THE EFFECT OF THERMAL ANNEALING ON THE OPTICAL BAND GAP OF Cd$_{1-x}$Zn$_x$S THIN FILMS DEPOSITED BY THE DIP TECHNIQUE

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ABSTRACT
The effect of thermal annealing on the optical band gap of Cd$_{1-x}$Zn$_x$S ($x=0.2, 0.4, 0.6, 0.8$) thin films have been investigated. The films were deposited using the dip technique. The fundamental optical property which has been investigated here is the absorbance of light at room temperature, using the KLB Ultraspec II 4050 (UV/Visible) spectrophotometer over the wavelength range 300 – 900 nm. The energy band gap and absorption coefficient of the films were determined from the absorption spectrum. The optical band gap of the as-deposited films varied from 2.42 eV ($x=0.2$) to 3.61 eV ($x=0.8$), that is, the band gap increased with increasing Zn concentration of the alloy. These values compare favorably well with that obtained from literature of similar films prepared using other deposition techniques. The as-deposited samples were thermally annealed in air for an hour at temperatures of 100°C, 200°C and 300°C and the absorption spectra again recorded. It was observed that thermal annealing decreased the band gap of the samples; this may be due to improving crystallinity or alternatively, a phase transformation taking place in the samples as a result of the heat treatment.

INTRODUCTION
Interest in the preparation and study of the physical properties of ternary chalcogenide compounds for their possible application in solar cells, light emitting diodes and non-linear optical devices has been increasing in recent years (Ortega-Lopez et al., 2003). Ternary compounds are found to be promising materials for optoelectronic device applications such as green light emitting devices and are suggested to be a possible material for the window layer of solar cells. These compounds are increasingly being studied for efficient solar energy conversion through photo-electrochemical solar cells and have become a potential candidate for such applications (Woon-Jo and Gye-Choon, 2003; Padam and Rao, 1986; Pawar et al., 1986).

Cadmium zinc sulphide (Cd, Zn)S ternary alloy is one of the promising materials in this respect (Kumar et al., 1998). Interest in (Cd, Zn)S has been driven by the expected improvement in performance of thin film photovoltaic cells of type CdTe- and CIS(CuInSe$_2$-based cells) using (Cd, Zn)S rather than the presently used CdS. This expectation arises mainly from the in-
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creased band gap of the Zn-containing solid solution, resulting in increased transparency to shorter wavelengths of light. Another consideration for heterojunction formation is the decrease in electron affinity of the semiconductor with increase in Zn content (ZnS has a smaller electron affinity than CdS). The electron affinity of a semiconductor is a measure of the position of the conduction band with respect to the vacuum energy level; a lower value means a higher conduction band. Thus the alignment of the conduction band of the (Cd, Zn)S with that of the second semiconductor can be controlled to a large extent by varying the film composition (Hodes, 2002).

Cd1-xZnS ternary compounds can form a continuous series of solid solution allowing systematic variation of the band gap from 2.43 eV for CdS to 3.7 eV for ZnS by adjusting the composition (Yokogawa et al., 1994). In CdS/CdTe solar cells, the replacement of CdS with the higher band gap ternary (Cd, Zn)S film can lead to a decrease in window absorption losses, and has resulted in an increase in the short-circuit current (Yamaguchi et al., 1996).

Although, much research has been done on (Cd, Zn)S thin films and their applications in optoelectronic devices, very little has been reported on how thermal annealing affects the optical properties of (Cd, Zn)S thin films prepared using the dip technique.

Optical properties such as the optical band gap, refractive index, extinction coefficient, transmittance and absorbance of a material are essential in characterizing materials for optoelectronic device fabrication. Also, being able to ‘tune’ the optical properties by thermal annealing can result in materials for specific applications.

In the present paper we report on the absorption coefficient and optical band gap of Cd1-xZn0.5S sulphide thin films (x = 0.2, 0.4, 0.6, and 0.8) prepared by the dip technique, as well as the effect of thermal annealing on the optical properties.

MATERIALS AND METHODS

The starting chemicals in the preparation of the films consisted of aqueous solutions of concentrated hydrochloric acid, concentrated nitric acid, for degreasing the glass slides to be used as substrate. Zinc nitrate Zn(NO3)2.6H2O, cadmium nitrate Cd(NO3)2.4H2O and thiourea, (NH2)2CS in methanol were used for the films formation. The chemicals were obtained from BDH chemicals Poole, England.

The substrates used in these experiments were cleaned in Genklene before the films were prepared. The cadmium nitrate was the source of cation (Cd2+), zinc nitrate was the source of another cation (Zn2+) and thiourea was the source of anion S2-. By varying the relative ratio of Cd and Zn ions Cd1-xZn0.5S thin films with composition parameter x = 0.2, 0.4, 0.6, and 0.8 were deposited on glass substrates with x defined by Song et al., (2005) as

\[
x = \frac{[Zn \; NO_{3/2}]}{Zn \; NO_{3/2} + Cd \; NO_{3/2}}
\]

The substrate was withdrawn vertically from a methanol solution of cadmium nitrate, zinc nitrate and thiourea at a controlled speed. The substrate was then transferred into an oven at a temperature of about 85°C and baked for five minutes. The reactions taking place are typically

\[
Cd \; NO_{3/2} \cdot 4H2O + NH2 \cdot CS \rightarrow CO2 + 6H2O + 2N2O
\]

\[
Zn \; NO_{3/2} \cdot 6H2O + NH2 \cdot CS \rightarrow ZnS + CO2 + 8H2O + 2N2O
\]

Where the compounds CdS and ZnS conflate in the ratio (1-x): x to form the alloy Cd1-xZnxS. The subscript x is the composition parameter defined above. The samples were then allowed to cool and the dipping-withdrawal-baking cycle repeated for about six times. This was done because according to Karanjai and Dasgupta (1986) the grain size increases rapidly with the number of dipping but levels off after about five or six dipping.

The thickness of the deposited films was measured by the gravimetric method using a sensitive electronic balance.

A KLB Ultraspec II 4050 (UV/Visible) spectrophotometer was used to determine the optical absorbance of the films as a function of wavelength at room temperature over the wavelength range 300 – 900 nm. As the films were examined along with the substrates on which they were formed, it was necessary to take into account the absorbance in the glass substrate even though it was small. Hence, the absorbance spectra of the glass substrates were taken and used for the elimination of the optical absorbance in the film-substrate combination to get the optical absorbance of the films. Aside the absorbance of the as deposited films, the samples were thermally annealed for one hour at temperatures of 100°C, 200°C, 300°C and the absorbance again recorded.

RESULTS AND DISCUSSION
The adherence of the films to the substrate was good except the one with x = 0.2, i.e. the one with high cadmium content and the colours of the films varied from yellow to white-yellowish, as the Zn-content increased in the sample. The calculated film thickness using the gravimetric method indicates that, generally, thicker films were formed with increasing Cd for the same number of dipping. The thickness of the films were 18.85 μm, 8.61 μm, 5.06 μm, 6.23 μm for x= 0.2, 0.4, 0.6, 0.8 respectively.

The absorption coefficient, \( \alpha \), of the thin films is calculated by using the expression;

\[
\alpha = \frac{2.303A}{d}
\]

Where \( A \) is the absorbance, and \( d \) is the thickness of the film.

Variation of absorption coefficient versus photon energy at different annealing temperatures
Typical absorption coefficient curve for composition x = 0.2 is shown in figure 1, displaying a shift of the fundamental absorption edge towards longer wavelengths (lower photon energies) as the annealing temperature is increased and also, raising the fundamental edge, leading to a high absorption coefficient. However, the shift is smaller from 200°C to 300°C annealing temperatures in both films. Shifting of the absorption edge which leads to high absorption coefficient may be attributed to the introduction of more electronic states inside the film structure or alternatively rearrangement of defect states as the heat treatment activates processes such as solid state diffusion in the film.

![Fig. 1: Absorption coefficient, \( \alpha \), versus photon energy, \( E \), for Cd_{0.8}Zn_{0.2}S sample](image-url)
Surface oxides which may have been formed during the annealing process could have also contributed to the increased absorption of the samples. Annealing temperature did not exceed 300°C because at 400°C the samples became dark, possibly due to the organic solvent methanol that was used in their preparation and the relatively long annealing time.

The absorption of photon energy less than the band gap energy involves localised tail states and hence does not obey Eq.1. Instead, there was an exponential dependence of absorption coefficient on photon energy giving rise to Urbach’s tail. The Urbach’s tail has been used to describe the extent of structural disorder in the sample, but the current understanding is that in amorphous solids it occurs due to both structural and thermal disorder (Cody, 1984).

**Optical Band Gap**

The electronic energy band parameters of semiconductor alloys and their dependence on alloy composition are very important. The energy band gap of a ternary alloy is dependent on the relative concentration of the constituent elements.

Almost all the II-IV compounds are direct band gap semiconductors. The optical band gap of the thin films were estimated from absorption coefficient data as a function of wavelength by using the Tauc Relation for direct band gap materials, which is given by

\[ \alpha h\nu = B (h\nu - E_g)^{\frac{1}{2}} \]  

Where \( h\nu \) is the photon energy, \( E_g \) the optical band gap and \( B \) is a constant.

By plotting a graph of \((\alpha h\nu)^2\) as ordinate and \( h\nu \) as abscissa, the optical band gap \( E_g \) can be determined by the extrapolation of best fit line between \((\alpha h\nu)^2\) and \( h\nu \) to intercept the \( h\nu \) axis at \((\alpha h\nu)^2 = 0\). This intercept gives the value of the optical band gap of the material.

Figure 2 shows the optical band gap for sample \( \text{Cd}_{0.8}\text{Zn}_{0.2}\text{S} \) at three different annealing temperatures. Figure 3 and 4 show a similar plot for sample \( \text{Cd}_{0.6}\text{Zn}_{0.4}\text{S} \) and \( \text{Cd}_{0.4}\text{Zn}_{0.6}\text{S} \) respectively. Thermal annealing is found to decrease the optical band gap of the films, for instance, band gap of the sample \( \text{Cd}_{0.8}\text{Zn}_{0.2}\text{S} \) varied from 2.42 eV as-deposited to 2.12 eV after annealing at 300°C for one hour.

![Graph](image_url)

**Fig. 2:** A graph of \((\alpha h\nu)^2\) plotted as a function of the photon energy, \( h\nu \), for \( \text{Cd}_{0.8}\text{Zn}_{0.2}\text{S} \) film annealed at different temperatures. Extrapolation of best fit line between \((\alpha h\nu)^2\) and \( h\nu \) to intercept the \( h\nu \) axis at \((\alpha h\nu)^2 = 0\) gives the band gap.
The band gap of the sample Cd$_{0.6}$Zn$_{0.4}$S varied from 3.36 eV as-deposited to 2.60 eV after annealing at 300°C. The decrease in band gap of the films after annealing may be due to improvement in the structure, i.e., improving crystallinity or alternatively, a phase transformation taking place in the samples as a result of the heat treatment. A similar effect of decreased band gap as a result of heat treatment of Cd$_{1-x}$Zn$_x$S thin films for photovoltaic applications has been reported by Chavhan et al., (2008).

Fig. 3: A graph of $(\alpha h\nu)^2$ plotted as a function of the photon energy, $h\nu$, for Cd$_{0.6}$Zn$_{0.4}$S film annealed at different temperatures. Extrapolation of best fit line between $(\alpha h\nu)^2$ and $h\nu$ to intercept the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ gives the band gap.

Fig. 4: A graph of $(\alpha h\nu)^2$ plotted as a function of the photon energy, $h\nu$, for Cd$_{0.4}$Zn$_{0.6}$S film annealed at different temperatures. Extrapolation of best fit line between $(\alpha h\nu)^2$ and $h\nu$ to intercept the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ gives the band gap.
It was observed that increasing Zn content in the sample increased the optical band gap. For example, in the as-deposited films, the band gap increased from 2.42 eV (x = 0.2) to 3.61 eV (x = 0.8). Increase in band gap in the solid solution of (Cd, Zn)S for higher Zn is a bulk property. On the other hand, as x increases particle size decreases, resulting in higher band gap due to increasing contribution of quantum size effect.

A summary of the optical band gap values with the sample constituent and at the various annealing temperatures is shown in table 1.

A plot of the optical band gap, Eg, against sample composition, x, when the samples had been annealed to 200°C is shown in figure 5, the somewhat linear variation of Eg with sample composition is a sign of solid solution formation. That is, as Zn content increases in the sample the energy gap of the ternary Cd$_{1-x}$Zn$_x$S approaches that of the binary ZnS which is quoted to be about 3.70 eV.

**CONCLUSION**

Optical studies of the films revealed that increasing zinc content and annealing temperature all increase the absorbance of the films. Absorbance spectra obtained from the films were used to evaluate the optical band gaps. Band gap of the as deposited films varied from 2.42 eV (x =0.2) to 3.61 eV (x =0.8), i.e. the band gap increase with increasing Zn concentration of the alloy. These band gap values compare favorably with literature values of similar films prepared using other deposition techniques. Thermal annealing however decreased the band gap of the samples; this may be due to improving crystallinity or alternatively, a phase transformation taking place in the samples as a result of the heat treatment.

**Table 1: Variation of sample composition with optical band gaps for Cd$_{1-x}$Zn$_x$S**

<table>
<thead>
<tr>
<th>Composition x</th>
<th>$E_g$(eV) for as-deposited sample</th>
<th>$E_g$(eV) sample annealed 100°C</th>
<th>$E_g$(eV) sample annealed 200°C</th>
<th>$E_g$(eV) sample annealed 300°C</th>
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<tbody>
<tr>
<td>0.2</td>
<td>2.42</td>
<td>2.32</td>
<td>2.14</td>
<td>2.12</td>
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<tr>
<td>0.4</td>
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<td>2.75</td>
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<td>2.60</td>
</tr>
<tr>
<td>0.6</td>
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<td>2.50</td>
<td>2.50</td>
<td>2.49</td>
</tr>
<tr>
<td>0.8</td>
<td>3.61</td>
<td>2.63</td>
<td>2.63</td>
<td>2.60</td>
</tr>
</tbody>
</table>

**Fig. 5: Optical band gap variation with zinc concentration in the samples**

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REFERENCES


