Optical absorption and transmission in Cu$_{x}$Zn$_{1-x}$Se pseudo-binary alloy

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The optical absorption and transmission in the pseudo-binary alloy of copper, zinc and selenium (Cu$_{x}$Zn$_{1-x}$Se) have been investigated. The transmission is high over most of the visible region but the absorption edge moves into the visible spectrum as the concentration of copper in the alloy increases. The energy gaps of the samples were found to be 1.58, 1.60 and 1.64 eV, respectively. These values fall within the requirement for visible transmission indicating that the films from such alloys can be used as visibly transmitting materials for use as warm climate windows to transmit visible radiation into buildings which have their windows coated with such films. Also, the decrease in energy gaps of the samples with a corresponding shift in the absorption edge towards the visible spectrum as the concentration of the copper impurity increases, leads to an improvement in the conductivity of the alloys examined.

Keywords: Optical absorption, Optical transmission, Pseudo-binary alloy, Optical band gap, Absorption coefficient

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1 Introduction

Over the years, considerable efforts have been made to develop high quality materials for practical device applications. Therefore, it is in furtherance of this objective that this investigation was undertaken in order to find out the optical parameters such as the absorption coefficient and optical band gap of Cu$_{x}$Zn$_{1-x}$Se pseudo-binary alloy which may be useful in the fabrication of optoelectronic devices.

ZnSe which is one of the constituents of the alloy under investigation, is of considerable interest because of its application in optoelectronic devices such as electroluminescence or light emitting diodes$^{1-5}$. Some of the properties which make it an attractive material for optoelectronic device applications are its direct band gap and it is transparent over a wide range of the visible spectrum$^{6-9}$. Some devices which utilize these properties include second harmonic generators, frequency mixers and electroluminescent display$^{10}$. Also, ZnSe is a primary material for applications in high power, high temperature electronics and it is presently the most advanced material for semiconductor laser applications$^{11}$. The present work was therefore partly inspired by these applications and the need to search for more applications for Cu$_{x}$Zn$_{1-x}$Se pseudo-binary alloy.

Copper is an important impurity in wide band gap zinc chalcogenides. In ZnSe, the incorporation of copper results in a variety of characteristic visible bands$^{12,13}$. However, there is a long-standing uncertainty about the role of copper in the aforementioned materials. Hence, there is need to develop new experimental techniques for incorporating copper into zinc chalcogenides in order to provide additional information on the behaviour of this important element. It is necessary to gain a clear understanding of the role of copper in zinc chalcogenides because copper is the most efficient known activator of luminescence in these compounds$^{14}$ and secondly because of the high diffusion rate of copper in the II-VI compound semiconductors$^{15}$.

The electrical and optical characteristics of semiconductor devices are governed principally by the type and distribution of the dopant impurities in the semiconductor material$^{13,16}$. It has been reported by Kim et al.$^{17}$ that the effect of heavy doping on the electrical and optical properties of compound semiconductor is important because of its application in many optoelectronic devices such as heterostructure bipolar transistor and laser diode. However, lightly and moderately doped semiconductors serve as major materials for extrinsic photoconductors$^{18}$. Hence, the present investigation was undertaken in order to discover whether the incorporation of Cu in ZnSe would yield some beneficial effects and improve the efficiency of devices made from ZnSe. It has been reported by Murayama et al.$^{19}$ that copper additions generally increase the kinetics of precipitation during artificial aging as well as reduce the deterioration of the age-hardening response arising from natural ageing of the
Al-Mg-Si alloy. Also, Akintunde observed that the absorbance, optical energy gap and the electrical conductivity of aluminium doped CdS thin films are dependent on aluminium dopant concentration. In addition, the behaviour of several dopants such as rare earth elements in \( p \)-GaSe, and other III-VI compounds is interesting because of their effect on crystal band structure and scattering anisotropy.

2 Experimental Details

Samples corresponding to atomic compositions \( x=1, 2, \) and 3 were weighed out and the composition by weight of the constituent elements is presented in Table 1. The alloy was treated as a unification of the binary alloys of \((\text{CuSe})_x\) and \((\text{ZnSe})_{1-x}\). The values of \( x \), which were obtained from the phase diagram of Cu and Zn were chosen such that the investigation could be carried out at the lowest possible temperature of about 350°C.

The percentages by weight were worked out from the following formulae connecting the weight percentages with atomic percentages equations:

\[
X = \frac{100 \ Y A}{Y A + B(100 - Y)} \quad \ldots (1)
\]

\[
Y = \frac{100 \ X B}{X B + B(100 - X)} \quad \ldots (2)
\]

where \( X \) is the percentage by weight and \( Y \) is the atomic percentage of the elements of atomic weight \( A \) in a binary alloy with another element which has atomic weight \( B \). The combined atomic weight of \( \text{Cu}_x\text{Zn}_{1-x}\text{Se} \) is 63.54\( x \) + 65.37 (1\( -x \)) + 78.96 = 144.33 – 1.83\( x \). The borosilicate glass ampoules used in this investigation were cleaned by first boiling in chromic acid and then ultrasonically in deionized water, trichloroethylene, acetone and ethanol. The materials which were 99.999% purity (Ventron, Germany) were placed in the clean ampoules and heated over a range of temperatures 200-400°C to form the molten alloy samples. They were homogenized in vacuum at 400°C for 3 hr. The samples were cut into flat circular tablets and polished with a fine grain sand paper. Each sample has a diameter of 2 cm and a thickness of 0.5 cm. The samples were used to carry out subsequent measurements. Optical absorbance and transmittance spectra of the samples were recorded using a Pharmacia LKB Biochron 4060 spectrophotometer.

3 Data Analysis

From the optical data, the transmittance \( (T) \) was determined from the expression:

\[
T = I/I_0 = \exp (-\alpha d) \quad \ldots (3)
\]

where \( I/I_0 \) are the intensities of the transmitted and incident optical radiations respectively, \( d \) the thickness of the sample under investigation and \( \alpha \) is the absorption coefficient.

From Eq. (3), the absorption coefficient can be expressed as:

\[
\alpha = \frac{1}{d} \ln(1/T) \quad \ldots (4)
\]

The energy gap is determined from the expression:

\[
\alpha = (h\nu - E_g)^{1/2} \quad \ldots (5)
\]

where \( h \nu \) is photon energy and \( E_g \) is the energy gap. By plotting \( \alpha^2 \) against \( h\nu \), the energy gap is obtained when \( \alpha^2 = 0 \).

4 Results and Discussion

Figure 1 shows the optical absorption and transmission spectra of the various samples of \( \text{Cu}_x\text{Zn}_{1-x}\text{Se} \) pseudo-binary alloy. A critical observation of the absorption spectrum of sample A shows that the absorbance falls to zero at 758 nm corresponding to energy of 1.64 eV. Similarly, in sample B, the absorption spectrum extends up to 776 nm, corresponding to an energy of 1.60 eV, while that of sample C falls to zero at 786 nm which is equivalent to an energy of 1.58 eV. By and large, the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Value of x in ( \text{Cu}<em>x\text{Zn}</em>{1-x}\text{Se} )</th>
<th>% by weight (x)</th>
<th>Wt of binary alloy for 50g</th>
<th>Wt of Se (g)</th>
<th>Energy gaps (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.25</td>
<td>99.15</td>
<td>49.55</td>
<td>0.45</td>
<td>1.64</td>
</tr>
<tr>
<td>B</td>
<td>0.30</td>
<td>98.20</td>
<td>49.10</td>
<td>0.90</td>
<td>1.60</td>
</tr>
<tr>
<td>C</td>
<td>0.40</td>
<td>97.34</td>
<td>48.65</td>
<td>1.35</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 1—Composition by weight of the constituent elements in the various samples of \( \text{Cu}_x\text{Zn}_{1-x}\text{Se} \) pseudo-binary alloy and their energy gaps.
sinusoidal variation in absorption and transmission spectra can be attributed to elastic scattering of charge carriers by phonons.

For all the samples of the Cu$_x$Zn$_{1-x}$Se alloy investigated, the transmittance is high over most of the visible region but the absorption edge moves into the visible spectrum as copper concentration increases. This result reduces reflectance considerably and improves the illumination. The introduction of acceptor levels above the valence band of the ZnSe band gap by the incorporation of copper impurity is indicated by the noticeable shift in the optical absorption edges as the impurity concentration increases. This results in the ease of electronic transition to the conduction band leading to an improvement in the conductivity of the material.

The variation of $\alpha^2$ with photon energy ($h\nu$) for the various samples of Cu$_x$Zn$_{1-x}$Se alloy is summarized in Fig. 2. The intercepts of Fig. 2 obtained by extrapolating the linear portion of the plots on the photon energy axis give the energy gaps of the various samples investigated and it is presented in Table 1. In Fig. 2, $\alpha^2 = 0$ for $h\nu \leq E_g$ and increases as $h\nu$ increases above $E_g$ in accordance with the expression given in Eq. (5). The region of $h\nu > E_g$ is due to transitions from the extended states at the top of the valence band to the localized states at the
bottom of the conduction band and also it is as a result of transitions from the localized states of the top of the valence band to extended states in the conduction band\textsuperscript{24}. The energy gaps of the various samples presented in Table 1 decrease with increase in dopant concentration. Due to the strong interactions either among the introduced Cu impurity themselves or with the host lattice atoms, the discrete impurity levels broaden into a band and the band tail gradually moves into the energy gap, resulting in the narrowing of the band gap of the alloy under investigation. This facilitates the ease of electronic transition from the valence band to the conduction band leading to an improvement in the conductivity of the material. For visible transmission, the energy gap requirement\textsuperscript{25,26} is from 1.5 to 3.0 eV. However, since the energy gaps of these alloys are in this region, it implies that films from such alloys can be used as visibly transmitting films for use as warm climate windows to transmit visible radiation into buildings\textsuperscript{27}. This will lead to a cool indoor temperature in buildings which have their windows coated with such films hence the increase in the transmittance can find applications in thermal control window coating and antireflection coating for solar thermal devices.

5 Conclusions

The following conclusions can be made from the present study:

1. The energy gaps of Cu\textsubscript{x}Zn\textsubscript{1-x}Se pseudo-binary alloy samples are 1.58, 1.60 and 1.64 eV and they satisfy the requirement for visible transmission which makes films of Cu\textsubscript{x}Zn\textsubscript{1-x}Se alloy promising materials for use as thermal control window coatings.

2. The increase in transmittance as a result of the incorporation of copper in ZnSe is desirable because it can be used as antireflection coating for solar thermal devices.

3. The incorporation of copper in ZnSe reduces the energy gap of the alloys which facilitates electronic transition to the conduction band thereby enhancing the conductivity of the materials.

References