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Characteristic behaviour of thermaly evaporated CdIn$_2$Se$_4$ thin films

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ABSTRACT

CdIn$_2$Se$_4$ thin films have been deposited by thermal evaporation technique of the pre-synthesized ingot material. X-ray diffraction study revealed that the prepared powder sample had polycrystalline structure corresponding to CdIn$_2$Se$_4$ single phase. The X-ray diffraction study indicated that the as-deposited films are amorphous in nature, while an amorphous-to-crystalline phase transition has been occurs at annealing temperature $T_a = 473$ K. The structural results have been confirmed using the transmission electron microscope and the corresponding electron diffraction pattern. The chemical analysis using the energy dispersive X-ray spectrometer indicates the nearly stoichiometric compositions of the bulk sample with chemical formula of Cd$_{1.02}$In$_{1.94}$Se$_{4.04}$. However, the chemical composition of the deposited films varies from sample to sample. The optical properties of the as-deposited films have been investigated as a function of the film composition in the wavelength range 500-2500 nm. The refractive index dispersion data has been adequately described by the well-known single oscillator model from which the dispersion parameters were determined. The analysis of the optical absorption coefficient revealed the presence of direct and indirect optical transitions. The energy corresponding such transition have been determined

Key words: Characterization, Deposition process, CdIn$_2$Se$_4$, Thin Films.

Introduction

Ternary compounds such as defect chalcopyrite semiconductors are currently being investigated due to their diversity of applications in areas like, non-linear optics, electro-optics, and acousto-optics (Suresh Babu, G., 2006; Tiginyanu, I.M., 2003; Reshak Ali, H., 2008). There is a wide range of semiconductors with different optical band gaps, refractive indices, electrical resistivity and other properties to suit the devices of interest. Ordered vacancy compound semiconductors form a class of ternary semiconducting compounds of the formula $A^{II}B^{III}_2X^{IV}_4$, where given atomic site is vacant in an ordered and stoichiometric fashion. These compounds form a natural bridge between impurity physics (where, e.g. vacancies exist as isolated entities) and crystal physics (where each site is repeated translationally to form a sublattice) (Millar, A., 1981). The important applications of these compounds for solar cells (Filipowicz, J., 1980), optoelectronic devices (Gracia, F.J., M.S. Tomar, 1980), memory switching (Yahia, I.S., 2010), electro-photographic layers and devices with high radiation stability (Shionoya, S., Y. Tamato, 1971; Zeyada, H.M., 2009) have been previously reported.

CdIn$_2$Se$_4$ that belongs to the $A^{II}B^{III}_2X^{IV}_4$ family has been prepared from its binary compounds, CdSe and In$_2$Se$_3$ in equivalent amounts by Hahn et al. (1955). The result of the X-ray analysis revealed that the CdIn$_2$Se$_4$ compound has a tetragonal structure with lattice parameters $a = b = 0.5815$nm and $c = 1.163$ nm (Chizhikov, V.I., 1981). The present work aims to investigate the structural characteristics, chemical analysis and optical properties of thin vacuum deposited films of CdIn$_2$Se$_4$.

Experimental techniques:

A polycrystalline ingot of CdIn$_2$Se$_4$ was prepared by the direct fusion of stoichiometric amounts of their constituting elements (Cd, In and Se) of purity 99.999% in a sealed evacuated silica tube (at pressure $10^{-3}$ Pa) of length 15 cm and internal diameter 1.5 cm. A homemade oscillatory furnace has been used to do this task. The furnace temperature was first raised gradually at a rate of 50 K h$^{-1}$ to 1300 K, where the mixture was left for 24 h, during which the oscillatory motion of the furnace was operated, to ensure homogeneity. The furnace temperature was then decreased slowly to the following temperatures: 1073, 873 and 573 K. Finally, the furnace was switched off and the tube was left to cool down to room temperature (300 K). The long duration of
synthesis and the mechanical shaking of the melt in the oscillatory furnace provide the high homogeneity of the investigated compound.

CdIn$_2$Se$_4$ thin films of different thicknesses were deposited by thermal evaporation of fine-grained powder onto clean glass substrates at room temperature, using a high-vacuum coating unit (Type Edward’s 306A) attached with quartz crystal thickness monitor. Several trials were conducted to adjust the conditions of evaporating the material in order to avoid its spillage or decomposition during the evaporation process. The evaporation was carried out at a vacuum pressure of 10$^{-4}$ Pa, from a molybdenum boat kept at a high temperature in order to evaporate the charge instantaneously. The substrate holder was rotated using a rotary drive mechanism to ensure film uniformity. The film thickness was measured during deposition process using a thickness monitor (Edwards, FTM4) and confirmed after deposition using interference fringes method.

The structural properties of the prepared ingot material as well as of the deposited films were examined by means of an X-ray diffractometer (Type PANalyticalX’Pert PRO diffractometer) with CuK$_\alpha$ radiation ($\lambda$ = 0.15408 nm), operated at 30 mA and 40 kV. A transmission electron microscope (Type JEOL-JEM 1230) operating at 120 kV was used to investigate the microstructure of the deposited films. The chemical composition of the prepared powder sample and the deposited films was investigated by means of energy dispersive X-ray analysis (EDX) interfaced with a transmission electron microscope. A double-beam spectrophotometer (Type Jasco, V-570, Refl-00), with automatic computer data acquisition, was employed at normal light incidence to record the optical transmission and reflection spectra of the deposited film in the wavelength range 500–2500 nm. The measurements were performed at room temperature on various parts of the deposited films, by scanning the entire sample. Very good reproducibility of spectra was generally achieved.

**Results and discussion**

**Structural characteristics of the deposited CdIn$_2$Se$_4$ films:**

The X-ray diffraction pattern of the prepared material in powder form is shown in **Fig. 1**. The analysis of this pattern confirms the polycrystalline nature of the investigated sample. Comparing the observed reflection planes with the standard XRD data (JCPDS cards No: 79-0835), indicates that the plane scan be indexed as to the tetragonal structure corresponding to the CdIn$_2$Se$_4$ single phase. Table 1 compares the observed interplaner spacing, $d_{hkl}$, with the standard XRD data. The lattice constants were calculated using the following formula (Fouad, S.S., 2011):

$$d_{hkl} = \frac{1}{\sqrt{(h^2+k^2)/a^2 + (l^2/c^2)}}$$  \hspace{1cm} (1)

$$a^2 = \frac{[(h^2+k^2)\ell_2^2-(h^2+k^2)\ell_1^2]d_1^2d_2^2}{\ell_1^2d_1^2-\ell_2^2d_2^2}$$  \hspace{1cm} (2)

$$c^2 = \frac{\ell_1^2d_1^2}{1-(h^2+k^2)d_1^2/a^2}$$  \hspace{1cm} (3)

**Table 1: X-ray diffraction pattern of CdIn$_2$Se$_4$ powdery sample.**

<table>
<thead>
<tr>
<th>2θ [Deg.]</th>
<th>d [nm]</th>
<th>2θ [Deg.]</th>
<th>d [nm]</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.519</td>
<td>0.4127</td>
<td>21.595</td>
<td>0.4112</td>
<td>101</td>
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<tr>
<td>26.502</td>
<td>0.3361</td>
<td>26.526</td>
<td>0.3357</td>
<td>111</td>
</tr>
<tr>
<td>34.494</td>
<td>0.2598</td>
<td>34.460</td>
<td>0.2601</td>
<td>102</td>
</tr>
<tr>
<td>44.022</td>
<td>0.2056</td>
<td>44.009</td>
<td>0.2056</td>
<td>220</td>
</tr>
<tr>
<td>46.781</td>
<td>0.1941</td>
<td>46.832</td>
<td>0.1938</td>
<td>221</td>
</tr>
<tr>
<td>49.601</td>
<td>0.1837</td>
<td>49.530</td>
<td>0.1839</td>
<td>310</td>
</tr>
<tr>
<td>52.046</td>
<td>0.1756</td>
<td>52.124</td>
<td>0.1753</td>
<td>311</td>
</tr>
<tr>
<td>59.411</td>
<td>0.1555</td>
<td>59.425</td>
<td>0.1554</td>
<td>321</td>
</tr>
<tr>
<td>64.018</td>
<td>0.1453</td>
<td>63.994</td>
<td>0.1454</td>
<td>400</td>
</tr>
<tr>
<td>68.343</td>
<td>0.1372</td>
<td>68.390</td>
<td>0.1371</td>
<td>114</td>
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<tr>
<td>70.599</td>
<td>0.1333</td>
<td>70.738</td>
<td>0.1334</td>
<td>313</td>
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<tr>
<td>80.942</td>
<td>0.1187</td>
<td>80.926</td>
<td>0.1187</td>
<td>422</td>
</tr>
<tr>
<td>86.740</td>
<td>0.1122</td>
<td>86.995</td>
<td>0.1119</td>
<td>511</td>
</tr>
</tbody>
</table>
The lattice constants of CdIn$_2$Se$_4$ calculated from the powder diffraction data were found to be $a = b = 0.5813, c = 2a = 1.1626$ nm which is in good agreement with the standard data (Chizhikov, V.I., 1981).

The X-ray studies, carried out on the as-deposited and argon annealed CdIn$_2$Se$_4$ films at different annealing temperatures (in the range from 373 to 523 K) for 1 h see Fig. 2, showed that the as-deposited films as well as those annealed at annealing temperature, $T_a < 423$ K are amorphous in nature, while, those annealed at $T_a \geq 473$ K showed a crystalline structure with a preferred orientation along the (111) plane. This finding indicates that the thermal annealing process has induced an amorphous-to-crystalline phase transition at annealing temperature $T_a = 473$ K. The crystallinity of the deposited film increases with increase in the annealing temperature to 523 K.

The structural studies have been confirmed throughout the transmission electron micrograph and the corresponding electron diffraction patterns for films of thickness ~80 nm suitable for transmission electron microscope investigation, as shown in Fig.3. It is clear from the figure that the diffraction patterns of CdIn$_2$Se$_4$ films annealed at 423 and 473 K, respectively, as typical samples. The figure depicts that the electron diffraction pattern of the film annealed at annealing temperature 423 K (Fig.3a), consist of diffused rings, beside no discernible structure observed in the corresponding transmission micrograph confirms the amorphous nature of the film as revealed by X-ray diffraction. As the films being annealed at temperature $T_a = 473$ K (Fig.3b), a distinct structure in the transmission mode has been observed, where the electron diffraction pattern consist of continuous spotty-rings pattern with different intensities indicating the crystalline nature of the films. The d-
Spacing obtained directly from the software of the transmission electron microscope for the film shown in Fig.3b as well as the values obtained from the X-ray diffraction analysis for the film annealed at 473 K (Fig.2) in comparison of the standard data are listed in Table 2.

Table 2: Analysis of the X-ray and electron diffraction pattern for CdIn2Se4 films annealed at 473 K.

<table>
<thead>
<tr>
<th>d-spacing [nm]</th>
<th>X-ray (Fig.2 curve d)</th>
<th>TEM Fig.3b</th>
<th>Standard</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3350</td>
<td>0.3359</td>
<td>0.3352</td>
<td>0.33572</td>
<td>111</td>
</tr>
<tr>
<td>0.2056</td>
<td>0.2041</td>
<td>0.2059</td>
<td>0.20559</td>
<td>220</td>
</tr>
<tr>
<td>0.1753</td>
<td>0.1746</td>
<td>0.17532</td>
<td>0.17532</td>
<td>311</td>
</tr>
<tr>
<td></td>
<td>0.1452</td>
<td>0.14537</td>
<td></td>
<td>400</td>
</tr>
</tbody>
</table>

EDX analysis has been carried out to examine the nominal composition of the prepared CdIn2Se4 bulk material and the corresponding deposited films with different thicknesses. The obtained data leads to the chemical formula Cd1.02In1.94Se4.04 for bulk which indicates the nearly stoichiometric compositions of the material. However, the EDX analysis for three representatives CdIn2Se4 thin film samples reveals that the compositional ratio of the deposited films varies from sample to sample. This variation may be attributed to the variation of the rate of deposition and/or the thickness of the deposited film. The variation of Cd, In and Se atomic percent for the investigated CdIn2Se4 samples are listed in Table 3.

Table 3: Chemical composition of CdIn2Se4

<table>
<thead>
<tr>
<th>Sample notation</th>
<th>Nominal composition</th>
<th>at %</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>In</td>
</tr>
<tr>
<td>506 nm</td>
<td>Cd1.06In2.15Se3.79</td>
<td>15.14</td>
<td>30.67</td>
</tr>
<tr>
<td>593 nm</td>
<td>Cd0.97In2.08Se3.95</td>
<td>13.83</td>
<td>29.74</td>
</tr>
<tr>
<td>678 nm</td>
<td>Cd1.03In1.99Se3.98</td>
<td>14.64</td>
<td>28.45</td>
</tr>
<tr>
<td>Bulk sample</td>
<td>Cd0.97In1.98Se4.04</td>
<td>13.97</td>
<td>28.33</td>
</tr>
<tr>
<td>Calculated</td>
<td></td>
<td>14.2857</td>
<td>28.5714</td>
</tr>
<tr>
<td>Theoretical ratio</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Optical properties of the CdIn$_2$Se$_4$ thin films:

Fig. 4 shows the spectral behavior of the transmittance $T$ and reflectance $R$ spectra at normal light incidence in the wavelength range from 500 to 2500 nm for the as-deposited CdIn$_2$Se$_4$ thin films of different thicknesses. In the figure above the absorption edge ($\lambda > 900$ nm, $\alpha \approx 0$), the presence of maxima of the interference fringes in the reflection spectra at the same wavelength position of the minima in the transmission spectra and vice versa reflects the optical homogeneity of the deposited films. In the region of strong absorption ($\lambda < 900$ nm, $\alpha \neq 0$), the transmission decreases drastically due to the influence of the absorption coefficient. An interference pattern appears when the wavelength of the incident radiation is comparable to the film thickness.

![Graph showing transmission and reflection spectra of three representative CdIn$_2$Se$_4$ samples.](image)

Fig. 4: Transmission and reflection spectra of three representative CdIn$_2$Se$_4$ samples.

The refractive index, $n$, the extinction coefficient, $k$ and the film thickness, $t$, of the investigated films were computed from the transmission spectra using the well-known Swanepoel method (Swanepoel, R., 1983). Fig. 5 shows the variation of the calculated refractive index for CdIn$_2$Se$_4$ films in the wavelength range 500-2500 nm. The symbols represent the set values of refractive index $n_F$ obtained using the Swanepoel envelope method, while the solid line represent the theoretical values calculated using the two-term Cauchy dispersion relationship; $n_F(\lambda) = a/\lambda^2 + b$ (where $a$ and $b$ are the Cauchy parameters). It is clearly seen that both the experimental and calculated values of the refractive index for all the investigated samples are in extension to each other. It is seen that the refractive index behavior of CdIn$_2$Se$_4$ thin films is quite similar, which is due to the normal dispersion. The refractive indices has a higher values at low wavelengths spectral region < 750 nm (strong absorption region), there after decrease with the increasing the wavelength and becomes fairly flat above 1500 nm. It was also seen that the magnitude of the refractive index at certain wavelength values varies notably from sample-to-sample depending on the ((Cd+In)/Se) at. %.

The obtained refractive index data can be analyzed using the well-known Wemple –DiDomenico single oscillator model through the following equation (Wemple, S.H., M. DiDomenico, 1971):

$$(n^2 - 1)^n = 1 + \frac{E_d E_e}{E_d^2 - (\hbar \omega)^2}$$
Fig. 5: Variation of the refractive index as a function of wavelength. Inset shows the plots of \((n^2-1)^{-1}\) vs. photon energy squared.

Where \(\hbar\omega\) is the photon energy, \(E_o\) is the energy of the effective dispersion oscillator, (an average energy gap) and \(E_d\) is the so-called dispersion energy and it measures the average strength of interband optical transitions. Plotting against \((n^2-1)^{-1}\) against photon energy squared (see inset of Fig. 6) and fitting a straight line allows us to determine the oscillator parameters \(E_o\) and \(E_d\). The calculated \(E_o\) and \(E_d\) values as well as the static refractive index, \(n_o(0)\); \(n_o(0) = \sqrt{1 + E_d/E_o}\) calculated via extrapolating the Wemple –DiDomenico optical-dispersion equation to \(\hbar\omega \to 0\) are listed in Table 4. It was clearly seen from the data reported in Table 4 that the dispersion parameters, \(E_o\) and \(E_d\) decreases with the decrease in the ((Cd+In)/Se) at. % of the cation to anion ratio (i.e. (Cd+In)/Se) at %.

Fig. 6: Plots of refractive index and W.D band gap, \(E_g^{WD}\) versus (Cd+In)/Se at %. It is clearly seen that the static refractive index varies in a reverse meaner with respect to the W.D band gap \(E_g^{WD}\).

Fig. 6: Plots of refractive index and W.D band gap, \(E_g^{WD}\) as a function (Cd+In)/Se at %.
The low wavelength absorption data for as-deposited CdIn$_2$Se$_4$ films are related to the fundamental absorption which refers to the band-to-band transition, i.e. the excitation of an electron from the valence band to the conduction band. The absorption coefficient, $\alpha$, as a function of the photon energy, $\hbar\omega$, is shown in Fig. 7. It is clearly seen that the films exhibit highest absorption coefficient, $\alpha \sim 10^5$ cm$^{-1}$ in the photon energy range to 2.25 eV. It can be seen also from the figure that the spectral variation of the absorption coefficient with the photon energy can be divided into two regions depending on the magnitude of the optical absorption coefficient: 1. Low energy absorption region in the photon energy range 1.74 - 1.92 eV, at which the magnitude of the optical absorption coefficient $\alpha < 10^4$ cm$^{-1}$ there is an Urbach tail (Tauc, J., 1974). The absorption coefficient can be described by the relation:

$$\alpha(\hbar\omega) = \alpha_o \exp (\hbar\omega / E_e)$$

where, $\alpha_o$ is constant and $E_e$ is the width of the band tail of the localized states at the optical band gap. The energy width of the localized states tails at the band gap, $E_e$, can be determined from the plots of log $\alpha$ versus $\hbar\omega$ as shown in Fig. 8. The determined $E_e$ values are listed in Table 4.

![Fig. 7: Variation of the optical absorption coefficient as a function of the photon energy.](image)

![Fig. 8: Plots of Log (\alpha) as a function of photon energy.](image)

**Table 4**: Optical parameters of CdIn$_2$Se$_4$ thin films.
2. High absorption region in the photon energy range 1.92-2.48 eV, where the magnitude of the optical absorption coefficient $\alpha > 10^4 \text{cm}^{-1}$ at which the optical absorption coefficient, $\alpha$ obeys the relation (Heavens, O.S., 1965; Pankov, I., J. Tauc (Ed.), 1971);

$$\alpha(\hbar\omega) = A(\hbar\omega - E_{g\text{opt}})\gamma$$

![Graphs showing absorption coefficient versus photon energy](image)

Fig. 9: Plots of $(\alpha \hbar \omega)^2$ and $(\alpha \hbar \omega)^{1/2}$ vs. photon energy.

The exponent, $\gamma$ is an index parameter, that characterize the type of the optical transition and is theoretically equal to 2, 1/2, 3 or 3/2 for indirect allowed, direct allowed, indirect forbidden, and direct forbidden transitions, respectively (Tauc, J., 1974; Heavens, O.S., 1965; Pankov, I., J. Tauc (Ed.), 1971). The analysis of the absorption coefficient of the investigated samples in the present work reveals that, in the region of strong absorption edge (2.1-2.48 eV); $(\alpha \hbar \omega)^2$ vary linearly with $\hbar \omega$ indicating the presence of direct optical transition. Extrapolating the straight part towards lower photon energy yields the corresponding value of the direct band gap. However in the photon energy range 1.9-2.1 eV, a straight line is attained from the plot of $(\alpha \hbar \omega)^{1/2}$ versus photon energy.
\( \hbar \omega \) indicates the presence of a non-direct optical transition. Fig.9a-c show the plots of \((\alpha \hbar \omega)^2\) and \((\alpha \hbar \omega)^{1/2}\) versus photon energy for the investigated samples. The determined energies corresponding to both direct and indirect optical transitions for those samples in comparison with the previously reported energy gap values for CdIn\(_2\)Se\(_4\) thin film are also listed in Table 4.

Conclusions:

CdIn\(_2\)Se\(_4\) thin films were prepared by thermal evaporation technique. The as-deposited and films annealed at annealing temperature 423 K are amorphous in nature. While, an amorphous-to-crystalline phase transition with a single phase of CdIn\(_2\)Se\(_4\) structure was obtained for the films annealed at 473 K. The optical properties of the deposited films were investigated. The refractive index of the films was found to follow the two-term Cauchy dispersion relation and is described by the single oscillator model. The refractive index, as well as the dispersion parameters was calculated as a function of \(((\text{Cd}+\text{In})/\text{Se})\) at. %. Where the refractive index increases from 2.426 to 2.458 as the \(((\text{Cd}+\text{In})/\text{Se})\) at % decreases from 0.845 to 0.757. The analysis of the optical absorption coefficient revealed the presence of direct and indirect optical transitions. The energy corresponding such transitions was found to be decrease with the decrease of the \(((\text{Cd}+\text{In})/\text{Se})\) at %.

References