International Journal of Engineering Research
Volume No.6, Issue No.5, pp :275-280
ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

Determination of Effective Masses of Electron an Evolution of the Lattice Parameters in no Stoichiometric $Cu(In_{1-x},Ga_x)Se_2$ Chalcopyrite Thin Film Solar Cell

Mouhamadou M. SOCE*, Alain K. EHEMBA*, Amsata NDIAYE, Gérôme SAMBOU*, Moustapha DIENG***

*Laboratoire des semiconducteurs et d'énergie solaire LASES, Cheikh Anta Diop University of Dakar, SENEGAL

** Laboratoire d'Electronique, Informatique, Télécommunications et Energies Renouvelables LEITER, Gaston Berger University of Saint-Louis, SENEGAL.

Corresponding author's email: ehembaalain@yahoo.fr

Abstract: ***In this paper, a study was carried out on the evolution of the effective mass of the electron and the effective mass of the crystal parameters in solar cells based on non-stoechiometric absorbers Cu ($In_{1-x}Ga_x$) Se_2. Usually the stoechiometry is defined for this type of cells in relation to the ratio*** $\frac{[Cu]}{[Ga]+[In]}$ ***for x between 0.1 and 0.9 with*** $x=\frac{[Ga]}{[Ga]+[In]}$***. For this work we have defined the stoechiometry according to the ratio*** $\frac{[Cu]}{[In]}$ ***for x values between 0.1 and 0.9. We have noted that the ratio*** $\frac{[Cu]}{[In]}$ ***increases with x and the energy gap Eg of the material, and that*** m_e ***also increases with this ratio. The lattice parameters increase with the ratio*** $\frac{[Cu]}{[In]}$ ***and with the gap energy Eg. In the end, two relations linking the crystal parameters and this ratio were determined.***

Keywords- $\frac{[Cu]}{[In]}$**, stoichiometry, effective mass, reduce masse, hole, electron, lattice parameter**

I. Introduction

Solar cells with $Cu(In_x,Ga_{1-x})Se_2$ absorber layers are the leading thin-film technology in terms of conversion efficiencies. Depending on the value of x, there may be different solar cells which the conversion efficiencies different. For $CuInSe_2$, $CuInGaSe_2$ and $CuGaSe_2$ solar cells, we obtained the conversion efficiencies between 20 and 22.3% [1].

With a theoretical efficiency of over 30%, these types of cells will be in the future leaders of PV technology. Despite the bright future and the many possible combinations and alloys, the major problem of these cell types is the lack of understanding of internal processes that impact on the final efficiency. [1]

For these cell types, the rate of the various compounds is very important because several parameters depend on it. Thus, the different ratios between compounds for this type of cells are the following: $\frac{[Cu]}{[In]}$, $\frac{[Cu]}{[Ga]+[In]}$, $x=\frac{[Ga]}{[Ga]+[In]}$, and $\frac{[Se]}{[Se]+[In]}$.These different ratios allow us to say whether we have absorbers that are Cu-poor or Cu-rich, Se-poor or Se-rich. About the ratio for Se, studies have shown that it is optimal at 2.

The stoechiometry is defined in relation to these ratios. A CIGS absorber is said to be stoechiometric if it is Cu-rich and not stoechiometric if it is Cu-poor. So far the best cell has been obtained with a Cu-poor absorber [2].

For $CuInSe_2$ (CIS), if the ratio $\frac{[Cu]}{[In]}\succ 1$, the cell is Cu-rich, a Cu_xSe secondary phase on the surface, formed by the excess copper [3]. If this ratio is less than 1, it is said to be Cu-poor. If the value of x is between 0 and 1 in Cu (InxGa1-x) Se_2 (CIGS) the stoechiometry will be studied according to the ratio $\frac{[Cu]}{[Ga]+[In]}$.

We propose to determine the effective mass of the electrons for x between 0 and 1 according to the bandgap energy, the stoichiometry and the ratio $\frac{[Cu]}{[In]}$ instead of $\frac{[Cu]}{[Ga]+[In]}$. The ratio $\frac{[Cu]}{[In]}$ is also very important in the various properties of the CIGS semiconductors. Structural changes were noted in the transition from CIS to CIGS with the addition of Ga. These structural changes directly affect the lattice parameters. A study on the evolution of this lattice parameter according to the ratio $\frac{[Cu]}{[In]}$ and the effective mass of the holes will be made for values of x between 0.1 and 0.9

II. Materials and Methodology

In Solid Physics, the effective mass is defined by the second-order tensor of the second derivatives of the energy E with respect to the wave vector k:

$$\frac{1}{m_{ij}}=\frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j} \qquad (1)$$

ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

From the dynamics of Bloch, the effective mass of the electron and the hole are given by [4]:

$$m_e^* = \hbar^2 \left(\frac{\partial^2 E_n}{\partial \vec{k}^2} \right)^{-1} \quad (2) \qquad m_e^* = -m_t^* \quad (3)$$

In this article we have another calculation approach, resulting from results of other research work. For stoechiometry we have based on two relationships from the literature: $x = \frac{[Ga]}{[Ga]+[In]}$ (4) and $\frac{[Cu]}{[Ga]+[In]} = 1$ (5)

We will determine a relation linking x to the ratio [Cu] / [In] using the equations (4) and (5).

$$x([Ga]+[In]) = [Ga] \quad (6) \Rightarrow x[Ga]+x[In] = [Ga] \quad (7)$$

$$\Rightarrow x[In] = [Ga] - x[Ga] \quad (8) \Rightarrow x[In] = [Ga](1-x) \quad (9)$$

$$\Rightarrow \frac{[In]}{[Ga]} = \frac{1-x}{x} \quad (10) \qquad \Rightarrow \qquad \frac{[Ga]}{[In]} = \frac{x}{1-x} \quad (11)$$

We have $\frac{[Cu]}{[In]+[Ga]} = \frac{[Cu]}{[In]\left(1+\frac{[Ga]}{[In]}\right)}$ (12)

$$\Rightarrow \frac{[Cu]}{[In]+[Ga]} = \frac{[Cu]}{[In]\left(1+\frac{x}{1-x}\right)} \quad (13) \qquad \frac{[Cu]}{[In]+[Ga]} = 1 \quad (12)$$

$$\Rightarrow \frac{[Cu]}{[In]\left(1+\frac{x}{1-x}\right)} = 1 \quad (13) \qquad \Rightarrow \frac{[Cu]}{[In]} = 1 + \frac{x}{1-x} \quad (14)$$

$$\Rightarrow \frac{[Cu]}{[In]} = \frac{1}{1-x} \quad (15)$$

For $Cu(In_{1-x},Ga_x)Se_2$, the absorber is Cu-poor (non-stoechiometric) if the following conditions are observed according to our model:

- For $Cu(In_{1-x}Ga_x)Se_2$ with $0.1 < x \leq 0.9$: if $\frac{[Cu]}{[In]} \succ 1$, the absorber is no stoechiometric.
- For the validation of our model we used experimental results with well-defined ratios of a cell with a Cu-poor absorber $\frac{[Ga]}{[Ga]+[In]} = x = 0.3$ (16) and $\frac{[Cu]}{[In]+[Ga]} = 0.95 \prec 1$ **(17)**

Using the equation (15), the ratio

$$\frac{[Cu]}{[In]} = \frac{1}{1-x} = 1.42 \succ 1 \quad (18).$$

It confirms our previous assertion.

This assertion is satisfied only if x is included in the interval $[0.1,0.9]$ $(0.1 < x \leq 0.9)$. In the following we determine the ratio $\frac{[Cu]}{[In]}$ for values of x in this interval.

Table 1: $\frac{[Cu]}{[In]}$ according to x

x	$1/(1-x)$	Cu/In	$CuIn_{1-x}Ga_xSe_2$
0.1	1.11	1.11	$CuIn_{0.9}Ga_{0.1}Se_2$
0.3	1.42	1.42	$CuIn_{0.7}Ga_{0.3}Se_2$
0.5	2	2	$CuIn_{0.5}Ga_{0.5}Se_2$
0.7	3.33	3.33	$CuIn_{0.3}Ga_{0.7}Se_2$
0.9	10	10	$CuIn_{0.1}Ga_{0.9}Se_2$

Given the work of Clas Pearson [6], the relation linking the effective mass of $Cu(In_{1-x}Ga_x)Se_2$ to the mass of the free electron and to x is given by:

$$me(CuIn_{1-x}Ga_xSe_2) = me(CuInSe_2) + (0.05x)m_0 \quad (19)$$

Where $me(CuInSe_2) = 0.09m_0$

$$(20)\ me(CuIn_{1-x}Ga_xSe_2) = [0.09 + 0.05x]m_0 \quad (21)$$

$\boldsymbol{m_0}$: free electron mass; ***me***: effective mass

Table 2 : effective mass values according to x

x	$CuIn_{1-x}Ga_xSe_2$	me
0.1	$Cu\ In_{0.9}Ga_{0.1}\ Se_2$	$0.095\times m_0$
0.3	$Cu\ In_{0.7}Ga_{0.3}\ Se_2$	$0.105\times m_0$
0.5	$Cu\ In_{0.5}Ga_{0.5}\ Se_2$	$0.115\times m_0$
0.7	$Cu\ In_{0.3}Ga_{0.7}\ Se_2$	$0.125\times m_0$
0.9	$Cu\ In_{0.1}Ga_{0.9}\ Se_2$	$0.135\times m_0$

Using the relation (4) and varying x, 0.1 to 0.9 steps 0.2, the values we obtain are mentioned in the table 2.

About the variation of the mass of electron according to the bandgap, referring to the work of Tinocco and al. [7], the bandgap is given by this relation:

$$E_g(y) = \left(1.620 - 0.840y + 0.175y^2\right)\text{eV} \quad (22)$$

Where y = 1-x.

Varying x for the values of 0.1 to 0.9 steps 0.2, we obtained the following table:

Table 3 : Variation of x according to the bandgap

x	$CuIn_{1-x}Ga_xSe_2$	me	Eg (eV)
0.1	$Cu\ In_{0.9}Ga_{0.1}\ Se_2$	$0.095\times m_0$	1.005
0.3	$Cu\ In_{0.7}Ga_{0.3}\ Se_2$	$0.105\times m_0$	1.118
0.5	$Cu\ In_{0.5}\ Ga_{0.5}\ Se_2$	$0.115\times m_0$	1.243
0.7	$Cu\ In_{0.3}Ga_{0.7}\ Se_2$	$0.125\times m_0$	1.383
0.9	$Cu\ In_{0.1}Ga_{0.9}\ Se_2$	$0.135\times m_0$	1.537

About the variation of the effective mass of hole according to the lattice parameters, we note that the evolution of the lattice parameters in CIGS semiconductors is related to different properties. These lattice parameters are directly related to the structural properties but also to the electrical, electronic and other properties. Two relationships linking the lattice parameters a and c to the stoechiometric ratio x have been shown from the ASTM sheets according to the Vegard law

ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

[8]. We will use these relationships to show the evolution of the mesh parameters as a function of the effective masses of the electron and the energy of the gap. These two relationships are:

$$a = -0.1715x + 5.7837 \quad (23)$$

$$c = -0.58113x + 11.6115 \quad (24)$$

where $x = \frac{[Ga]}{[Ga]+[In]}$; x being related to ratio $\frac{[Cu]}{[In]}$ according to the equation (8)

In the Table 4, the values of the lattice parameters as according to the ratio $\frac{[Cu]}{[In]}$ are mentioned:

Table 4 : Variation of x according to lattice parameters.

x	$Cu(In_{1-x}Ga_x)Se_2$	$[Cu]/[In]$	a(nm)	c(nm)
0.1	$Cu(In_{0.9}Ga_{0.1})Se_2$	1.11	5.76	11.55
0.3	$Cu(In_{0.7}Ga_{0.3})Se_2$	1.42	5.73	11.44
0.5	$Cu(In_{0.5}Ga_{0.5})Se_2$	2	5.69	11.32
0.7	$Cu(In_{0.3}Ga_{0.7})Se_2$	3.33	5.66	11.20
0.9	$Cu(In_{0.1}Ga_{0.9})Se_2$	10	5.63	11.09

III. RESULTS AND DISCUSSION

The results of all calculations are mentioned in the table 5. We have mentioned the variation of the bandgap Eg and the variation of the lattice parameters according to the $\frac{[Cu]}{[In]}$ ratio.

For the no stoichiometric $Cu(In_{1-}x, Ga_x)Se_2$ solar cells, Cu-poor, the $\frac{[Cu]}{[In]}$ ratio is greater than 1 for the x values between 0.1 and 0.9. And this ratio increases with the x increasing as shown in Figure 1-a. This ratio indicates whether the cell absorber is Cu-rich or Cu-poor.

Table 5 : Recapitulative of all results

x	$CuIn_{1-x}Ga_xSe_2$	m_e	[Cu]/[In]	a (nm)	c (nm)	Eg (eV)
0.1	$Cu\ In_{0.9}Ga_{0.1}\ Se_2$	$0.095\times m_0$	1.11	5.76	11.55	1.005
0.3	$Cu\ In_{0.7}Ga_{0.3}\ Se_2$	$0.105\times m_0$	1.42	5.73	11.44	1.118
0.5	$Cu\ In_{0.5}\ Ga_{0.5}\ Se_2$	$0.115\times m_0$	2	5.69	11.32	1.243
0.7	$Cu\ In_{0.3}Ga_{0.7}\ Se_2$	$0.125\times m_0$	3.33	5.66	11.20	1.383
0.9	$Cu\ In_{0.1}Ga_{0.9}\ Se_2$	$0.135\times m_0$	10	5.63	11.09	1.537

Indeed, this ratio is very important because it must be optimized to have a high performance cell. In this interval of x, we have Cu-poor absorbers, because the ratio $\frac{[Cu]}{[In]} \succ 1$.

From $CuInSe_2$ to $CuGaSe_2$, the increase of the bandgap is noticeable because of the insertion of Ga. Indeed the more the Ga level is increased on the $CuInSe_2$, the more the Ga substitutes for the Indium and the more the energy of the gap increases. Thus, from x between 0.1 to 0.9, we have an increase in the [Cu] / [In] ratio according to the bandgap Eg (Figure1b).

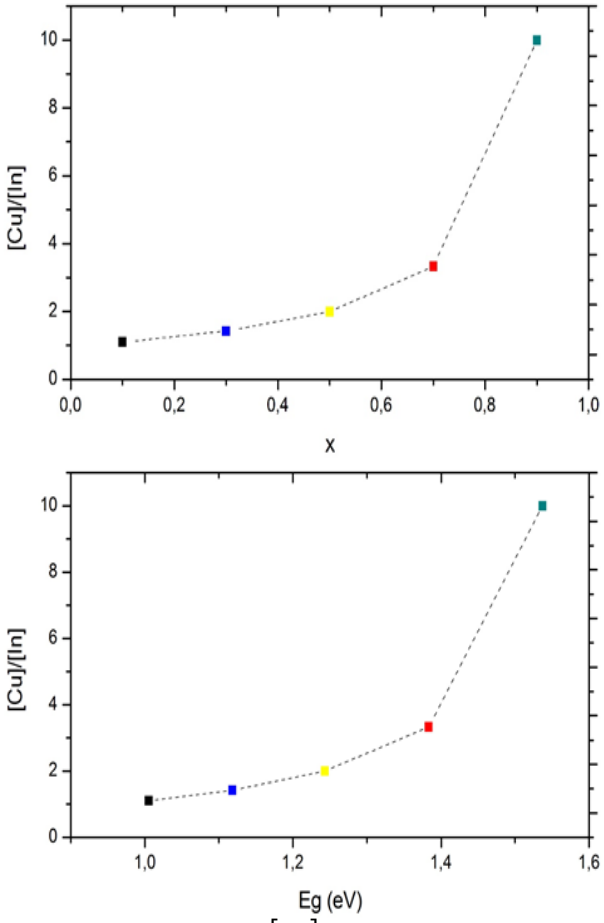


Figure 1: Variation of $\frac{[Cu]}{[In]}$ ratio according to x (a) and the bandgap Eg (b).

About the effective mass of the electron, its evolution with the $\frac{[Cu]}{[In]}$ ratio is increasing. Indeed, there is a rapid increase in me as according to the $\frac{[Cu]}{[In]}$ ratio (figure 2).

ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

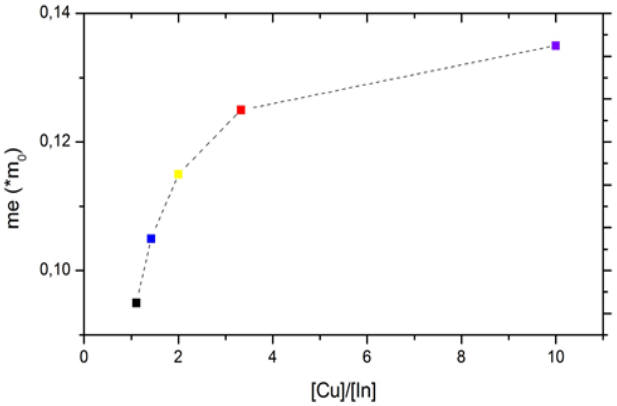
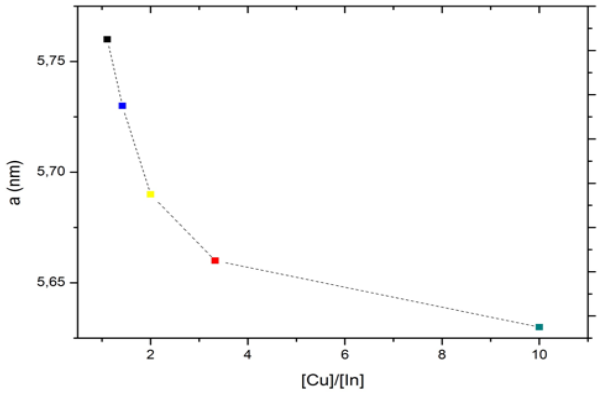


Figure 2: Variation of the effective masse of electron (m_e) according to ratio $\frac{[Cu]}{[In]}$

The optimal effective mass of the electron for a high quality cell is between: $m_e = 0.10m_0 - 0.11m_0$

We note that if the ratio is too great compared to the unit (numerical sequence of reason 1), the absorber in this case will be far from the optimal zone. Indeed, the best cell obtained in laboratory has an absorber layer with $\frac{[Cu]}{[In]}$ ratio equal to 1.30 to 1.42. The evolution of the crystal parameters also depends on this ratio. A study of this relation has been done. Indeed, the lattice parameters depend strongly on the composition of the material, and according to the value of the $\frac{[Cu]}{[In]}$ ratio. The Figures 3-y and 3-w gives us an illustration of this evolution. A similar evolution of the crystal parameters is noted (a and c). Indeed, a and c decrease sharply with the increase in the $\frac{[Cu]}{[In]}$ ratio. This increase in this ratio is related to x. The reduction of the lattice parameters is directly related to the composition of the CIGS materials. If the Ga level increases, we will have a decrease in the values of the crystal parameters (a and c). The addition of Ga on the $CuInSe_2$ also affects the crystal parameters (a, c) by affecting the mean grain size which will therefore decrease in favor of the grain boundaries. We note then a significant recombination and a decrease in the electrical performance.



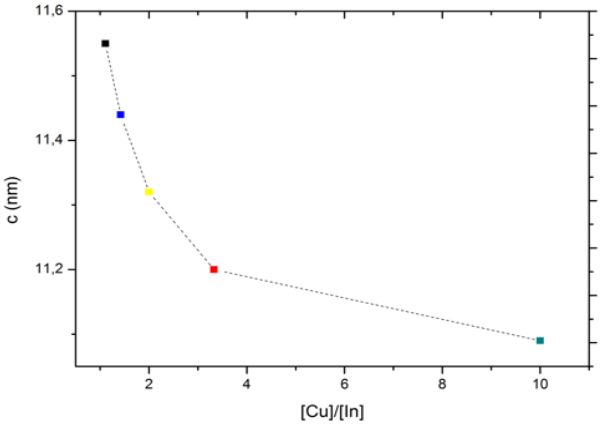


Figure 3: Evolution of the lattice parameter according to ratio $\frac{[Cu]}{[In]}$. (y) a ;(w) b

This observation can also be related to the bandgap, in fact the increase of the gap is proportional to the level of Ga in the $Cu(In_{1-x},Gax)Se_2$. Thus, the evolution of the gap according to the crystalline parameters will be identical to the evolution of the crystalline parameters according to $\frac{[Cu]}{[In]}$ ratio (figure 4).

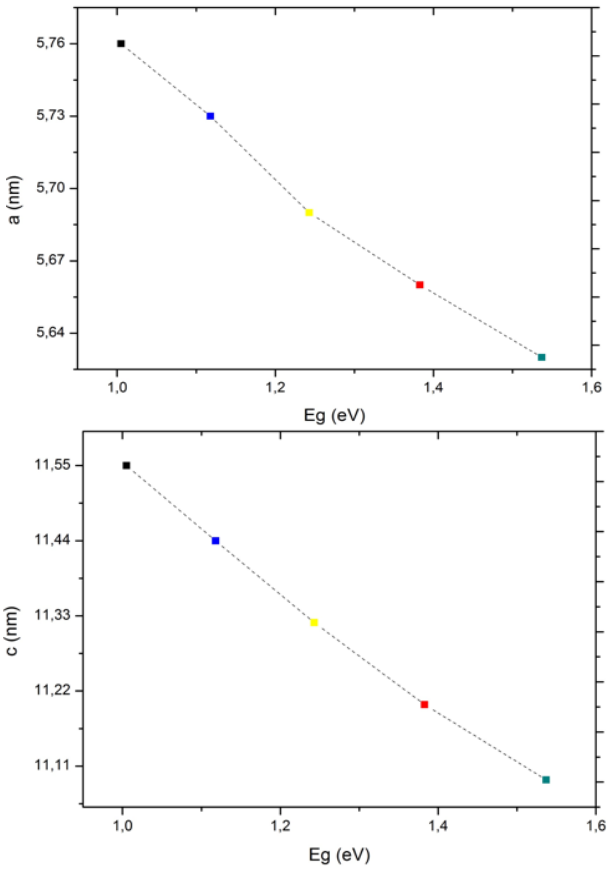


Figure 4: Lattice Parameters (a; c) according to bandgap Eg.

We note a linear regression of the crystal parameters according to the bandgap. Here mathematical relations can be

ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

drawn from these two graphs. A relation linking a and Eg, and another linking c to Eg. We can use Excel to make two trend curves: one linear and another polynomial. We can give in these two cases the equations which govern these curves.

III.1 Linear variation

Assuming that these graphs are straight lines and characteristics of a y = ax + b equation type. We obtain the following equations:

$$a = a_{a,Eg}E_g + b_{a,Eg} \quad (25) \text{ and } c = a_{c,Eg}E_g + b_{c,Eg} \quad (26)$$

With $y_{a,Eg}$ the equation wich give the variation of **a** according to Eg and $y_{c,Eg}$ the evolution of c according to Eg. The determination of the equations of these lines was done by Excel with a linear option for the trend (figures 5a and 5b).

The equations governing a and c as a function of Eg are given by (27) and (28):

$$a = -0.247\,E_g + 6.0045 \quad (27)$$

$$c = -0.8695E_g + 12.413 \quad (28)$$

Relationships directly linking the crystal parameters to $\frac{[Ga]}{[Ga]+[In]}$ and $\frac{[Cu]}{[In]}$ ratios can be given using equations (15), (22), (27) and (28). We have the following relations by integrating the relation (12)

$$a = -0.247\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right] + 6.0045$$

$$c = -0.8695\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right] + 12.413$$

Using the equation (8), we have the expression $(1-x) = \left(\frac{[Cu]}{[In]}\right)^{-1}$. Then integrating it into (29) and (30), we will have (31) and (32) respectively:

$$a = -0.247\left[1.620 - 0.840\left(\frac{Cu}{In}\right)^{-1} + 0.175\left(\frac{Cu}{In}\right)^{-2}\right] + 6.0045$$

$$c = -0.8695\left[1.620 - 0.840\left(\frac{Cu}{In}\right)^{-1} + 0.175\left(\frac{Cu}{In}\right)^{-2}\right] + 12.413$$

By assembling constants and monomials of the same degree, the final expressions will be:

$$a = 5.60 + 0.2\left(\frac{Cu}{In}\right)^{-1} - 0.043\left(\frac{Cu}{In}\right)^{-2} \quad (33)$$

$$c = 11 + 0.73\left(\frac{Cu}{In}\right)^{-1} - 0.152\left(\frac{Cu}{In}\right)^{-2} \quad (34)$$

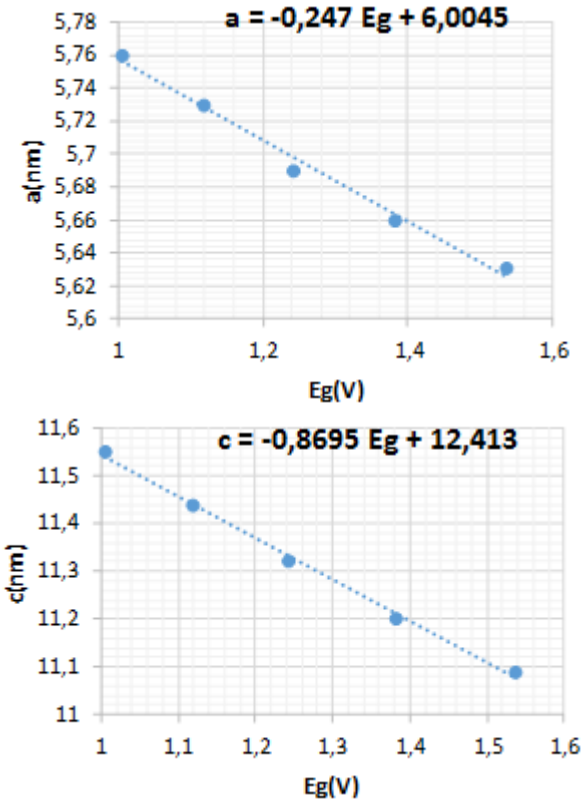


Figure 5: Variation of the lattice parameters a and c according to the bandgap Eg

III.2 Polynomial variation

The two curves are given in the FIGS.6a-6b. Two polynomial type relations were determined between **a, c** and **Eg**. These two equations are:

$$a = 0.1419(E_g)^2 - 0.6078E_g + 6.2289 \quad (35)$$

$$c = 0.3508(E_g)^2 - 1.7618E_g + 12.968 \quad (36)$$

Replacing Eg with its expression given by (22), we will have:

$$a = 0.1419\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right]^2 - 0.6078\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right] + 6.2289 \quad (37)$$

$$c = 0.3508\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right]^2 - 1.7618\left[1.620 - 0.840(1-x) + 0.175(1-x)^2\right] + 12.968 \quad (38)$$

ISSN:2319-6890 (online),2347-5013(print)
1 May 2017

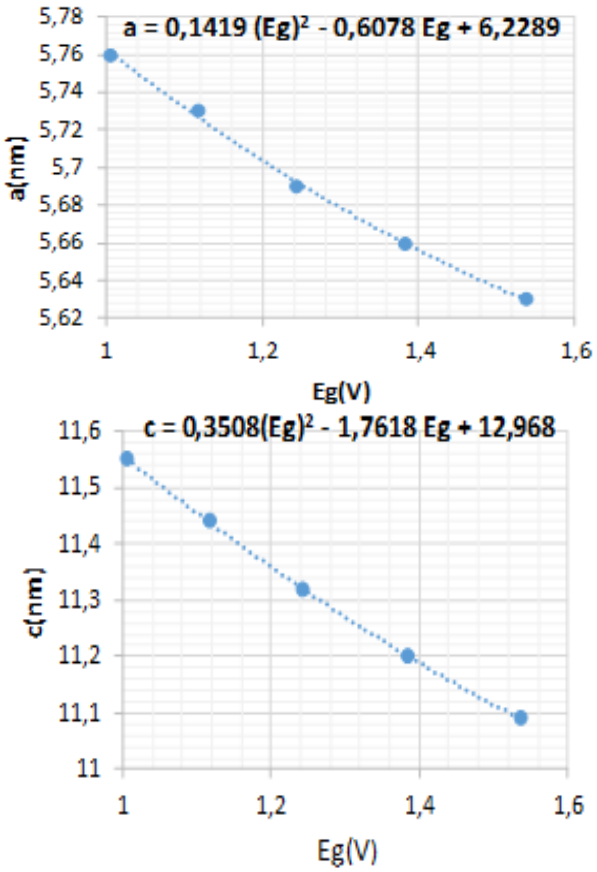


Figure 6: Variation of lattice parameters a and c according to Eg.

Using equation (8) $(1-x)=\left(\frac{[Cu]}{[In]}\right)^{-1}$ and integrating it into (37) and (38), we will have:

$$a = 0.1419\left[1.620 - 0.840\left(\frac{[Cu]}{[In]}\right)^{-1} + 0.175\left(\left(\frac{[Cu]}{[In]}\right)^{-1}\right)^2\right]^2$$
$$- 0.6078\left[1.620 - 0.840\left(\frac{[Cu]}{[In]}\right)^{-1} + 0.175\left(\left(\frac{[Cu]}{[In]}\right)^{-1}\right)^2\right] + 6.2289 \quad (39$$

$$b = 0.3508\left[1.620 - 0.840\left(\frac{[Cu]}{[In]}\right)^{-1} + 0.175\left(\left(\frac{[Cu]}{[In]}\right)^{-1}\right)^2\right]^2 \quad (40)$$
$$- 1.7618\left[1.620 - 0.840\left(\frac{[Cu]}{[In]}\right)^{-1} + 0.175\left(\left(\frac{[Cu]}{[In]}\right)^{-1}\right)^2\right] + 12.968$$

And finally after development, we get the following relationships (41) and (42):

$$a = 0.004\left(\frac{[Cu]}{[In]}\right)^{-4} - 0.04\left(\frac{[Cu]}{[In]}\right)^{-3} + 0.08\left(\frac{[Cu]}{[In]}\right)^{-2} + 0.13\left(\frac{[Cu]}{[In]}\right)^{-1} + 5.62$$

$$b = 0.01\left(\frac{[Cu]}{[In]}\right)^{-4} - 0.10\left(\frac{[Cu]}{[In]}\right)^{-3} + 0.14\left(\frac{[Cu]}{[In]}\right)^{-2} + 0.53\left(\frac{[Cu]}{[In]}\right)^{-1} + 11.02$$

III.3 Conclusion

Several results have been obtained by this work. For the study of stoichiometry in CIS and CIGS ($0.1 < x \leq 0.9$) , the use of the $[Cu]/[In]$ ratio may be indicative but with well-defined intervals. Indeed if $\frac{[Cu]}{[In]} \succ 1$, we have a Cu-poor CIS sample and Cu-rich CIGS sample ($0.1 < x \leq 0.9$). If $\frac{[Cu]}{[In]} \prec 1$, we have a Cu-rich CIS and a Cu-poor CIGS. We have also shown that the effective mass of the electrons in the CIGS ($0.1 < x \leq 0.9$) increases with the $\frac{[Cu]}{[In]} \succ 1$ ratio. We note that the bandgap and x also increases with this ratio. Compared to the lattice parameters, we note their decrease with the increase of this ratio or the increase of the bandgap. Finally two relations linking the lattice parameters a and c to the $[Cu]/[In]$ ratio are determinate using a linear and a polynomial approach.

References:

[1]. White paper for CIGS thin film solar cell technology 2015

[2] S. Siebentritt, L. Gütay, D. Regesch, Y. Aida, V. Deprédurand.2013. Why do we make Cu(In,Ga)Se_2 solar cells non-stoichiometric? Journal Solar Energy Materials & Solar Cells 119 (2013) 1825.DOI.org/10.1016/J.SOLMAT.2013.04.01.04

[3] Levent Gütay, David Regesch, Jes K. Larsen, Yasuhiro Aida, Valérie Depredurand, Susanne Siebentritt, Influence of copper excess on the absorber quality of CuInSe2, Appl. Phys. Lett. 99, 151912 (2011); doi: DOI/10.1063/1.3648111

[4] Cours dynamique de bloch (Chapitre 4), Grenoble Inp

[5] Roland Scheer, Hans-Werner Schock.2011.Chalcogenide Photovoltaics Physics, Technologies, and Thin Film Devices.WILEY-VCH Verlag& Co. KGaA.ISBN: 978-3-527-31459-1.

[6] Clas Persson.2008.Anisotropic hole-mass tensor of CuIn1−xGax(S,Se)$_2$: Presence of free carriers narrows the energy gap.Appl. Phys. Lett. 93, 072106; DOI: 10.1063/1.2969467

[7] T. Tmoco, C. Rincon, M. Quintero and G. S Perez.1991. Phase Diagram and Optical Energy Gaps for CuInyGa 1-y Se2alloys.Phys. stat. sol. (a) 124, 427

[8] Ullal, H.S.; Roedern, B.V. Proceedings of the 22nd European Photovoltaic Solar Energy Conference, Milan, Italy, Vol. 1926, 2007.