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Identification of Optical Transitions by Spectroscopic Ellipsometry (SE) on $CuIn_3Se_5$ Bulk Compounds

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Abstract

Bulk materials were synthesized by the Bridgman technique using the elements Cu, In and Se. These samples were characterized by Energy Dispersive Spectrometry (EDS) to determine the elemental composition, as well as by X-ray diffraction for structure, hot point probe method for type of conductivity, Optical response (Photoconductivity) and Photoluminescence (PL) to determine the band gap value and Spectroscopic Ellipsometry to find energy levels above the gap in the band scheme at room-temperature. They show a nearly perfect stoechiometry and present a p-type conductivity. $CuIn_3Se_5$ either has a Stannite structure, an Ordered Defect Chalcopyrite structure (ODC), or an Ordered Vacancy Chalcopyrite structure (OVC). The gap energy obtained for the different samples was 1.23 eV. Energy levels above the gap in the band scheme were determinate by measuring the dielectric function at room temperature for energies lying between 1.5 and 5.5 eV. Many transitions were observed above the gap for different samples. Spectroscopic Ellipsometry gave evidence for the interpretation of the choice of gap values which were compatible with that obtained from solar spectrum.

Keywords

Chalcopyrite, Photovoltaic, Bulk Materials, Stannite, Photoluminescence, Optical Response, X-Ray Diffraction, Photoconductivity, Spectroscopic Ellipsometry

1. Introduction

$CuIn_{1-x}Ga_xSe_2$ semiconductor compounds with chalcopyrite structure are good candidates for absorbers in high-efficiency photovoltaic devices. Some studies have shown that higher efficiency was reached in samples where a $Cu(In_{1-x}Ga_x)_3Se_5$ phase was formed at the surface of the $CuIn_{1-x}Ga_xSe_2$ layer [1] [2] [3] [4]. Another attractive property is their tolerance to large range of anion-to-cation off stoechiometry, manifested by the existence of an ordered defect compounds (ODC) with large variations in their Cu/In/Se ratio [5]. These ODCs, like $CuIn_3Se_5$, generally possess wider band gap and the formation of ternary Cu-In-Se compounds enables the formation of hetero-junctions used in the design of high-performance electronic and optoelectronic devices. Therefore, $CuIn_3Se_5$ has been of interest to many groups [6]. In this work, crystals of $CuIn_3Se_5$ were grown by the horizontal Bridgman methods [7] using a direct combination of high purity 5N for Cu, 6N for Se and Ga. The elements were placed in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. Energy Dispersive Spectrometer (EDS) and X-ray diffraction (XRD) were used to calculate the compositions of the ingots considered as very important parameters. The hot point probe method is used in order to determine the conduction types of these ingots; Photoconductivity (PC) and Photoluminescence (PL) allowed us to check their optical properties. Spectroscopic Ellipsometry (SE) is used to determine the energy levels above the gap in the band scheme at room temperature. Spectroscopic Ellipsometry (SE) technique is an experimental tool for measuring simultaneously the real and imaginary parts of the dielectric function versus photon energy for any semiconductor. The critical point structures in the dielectric function of a semiconductor are due to the optical-point transitions between valence and conduction bands where there exists a large joint density of states, thus providing valuable information on the electronic energy-band structure of the material. The paper proposed a new method used for determining with precision the optical transition that occurred in semiconductor, obtained from the experimental results of (SE). A harmonic oscillator approximation (HOA) was fitted to data for monocrystal silicon and $CuIn_3Se_5$. Room-temperature measurements were reported for the-pseudo dielectric function $\langle \varepsilon \rangle$ at energies from 1.5 to 5.5 eV.

2. Experiments

Crystals with different compositions were synthesized by direct combination of high purity 5 N for Cu and In and 6 N for Se in the desired proportions. The elements were placed in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. This tube was placed in a horizontal heater that reached a temperature exceeding the melting point of the compound. It was left in the heater for 72 hours at which point it was allowed to slowly cool down [7]. To characterize the crystals, X-ray diffraction was carried out using a Seifert MZIV powder diffractometer (θ, 2θ geometry) with Cu (Kα) radiation ($\lambda = 1.5406$ Å). The chemical compositions of the obtained samples were given by EDS. The Photoluminescence (PL) measurements were performed at 4.2 K by directly immersing the samples into liquid helium. To get the gap energy value at room temperature, we used the photoconductivity technique. The samples spectral response was measured at a constant light power over the wavelengths range 400 nm - 2000 nm. To find the energy levels above the gap in the band scheme at room temperature, the Spectroscopic Ellipsometry method was used. The ellipsometer consists of:

- a source (75 watt xenon arc lamp) having a sufficiently high light intensity in the spectral range (λ from 0.2 µm to 1 µm), with a high stability (±0.2%). The lamp arc is very short ($\Phi \approx 0.3$ mm) and can achieve a well-collimated beam.
- a monochromator of H10D type, manufactured by Jobin Yvon in holographic gratings. It covers the spectral range 200 - 800 nm with a maximum resolution of 0.5 nm.
- a polarizer and an analyzer used in the range of 220 nm to 3000 nm, with extinction rates of 10^{-5}. They are mounted on rotating turntables with an accuracy of one minute.
- a photo-elastic modulator and a photomultiplier (Hamamatsu, $\Phi = 12$ mm).

3. Results and Discussion

3.1. Characterization by EDS

In **Table 1** the characterization results of $CuIn_3Se_5$ materials by EDS are presented. The samples show a nearly perfect stoechiometry since the magnitude of deviation from stoechiometry, Δy ($\Delta y = (3\times \mathrm{Cu})/\mathrm{In} - 1$), is very small [8]. The results of the chemical compositions of a $CuIn_3Se_5$ sample have a large value of Δy (0.3). A detailed analysis is done in order to study the secondary phases that appear in this sample which will be discussed later on. The $CuIn_3Se_5$ samples present a n-type conductivity.

3.2. Characterization by X-Ray Diffraction (XRD)

The spectra of different $CuIn_3Se_5$ samples obtained by X-ray diffraction are shown in **Figure 1**. These samples are well-crystallized and all existent peaks are similar to those found in previous publications [9] [10] [11]. Thus, our XR spectra show the presence of several preferential orientations according to planes (112), (220) and (312) for all samples. Since the characteristic peaks concerning the chalcopyrite structure were not observed, the conclusion was made that unlike the $CuInSe_2$ compounds, the $CuIn_3Se_5$ compounds do not have a chalcopyrite structure [1] [12]. They either have a Stanite structure [6], an Ordered Defect Chalcopyrite structure (ODC), or an Ordered Vacancy Chalcopyrite structure (OVC).

Table 1. Chemical compositions of $CuIn_3Se_5$ bulk samples obtained by EDS.

		$CuIn_3Se_5$			
Samples	% Cu	% In	% Se	Δy	Conductivity type
A	11.2	32.4	56.4	+0.037	n
B	11.3	32.9	55.8	+0.030	n
C	11.2	32.5	56.3	+0.034	n

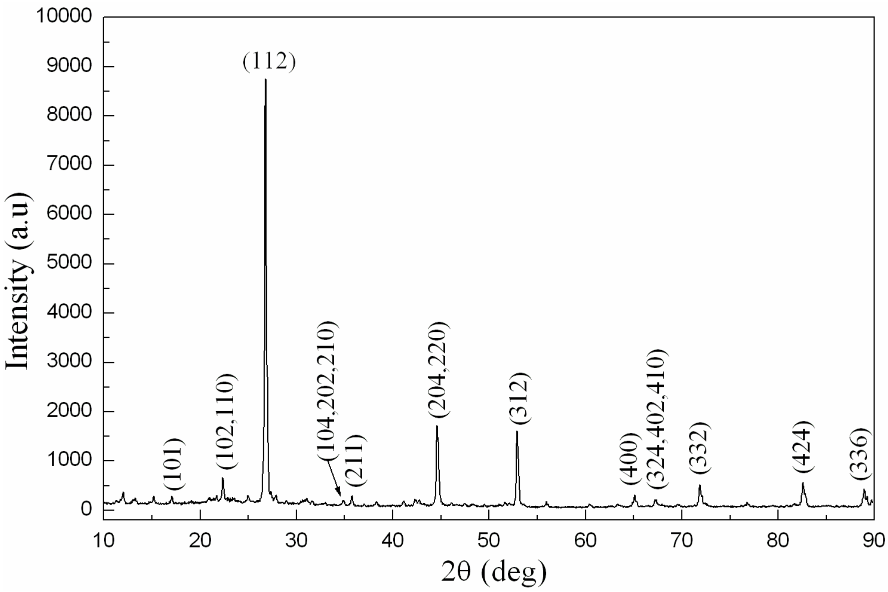


Figure 1. Spectrum of $CuIn_3Se_5$ obtained by X-Ray Diffraction for one sample.

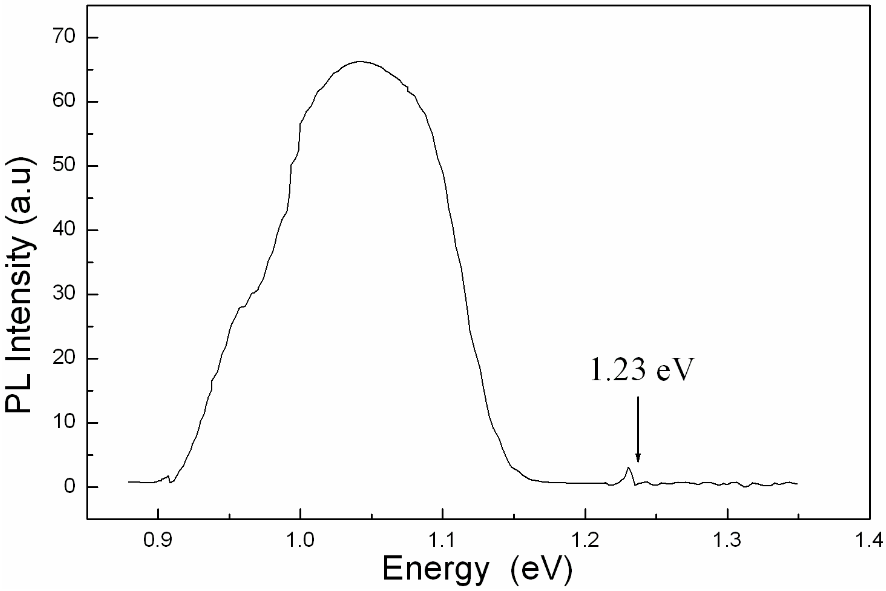


Figure 2. Photoluminescence spectrum of $CuIn_3Se_5$ at 4.2 K for one sample.

The *a* and *c* lattice parameters of $CuIn_3Se_5$ have been calculated from the spectra where $a = 5.76$, $c = 11.52$. These values of *a* and *c* are in agreement with those reported in G. Marin *et al.* and T. Negami *et al.* [13] [14].

3.3. Characterization by Photoluminescence (PL)

Figure 2 presents the photoluminescence spectrum of $CuIn_3Se_5$ obtained at 4.2 K. The spectrum shows the exciton position which is required to determine the gap value of 1.23 eV [15]. The activation energy level implicated in the optical transition is found by subtracting the emission peak located at 1.09 eV from the gap value. In other words the activation energy is equal to $1.23 - 1.09 = 0.140$ eV

(140 meV).

3.4. Characterization by Photoconductivity (PC)

We have determined the band gap energy value by analyzing our samples using spectral Photoconductivity [16]. **Figure 3** illustrates the Photoconductivity spectrum ($(ah\nu)^2$ as a function of $h\nu$) of $CuIn_3Se_5$. This spectrum denotes high speeds of surface recombination. A saturation level at high energy was not observed. In these cases, the gap value is given by an approximate value which was found by taking the abscissa of each curve at $PC_{max}/2$ [17]. The gap value at room temperature is 1.22 eV, which match those found by Photoluminescence and in literature [18].

3.5. Spectroscopic Ellipsometry (SE)

a) Method

Spectroscopic Ellipsometry (SE) is a characterization technique which allows the determination of energy levels above the gap in the band scheme. The real part of the dielectric pseudo-function $\langle \varepsilon_r \rangle$ is related to the substrate densities of state D_n. The calculation of the 3rd order derivative of the quantity $E^2\varepsilon_r(E)$ [18], is given by:

$$D_n(E) = \frac{1}{E^2}\frac{d^3}{dE^3}\left[E^2\varepsilon_r(E)\right]$$

where $E = \hbar\omega$ is the photon energy, allows the determination of the energy levels of optical transitions that correspond to the peaks of D_n. In order to illustrate this fact, a harmonic oscillator model, centred at the frequency ω_0 is used. Its' Lorentz nature is characterized by an elastic amplitude α_e and an absorption one α_a:

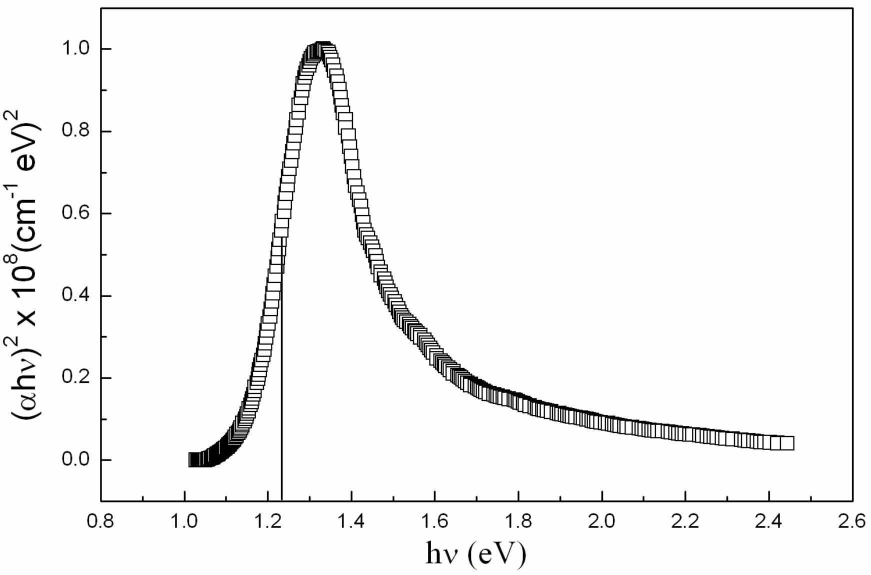


Figure 3. Photoconductivity spectrum ($(ah\nu)^2$ as a function of $h\nu$) of $CuIn_3Se_5$ at room temperature for one sample.

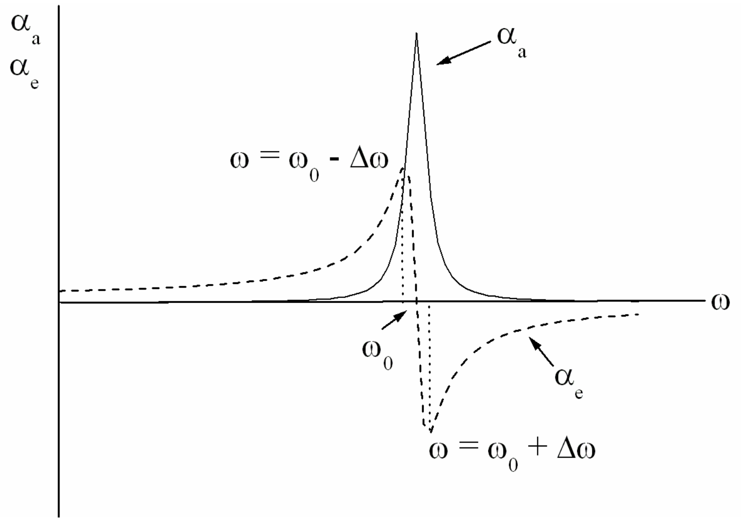


Figure 4. The variation of α_e and α_a as a function of ω.

$$\alpha_e = \frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + r^2\omega^2}$$

$$\alpha_a = \frac{r^2\omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + r^2\omega^2}$$

where r is the damping constant.

α_e and α_a functions are shown in **Figure 4**. The frequency ω_0 is determined by the maximum of α_a and the zero of α_e. The 3rd and 4th order derivatives of functions α_e and α_a are respectively calculated. The numerical calculation of the nth derivative is made by repeating n times the standard algorithm of the derivative calculation using three points, which is expressed as:

$$f'(x_i) = \frac{f(x_{i+1}) - f(x_{i-1})}{2\Delta x}$$

Figure 5 illustrates the spectra of $\alpha_a(\omega)$ and of its 4th order derivative. **Figure 6** shows the spectra of $\alpha_e(\omega)$ and of its 3rd order derivative. In the 2 cases, ω_0 value was determinate. The function $\alpha_a(\omega)$ presents a narrow peak which permit to determine ω_0 with precision. The peaks fineness in the $\alpha_a(\omega)$ 4th derivative and in the $\alpha_e(\omega)$ 3rd derivative spectra, respectively (Full Width Half Maximum (FWHM) lower than that of the initial function), shows that this method is a great way to determine the ω_0 position.

To verify the accuracy of the determination of E_1, E_2... levels, this method was applied to the case of Si. ε_i and ε_r represent α_e and α_a type for each harmonic oscillator, where the energy level is an optical transition described in the band scheme. The spectra of ε_i and ε_r functions are shown in **Figure 7**.

The maximum 3rd and 4th order derivatives of ε_r and ε_i are shown in **Figure 8** representing the transitions of energy levels in the band scheme [19]. The three energy levels observed E_1 (3.6 eV), E_2 (4.2 eV), and E_3 (5 eV) are identical to those found by Aspnes *et al.* [19], which shows the efficiency of our method.

b) Case of $CuIn_3Se_5$

$CuIn_3Se_5$ samples were characterized by Spectroscopic Ellipsometry, and the observed transitions were determined by the method described above. The different spectra of the imaginary part (ε_i) and the real part (ε_r) respectively of the dielectric function, for different $CuIn_3Se_5$ samples are shown in **Figure 9**. **Figure 10** illustrates the results of spectra at 3rd and 4th order derivatives of ε_r and ε_i respectively, of one sample of $CuIn_3Se_5$.

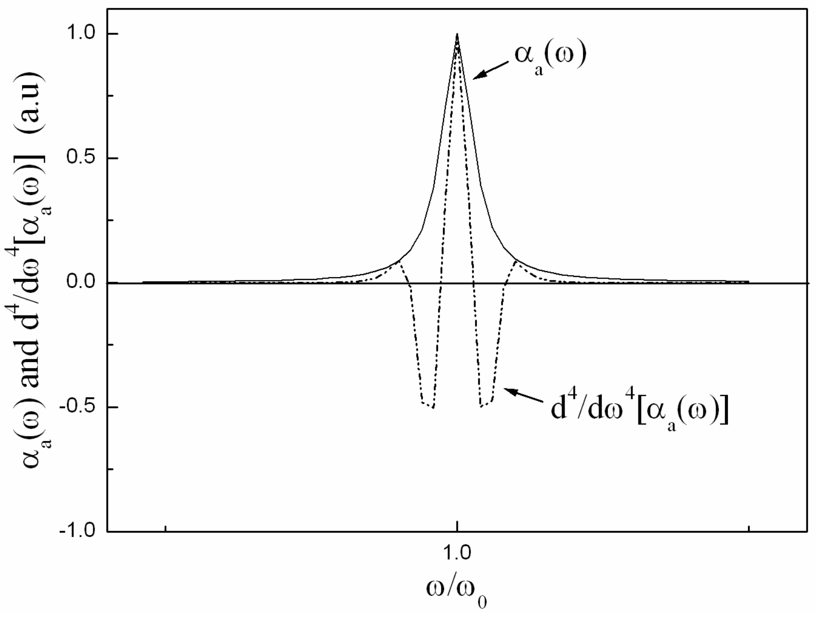


Figure 5. $\alpha_a(\omega)$ and $\frac{d^4}{d\omega^4}\left[\alpha_a(\omega)\right]$.

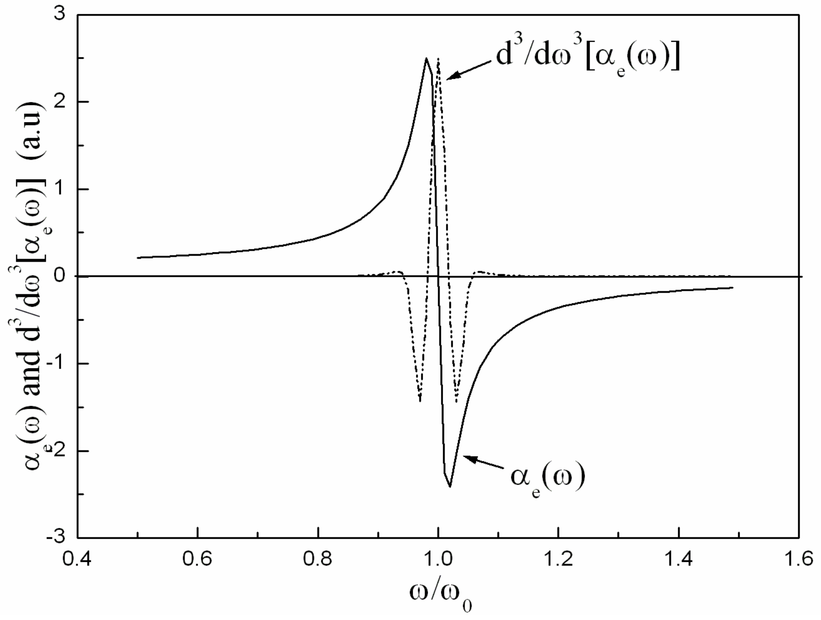


Figure 6. $\alpha_e(\omega)$ and $\frac{d^3}{d\omega^3}\left[\alpha_e(\omega)\right]$.

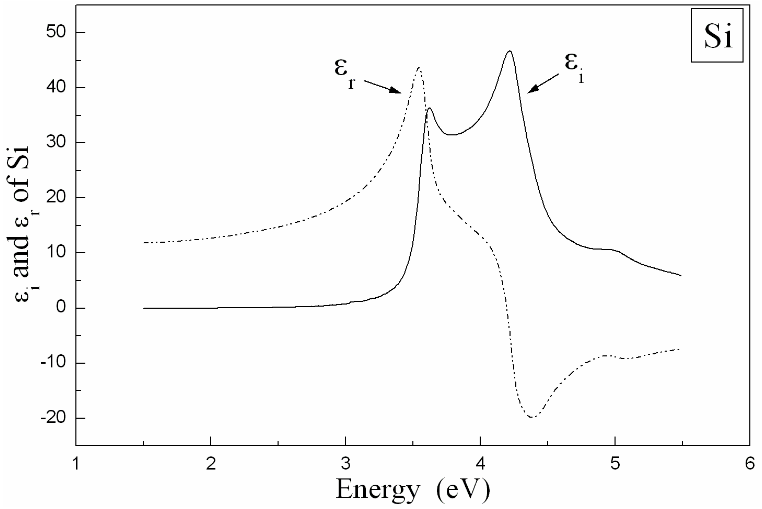


Figure 7. The dielectric functions ε_i and ε_r of Si.

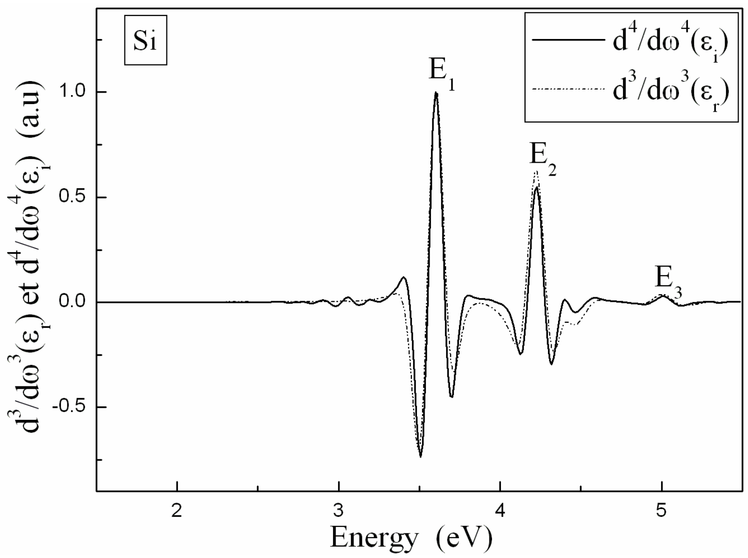
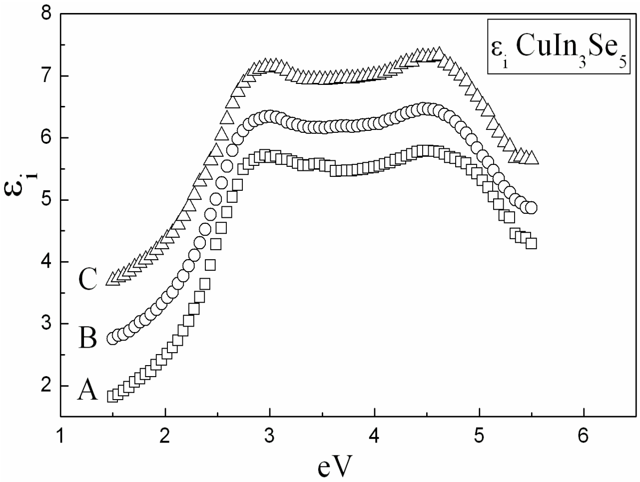
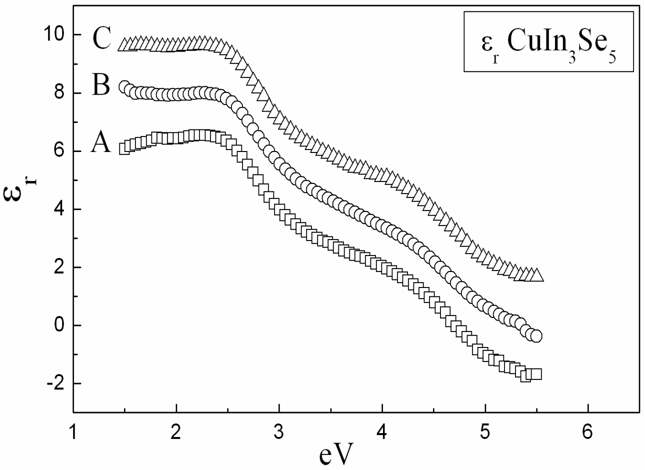


Figure 8. The 3rd order derivative of ε_r and the 4th order derivative of ε_i of Si.



(a)



(b)

Figure 9. Evolution of spectrum: (a) the imaginary part of dielectric function; (b) its real part, for different samples A, B and C.

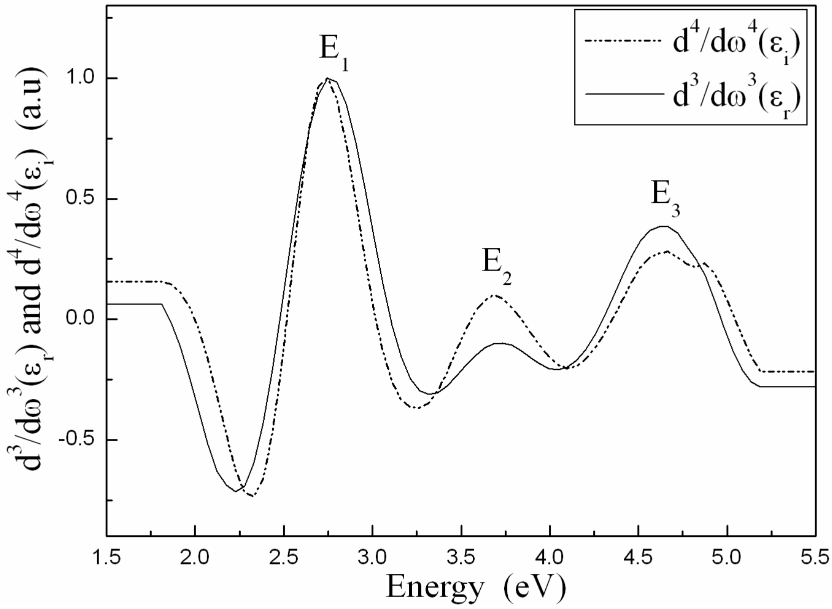


Figure 10. The 3rd order derivative of ε_r and the 4th order derivative of ε_i of one sample of $CuIn_3Se_5$.

Zeaiter *et al.* [20] were studied the stœchiometry effect on the dielectric functions. They found that the imaginary dielectric function (ε_i) of $CuInSe_2$ evolves for different values of Cu/In ratio. In fact the peaks widen when the percentage of indium is increased, because the dielectric function is directly related to the crystal structure. Since the crystal is rich in In, involves a disorder in the crystal lattice and a loss of crystallinity which proved more significantly for high energies. This effect was observed in the case of silicon [21] [22]. So the excess of In has the effect of expanding and decreasing the intensity peaks of the imaginary dielectric function (ε_i). We noticed the same effects on our spectra of $CuIn_3Se_5$.

Table 2. The transitions energies obtained by the 3rd order derivative of ε_r and the 4th order derivative of ε_i for the samples of $CuIn_3Se_5$.

Samples	E_1 (eV)	E_2 (eV)	E_3 (eV)
A	2.75	3.68	4.62
B	2.73	3.70	4.64
C	2.75	3.69	4.61

Table 2 shows the observed transitions (E_1, E_2 and E_3) for different samples A, B and C. The transitions E_1 and E_3 can be attributed to the d levels ionization of Cu. In contrary, the transition E_2 is related to the hybridization s-s between the s-levels of In and that of Cu. The highest levels of the valence band are essentially constituted by the 4p levels of Se and the d-levels of high density localized of Cu.

4. Conclusion

Samples of $CuIn_3Se_5$ have been prepared by the Bridgman method. The different samples have then been characterized by several techniques (EDS, XR, hot point probe, photoluminescence, Photoconductivity and Spectroscopic Ellipsometry). Our samples present good stoechiometry and are well crystallized. Their lattice parameters $a = 5.76$, and $c = 11.52$ are similar to those in previous publications, specifically $c/a \approx 2$. The $CuIn_3Se_5$ samples present p-type conductivity. The characterization by photoluminescence and Photoconductivity allowed the gap value of 1.23 eV to be determined for these compounds. The characterization by Spectroscopic Ellipsometry allowed the determination of energy levels above the gap in the band scheme. This study made possible the preparation of a more efficient hetero-junction based on $CuIn_3Se_5$.

References

[1] Habib, D., Al Asmar, R., El Helou, Z. and El Haj Moussa, G. (2013) Influence of Iodine Pressure on the Growth of $CuIn_{1-x}Ga_xSe_2$ Thin Films Obtained by Close-Spaced Vapor Transport "CSVT". *World Journal of Condensed Matter Physics*, **3**, 164-168. https://doi.org/10.4236/wjcmp.2013.34026

[2] Lee, J.Y., Seong, W.K., Kim, J.-H., Cho, S.-H., Park, J.-K., Lee, K.-R., Moon, M.-W. and Yang, C.-W. (2015) Synthesis and Characterization of Single-Crystal $Cu(In,Ga)Se_2$ Nanowires: High Ga Contents and Growth Behavior. *CrystEngComm*, **17**, 4950-4957.

[3] Souilah, M., Rocquefelte, X., Lafond, A., Guillot-Deudon, C., Morniroli, J.-P. and Kessler, J. (2009) Crystal Structure Re-Investigation in Wide Band Gap CIGSe Compounds. *Thin Solid Films*, **517**, 2145-2148. https://doi.org/10.1016/j.tsf.2008.10.077

[4] Habib, D., El Haj Moussa, G. (2016) Crystal Growth, Structural and Optical Studies of $CuGa_3Se_5$ Bulk Compounds. *World Journal of Condensed Matter Physics*, **6**, 27-34. https://doi.org/10.4236/wjcmp.2016.61004

[5] Zhang, S.B., Wei, S.H., Zunger, A. (1998) Defect Physics of the $CuInSe_2$ Chalcopyrite Semiconductor. *Physical Review B*, **57**, 9642-9656.

https://doi.org/10.1103/PhysRevB.57.9642

[6] Habib, D., Aoudé, O., Karishy, S., El Haj Moussa, G. (2015). Fabrication, Characterization and Optical Properties of $CuIn_3Se_5$ Bulk. Compounds. *World Journal of Condensed Matter Physics*, **5**, 201-208. https://doi.org/10.4236/wjcmp.2015.53021

[7] El Haj Moussa, G.W., Ariswan, Khoury, A., Guastavino, F. and Llinarés, C. (2002) Fabrication and Study of Photovoltaic Material $CuIn_{1-x}Ga_xSe_2$ Bulk and Thin Films Obtained by the Technique of Close-Spaced Vapor Transport. *Solid State Communications*, **122**, 391-396. https://doi.org/10.1016/S0038-1098(02)00100-X

[8] Marin, G., Tauleigne, S., Wasim, S.M., Rincon, C., Guervara, R., Delgado, J.M., Mora, A.E. and Sanchez Perez, G. (1998) X-ray Powder Diffraction and Optical Characterizations of the $Cu(In_{1-x}Ga_x)_3Se_5$ Semiconducting Systems. *Materials Research Bulletin*, **33**, 1057-1068.

[9] Wang, H.P., Lam, W.W. and Shih, I. (1999) Crystal Growth of $Cu(In_{1-x}Ga_x)_3Se_5$ by Horizontal Bridgman Method. *Journal of Crystal Growth*, **200**, 137-142. https://doi.org/10.1016/S0022-0248(98)01300-1

[10] Wang, H.P., Schih, I. and Champness, C.H. (2001) Effect of Sodium on Bridgman-Grown $Cu(In_{1-x}Ga_x)_3Se_5$ Crystalline Materials. *Thin Solid Films*, **387**, 60-62. https://doi.org/10.1016/S0040-6090(00)01840-X

[11] Djellal, L., Bellal, B. and Trari, M. (2012) Physical, Photoelectrochemical Properties of $CuIn_3Se_5$ and Relevance for Hydrogen Production. *Materials Chemistry and Physics*, **137**, 340-345. https://doi.org/10.1016/j.matchemphys.2012.01.131

[12] Meadows, H.J., Bhatia, A., Stephan, C., Schorr, S., Scarpulla, M.A. and Dale, P.J. (2013) Crystallographic Study of Phases Present in CuInSe2 Absorber Layers Produced by Laser Annealing Co-Electrodeposited Precursors. *Proceedings of SPIE* 8823, *Thin Film Solar Technology V*, San Diego, California, 11 September 2013, 882302.

[13] Marin, G., Tauleigne, S., Guevara, R., Delgado, J.M., Wasim, S.M., Bocaranda, P., Sanchez Perez, G. and Bacquet, G. (1997) Crystal Growth Structural Characterization and Room Temperature Band Gap of $CuIn_3Se_5$ and $CuGa_3Se_5$. *Proceedings of the 11th International Conference on Ternary and Multinary Compounds*, Salford, 8-12 September 1997, 573-577.

[14] Negami, T., Kohara, N., Nikihiko, M., Wada, T. and Hirao, T. (1995) Preparation and Characterization of $Cu(In_{1-x}Ga_x)3Se_5$ Thin Films. *Applied Physics Letters*, **67**, 825-827. https://doi.org/10.1063/1.115456

[15] Hofmann, A. and Pettenkofer, C. (2012) The $CuInSe_2$-$CuIn_3Se_5$ Defect Compound Interface: Electronic Structure and Band Alignment. *Applied Physics Letters*, **101**, Article ID: 062108. https://doi.org/10.1063/1.4739790

[16] Ariswan, El Haj Moussa, G., Abdelali, M., Guastavino, F. and Llinares, C. (2002) Structural, Optical and Electrical Properties of the Ordered Vacancy Compound $CuIn_3Se_5$ Thin Films Fabricated by Flash Evaporation. *Solid State Communications*, **124**, 391-396. https://doi.org/10.1016/S0038-1098(02)00603-8

[17] DeVore, H.B. (1956) Spectral Distribution of Photoconductivity. *Physical Review*, **102**, 86. https://doi.org/10.1103/PhysRev.102.86

[18] Negami, T., Kohara, N., Nikihiko, M., Wada, T. and Hirao, T. (1995) Preparation and Characterization of $Cu(In_{1-x}Ga_x)_3Se_5$ Thin Films. *Applied Physics Letters*, **67**, 825-827. https://doi.org/10.1063/1.115456

[19] Aspnes, D.E. and Studna, A.A. (1983) Dielectric Functions and Optical Parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV. *Physical Review*

B, **27**, 985.

[20] Zeaiter, K., Yanuar, A. and Llinares, C. (2001) Off-Stoichiometry Effect on the $CuInSe_2$ Dielectric Function. *Solar Energy Materials & Solar Cells*, **70**, 213-218.

[21] Aspnes, D.E. (1982) Optical Properties of Thin Films. *Thin Solid Films*, **89**, 249-262.

[22] Aspnes, D.E. (1985) In the Accurate Determination of Optical Properties. In: Palik, E.D., Ed., *Ellipsometry Handbook of Optical Constant of Solid*, Academic Press, Chapter 5, 88-110.