Identification of Optical Transitions by Spectroscopic Ellipsometry (SE) on CuIn$_3$Se$_5$ 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$_3$Se$_5$ 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$_x$Se$_2$ 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$_x$)$_2$Se$_3$ phase was formed at the surface of the CuIn$_{1-x}$Ga$_x$Se$_2$ layer [1] [2] [3] [4]. Another attractive property is their tolerance to large range of anion-to-cation off stoichiometry, manifested by the existence of an ordered defect compounds (ODC) with large variations in their Cu/In/Se ratio [5]. These ODCs, like CuIn$_3$Se$_5$, 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$_3$Se$_5$ has been of interest to many groups [6]. In this work, crystals of CuIn$_3$Se$_5$ 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 $5 \times 10^{-6}$ 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$_3$Se$_5$. 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 5N for Cu and In and 6N for Se in the desired proportions. The elements were placed in a quartz tube sealed under a vacuum of $5 \times 10^{-6}$ 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 ($\theta$, $2\theta$ 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 con-
stant 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 ($\lambda$ from 0.2 $\mu$m to 1 $\mu$m), with a high stability ($\pm 0.2\%$). 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$_3$Se$_5$ materials by EDS are presented. The samples show a nearly perfect stoechiometry since the magnitude of deviation from stoechiometry, $\Delta y (\Delta y = (3 \times \text{Cu})/\text{In} - 1)$, is very small [8]. The results of the chemical compositions of a CuIn$_3$Se$_5$ sample have a large value of $\Delta y$ (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$_3$Se$_5$ samples present a n-type conductivity.

3.2. Characterization by X-Ray Diffraction (XRD)

The spectra of different CuIn$_3$Se$_5$ 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$_3$Se$_5$ 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>
<thead>
<tr>
<th>Table 1. Chemical compositions of CuIn$_3$Se$_5$ bulk samples obtained by EDS.</th>
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<tr>
<td>Samples</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
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</table>
The $a$ and $c$ lattice parameters of CuIn$_3$Se$_5$ 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$_3$Se$_5$ 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 \((\alpha h\nu)^2\) as a function of \(h\nu\) of CuIn3Se5. 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 \(PC_{\text{max}}/2\) \[17\]. 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 \(\langle \epsilon_r \rangle\) is related to the substrate densities of state \(D_n\). The calculation of the 3rd order derivative of the quantity \(E^2 \epsilon_r (E)\) \[18\], is given by:

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

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 \(\alpha_a\):

\[\text{Figure 3.} \] Photoconductivity spectrum \((\alpha h\nu)^2\) as a function of \(h\nu\) of CuIn3Se5 at room temperature for one sample.
The variation of $\alpha_e$ and $\alpha_a$ as a function of $\omega$.

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

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

where $r$ is the damping constant.

$\alpha_e$ and $\alpha_a$ functions are shown in Figure 4. The frequency $\omega_0$ is determined by the maximum of $\alpha_a$ and the zero of $\alpha_e$. The 3rd and 4th order derivatives of functions $\alpha_e$ and $\alpha_a$ 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 $\alpha_e(\omega)$ and of its 4th order derivative. Figure 6 shows the spectra of $\alpha_a(\omega)$ and of its 3rd order derivative. In the 2 cases, $\omega_0$ value was determinate. The function $\alpha_a(\omega)$ presents a narrow peak which permit to determine $\omega_0$ 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 $\omega_0$ position.

To verify the accuracy of the determination of $E_1$, $E_2$,... levels, this method was applied to the case of Si. $e_i$ and $e_r$ represent $\alpha_e$ and $\alpha_a$ type for each harmonic oscillator, where the energy level is an optical transition described in the band scheme. The spectra of $e_i$ and $e_r$ functions are shown in Figure 7.

The maximum 3rd and 4th order derivatives of $e_i$ and $e_r$ are shown in Figure 8 representing the transitions of energy levels in the band scheme [19]. The three energy levels observed $E_i$ (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$_3$Se$_5$

CuIn$_3$Se$_5$ samples were characterized by Spectroscopic Ellipsometry, and the observed transitions were determined by the method described above. The different spectra of the imaginary part ($\varepsilon_i$) and the real part ($\varepsilon_r$) respectively of the dielectric function, for different CuIn$_3$Se$_5$ samples are shown in Figure 9. Figure 10 illustrates the results of spectra at $3^{rd}$ and $4^{th}$ order derivatives of $\varepsilon_r$ and $\varepsilon_i$ respectively, of one sample of CuIn$_3$Se$_5$.
Figure 7. The dielectric functions $\varepsilon_i$ and $\varepsilon_r$ of Si.

Figure 8. The 3rd order derivative of $\varepsilon_i$ and the 4th order derivative of $\varepsilon_r$ of Si.
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 $\varepsilon_r$ and the 4th order derivative of $\varepsilon_i$ of one sample of CuIn$_3$Se$_5$.

Zeaiter et al. [20] studied the stoichiometry 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 [21] [22]. So the excess of In has the effect of expanding and decreasing the intensity peaks of the imaginary dielectric function ($\varepsilon_i$). We noticed the same effects on our spectra of CuIn$_3$Se$_5$. 
Table 2. The transitions energies obtained by the 3rd order derivative of $\varepsilon_1$ and the 4th order derivative of $\varepsilon_2$ for the samples of CuIn$_3$Se$_5$.

<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>A</td>
<td>2.75</td>
<td>3.68</td>
<td>4.62</td>
</tr>
<tr>
<td>B</td>
<td>2.73</td>
<td>3.70</td>
<td>4.64</td>
</tr>
<tr>
<td>C</td>
<td>2.75</td>
<td>3.69</td>
<td>4.61</td>
</tr>
</tbody>
</table>

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$_3$Se$_5$ 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 stoichiometry 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$_3$Se$_5$ 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$_3$Se$_5$.

References


B, 27, 985.

