International Journal of Scientific Engineering and Technology
Volume No.5 Issue No.5, pp: 252-255

ISSN:2277-1581
01 May 2016

Effect of [Ga]/[In+Ga] Atomic Ratio on Electric Parameters of Cu(In,Ga)Se_2 Thin Film Solar Cells

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Abstract: In this paper we study the influence of [Ga]/[In + Ga] atomic ratio on electric parameters of the CIGS solar cell. We conduct the simulation of a solar cell constituted of window layer (ZnO)/ buffer layer (CdS)/ absorber Cu(In,Ga)Se₂ using the SCAPS-1D program. We vary the [Ga]/[In + Ga] atomic ratio according to the values 0.3; 0.5 and 0.7. This variation intended to study the behavior of macroscopic electrical parameters (Voc, Jsc, FF, η), characteristic J/V, conductance G/V, capacitance C/V and external quantum efficiency EQE of the cell. The results obtained show that the performance of CIGS solar cells decrease with increasing in [Ga]/[In+Ga] ratio. A conversion efficiency of about 21.54% is obtained with the cell having a ratio of 0.3. This makes it the most promising approach of our cells studied.

Keywords— CIGS solar cells, [Ga]/[In+Ga], electric parameters, external quantum efficiency, SCAPS-1D.

I. Introduction

Nowadays, the Photovoltaic technology based on CIGS has considerable growth potential in improving performance and lower production costs. The best way to understand the working mechanisms of these devices such as currents transport, electron-hole generation and recombination phenomena is the construction of numerical models for simulation. For this we used a numerical simulation software called SCAPS-1D (Solar Cell Capacitance Simulator one dimension), developed in the laboratory ELIS (Electronics and Information Systems) from the University of Gent, Belgium **[1]**. This allows elucidating the processes which limit the cell performance and give an optimal design of the structures at the base of these devices. In this article, we study the influence of [Ga]/[In + Ga] atomic ratio on electrical parameters of CIGS solar cell. Different cells with varying atomic ratios are used. The parameters studied are the current-voltage characteristic (J/V), the open circuit voltage (Voc), the short-circuitcurrent density (Jsc), the fill factor (FF), the conversion efficiencies (η), the capacitance-voltage characteristic, the conductance-voltage characteristic and the quantum efficiency (QE). This work allows us to take note of the atomic ratio which would lead to an optimal CIGS cell.

II. Numerical simulation

- **SCAPS-1D Numerical Simulation Program**

The SCAPS-1D is Windows application software. It was developed to simulate the electrical characteristics of heterojunction solar cells and thin film. It has been extensively tested in solar cells made of CdTe and Cu(In, Ga)Se_2 by M.Burgelman et al [1].

The simulation software proceeds by solving three fundamental equations of a semiconductor which is the Poisson equation and the continuity equations:

$$\nabla.\ \varepsilon\nabla\emptyset = -q(p - n + N_{D+} - N_{A-}) \quad (1)$$

$$\nabla.\overrightarrow{Jn} = q(R - G) + q\frac{\partial n}{\partial t} \quad (2)$$

$$\nabla.\overrightarrow{Jp} = q(R - G) + q\frac{\partial p}{\partial t} \quad (3)$$

Where ε is the dielectric constant; φ the electrostatic potential; n and p are the concentrations of free carriers; N_{D+} and N_{A-} the densities of the ionized acceptors and donors. J_n and J_p are the current densities of electrons and holes; R is the recombination rate and G the electron-hole generation rate.

- **Cell Structure and Materials Properties**

The cell structure that is simulated in this study is an *"window layer n-ZnO/emitter n-CdS /base Cu(In, Ga)Se_2"*. This enables us to study the influence of [Ga]/[In + Ga] ratio on electric parameters. The experimental conditions are an ambient temperature of 300K, a low series resistance, an "infinite" shunt resistance compared to series resistance, under an illumination spectrum of AM_1.5 and an incident light power of 1000W.m^{-2}.The baseline set of parameters for electrical modelling was obtained from measurements done in the group, measurement data found in literature and previous work by others dealing with modelling of CIGS solar cells [2]. This parameter set is presented in Table 1.

Table 1: The baseline parameters for modelling CIGS cells with CdS buffer layer

Layer properties				
	CIGS	CdS	ZnO	ZnO/ Al
Thickness [µm]	1.8	0.05	0.1	0.3
E_g [eV]	Variant	2.4	3.3	3.3
ε_r	13.6	5.4	9	9
N_c[cm^{-3}]	6.8×10^{17}	1.3×10^{18}	3.0×10^{18}	3.0×10^{18}
N_v[cm^{-3}]	1.5×10^{19}	9.1×10^{18}	1.7×10^{19}	1.7×10^{19}

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V_{th}^{e}[cm/s]	3.9×10^{7}	3.1×10^{7}	2.4×10^{7}	2.4×10^{7}
V_{th}^{p}[cm/s]	1.4×10^{7}	1.6×10^{7}	1.3×10^{7}	1.3×10^{7}
μ_e [cm/Vs]	100	72	100	100
μ_p [cm/Vs]	12.5	20	31	31
Doping [cm^{-3}]	10^{16} (a)	5×10^{17} (d)	10^{17} (d)	10^{20} (d)

In the table 1, (a) and (d) denote shallow acceptor and donor defects when (A), (D) and (N) denote deep acceptor, donor and neutral defects. The absorber layers were deposited in a system that produces layers of graded composition with regards to the group III elements [3]. This can be described with the compositional ratio defined in Eq. (4):

$$GGI = \frac{[Ga]}{[Ga]+[In]} \quad (4)$$

In simulation the band gap and the electronic affinity were set to vary with composition. The dependence of the band gap on GGI was implemented using Eq. (5) [4-5].

$$Eg = 1.01 + 0.626 * GGI - 0.167 * (1 - GGI) \quad (5)$$

Almost all of the band gap widening is due to a change in the energetic position of the conduction band minimum [6]. In addition to the band gap also the absorption coefficients of CIGS are set to vary with composition based on the optical constants. [7-8]. Optical constants of CBD CdS were drawn from the same work while absorption coefficients of the undoped and Al-doped ZnO layers were obtained from reflection-transmission (RT) [9]. Density of states at the conduction band minimum (N_c) and valence band maximum (N_v) are calculated using Eq. (6) [10].

$$N_{c/v} = 2\left(\frac{2\pi m^*_{e/p} kT}{h^2}\right)^{3/2} \quad (6)$$

Where $m^*_{e/p}$ the effective band masses of electrons/holes, h are is Planck's constant and k is the Boltzmann constant. Thermal velocities for electrons (V_{th}^{e}) and holes (V_{th}^{p}) are obtained from Eq. (7) [10].

$$V_{th}^{e/p} = \sqrt{\frac{3kT}{m^*_{e/p}}} \quad (7)$$

The nobilities are chosen in such a way that the following approximate relation holds [10].

$$\frac{\mu_p}{\mu_e} \approx \frac{m^*_e}{m^*_p} \quad (8)$$

In the CIGS the mobility is chosen so that the electron diffusion length has a reasonable value of about 0.8 µm [11].Following the results [12], no conduction band offset (CBO) was introduced between the CIGS and CdS layers. All layers are polycrystalline and therefore contain a large number of different defects which may be process dependent. This is especially true for the CIGS layer [13].

III. Results and discussions

- **Impact of GGI atomic ratio on the electrical characteristics**

The GGI atomic ratio plays a very important role on the performance of solar cell. The results of simulation show his influence on macroscopic electrical parameters. The table 2 shows down results of this simulation.

Table 2: simulation results for different values of atomic ratios

Ratio [Ga]/[In+Ga]	Voc (V)	Jsc (mA/cm²)	FF (%)	η (%)
0.3	0.7383	36.368	80.2314	21.5429
0.5	0.7877	31.4719	80.6735	19.9991
0.7	0.8376	27.3192	81.0356	18.543

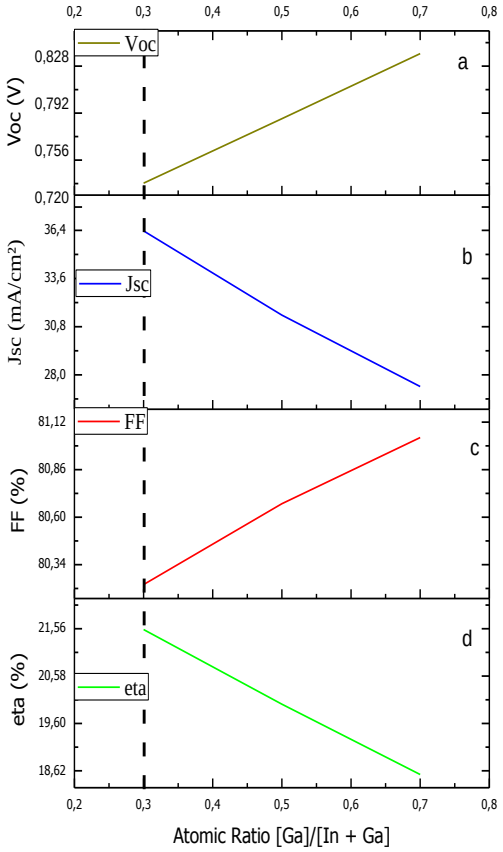

Fig.1: Effect of GGI atomic ratio on the macroscopic electrical parameters

The Figures 1a; 1b; 1c and 1d respectively show the characteristics of the open circuit voltage (Voc), the short circuit current density (Jsc), the fill factor (FF) and conversion efficiency (η) with GGI composition ratio. The open-circuit voltage (Voc) increases weakly with the [Ga] content and reaches a saturation value at high concentration. By against the increase of GGI ratio causes a drop on the short-circuit current density (Jsc), due to the decrease of the absorption coefficient with increasing band gap**[7-8]**. The fill factor (FF) also

ISSN:2277-1581
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increases weakly with the [Ga] content. This shows that the variation of the atomic ratio [Ga]/[In+Ga] so doesn't affect quality of the cell. The conversion efficiency (η) reaches its maximum value when the atomic ratio is 0.3 and drastically decreases with increasing [Ga] concentration.

- **Current-voltage characteristics (J/V)**

The Fig.2 shows the current-voltage characteristic (J/V) of CIGS-0.3, CIGS-0.5 and CIGS-0.7 samples. The black pattern for each curve represents the maximum power point (MPP) reached by the cell.

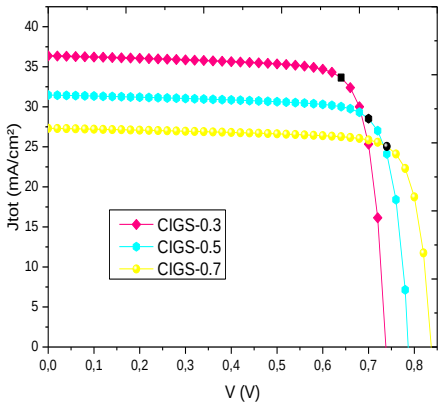

Fig.2: Current-voltage characteristics (J/V) of CIGS samples

This graph summarizes perfectly the effect of GGI atomic ratio on macroscopic electrical parameters. Indeed we note a big decrease in short-circuit current density (Jsc) and a low change in open circuit voltage. The maximum power point reached by the cell also decreases with increasing gallium rate. This is what causes the decrease in conversion efficiency with the GGI ratio according to fig.1.d.

- **Conductance-voltage characteristics (G/V)/ Capacitance-voltage characteristics (C/V)**

The (G/V) conductance method [14] is the most complete method to characterize the interface states: it measures the density of interface states, the capture cross section of majority carriers by interface states and it also gives information on changes of the surface potential. The G/V technical is based on the measurement of the equivalent parallel conductance of a heterojunction with the frequency and the voltage V applied. The conductance which represents losses due to the capture and emission of carriers by the interface traps is a measure of the density of interface states. The Figure 3 shows the conductance of CIGS samples studied depending of voltage applied for a frequency set at 10^{+5}Hz.

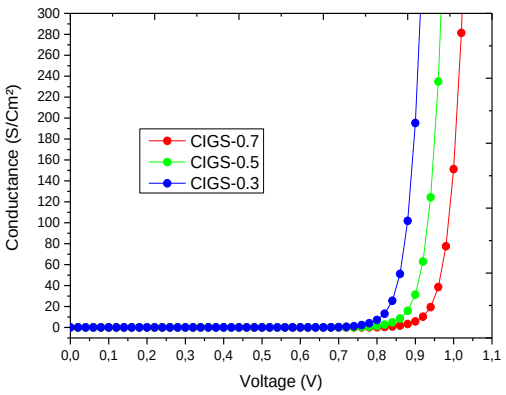

Fig. 3: Conductance-voltage characteristics (G/V)

The Conductance curves of fig.3 contain all necessary information to define the interface states. A trap at the interface is characterized by its energy position and constant capture time. The energy level (trap) probed the band gap depends on position of the Fermi level and thus voltage V applied. Consequently, for a fixed frequency value, the variation of V that a given trap will respond to the signal and therefore the conductance G also shows a peak at this point. The peak amplitude gives the density of interface states and the voltage V gives the energy position of traps. To confirm the determination of the density of interface states, measurements C/V (capacitance-voltage) at frequency (10^{+5}Hz) were performed. Fig.4 shows the characteristics C/V of CIGS-0.3, CIGS-0.5 and CIGS-0.7 samples.

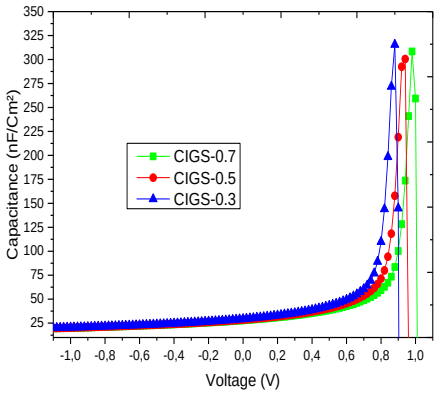

Fig.4: Capacitance-voltage characteristics (C/V)

Results presented with G/V (Fig.3) and C/V (Fig.4) characteristics show a shifting of traps towards high energy positions. So we can say that increasing the concentration of [Ga] doesn't influence too on the density of interface states but against causes a progressive shift of traps towards high energy positions.

ISSN:2277-1581
01 May 2016

- **Quantum efficiency (QE)**

The electric parameters of the photovoltaic cell obtained with (J/V) characterization tell us about overall performance of them without specifically indicate their origins. The spectral response and quantum efficiency in particular determine the response of the cell as a function of the wavelength and can be located in cell the sources that limit (or not) its performance. CIGS absorption coefficient varies with radiation wavelength. Of short wavelength photons are absorbed near the surface (in the transmitter), while those of higher wavelength are absorbed mainly in the heart of the cell (in the base). It is therefore possible to access the behavior and efficiency of each cell region. The fig.5 show the quantum efficiency of CIGS samples studied.

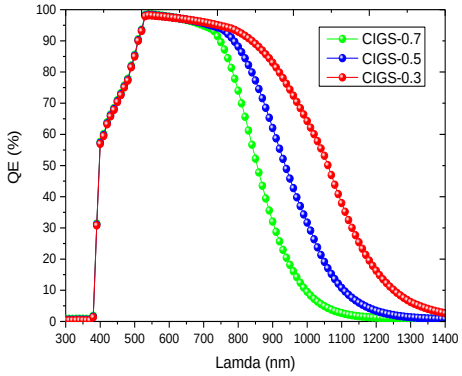

Fig.5: quantum efficiency of CIGS samples

We note that the CIGS sample with the lowest GGI atomic ratio absorbs photons over a wider range of wavelengths. Indeed, this can be explained by the fact that no photon whose energy is less than the band gap is absorbed. Now the band gap increases gradually as the GGI atomic ratio increases. Therefore, samples having a larger gap can't absorb lower energy photons (high wavelength).

IV. Conclusion

This simulation allowed the study of photovoltaic cells based on CIGS. Our objective was to gain knowledge about the effect of composition on cell parameters. The results obtained clearly show the photovoltaic characteristics are greatly affected by [Ga]/[In + Ga] composition of the absorbent layer. In addition the calculated parameters showed the drop in efficiency with increasing GGI atomic ratio. Therefore, we can say unequivocally that the CIGS-0.3 cell (*[Ga]/[In + Ga]= 0.3*) is the most efficient cells studied in this article.

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