CHAPTER 4
OPTICAL STUDIES ON CuInSe$_2$, AgInSe$_2$
AND CuAlSe$_2$ THIN FILMS
4.1 Introduction

For probing the band structure of the semiconductors, most direct method is the optical absorption studies. We can determine the energy gap of the material as well as determine whether the valence band and conduction band extrema occur at the same or different points in the k-space knowing the frequency dependence of the absorption coefficient. There are different types of absorption processes such as fundamental absorption, free carrier absorption, excitonic absorption and impurity absorption. Electrons can be excited from the valence band to the conduction band with the absorption of a photon of energy equal to the band gap of the material. In this case, the absorption coefficient is $10^5$ to $10^6 \text{cm}^{-1}$. Rapid drop in the absorption coefficient on the low energy side of the absorption band leads to the absorption edge in semiconductors. Beyond this, the material becomes transparent.

I-III-VI$_2$ type ternary semiconductors which belong to the space group I42d gives anisotropic, non-centro symmetric crystal structure which permits non-linear optical properties and birefringence and also is suitable for phase-matched parametric optical mixing (1). The band gaps of I-III-VI$_2$ compounds are low relative to their
binary analogues due to a partial cancellation of the positive spin–orbit parameters for p–levels and negative ones for d–levels as observed in electroreflectance spectra (2–4). The technique of optical absorption has been used by various workers (5–7) to identify the three basic energy gaps A, B and C which correspond to the forbidden band gap, crystal field split and the spin–orbit split levels respectively. In this chapter, we have employed optical absorption technique for identifying the energy gaps of CuInSe2, AgInSe2 and CuAlSe2 thin films.

4.2 Theory

When the energy of the incident photon is greater than the band gap \( (h\nu > E_g) \), we have the relation for absorption coefficient \( \alpha \) given by (8),

\[
\alpha(h\nu) = \frac{A}{h\nu} \left\{ (h\nu - E_g)^{3/2} + \frac{\pi}{2} B - B \arcsin \left( \frac{h\nu - E_g}{h\nu - E_g + B^2} \right)^{1/2} \right\} \quad \cdots (1)
\]

where \( B^2 = \frac{(c_c + c_v)^2}{4(b_c + b_v)} \) and the constants \( b_c, b_v > 0; c_c, c_v \geq 0 \).

For \( h\nu - E_g \leq B^2 \), equation 1 simplifies to,

\[
\alpha (h\nu) = \frac{A}{3B^2h\nu} (h\nu - E_g)^{3/2} \quad \text{and at} \ (h\nu - E_g) \gg B^2,
\]

equation 1 becomes,
\[ \alpha (h\nu) = \frac{A}{h\nu} (h\nu - E_g)^{1/2} \]

where \( A \) is a constant.

When the energy of the incident photon exceeds the band gap \( E_g \) of the material (\( E_g > h\nu \)), an electron is excited from the valence band into the conduction band. There are two types of transitions: direct and indirect. Transition involving photons is direct and that involving photon and phonon is indirect. A direct vertical optical transition near the fundamental absorption edge in a semiconductor is shown schematically in figure 4.1. It can be seen that the valence band maximum and conduction band minimum appear at the same point in the Brillouin zone at \( k = 0 \). When a transition requires a change in both energy and momentum, a double transition process is required because the photon cannot provide a change in momentum. For overcoming this, emission or absorption of phonons occurs. Momentum is conserved through a phonon interaction resulting in indirect transition as shown in figure 4.2. The plot of \((\alpha h\nu)^2\) versus \(h\nu\) for direct allowed transition, \((\alpha h\nu)^{2/3}\) versus \(h\nu\) for direct forbidden transition, \((\alpha h\nu)^{1/2}\) versus \(h\nu\) for indirect allowed transition and \((\alpha h\nu)^{1/3}\) versus \(h\nu\) for indirect forbidden transition would always be straight lines. We can obtain the band gap of the material by extrapolating these lines to \( \alpha = 0 \). However, if we calculate \( \alpha_1 \) using slope \( A_1 \) and intercept \( E_{g1} \) determined from the \((\alpha h\nu)^2\) versus \(h\nu\) graph at higher energies, we find that \( \alpha_1 \) becomes considerably smaller than the absorption coefficient \( \alpha \) measured experimentally.
Fig. 4.1. Direct transition

VB - valence band, CB - conduction band, \( E_g \) - band gap
Fig. 4.2. Indirect transition

VB - valence band, CB - conduction band, Eg - band gap
which is explained by the existence of an additional absorption process. The absorption due to this additional process is denoted by $\alpha_2$ defined by $\alpha_2 = \alpha_{(\text{exp.})} - \alpha_{(\text{cal.})}$. A plot of $(\alpha_2 \nu)^2$ versus $\nu \nu$ yields straight line indicating the presence of a second direct allowed transition and extrapolated intercept gives the band gap $E_g = E_{g2}$. $\alpha_2$ is explained as the transitions from the split-off valence bands to the conduction band. The difference between two direct allowed transitions ($E_{g2} - E_{g1}$) gives the spin-orbit splitting value ($\Delta \sigma_0$). The values for the direct band to conduction band transition energies and the corresponding valence band splitting due to the spin-orbit interaction can also be extracted from the optical data.

4.3 CuInSe$_2$ thin films

The optical properties of CuInSe$_2$ near the fundamental absorption edge have been studied by several workers by electroreflectance (9-11), reflection (12,13), absorption (14), photovoltage measurements (15) and luminescence measurements (16). At present, it is well established that CuInSe$_2$ is a direct gap semiconductor with an energy gap of about 1.0eV. CuInSe$_2$ has an absorption coefficient higher than $10^4$ cm$^{-1}$ near the absorption edge. These properties, together with an excellent thermal stability, make it a suitable material for application in low cost solar cells. The use of CuInSe$_2$ thin films in solar cells require the knowledge of its optical properties due to its influence on efficiency. In the present work, an attempt is made to get more
detailed information about the optical transition probabilities in CuInSe$_2$ by measuring and analyzing optical absorption spectra of CuInSe$_2$ thin films. The optical properties of CuInSe$_2$ films with varying thickness are studied. CuInSe$_2$ films of thickness 1900Å, 3300Å and 6100Å are deposited in a vacuum of $10^{-6}$ torr in Hind Hivac coating unit keeping the substrate at room temperature. Absorption coefficient $\alpha$ is calculated from the transmittance spectra using the relation $\alpha t = \ln I_0/I$, where $I_0$ and $I$ are the intensities of the incident and transmitted radiation respectively and $t$ is the thickness of the film. The values of $\alpha$ obtained near the band edge for CuInSe$_2$ are $6.5 \times 10^4$cm$^{-1}$ and $1.4 \times 10^5$cm$^{-1}$ for thicknesses 3300Å and 1900Å respectively. A plot of $\alpha$ versus $h\nu$ for CuInSe$_2$ thin films for thicknesses 1900Å and 3300Å is shown in figure 4.3. For a film of thickness 6100Å, the transmittance is zero in the whole wavelength region. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is given for CuInSe$_2$ films of thicknesses 1900Å and 3300Å in figure 4.4. The obtained extrapolated intercept $E_g$ are 0.98eV and 0.92eV for 1900Å and 3300Å respectively. The narrowing of band gap with thickness has been observed (17). The reported values for $E_g$ is 0.94eV for bulk CuInSe$_2$ (14). Value of $E_g$ for single crystal CuInSe$_2$ obtained by electroreflectance spectra is 0.96eV (10) and 0.95eV by Schottky barrier photovoltage measurements (15). Our values agree with the reported ones.
Fig. 4.3. Plot of \( \alpha \) versus \( h\nu \) of CuInSe\(_2\) thin film of thickness \( \times \) 1900Å and \( \bullet \) 3300Å.

Fig. 4.4. Plot of \((\alpha h\nu)^2\) versus \(h\nu\) for different thickness \( \times \) 1900Å and \( \bullet \) 3300Å.
a. **Effect of substrate temperature**

The intrinsic defect equilibrium is rather cumbersome in CuInSe$_2$ that growth and annealing experiments under controlled conditions combined with a comprehensive optical characterization of the samples are necessary to elucidate the defect formation processes in the material. CuInSe$_2$ films of thickness 2000Å are deposited at different substrate temperatures 350, 400, 450 and 500°C. The value of $\alpha$ obtained at various wavelengths is plotted as $\alpha$ versus $h\nu$ and is given in figure 4.5. The value of $\alpha$ at 500nm ($\alpha_{500}$) increases from 1.25 $\times$ 10$^5$cm$^{-1}$ (deposited at 30°C) to 2.1 $\times$ 10$^5$cm$^{-1}$ (deposited at 500°C). Close to the band edge, $\alpha$ is around 5 $\times$ 10$^5$cm$^{-1}$ (deposited at 350°C) which is higher than the earlier reported values (18,19). A plot of $(\alpha h\nu)^2$ versus $h\nu$ gives $E_g = E_{g1}$ from the extrapolated intercept is shown in figure 4.6 for CuInSe$_2$ film of thickness 2000Å for two typical substrate temperatures 450°C and 500°C. The band gap $E_{g1}$ obtained from the extrapolated intercept in figure 4.6 is included in table 4.1. Tuttle et. al. (18) have shown that $E_{g1}$ increases from 0.94 to 1.02eV as the substrate temperature increases from 350°C to 450°C. If we calculate $\alpha$, with slope $A_1$ and intercept $E_{g1}$ determined from the $(\alpha h\nu)^2$ versus $h\nu$ graph (Fig.4.6), $\alpha_1$ becomes considerably smaller than the absorption coefficient $\alpha$ measured experimentally which is explained by the existence of an additional absorption process. The value of $E_{g1}$ and slope $A_1$ obtained from figure 4.6 is then used to calculate $\alpha_1$ which in turn is used to calculate $\alpha_2$. For $h\nu > 1.2$eV, an analysis of the absorption spectra yields an additional absorption coefficient, $\alpha_2 = \alpha - \alpha_1$, indicating
Fig. 4.5. Plot of $\alpha$ versus $h\nu$ of CuInSe$_2$ thin film of thickness 2000Å deposited at substrate temperatures $\Delta$ 30°C; □ 350°C; ○ 400°C; • 450°C and × 500°C.

Fig. 4.6. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CuInSe$_2$ thin film of thickness 2000Å deposited at substrate temperatures ○ 450°C and × 500°C.
a direct allowed transition with band gap $E_g = E_{g2}$. From a plot of $(\alpha_2 h \nu)^2$ against $h \nu$, $E_{g2}$ is obtained as the intercept and is shown in figure 4.7. $'\alpha_2'$ is assigned to the transitions from the split off valence band to the lowest conduction band. The value of $E_{g2}$ for the films deposited at 450°C and 500°C is less than the room temperature (RT) deposited sample (1.3eV). The spin orbit splitting value $(\Delta_{so})$ is 0.2eV for the RT deposited film and it increases to 0.23eV for the film deposited at 500°C which is in agreement with the values reported by photoreflectance and optical studies (10, 20). The values of $(\Delta_{so})$ indicate near stoichiometric and copper rich film (21). From the photoluminescence spectra (28), the values of $E_{g1}$ and $E_{g2}$ are 1.04eV and 1.27eV and $\Delta_{so}$ is 0.233eV for bulk CuInSe$_2$. The values of $E_{g1}$ and $E_{g2}$ are 0.99eV and 1.22eV respectively for laser evaporated CuInSe$_2$ thin films (22).

Table 4.1. $E_{g1}$ and $E_{g2}$ of CuInSe$_2$ thin films of thickness 2000Å for substrate temperatures 350, 400, 450 and 500°C.

<table>
<thead>
<tr>
<th>Substrate temperature $T_s$ °C</th>
<th>Band gap $E_g$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{g1}$</td>
<td>$E_{g2}$</td>
</tr>
<tr>
<td>350</td>
<td>1.11</td>
</tr>
<tr>
<td>400</td>
<td>1.15</td>
</tr>
<tr>
<td>450</td>
<td>1.02</td>
</tr>
<tr>
<td>500</td>
<td>1.05</td>
</tr>
</tbody>
</table>
b. Effect of air annealing

Thin film CuInSe₂ solar cells prepared by most techniques, require a post deposition anneal in air to optimize their photovoltaic performance (23, 24). Steady progress has been made in describing the anneal's chemical effects and their influence on the electronic properties of the cell (25 - 34). CuInSe₂ films for CuInSe₂ cells synthesized by three source evaporation reach their optimum efficiency only when it is annealed for 30 minutes at 200°C in air (35). The present work investigates the sensitivity of CuInSe₂ thin films to the oxygen environment.

Room temperature deposited CuInSe₂ thin films of thickness 2400Å are air annealed in a rocking furnace at various temperatures of 50, 100, 150, 200, 250 and 300°C for one hour. Films thus obtained are used for optical characterization. %T versus ℎν for a CuInSe₂ film of thickness 2400Å annealed at 200°C in air is shown in figure 4.8.

The band gap E₁ as obtained from (αhν)² versus ℎν graph (Fig. 4.9.) is given in table 4.2. The value of E₁ is ~1.0eV for all the films. In order to study the metal-oxygen bonds present in the air annealed films infrared (IR) spectra in the range 400-1200 cm⁻¹ is taken with the material suspended in Nujol. The measurements are
Fig. 4.7. $\alpha \propto h\nu$ versus $h\nu$ of CuInSe$_2$ thin film of thickness 2000Å deposited at substrate temperatures ○ 450°C and × 500°C.

Fig. 4.8. %T versus $h\nu$ of CuInSe$_2$ thin film of thickness 2400Å air annealed at 200°C for one hour.
done in the wavelength range 400 - 600 cm⁻¹ in order to study the indium-oxygen bonding. A typical IR spectra of the CuInSe₂ thin film of thickness 2400 Å annealed at 300°C for one hour is given in figure 4.10. From the spectra, distinct peaks are available at 413, 432, 498, 514, 568 and 600 cm⁻¹. The chemical environment of oxygen in oxidized CuInSe₂ thin films has been studied using infrared absorption spectroscopy (36) and the obtained peaks corresponding to In₂O₃ are at 420, 540, 570 and 600 cm⁻¹ for oxidized CuInSe₂ thin films (37, 38). The absorption peak at 1150 cm⁻¹ for molecular oxygen (39) is absent in our samples. Thus the peaks obtained in our films correspond to vibrational modes characteristic of indium-oxygen bonds. IR measurements on p-CuInSe₂ films provide evidence for In-O bond formation (40). At the surface, some co-ordinatively unsaturated indium will be present. This implies that one or more selenium vacancies exist there. In their normalized state, charge neutrality is preserved by one (or more) lone pair(s) of electrons to the conduction band of CuInSe₂. Oxygen, absorbed on the grain surface, can pick up electrons from the conduction band while reacting chemically with the indium to form an In-O bond (chemisorption), thus neutralizing the selenium vacancy via formation of selenium in oxygen vacancy, which is a weak acceptor (40).
Fig. 4.9. $(\alpha h\nu)^2$ versus $h\nu$ of CuInSe$_2$ thin film of thickness 2400Å air annealed at different temperatures × 50°C; △ 100°C; ◊ 150°C and ◆ 200°C for one hour.

Fig. 4.10. IR spectra of CuInSe$_2$ thin film of thickness 2400Å air annealed at temperature 300°C for one hour.
Table 4.2. Band gap values of air annealed CuInSe₂ thin films
for temperatures 50, 100, 150 and 200°C.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta °C</td>
<td>Eg₁ eV</td>
</tr>
<tr>
<td>50</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>1.03</td>
</tr>
<tr>
<td>150</td>
<td>0.96</td>
</tr>
<tr>
<td>200</td>
<td>1.00</td>
</tr>
</tbody>
</table>

c. Effect of vacuum annealing

Room temperature deposited CuInSe₂ thin films of thickness 2000Å are vacuum (10⁻⁶ torr) annealed for one hour at different temperature 50, 100, 150 and 200°C. These films are used for optical studies. %T versus λ for vacuum annealed CuInSe₂ thin films are given in figure 4.11. Values of α are calculated from the spectra and it increases with annealing temperature. α values at 800nm is given in table 4.3 for the films. Values of band gap as obtained from (αhν)² versus hν graph (Fig. 4.12) varied between 0.95eV and 0.98eV. Values of Eg₂ decrease from 1.4eV to 1.3eV as the annealing temperature increases from 50°C to 200°C. Gap narrowing has been observed similar to an early report for a 350°C deposited CuInSe₂ thin film post annealed at 450°C (18). Vanishing of sub gap
Fig. 4.11. $\% T$ versus $\lambda$ of CuInSe$_2$ thin film of thickness 2000Å vacuum annealed at different temperatures
- $50^\circ C$; $x$ $100^\circ C$; $\triangle$ $150^\circ C$ and $\Delta$ $200^\circ C$

Fig. 4.12. $(\alpha h \nu)^2$ versus $h \nu$ of CuInSe$_2$ thin film of thickness 2000Å vacuum annealed at different temperatures
- $\circ$ $50^\circ C$; $\triangle$ $100^\circ C$; $x$ $150^\circ C$ and $\triangledown$ $200^\circ C$
absorption is also observed for the vacuum annealed CuInSe$_2$ films under present study. For a chemical bath deposited CuInSe$_2$ film post annealed at 300°C for one hour in 10$^{-2}$ torr, decrease of $E_g$ from 1.3eV to 1.02eV has been observed (41). The change in the optical properties of the films due to post deposition vacuum annealing is attributed to the improvement in the uniformity of composition and crystallinity of the film (42).

Table 4.3. $\alpha_{800\text{nm}}$, $E_g1$ and $E_g2$ of CuInSe$_2$ thin films of thickness 2000Å vacuum annealed at temperatures 50, 100, 150 and 200°C.

<table>
<thead>
<tr>
<th>Annealing temperature $T_a$ °C</th>
<th>Absorption coefficient $\alpha_{800\text{nm}}$ $10^4 \times \text{cm}^{-1}$</th>
<th>Band gap $E_g$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.5</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>9.1</td>
<td>0.96</td>
</tr>
<tr>
<td>150</td>
<td>9.6</td>
<td>0.95</td>
</tr>
<tr>
<td>200</td>
<td>9.4</td>
<td>0.95</td>
</tr>
</tbody>
</table>
d. Effect of composition

Study on the variation of the optical properties of CuInSe₂ thin films keeping selenium concentration constant is investigated here. Films of Cu₁₁In₁Se₂ of thickness 2000Å are deposited keeping the substrate at room temperature. α values are obtained from the optical transmission spectra. From the spectra (Fig.4.13), it has been observed that the onset of absorption increases for the copper rich film. Significant sub band gap absorption is also seen in the spectra. A plot of (αhv)² versus hv for Cu₁₁In₁Se₂ of thickness 2000Å is shown in figure 4.14 and Eg is obtained from its intercept. Value of α at 500nm (α₅₀₀) for Cu₁₁In₁Se₂ is compared with the stoichiometric film in table 4.4. ‘α’ decreases while band gap increases to 1.24eV on deviation from stoichiometry. Usually, Cu₂Se phase with higher band gap is dominated in copper rich CuInSe₂ thin films. Cu₁In₁Se₂.₅ thin films of thickness 2000Å are deposited at room temperature and is used for optical characterization. α value is in the same range for the stoichiometric film while band gap increases to 1.54eV. A plot of (αhv)² versus hv for a Cu₁In₁Se₂.₅ thin film of thickness 2000Å is given in figure 4.15 and the intercept gives a band gap of 1.54eV. The increase in band gap is ascribed to the binary phase formation in the films. It is seen that α is highest for the stoichiometric film.
Fig. 4.13. $\alpha$ versus $h\nu$ of Copper Indium Selenide thin film of thickness 2000Å $\bullet$ Cu$_{1.1}$In$_{1}$Se$_{2}$; $\circ$ Cu$_{1}$In$_{1}$Se$_{2.5}$

Fig. 4.14. $(\alpha h\nu)^2$ versus $h\nu$ of Cu$_{1.1}$In$_{1}$Se$_{2}$ thin film of thickness 2000Å
Table 4.4. $\alpha_{500\text{nm}}$ and $E_g$ values of Copper Indium Selenide thin films.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\alpha_{500\text{nm}}$ (cm$^{-1}$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{1.1}$In$_1$Se$_2$</td>
<td>$1.3 \times 10^5$</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu$_{1.1}$In$<em>1$Se$</em>{2.5}$</td>
<td>$7.0 \times 10^4$</td>
<td>1.24</td>
</tr>
<tr>
<td>Cu$_{1.1}$In$_1$Se$_2$</td>
<td>$1.2 \times 10^5$</td>
<td>1.54</td>
</tr>
</tbody>
</table>

4.4 AgInSe$_2$ thin films

AgInSe$_2$ is a direct gap material with a value 0.5eV below that of its binary analog CdSe (10). Measurement of the optical properties allows to obtain critical information about the electronic band structure, optical transitions and relaxation mechanisms. Apart from a 17% hybridization with silver 4d levels, the uppermost valence bands in AgInSe$_2$ are equivalent to those which would occur in a cubic CdSe compressed to achieve the built-in distortion of AgInSe$_2$. AgInSe$_2$ films of thickness 1500Å, 3000Å and 6500Å are deposited using a vacuum coating unit at the rate of 30Ås$^{-1}$ keeping the substrate at room temperature. AgInSe$_2$ film of thickness 6500Å is having zero transmittance in the whole wavelength region. A typical plot of absorbance ($A$) versus $\lambda$ is shown in figure 4.16 for a AgInSe$_2$ film of thickness 3000Å. A plot of $(\alpha\nu)^2$ versus $\nu$ yielded
Fig. 4.15. \((\alpha h \nu)^2\) versus \(h \nu\) of CuIn\(_1\)Se\(_{2.5}\) thin film of thickness 2000Å

Fig. 4.16. \(A\) versus \(\lambda\) of AgInSe\(_2\) thin film of thickness 3000Å
band gap 1.18eV and is given in figure 4.17 for AgInSe2. Band gap is found to decrease from 1.24eV to 1.18eV as the thickness increases from 1500Å to 3000Å. The values obtained in an early report for vacuum deposited AgInSe2 films are 1.44eV, 1.34eV and 1.27eV for thicknesses 883Å, 1605Å and 2140Å respectively (17).

a. Effect of substrate temperature

AgInSe2 thin films of thickness 2000Å are deposited for different substrate temperatures 30, 350, 400, 450 and 500°C. A plot of %T versus λ for AgInSe2 films for different substrate temperatures is shown in figure 4.18. %T increases on increasing the substrate temperature from RT to 500°C. The value of α at 500nm increases from $3.1 \times 10^4$ cm$^{-1}$ (for sample deposited at RT) to $2.0 \times 10^5$ cm$^{-1}$ (for sample deposited at 350°C). Close to the band edge, the value is $4.2 \times 10^5$ cm$^{-1}$ (for sample deposited at 500°C), which is fairly high. A plot of $(\alpha h\nu)^2$ versus hν (Fig. 4.19) yielded the optical band gap which varies from 1.18eV to 1.42eV and is collected in table 4.5. The photoluminescence experiment (10) shows that AgInSe2 has an anomalous temperature dependence on the energy gap dominated by self-energies associated with the phonon scattering. There is one single conduction band and three closely spaced valence band levels V1, V2 and V3 for AgInSe2. Eg1, Eg2 and Eg3 are obtained by transitions from V1, V2 and V3 to the conduction band. The obtained values of Eg1, Eg2 and Eg3 from luminescence experiments are 1.24,
Fig. 4.17. $(\alpha h \nu)^2$ versus $h \nu$ of AgInSe$_2$ thin film of thickness 3000Å

Fig. 4.18. %T versus $\lambda$ of AgInSe$_2$ thin film of thickness 2000Å for different substrate temperatures: ▽ 30°C; ● 350°C; △ 400°C; ○ 450°C and × 500°C
1.33 and 1.6eV respectively. The band at 1.19eV is attributed to impurities and the shoulder near 1.245eV is assigned to result from the decay of free exciton (10).

Table 4.5. Band gap values of AgInSe₂ thin films of thickness 2000Å for substrate temperatures 30, 350, 400, 450 and 500°C

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>Band gap Eg₁ (eV)</th>
</tr>
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<tbody>
<tr>
<td>Ts °C</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.22</td>
</tr>
<tr>
<td>350</td>
<td>1.34</td>
</tr>
<tr>
<td>400</td>
<td>1.42</td>
</tr>
<tr>
<td>450</td>
<td>1.18</td>
</tr>
<tr>
<td>500</td>
<td>1.18</td>
</tr>
</tbody>
</table>

b. Effect of air annealing

AgInSe₂ thin films of thickness 2800Å are deposited at room temperature in a vacuum of 10⁻⁶ torr and are air annealed at temperatures 50, 100, 150, 200, 250 and 300°C for one hour. Band gap values as obtained from the (αhυ)² versus hυ (Fig. 4.20) and is given in table 4.6.
Fig. 4.19. A typical plot of $(\alpha h\nu)^2$ versus $h\nu$ for a AgInSe$_2$ thin film of thickness $2000\AA$ deposited at $300\, K$.

Fig. 4.20. $(\alpha h\nu)^2$ versus $h\nu$ of AgInSe$_2$ thin film of thickness $2800\AA$ air annealed at different temperatures:
- $50^\circ C; \Delta 100^\circ C; \times 150^\circ C; \bullet 200^\circ C; \nabla 250^\circ C$ and $o 300^\circ C$.
Table 4.6. Band gap values of AgInSe2 thin films air annealed at temperatures 50, 100, 150, 200, 250 and 300°C for one hour.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Band gap</th>
</tr>
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<tbody>
<tr>
<td>Ta °C</td>
<td>Eg eV</td>
</tr>
<tr>
<td>50</td>
<td>1.24</td>
</tr>
<tr>
<td>100</td>
<td>1.24</td>
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<td>1.18</td>
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<tr>
<td>250</td>
<td>1.18</td>
</tr>
<tr>
<td>300</td>
<td>1.18</td>
</tr>
</tbody>
</table>

c. Effect of vacuum annealing

Room temperature deposited AgInSe2 thin films of thickness 1500Å are vacuum annealed at different temperatures 50, 100, 150 and 200°C for one hour. The optical spectra of the films are taken in a Shimadzu 170A spectrophotometer. A plot of A versus λ is shown in figure 4.21. Absorption peak sharpens with annealing temperature upto 150°C and then starts broadening on increase of temperature. α value at 500nm is given in table 4.7. A plot of
$(\alpha h\nu)^2$ versus $h\nu$ is given in figure 4.22. The band gap $E_g$ given in table 4.7 decreases with decrease in annealing temperature and approaches the value of bulk samples.

**Table 4.7.** $a_{500\text{nm}}$ and $E_g$ values of vacuum annealed AgInSe$_2$ thin films.

<table>
<thead>
<tr>
<th>Annealing temperature $T_a$ °C</th>
<th>Absorption coefficient $\alpha_{500\text{nm}} \text{cm}^{-1} \times 10^5$</th>
<th>Band gap $E_g$ eV</th>
</tr>
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<tbody>
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<td>50</td>
<td>2.0</td>
<td>1.18</td>
</tr>
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<td>100</td>
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</tr>
<tr>
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<td>1.22</td>
</tr>
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</tr>
</tbody>
</table>

4.5 CuAlSe$_2$ thin films

The optical properties of bulk CuAlSe$_2$ have been studied in detail (43, 44). However, those of thin films are rather scarce. The high band gap of 2.7eV of this material makes it useful in opto-electronic devices such as blue light-emitting diodes and blue laser diodes. It is very difficult to grow good quality CuAlSe$_2$ charge due to the existence of chemically active aluminium in the matrix and the quartz tubes used for the growth often exploded. We have produced compound of CuAlSe$_2$ for deposition in small amounts.
Fig. 4.21 A versus $\lambda$ of AgInSe$_2$ thin film of thickness 1500Å vacuum annealed at different temperatures
(1) 50°C; (2) 100°C; (3) 150°C and (4) 200°C

Fig. 4.22. $(\alpha \nu)^2$ versus $\nu$ of AgInSe$_2$ thin film of thickness 1500Å vacuum annealed at different temperatures
$\Delta$ 50°C; o 100°C; ● 150°C and x 200°C
avoiding explosion. CuAlSe₂ films of thickness 2000Å, 4000Å and 5800Å are deposited in a vacuum of 10⁻⁶ torr onto glass substrate at room temperature. The optical spectra yield α values at 500nm for the CuAlSe₂ films and is given in table 4.8. A plot of A versus λ is shown in figure 4.23 for different thicknesses. A plot of (αhv)² versus hv (Fig. 4.24) yields band gaps and is given in table 4.8. Eg obtained for the bulk material is 2.7eV (45). The value 2.5 eV obtained by iodine transport method (46) is low. By photoreflectance measurement, the peaks are obtained at 2.739eV (assigned to free exciton emission) and 2.677eV (assigned to bound exciton emission) for CuAlSe₂ epilayers grown by MOCVD (47).

Table 4.8. α500nm and Eg values of CuAlSe₂ thin films

for thicknesses 2000Å, 4000Å and 5800Å.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Absorption coefficient (α500nm cm⁻¹)</th>
<th>Band gap (Eg eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>2.1 × 10⁵</td>
<td>2.80</td>
</tr>
<tr>
<td>4000</td>
<td>9.8 × 10⁴</td>
<td>2.75</td>
</tr>
<tr>
<td>5800</td>
<td>5.7 × 10⁴</td>
<td>2.70</td>
</tr>
</tbody>
</table>
Fig. 4.23 $A$ versus $\lambda$ of CuAlSe$_2$ thin film of thickness:
(1) 2000Å; (2) 4000Å and (3) 5800Å

Fig. 4.24. $(\alpha h\nu)^2$ versus $h\nu$ of CuAlSe$_2$ thin films for different thickness
  • 2000Å;  × 4000Å and △ 5800Å
a. Effect of vacuum annealing

Room temperature deposited CuAlSe₂ films of thickness 2000 Å are vacuum (10⁻⁶ torr) annealed at temperatures 50, 100, 150 and 200°C for one hour and is used for optical characterization. 'A' versus λ is shown in figure 4.25 for CuAlSe₂ films of thicknesses 2000Å vacuum annealed at temperatures 50, 100, 150 and 200°C. α₅₀₀nm decreases from 1.9 x 10⁵ cm⁻¹ to 1.7 x 10⁵ cm⁻¹ as the temperature increases from 50°C to 100°C and then increases to 2.2 x 10⁵ cm⁻¹ at 200°C. Optical band gap Eg as obtained from the (αhv)² versus hv graph (Fig. 4.26) is given in table 4.9. Band gap decreases from 2.8eV to 2.72eV as the temperature decreases from 200°C to 50°C. Narrowing of the band gap can also be observed.

Table 4.9. α₅₀₀nm and Eg values of CuAlSe₂ thin films of thickness 2000Å vacuum annealed at temperatures 50, 100, 150 and 200°C.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Absorption coefficient</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta °C</td>
<td>α₅₀₀nm cm⁻¹ x 10⁵</td>
<td>Eg eV</td>
</tr>
<tr>
<td>50</td>
<td>1.9</td>
<td>2.80</td>
</tr>
<tr>
<td>100</td>
<td>1.7</td>
<td>2.75</td>
</tr>
<tr>
<td>150</td>
<td>2.2</td>
<td>2.72</td>
</tr>
<tr>
<td>200</td>
<td>2.2</td>
<td>2.72</td>
</tr>
</tbody>
</table>
Fig. 4.25. $A$ versus $\lambda$ of CuAlSe$_2$ thin film of thickness 2000Å vacuum annealed at different temperatures
(1) 50°C; (2) 100°C; (3) 150°C and (4) 200°C

Fig. 4.26. $(\alpha \nu)^2$ versus $\nu$ of CuAlSe$_2$ thin film of thickness 2000Å vacuum annealed at different temperatures
× 50°C; ● 100°C; ○ 150°C and △ 200°C
4.6 Conclusion

The absorption coefficient $\alpha$ increases with decrease in film thickness for CuInSe$_2$ films. Band gap narrowing with thickness is observed for these films. Higher substrate temperatures minimized the residual absorption below the band gap. IR spectra of the air annealed CuInSe$_2$ thin films indicate distinct peaks corresponding to indium–oxygen bonds. Narrowing of the band gap is observed for vacuum annealed CuInSe$_2$ thin films. It has been found that $\alpha$ is highest for the stoichiometric CuInSe$_2$ thin film. Narrowing of band gap with thickness is also observed for AgInSe$_2$ thin films. For AgInSe$_2$ thin films, band gap decreases with decrease in vacuum annealing temperature. Similar to CuInSe$_2$ and AgInSe$_2$ thin films, CuAlSe$_2$ thin films show narrowing of band gap with thickness. $\alpha$ and $E_g$ values decrease with decrease in annealing temperature for CuAlSe$_2$ films.
References


