

Spectroscopic Ellipsometry Study of the Dielectric Function of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ Bulk Compounds: Identification of Optical Transitions

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Abstract

Using Spectroscopic Ellipsometry (SE), the optical properties of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ bulk compounds, grown by the Bridgman method, were analyzed by varying x composition ($0 \leq x \leq 1$). Energy levels above the gap in the band scheme were determined by measuring the complex dielectric function $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$ at room-temperature for energies between 1.5 and 5.5 eV using a variable angle of incidence ellipsometer. The transitions values E_1 , E_2 and E_3 were observed above the gap for different samples of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ alloy. When a gallium atom replaces an indium atom, one assumes globally that the levels related to selenium and copper are unchanged. Conversely, the levels corresponding to the conduction band are shifted towards higher energies. Thus, the gap increases as the composition of gallium increases. Spectroscopic Ellipsometry (SE) gave evidence for the interpretation of the choice of gap values which were compatible with that obtained from solar spectrum. Several other characterization methods like Energy Dispersive Spectrometry (EDS), hot point probe method, X-ray diffraction, Photoluminescence (PL), Optical response (Photoconductivity) were presented in this paper. The $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ have an Ordered Vacancy Chalcopyrite-type structure with lattice constants varying as a function of the x composition. The band gap energy of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ compounds is found to vary from 1.23 eV to 1.85 eV as a function of x.

Keywords

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

1. Introduction

Chalcopyrite compound semiconductors $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ are leading candidates for the absorbers in high efficiency photovoltaic devices [1]. A p-n junction model has been proposed by Schmidt *et al.* [2] that is based on the identification of a thin n-type surface layer atop the ternary p-type CuInSe_2 PV-quality absorber. This surface material is reported to show composition near CuIn_3Se_5 . In the present work, $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ ingots were grown using a horizontal Bridgman method. Energy Dispersive Spectrometry (EDS) and X-ray diffraction (XRD) were used to calculate the compositions of the ingots. The hot point probe method is used to determine the conduction types. The optical properties are investigated using Photoconductivity and Photoluminescence characterization.

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. In this paper, the method illustrates the accuracy of transitions, in semiconductor, obtained from the experimental results of SE. A harmonic oscillator approximation (HOA) was fitted to the data for monocrystal silicon and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$. Room-temperature measurements were reported for the-pseudo dielectric function $\langle \epsilon \rangle$ at energies from 1.5 to 5.5 eV.

2. Experiment and Results

Crystals with different compositions were synthesized by direct combination of high purity 5N for Cu and In, 6N for Ga and Se in the desired proportions. The elements were put in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. This tube is then introduced in a horizontal furnace at a temperature higher than the melting temperature of the compounds for 72 hours and then slowly cooled down.

The crystals were characterized by X-ray measurements, using a Seifert MZIV powder diffractometer ($\theta, 2\theta$ geometry) with Cu ($K\alpha$) radiation ($\lambda = 1.5406 \text{ \AA}$). The chemical composition of the obtained samples were given by EDS (Link type AN 1000 55/S) coupled to a scanning microscope (Cambridge type S360). The Photoluminescence (PL) measurements were performed at temperature 4.2 K by directly immersing the samples into liquid helium. The optical responses or Photoconductivity were performed at room temperature. Spectroscopic Ellipsometry used to determine the energy levels above the gap in the band scheme.

2.1. Characterization by EDS

Figure 1 and **Table 1** show the results of characterization by EDS of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ films.

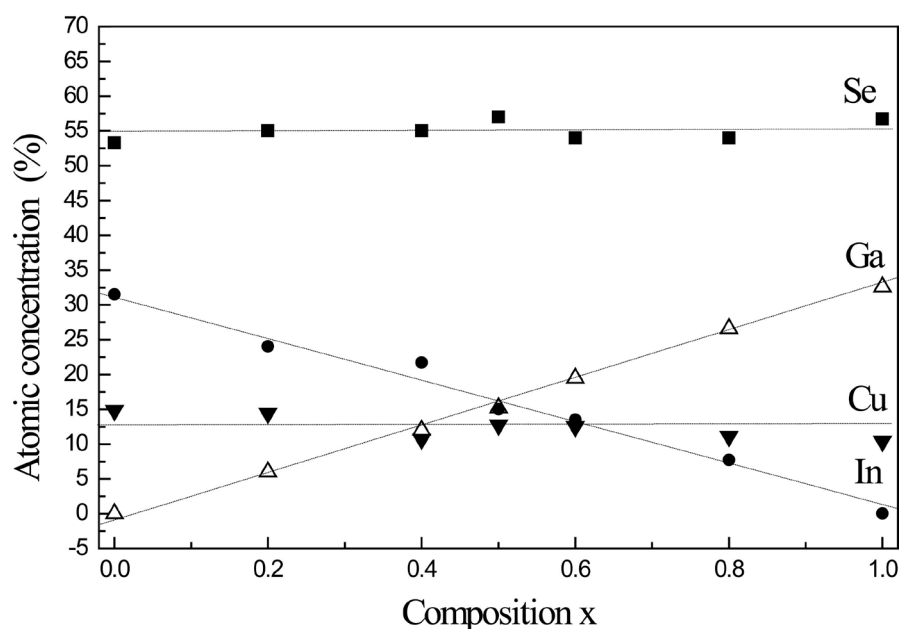


Figure 1. Composition of the bulk of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ determined by EDS as a function of the composition x: ■ Se; ▼ Cu; ● In ; Δ Ga.

Table 1. Composition and deviation from stoichiometry for the $\text{Cu}(\text{In}_x\text{Ga}_{1-x})_3\text{Se}_5$ crystals.

$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$							
Starting (x)	Samples (x)	% Cu	% In	% Ga	% Se	The deviation from stoichiometry $\Delta y = \frac{3 * \text{Cu}}{\text{Ga} + \text{In}} - 1$ [2]	Conduction type
0	0	11.2	32.5	0	56.3	+0.03	n
0.2	0.21	12	24.5	6.8	56	+0.15	p
0.4	0.4	10.7	21.7	12	55	-0.05	p
0.5	0.59	11.7	16	16.2	56	+0.09	p
0.6	0.64	11.1	11.8	21.8	55.3	-0.01	p
0.8	0.78	11.1	7.7	26.6	54	-0.03	p
1	1	10.4	0	32.6	56.7	-0.04	p

The good stoichiometry is well observed in our samples and its magnitude deviation Δy is slight; so, our samples present a nearly perfect stoichiometry ($\Delta y = 0$) [3]. The composition x in gallium for the studied samples, from EDS measurements, is very close to the starting composition of the elements in the sealed tube. The CuIn_3Se_5 samples show a conductivity of type n and the other samples ($x \neq 0$) are all of type p.

2.2. Characterization by X-Ray Diffraction

The X-Ray diffraction spectra of different samples $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ are illustrated in **Figure 2(a)**. Our samples are of good crystalline quality and all excitation peaks in the resulting spectra are the same as those found in references [4]

[5] [6] [7]. Thus, X-Ray diffraction patterns show the presence of many preferential orientations according to the planes (112), (220) and (312) of all the samples. Also, it shows a linear shifting of peaks towards the higher magnitudes of 2θ when the x composition increases.

The (112) peak position as function of the composition x ($0 \leq x \leq 1$) is shown on **Figure 2(b)** and it may be written under the following linear form:

$$2\theta = 26.84 + 1.2x \quad (1)$$

The compounds $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ do not have a chalcopyrite structure as for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ since the characteristic peaks concerning the chalcopyrite

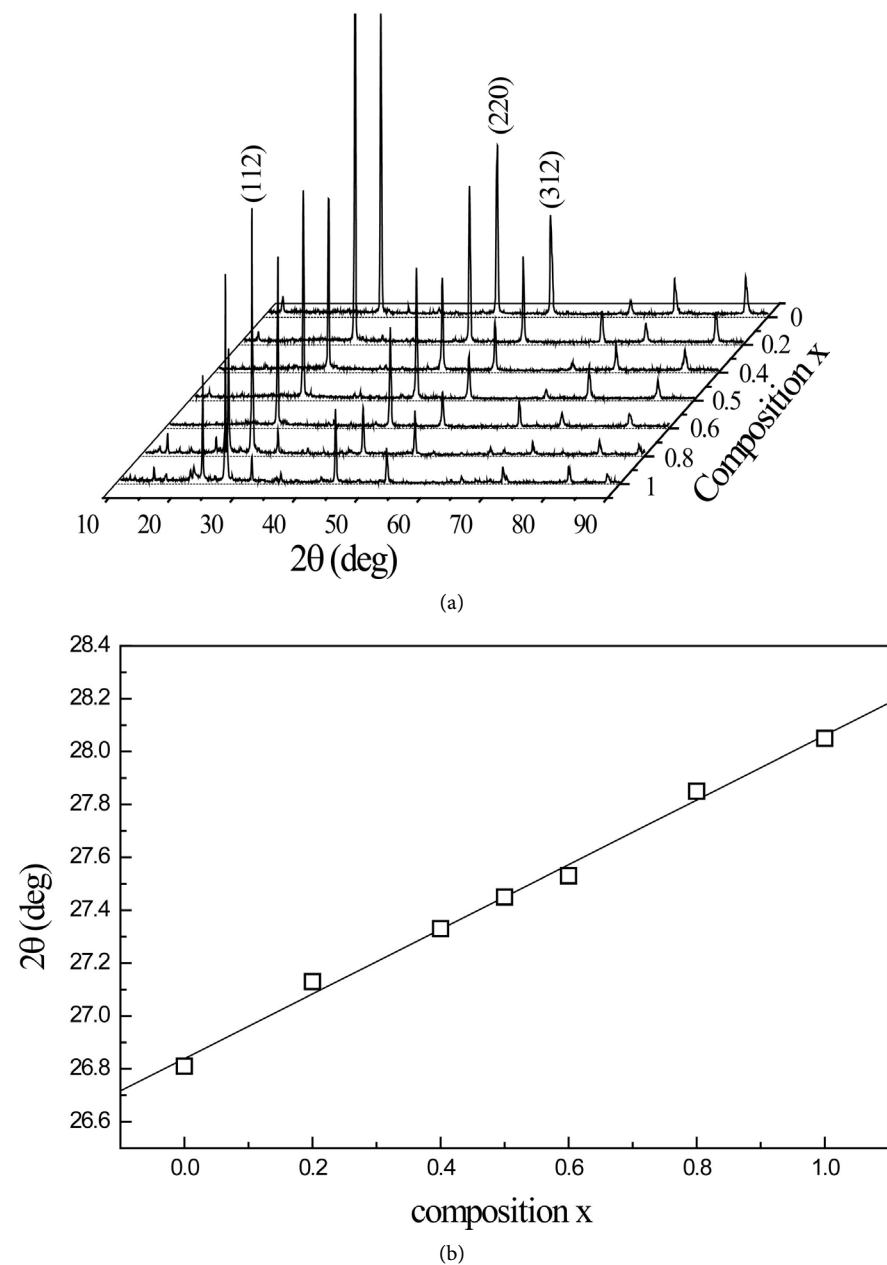


Figure 2. (a) X-ray diffraction patterns of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$; (b) The (112) peak position as a function of the composition x .

Table 2. Lattice parameters (a, c and c/a) for near-stoichiometry $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ crystals.

x	a	c	c/a	Δ (c/a)
0	5.76	11.52	2.0015	+0.0015
0.2	5.72	11.43	1.9995	-0.0005
0.4	5.65	11.295	1.999	-0.0010
0.5	5.62	11.262	2.0032	+0.0032
0.6	5.59	11.28	2.016	+0.0160
0.8	5.56	11.17	2.007	+0.0070
1	5.49	10.93	1.9896	-0.0105

structure could not be observed. These compounds can be of stannite structure [6] [7] [8] or an Ordered Vacancy Chalcopyrite structure (OVC) or Ordered Defect Chalcopyrite Structure (ODC).

The lattice parameters a and c for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ given in **Table 2**, have been calculated from our spectra. These values decrease when the Gallium concentration increases [9] [10] [11] [12]. They vary between: a = 5.76, c = 11.2 for the CuIn_3Se_5 and a = 5.49, c = 10.93 for the CuGa_3Se_5 ; *i.e.* the Gallium atom is smaller than the Indium one. Our values obtained for a and c are in good agreement with those reported in the literature [9] [10] [11] [12].

2.3. Characterization by Photoluminescence

Zott *et al.* [13] [14] and Orsal *et al.* [15] have studied the gap variation of CuInSe_2 and CuGaSe_2 as a function of the ratio Cu/In and Cu/Ga respectively; they have observed an increase of the gap value with the concentration of Indium or Gallium. The compounds $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ are equivalent to the compounds $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ with an excess of Indium or Gallium according to the composition x. Then, the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ compounds shows a gap value higher than that of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ for each value of the composition x.

The different Photoluminescence response spectra of the alloy $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ ($0 \leq x \leq 1$) at liquid helium temperature (4.2 K) are presented in **Figure 3(a)**. For x = 0 we have been able to detect the exciton position which allows us to specify the exact position of the band gap. The arrows pointing upward indicate the gap values of literature [10] [12], and the arrows pointing downward indicate our values (for x = 1 and x = 0). These spectra shift towards higher energies when gallium concentration increases. Each of the spectra is formed by one large peak, which is probably caused by the impurity band transitions. **Figure 3(b)** presents the PL dominant peak variation as function of the composition x. We notice that our samples have band gap energy values that are well conform to those of literature [10] [12].

2.4. Characterization by Photoconductivity

We have determined the band gap energy value at room-temperature by analyzing

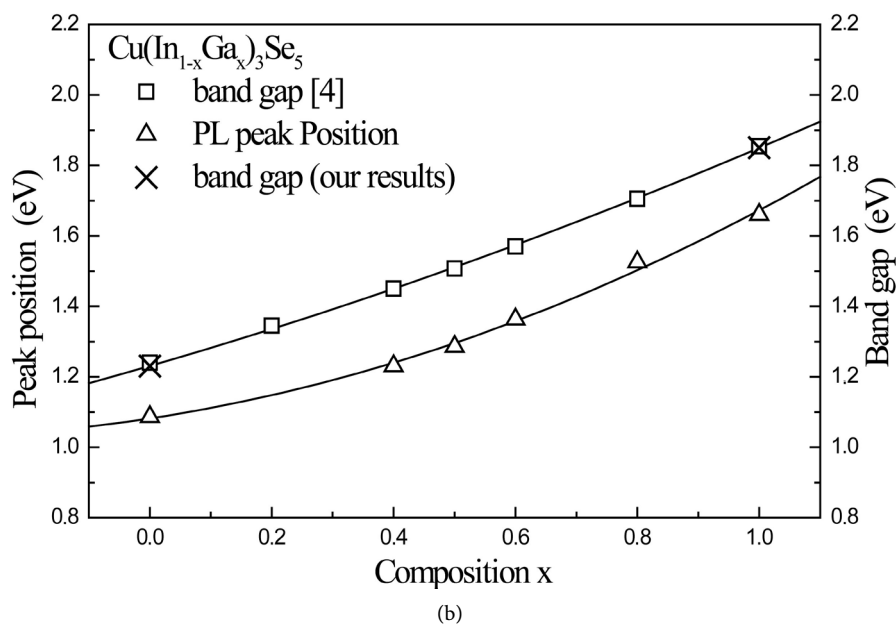
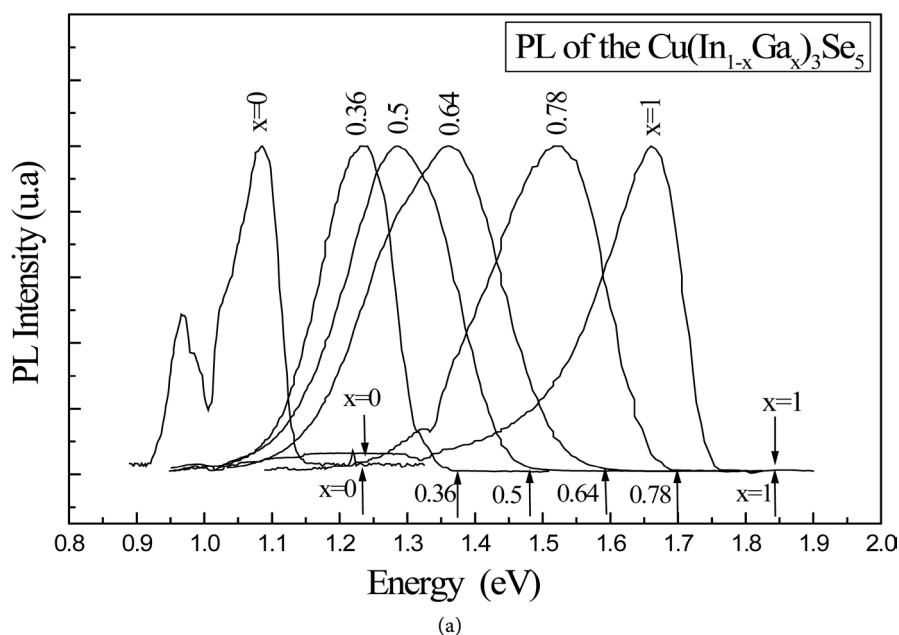


Figure 3. (a) Photoluminescence response at 4.2 K of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ crystals ($0 \leq x \leq 1$), The arrows pointing upward indicate the gap values of literature [6] [7] [9], and the arrows pointing downward indicate our values (for $x = 1$ and $x = 0$); (b) Variation of PL dominant peak in function of composition x of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ (Δ). The band gap energy at 4.2 K given by [4] (\square), our gap values (\times).

our compounds using spectral Photoconductivity [16].

Figure 4(a) illustrates the different spectra of Photoconductivity $((ah\nu)^2$ as a function $h\nu$) of the alloy $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$. These spectra denote high speeds of surface recombination. We do not observe a saturation level at high energy. In these cases, the gap value is given by an approximate value by taking the abscissa of each curve at $PC_{\max}/2$. We have observed a variation of band gap energy as a function of the composition x at room temperature, the band gap value varies

from 1.23 eV [6] [7] [12] for $x = 0$ to 1.85 eV for $x = 1$, these values match those found by Photoluminescence and in literature [4] [6] [7] [10]. **Figure 4(b)** shows the variations of band gap energy at 300 K as a function of the composition x . These variations can be expressed by the following equation:

$$E_g(x)[\text{eV}] = 1.22 + 0.42x + 0.21x^2 \quad (2)$$

2.5. Characterization by Spectroscopic Ellipsometry (SE)

Spectroscopic Ellipsometry (SE) is a characterization technique which allows the

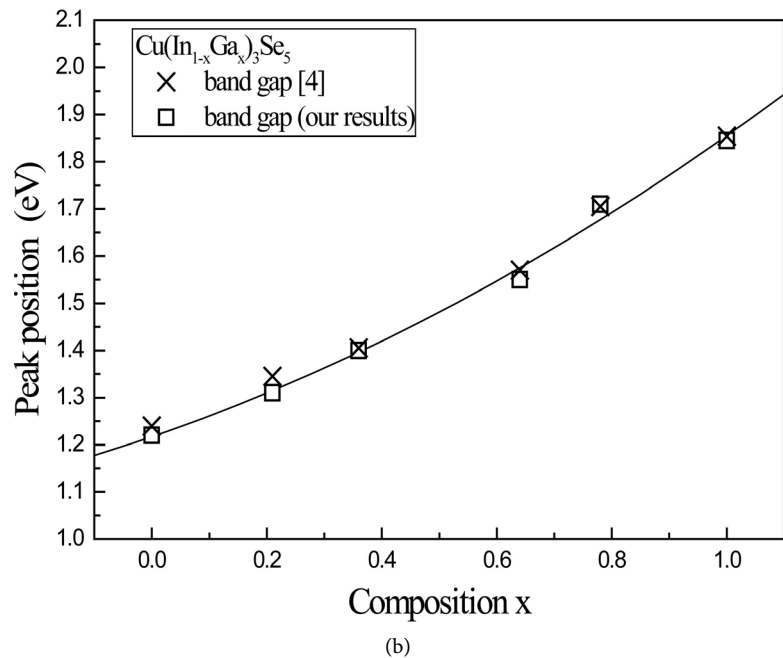
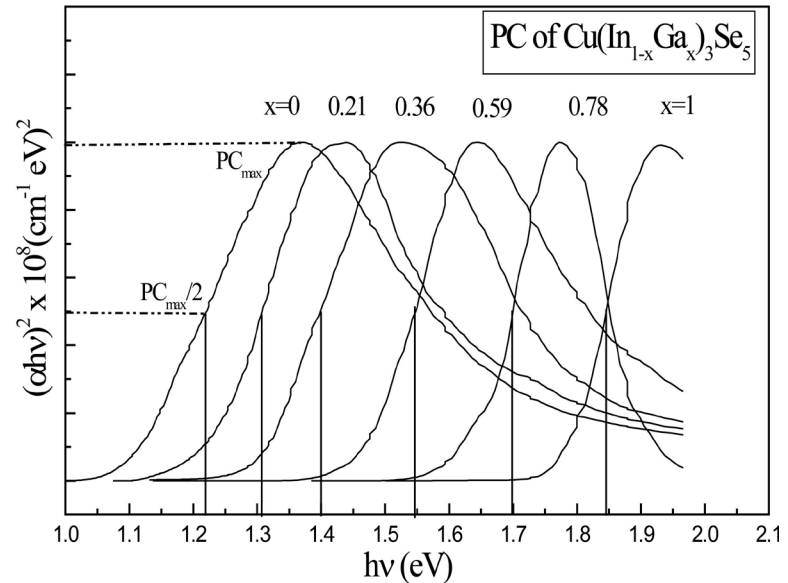


Figure 4. (a) Photoconductivity spectra $((ah\nu)^2$ as a function $h\nu$) of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ alloy; (b) Optical band gap at 300 K by Photoconductivity of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$.

determination of energy levels above the gap in the band scheme. The real part of the dielectric pseudo-function $\langle \epsilon_r \rangle$ is related to the substrate densities of state D_n . The calculation of the 3rd order derivative of the quantity $E^2 \epsilon_r(E)$ [17], is given by:

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

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 :

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

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

where r is the damping constant.

The $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ bulk compounds were characterized by Spectroscopic Ellipsometry, and the observed transitions were determined by the method described above. **Figure 5** illustrates the evolution of the imaginary part (ϵ_i) and the real part (ϵ_r) of the dielectric function, for

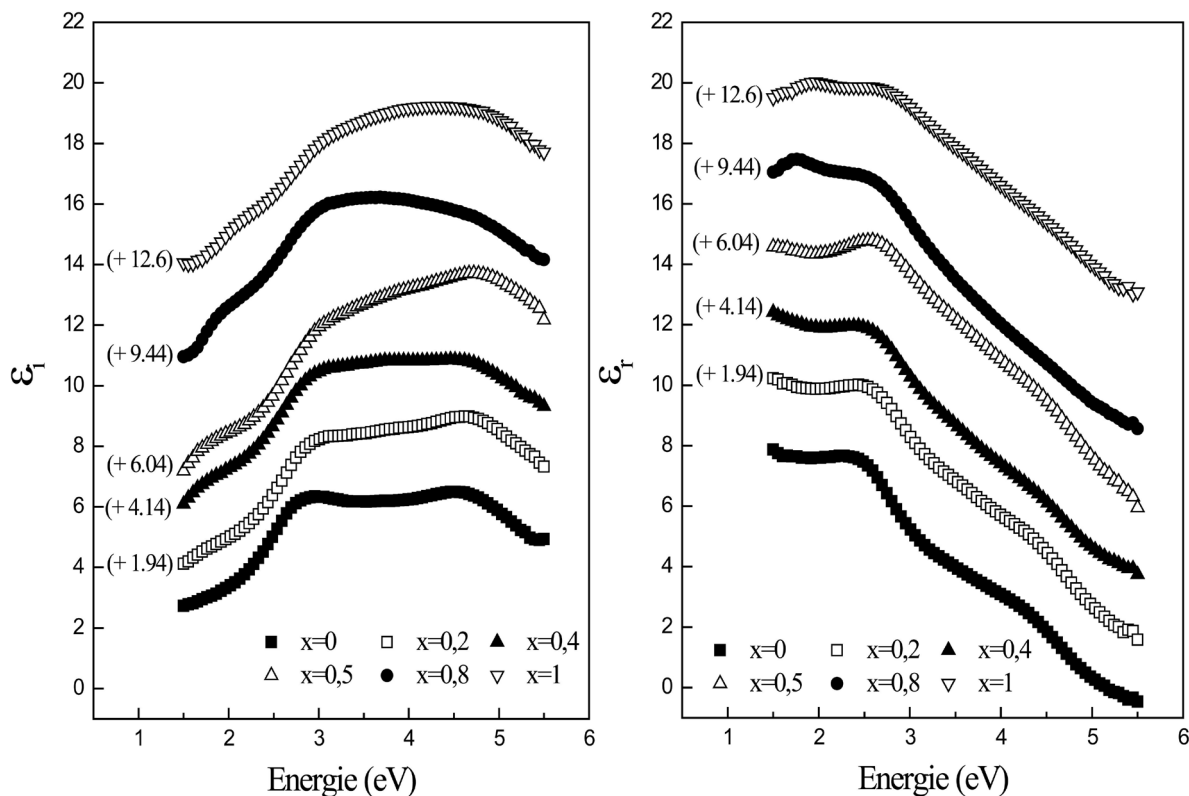


Figure 5. Evolution of the spectrum of the imaginary part (ϵ_i) and the real part (ϵ_r) of the dielectric function, for different compositions of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$. The different spectra are identified by labeled symbols in the figure.

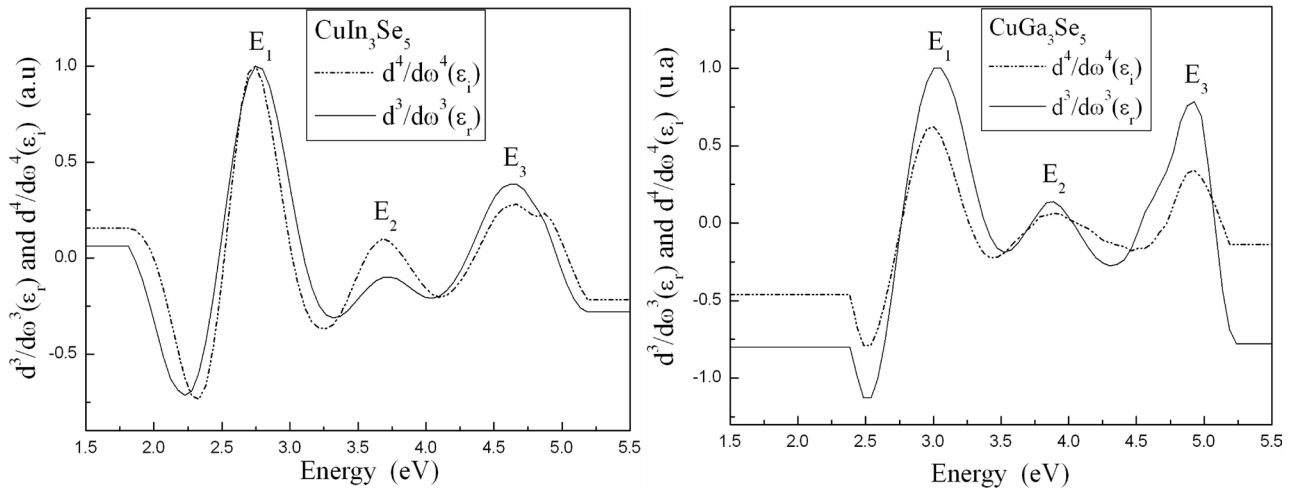


Figure 6. 3rd order derivative of ϵ_r and the 4th order derivative of ϵ_i of CuIn_3Se_5 and CuGa_3Se_5 .

the real one (ϵ_r) for the dielectric function in terms of the composition of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ alloy for different values of x ($x = 0, 0.21, 0.36, 0.5, 0.64, 0.78$ and 1). For the sake of clarity of spectra, each spectrum was shifted by the quantity given in parenthesis on the left.

The spectrum of the imaginary part of dielectric function was observed to shift towards higher energies as gallium concentration increases.

The method described above has been applied to the case of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ bulks. **Figure 6** shows the results of the spectra at 3rd and 4th order derivatives of ϵ_i for a sample of CuIn_3Se_5 and CuGa_3Se_5 .

Zeaiter *et al.* [18] were studied the stoichiometry 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 [19] [20].

Therefore, the implementation has the effect of widening the peaks and simultaneously decreasing the intensity of the peaks of the imaginary dielectric function (ϵ_i). The same effects were noticed on the spectra of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ compounds [21]. $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ compounds are like $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ compounds.

Table 3 shows the observed transitions values (E_1 , E_2 and E_3) for different samples of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ ($0 \leq x \leq 1$) alloy. **Figure 7** illustrates the variation of these transitions as a function of the initial composition x . Parabolic variations are obtained for E_1 , E_2 and E_3 (as a function of the composition x). The equations for the fitted curves are:

$$E_1 = 2.76 + 0.29x - 0.06x^2$$

$$E_2 = 3.73 + 0.27x - 0.146x^2$$

$$E_3 = 4.64 + 0.245x - 0.033x^2$$

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

Samples	E_1 (eV)	E_2 (eV)	E_3 (eV)
x = 0	2.75	3.68	4.62
x = 0.21	2.85	3.86	4.72
x = 0.36	2.85	3.78	4.73
x = 0.5	2.9	3.84	4.773
x = 0.78	2.95	3.786	4.83
x = 1	3	3.89	4.93

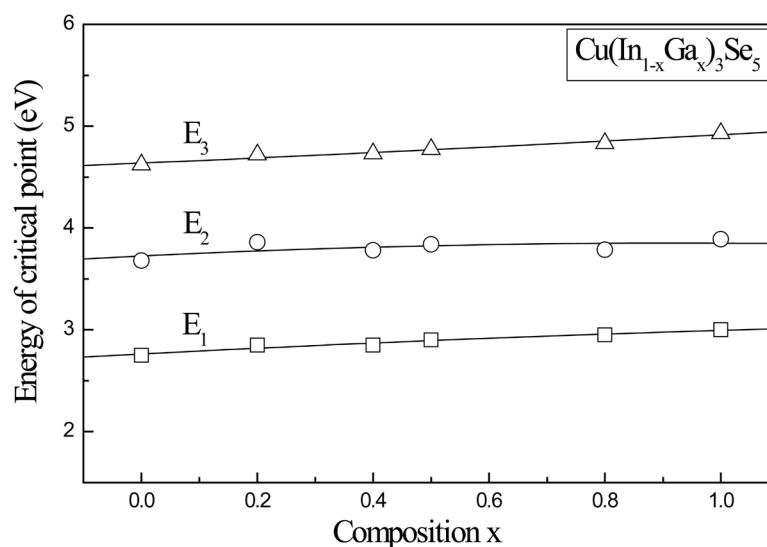


Figure 7. Variation of inter-band transitions: E_1 (\square), E_2 (\circ), E_3 (Δ) of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ as a function of the composition x.

The transitions E_1 and E_3 can be attributed to the ionization of levels d of Cu. In contrary, the transition E_2 is related to the hybridization s-s between the s-levels of indium and that of Cu.

The highest levels of the valence band are essentially composed of the 4p-levels of Se and the localized strong density d-levels of Cu. Thus, the valence band is nearly independent of the variation of composition.

The lowest levels of the conduction band are essentially composed of s-levels for copper and indium. Gallium is specified by a 4 s band with higher energy than that of 3 s of indium. When a gallium atom replaces an indium atom, one assumes globally that the levels related to selenium and copper are unchanged. Conversely, the levels corresponding to the conduction band are shifted towards higher energies. Thus, the gap increase as the composition of gallium increases.

3. Conclusion

The $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ for ($0 \leq x \leq 1$) compounds were prepared by the Bridgman method. The different samples have been characterized by several techniques of

characterization. Samples show a good stoichiometry. These materials are well crystallized having a preferential orientation. In addition, they have a stannite structure, an Ordered Vacancy Chalcopyrite (OVC) or an Ordered Defect Chalcopyrite (OVC). The lattice parameters (a and c) vary between $a = 5.76$, $c = 11.2$ for the CuIn_3Se_5 and $a = 5.49$, $c = 10.93$ for the CuGa_3Se_5 . These samples have p-type conductivity for the values of $x \neq 0$, the band gap energy values of these compounds, which vary from 1.23 eV for the CuIn_3Se_5 to 1.85 eV for the CuGa_3Se_5 . Spectroscopic Ellipsometry was used to determine the energy levels above the gap in the band scheme. We measured the dielectric function $\langle \epsilon \rangle$ at room temperature by varying the energy between 1.5 to 5.5 eV. We observed several transitions (E_1 , E_2 , E_3) above the gap for the different samples of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ alloy ($0 \leq x \leq 1$). These transitions vary parabolically as a function of the starting composition x. When a gallium atom replaces an indium atom, the levels of the conduction band move to higher energies. Thus the gap will increase when the gallium composition increases. The study by spectroscopic ellipsometry allowed us to explain the increase in the energy gap as a function of the Gallium concentration, and consequently to prepare a more efficient junction, simply by choosing the correct x value of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ alloy when the gap value is matched to the solar spectrum.

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