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

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Abstract

Using Spectroscopic Ellipsometry (SE), the optical properties of Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ bulk compounds, grown by the Bridgman method, were analyzed by varying x composition (0 ≤ x ≤ 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 Cu(In$_{1-x}$Ga$_x$)$_3$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 Cu(In$_{1-x}$Ga$_x$)$_3$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 Cu(In$_{1-x}$Ga$_x$)$_3$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 CuIn_{1-x}Ga_xSe_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_{3}Se_5. In the present work, Cu(In_{1-x}Ga_x)Se_2 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 Cu(In_{1-x}Ga_x)Se_2. Room-temperature measurements were reported for the-pseudo dielectric function \( \langle \varepsilon \rangle \) 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 \( 5 \times 10^{-6} \) 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 (Ka) radiation (\( \lambda = 1.5406 \) Å). 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 Cu(In_{1-x}Ga_x)_3Se_5 films.
Figure 1. Composition of the bulk of the Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)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 Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)Se\(_5\) crystals.

<table>
<thead>
<tr>
<th>Starting (x)</th>
<th>Samples (x)</th>
<th>% Cu</th>
<th>% In</th>
<th>% Ga</th>
<th>% Se</th>
<th>The deviation from stoichiometry (\Delta y = \frac{3 \times Cu}{Ga + In} - 1)</th>
<th>Conduction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>11.2</td>
<td>32.5</td>
<td>0</td>
<td>56.3</td>
<td>+0.03</td>
<td>n</td>
</tr>
<tr>
<td>0.2</td>
<td>0.21</td>
<td>12</td>
<td>24.5</td>
<td>6.8</td>
<td>56</td>
<td>+0.15</td>
<td>p</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>10.7</td>
<td>21.7</td>
<td>12</td>
<td>55</td>
<td>−0.05</td>
<td>p</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59</td>
<td>11.7</td>
<td>16</td>
<td>16.2</td>
<td>56</td>
<td>+0.09</td>
<td>p</td>
</tr>
<tr>
<td>0.6</td>
<td>0.64</td>
<td>11.1</td>
<td>11.8</td>
<td>21.8</td>
<td>55.3</td>
<td>−0.01</td>
<td>p</td>
</tr>
<tr>
<td>0.8</td>
<td>0.78</td>
<td>11.1</td>
<td>7.7</td>
<td>26.6</td>
<td>54</td>
<td>−0.03</td>
<td>p</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>10.4</td>
<td>0</td>
<td>32.6</td>
<td>56.7</td>
<td>−0.04</td>
<td>p</td>
</tr>
</tbody>
</table>

The good stoichiometry is well observed in our samples and its magnitude deviation \(\Delta y\) 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\(_3\)Se\(_5\) 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 Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)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].
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 $2\theta$ 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:

$$2\theta = 26.84 + 1.2x$$

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

![Figure 2](image-url)

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

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

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

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 Cu(In$_{1-x}$Ga$_x$)$_3$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$_3$Se$_5$ and a = 5.49, c = 10.93 for the CuGa$_3$Se$_5$; 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 Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ are equivalent to the compounds Cu(In$_{1-x}$Ga$_x$)$_2$Se$_2$ with an excess of Indium or Gallium according to the composition x. Then, the Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ compounds shows a gap value higher than that of Cu(In$_{1-x}$Ga$_x$)$_2$Se$_2$ for each value of the composition x.

The different Photoluminescence response spectra of the alloy Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ (0 ≤ x ≤ 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 Cu(In_{1-x}Ga_x)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 Cu(In_{1-x}Ga_x)Se_5 (\Delta). The band gap energy at 4.2 K given by [4] (□), our gap values (×).

Figure 4(a) illustrates the different spectra of Photoconductivity (\((a\nu)^2\) as a function \(\nu\)) of the alloy Cu(In_{1-x}Ga_x)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 \(PC_{\text{max}}/2\). We have observed a variation of band gap energy as a function of the composition x at room temperature, the band gap value varies our compounds using spectral Photoconductivity [16].
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]. \textbf{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:

\[ E_g(x)[eV] = 1.22 + 0.42x + 0.21x^2 \]  

(2)

\subsection*{2.5. Characterization by Spectroscopic Ellipsometry (SE)}

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 \( \varepsilon_r \) is related to the substrate densities of state \( D_n \). The calculation of the 3rd order derivative of the quantity \( E^2 \varepsilon_r (E) \) [17], 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 \( \omega_0 \) is used. Its’ Lorentz nature is characterized by an elastic amplitude \( \alpha_e \) and an absorption one \( \alpha_a \):

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

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

where \( r \) is the damping constant.

The Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)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 \( \varepsilon_i \) and the real part \( \varepsilon_r \) of the dielectric function, for different compositions of Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)Se\(_5\). The different spectra are identified by labeled symbols in the figure.

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**Figure 5.** Evolution of the spectrum of the imaginary part \( \varepsilon_i \) and the real part \( \varepsilon_r \) of the dielectric function, for different compositions of Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)Se\(_5\). The different spectra are identified by labeled symbols in the figure.
Figure 6. 3rd order derivative of $\varepsilon_r$ and the 4th order derivative of $\varepsilon_i$ of CuIn$_3$Se$_5$ and CuGa$_3$Se$_5$.

the real one ($\varepsilon_r$) for the dielectric function in terms of the composition of Cu(In$_{1-x}$Ga$_x$)$_3$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 Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ bulks. Figure 6 shows the results of the spectra at 3rd and 4th order derivatives of $\varepsilon_i$ for a sample of CuIn$_3$Se$_5$ and CuGa$_3$Se$_5$.

Zeaiter et al. [18] were studied the stœchiometry effect on the dielectric functions. They found that the imaginary dielectric function ($\varepsilon_i$) 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 ($\varepsilon_i$). The same effects were noticed on the spectra of Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ compounds [21]. Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ compounds are like CuIn$_{1-x}$Ga$_x$Se$_2$ compounds.

Table 3 shows the observed transitions values ($E_1$, $E_2$ and $E_3$) for different samples of the Cu(In$_{1-x}$Ga$_x$)$_3$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 $\varepsilon_i$ and the 4th order derivative of $\varepsilon_i$ for different samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_1$ (eV)</th>
<th>$E_2$ (eV)</th>
<th>$E_3$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>2.75</td>
<td>3.68</td>
<td>4.62</td>
</tr>
<tr>
<td>$x = 0.21$</td>
<td>2.85</td>
<td>3.86</td>
<td>4.72</td>
</tr>
<tr>
<td>$x = 0.36$</td>
<td>2.85</td>
<td>3.78</td>
<td>4.73</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>2.9</td>
<td>3.84</td>
<td>4.773</td>
</tr>
<tr>
<td>$x = 0.78$</td>
<td>2.95</td>
<td>3.786</td>
<td>4.83</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>3</td>
<td>3.89</td>
<td>4.93</td>
</tr>
</tbody>
</table>

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 4s band with higher energy than that of 3s 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 Cu(In$_{1-x}$Ga$_x$)$_3$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\(_3\)Se\(_5\) and \(a = 5.49, c = 10.93\) for the CuGa\(_3\)Se\(_5\). These simples 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\(_3\)Se\(_5\) to 1.85 eV for the CuGa\(_3\)Se\(_5\).

Spectroscopic Ellipsometry was used to determine the energy levels above the gap in the band scheme. We measured the dielectric function \(\langle \varepsilon \rangle\) 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 Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)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 Cu(In\(_{1-x}\)Ga\(_x\))\(_3\)Se\(_5\) alloy when the gap value is matched to the solar spectrum.

References


