria, P.O. Box 6091, Damascus, Syria

E-mail: pscientific2@aec.org.sy

Received 2 November 2013; revised 24 September 2014; accepted 22 February 2015

Power conversion efficiency of solar cells is theoretically expected to have its maximum at an absorber energy band gap of $E_g \approx 1.4$ eV, but experimentally it is found at $E_g = 1.18$ eV for ZnO/CdS/Cu(In,Ga)Se_2 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)Se_2 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[1] of approximately $E_g = 1.4$ eV. The chalcopyrite compound system Cu(In,Ga)Se_2 provides an absorber material with a continuously adjustable energy band gap between $E_g = 1.02$ eV (for $CuInSe_2$) and $E_g = 1.68$ eV (for $CuGaSe_2$), 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 [$x = |Ga|/(|Ga|+|In|)$] in the absorber system. In the first approximation, a simple linear relation between E_g and x is assumed [$E_g(x) = E_{gCuInSe_2} + x\,(E_{gCuGaSe_2} - E_{gCuInSe_2})$]. Solar cells based on this system exhibited a record power conversion efficiency of $\eta = 20.3\%$ for a cell with an energy band gap[2] 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)Se_2 solar cells with no 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 inhomogenity[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[16,17] 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/$CuGaSe_2$ 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:

$$j_{L0} = q \int_{AM1.5} Q(\lambda) \cdot \Phi(\lambda) \cdot d\lambda \qquad \ldots(1)$$

where q represents the electron charge, λ the wavelength and $\Phi(\lambda)$ the AM1.5 solar spectrum[22], $Q(\lambda)$ 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 λ_g represents the wavelength equivalent to the energy band gap ($\lambda_g = hc/E_g$), 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:

$$j_0 = 1.5\times10^8 \exp\left(-\frac{E_g}{k_B T}\right) \quad \ldots(2)$$

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]:

$$ff = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \quad \ldots(4)$$

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

The power conversion efficiency η 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 η 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[23]. In the model, the saturation current density j_0 and the diode ideality factor n relate to the interface state density N_{ir} as follows:

$$j_0 = q\, v_{th} \sigma_p N_{ir} N_2 \exp\left[\frac{-qV_d}{n k_B T}\right] \quad \ldots(6)$$

$$N_{ir} = \sqrt{\frac{2\varepsilon_{r1}\varepsilon_0 N_1 V_d}{q}\frac{(n-1)}{n}} - \sqrt{\frac{2\varepsilon_{r2}\varepsilon_0 N_2 V_d}{q\, n}} \quad \ldots(7)$$

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

$$j_{sc} = \frac{j_{L0}}{1 + \frac{\sigma_p v_{th} N_{ir} \varepsilon_{r1}\varepsilon_0}{q\mu_{CdS} N_1 W_1}} \quad \ldots(8)$$

$$W_1 = \sqrt{\frac{2\varepsilon_{r1}\varepsilon_0 V_d (n-1)}{q N_1 n}} \quad \ldots(9)$$

where v_{th} is the thermal velocity, σ_p the capture cross-section for holes at the interface, N_1 the donor concentration, N_2 the acceptor concentration, ε_{r1}, ε_{r2} are the relative dielectric constant of CdS and $Cu(In,Ga)Se_2$, respectively, ε_0 is the dielectric constant of free space and V_d is the diffusion voltage. W_1 represents the depletion layer width in the window layer and μ_{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:

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

The illuminated j-V characteristic can then be drawn and the fill factor ff can be calculated through:

$$ff = \left| \frac{P_m}{j_{sc} V_{oc}} \right| \quad \ldots(11)$$

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[24] by:

$$V_d = \frac{E_g - \delta_n - \delta_p - \Delta E_C}{q} \quad \ldots(12)$$

where $\delta_n = E_C - E_F$ and $\delta_p = E_F - E_V$. 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[25] using the Eqs (13 and 14):

$$E_F - E_C = k_B T \ln \frac{N_1}{N_C} \text{ (for } n\text{-type semiconductor)} \ldots(13)$$

and

$$E_V - E_F = k_B T \ln \frac{N_2}{N_V}$$

(for p-type semiconductor) …(14)

The conduction band effective density of states[26] can be written as:

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

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

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

The conduction band offset ΔE_C is defined as:

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

where χ_{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 ΔE_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[20] 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 ΔE_C changes linearly with Ga content x according to the following relation:

$$\Delta E_C = 0.1 + 0.1x \quad \ldots(15)$$

The effective mass of holes is assumed to change as:

$$m_{eff,h} = 0.73 m_0 + x\left(m_{eff,h2} - m_{eff,h1}\right) \quad \ldots(16)$$

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:

$$v_{th} = 2\sqrt{\frac{kT}{m_{eff}}} . \quad \ldots(17)$$

The relative dielectric constant[33] 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 ε_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_{ir} 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 $N_1 = 1\times10^{18}$ cm^{-3}, acceptor concentration in the absorber $N_2 = 1\times10^{16}$ cm^{-3}, mobility of electrons in CdS $\mu_{CdS} = 0.005$ cm^2/Vs, and capture cross-section for holes at the interface $\sigma_p = 5\times10^{-17}$ cm^2.

3 Results and Discussion

Figure 1 shows the calculation results of the photovoltaic parameters (j_{sc}, V_{oc}, ff, η) 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_{sc}, it is clear that very low values of N_{ir} lead to a rapid reduction in j_{sc} and that a further significant increase in N_{ir} does not lead to a further decrease in j_{sc}. Concerning the open-circuit voltage, Fig. 2 shows that the curves $V_{oc}(N_{ir})$ 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_{oc} changes from $V_{oc} = 0.62$ V to $V_{oc} = 1.16$ V for a low N_{ir} value ($N_{ir} = 1\times10^{12}$ cm^{-2}), while for a moderate N_{ir} value ($N_{ir} = 2.5\times10^{12}$ cm^{-2}) V_{oc} changes from $V_{oc} = 0.30$ V to $V_{oc} = 1.04$ V. The behaviour of the fill factor ff is similar to that of V_{oc}, however, more pronounced: while it exhibits only a small change from $ff = 0.82$ to $ff = 0.89$ for $N_{ir} = 1\times10^{12}$ cm^{-2}, it shows a significant increase from $ff = 0.44$ to $ff = 0.82$ for $N_{ir} = 2.5\times10^{12}$ cm^{-2}. Solar cell efficiency η as a product of j_{sc}, V_{oc} and ff behaves in a more complex

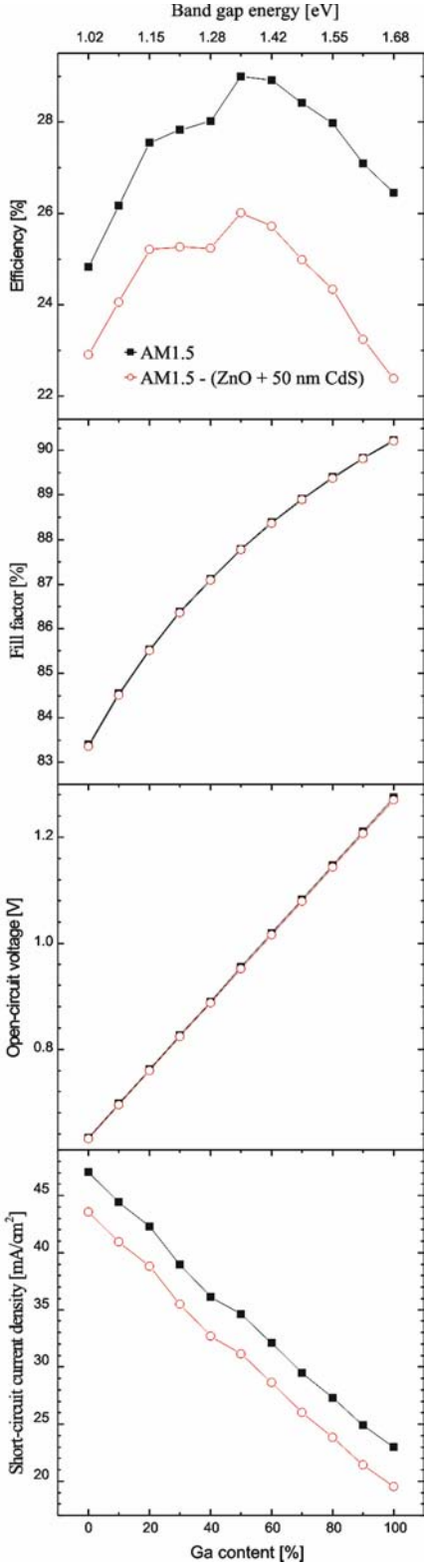

Fig. 1 — Calculation results of the photovoltaic parameters for the ideal case and the realistic case depending on Ga content without any recombination losses

manner: unlike other parameters, the curves of η intersect, resulting in a maximum of η 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[34-39] 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, η) 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

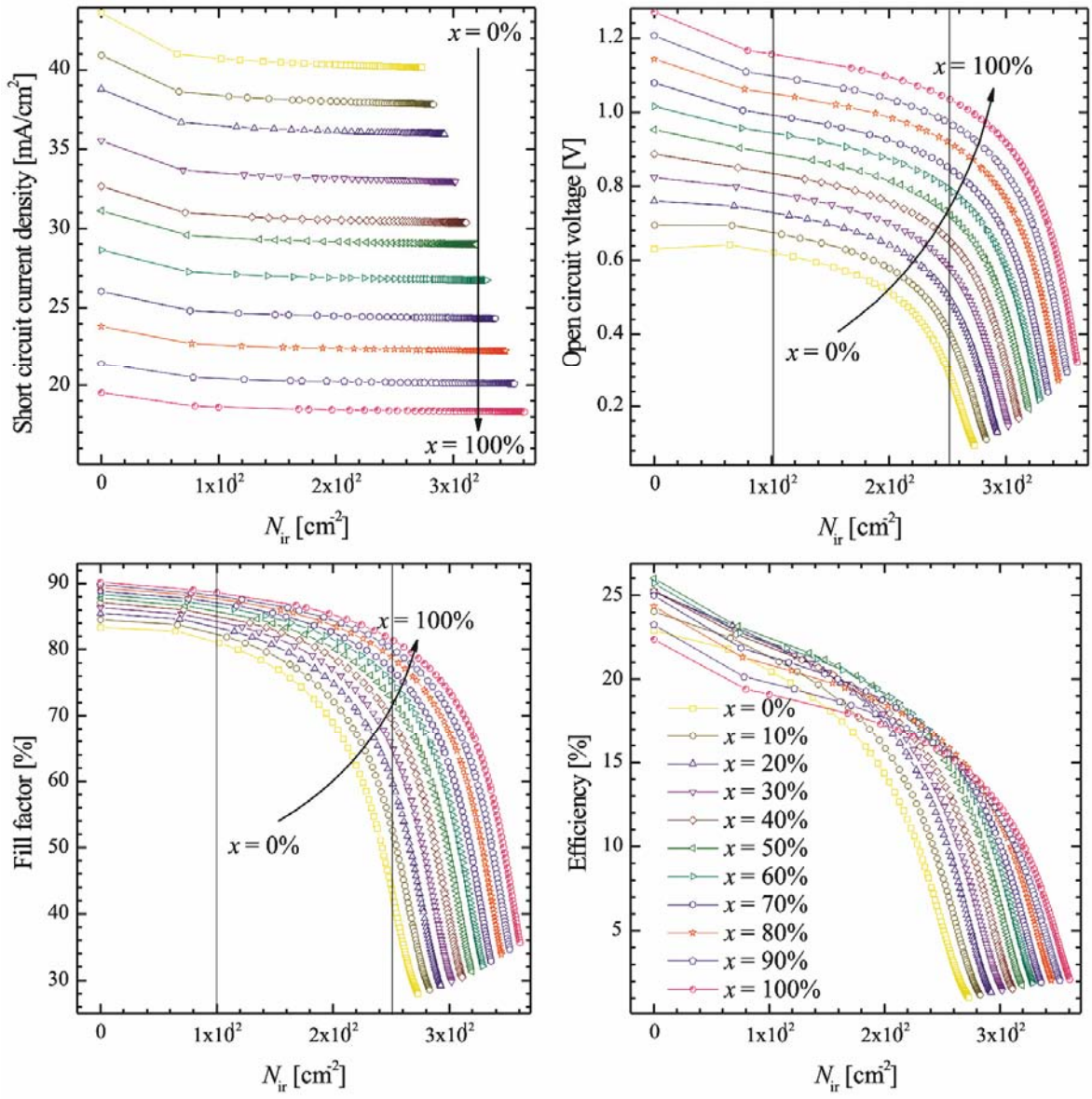

Fig. 2 — Calculation results of the photovoltaic parameters depending on the interface state density N_{ir} depending on Ga content. Two lines are drawn for guidance at $N_{ir} = 1\times10^{12}\,cm^{-2}$ and $N_{ir} = 2.5\times10^{12}\,cm^{-2}$ in the graphs for open circuit voltage and fill factor

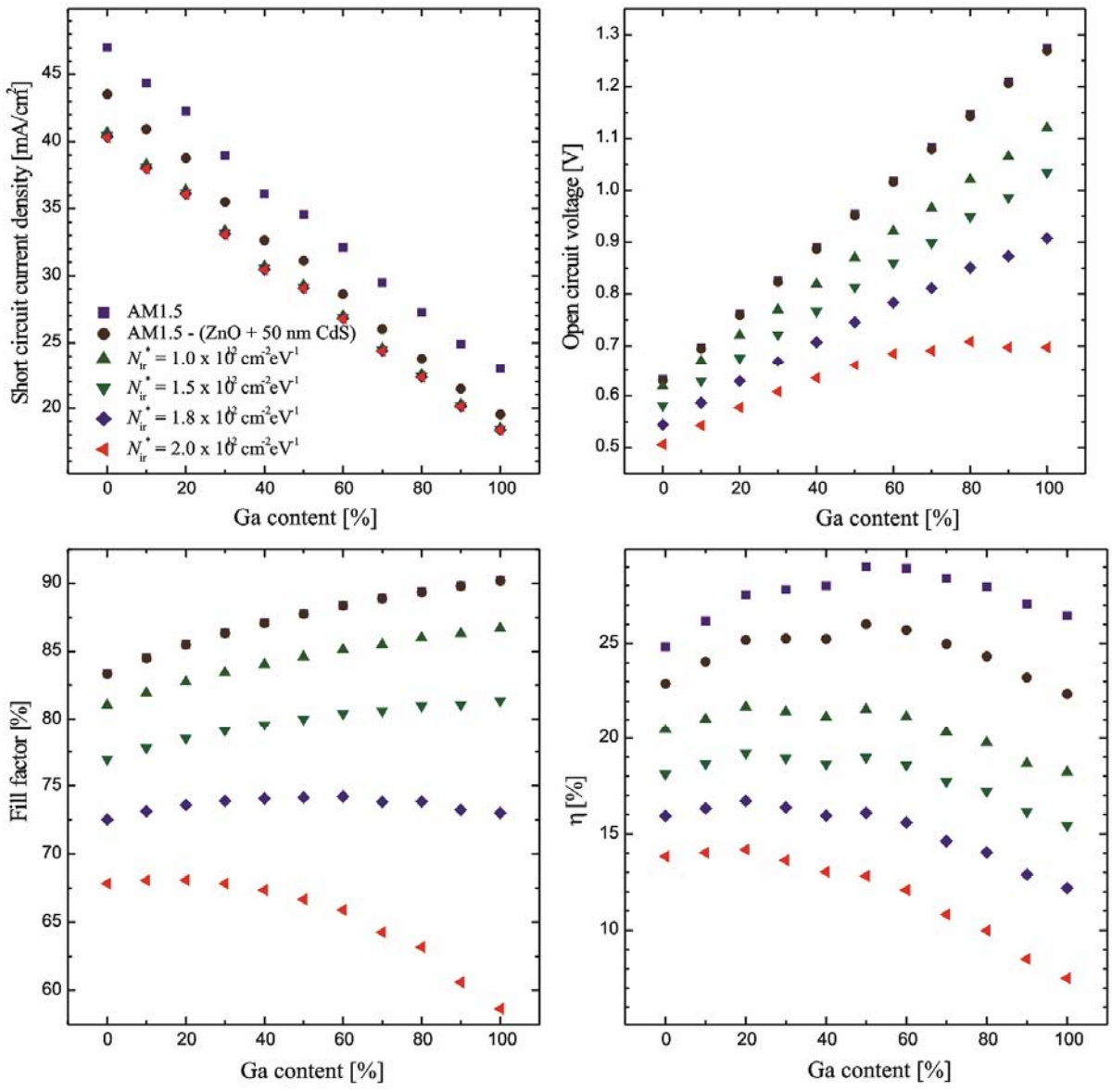

Fig. 3 — Photovoltaic parameters depending on Ga content for 4 different values of interface state density per energy unit N^*_{ir}. For comparison, the parameters calculated for the ideal case and the realistic case are also plotted

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/cm^2 for $x = 0\%$ and of approximately 1 mA/cm^2 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 $N^*_{ir} = 2\times10^{12}$ 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 η at about $x = 50\%$, the effect of interface states further reduces η 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 η 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 η 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 η at higher Ga content x leading to the maximum of η 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

1 Green M A, *Solar Cells*, Englewood Cliffs, (1982) 88.

2 Jackson P, Hariskos D & Lotter E, *Prog Photovolt Res Appl*, 19(7) (2011) 894.

3 Gloeckler M, Fahrenbruch A L & Sites J R, *Photovoltaic Energy Conversion*, Osaka Japan, (2003) 491.

4 Gloeckler M & Sites J R, *J Phys & Chem of Solids*, 66 (2005) 1891.

5 Gloeckler M & Sites J R, *Thin Solid Films*, 480-481 (2005) 241.

6 Yamada A, Matsubara K & Sakurai K, *Appl Phys Lett*, 85 (2004) 5607.

7 Ludwig C D R, Gruhn T & Claudia F, *Phys Rev Lett*, 105 (2010) 25702.

8 Gütay L & Bauer G, *Thin Solid Films*, 515 (2007) 6212.

9 Mattheis J, Rau U & Werner J H, *J Appl Phys*, 101 (2007) 113519.

10 Mattheis J, Schlenker T & Rau U, *MRS Proc*, 865 (2005) F16.4.

11 Hanna G, Jasenek A, Rau U & Schock H W, *Thin Solid Films*, 387 (2001) 71.

12 Rau U, Schmidt M & Jasenek A, *Sol Energy Mater & Sol Cells*, 67 (2001) 137.

13 Shafarman W N, Klenk R & Mc Candless B E, *J Appl Phys*, 79 (1996) 7324.

14 Shafarman W N, Klenk R & Mc Candless B E, *Proc 25th PVSC*, Washington, D C, (1996) 763.

15 Heath J T, Cohen J D & Shafarman W N, *Appl Phys Lett*, 80 (2002) 4540.

16 Jiang C-S, Noufi R & Ramanathan K, *IEEE photovolt Special Conf and Exhib*, (2005) 251.

17 Jiang C-S, Contreras M A & Repins I, *IEEE photovolt Special Conf and Exhib*, (2012)1486.

18 Saad M & Kassis A, *Sol Energy Mater & Sol Cells*, 77 (2003) 415.

19 Saad M & Kassis A, *Renewable Energy*, 33 (2008) 974.

20 Saad M & Kassis A, *Sol Energy Mater & Sol Cells*, 95 (2011) 1927.

21 Singh L, Saxena M & Bhatnagar P K, *Indian J Pure & Appl Phys*, 42 (2004) 841.

22 Reference Solar Spectral Irradiance: ASTM G-173 available at http://rredc.nrel.gov/solar/spectra/am1.5/ASTMG173/ASTMG173.html

23 Saad M & Kassis A, *Sol Energy Mater & Sol Cells*, 79 (2003) 507.

24 Fahrenbruch A L & Bube R H, *Fundamentals of solar cells*, Academic Press, New York, (1983) 133.

25 Sze S M, *Physics of semiconductor devices*, John Wiley & Sons, New York, (1981) 849.

26 Ashcroft N W & Mermin N D, *Solid state physics*, Sounders college publishing, New York, (1976) 574.

27 Wei S H & Zunger A, *Appl Phys Lett*, 63 (1993) 2549.

28 Sugiyama M, Nakanishi H & Chichibu S F, *Jpn J Appl Phys*, 40 (2001) 428.

29 Swank R K, *Phys Rev*, 153 (1967) 844.

30 Zott S, Leo K, Ruckh M & Schock H W, *J Appl Phys*, 82 (1997) 356.

31 Mandel L, Tomlinson R D, Hampshire M J & Neumann H, *Solid State Comm*, 32 (1979) 201.

32 Flietner H, *Phys Stat Solidi B*, 54 (1972) 201.

33 Boer K W, *Survey of Semiconductor Physics,* Van Nostrand Reinhold, New York, (1990) 444.

34 Gudovskikh A S, Kleider J P & Stangl R, *J Non-Crystalline Solids*, 352 (2006) 1213.

35 Saha A R, Chattopadhyay S, Bose C & Maiti C K, *Thin Solid Films*, 504 (2006) 86.

36 Gomila G, *J Phys D Appl Phys*, 32 (1999) 64.

37 Karatas S, Altındal S & Cakar M, *Physica B*, 357 (2005) 386.

38 Bülbül M M & Zeyrek S, *Microelectronic Engineering*, 83 (2006) 2522.

39 Turcu M & Rau U, *Springer Series in Materials Sci*, 86 (2006) 91.