THE EFFECT OF THERMAL ANNEALING ON THE OPTICAL BAND GAP OF CADMIUM SULPHIDE THIN FILMS, PREPARED BY THE CHEMICAL BATH DEPOSITION TECHNIQUE

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ABSTRACT
Cadmium sulphide thin films have been prepared by the chemical bath deposition technique (pH 11, 70°C). Two different sets of films were prepared under varied conditions and concentrations of their ions sources (Cd²⁺ from cadmium nitrate, S²⁻ from thiourea) and Na₂EDTA as a complexing agent. A UV mini Schimazu UV–VIS Spectrophotometer was used to determine the optical absorbance of the films as a function of wavelength at room temperature over the wavelength range 200 – 600 nm. The samples were then thermally annealed for thirty (30) minutes, at temperatures of 100°C, and 200°C, after which the absorbance of the films were again recorded. The band gap values obtained for the sample with 0.5 M CdS as deposited, annealed at 100°C and annealed 200°C were 2.1 eV, 2.2 eV and 2.3 eV respectively. Whilst the values obtained for the sample 0.15M CdS as deposited, annealed at 100°C and annealed at 200°C were 2.0 eV, 2.01eV and 2.02 eV respectively. The increase in band gap with annealing temperature might be attributed to the improvement in crystallinity in the films.

INTRODUCTION
Cadmium Sulphide in the bulk form and thin films has been extensively studied in the past forty years due to the interest in this material for a large variety of applications ranging from photovoltaic to luminescent devices (Boakye and Nusenu, 1996). Cadmium sulphide (CdS) is a II – VI semiconductor with an energy band gap (Eg) of 2.42 eV in bulk materials at room temperature (Reddy et al., 2007). CdS has been known for many decades as a photocatalytic semiconductor material for solar hydrogen generation in the visible wavelength range (Uchihara et al., 2007). CdS is also one of the most promising materials for application in electronic and optoelectronic devices such as solar cells, photo sensors, laser materials, optical waveguides and nonlinear integrated optical devices (Pantoja et al., 2003; Zhan et al., 2003; Tiwari and Tiwari, 2006). Polycrystalline CdS films are generally used in CuInSe₂ (CIS) and CdTe solar cells as a window material for transmitting the light absorbed by CIS or CdTe, and also as an n-type material for p-n junction of solar cells (Romeo et al., 2001). For increased efficiency of solar cells, a semiconductor with optimum band gap, low resistivity and high absorption coefficient is required (Hiie et al., 2006).

Cadmium sulphide has crystal cubic structure
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(zinc-blende) or hexagonal structure (wurtzite), or mixture of them according to growth deposition (Kaur et al., 1980). The films have a strong preferential orientation of either hexagonal H[002] or cubic C[111] planes parallel to the substrate surface (Haider et al., 2008). The material properties that are of interest for these films are the optical properties within the range of UV, visible, and near infrared (NIR) which strongly depend on the dielectric constants, refractive index, and the band-gap of the thin film and depends very much on the nature of the film material properties (Ugwu, 2006).

A large variety of deposition techniques which include vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy (MBE), vapour phase epitaxy, chemical vapour deposition (CVD), solution growth, screen printing and electrophoresis have been used for the preparation of these films (Chopra and Kaur, 1983). Among these techniques, chemical bath deposition (CBD) is a low cost and suitable technique to prepare high quality well adhered film reproducibly (Metin et al., 2009). The deposition process is based on the slow release of sulphide ions via the controlled hydrolysis of thiourea [SC(NH$_2$)$_2$] in an alkaline medium in the presence of Cd salt and a chelating agent such as NH$_3$.

The physical and chemical properties of not only CdS films but also most of the binary metal chalcogenides of II–VI semiconductors obtained by CBD critically depend on the preparative parameters such as the source and concentration of metal and chalcogenide ions, pH of the deposition solution, deposition time and temperature, and gas phase pressure, and the time of annealing. The annealing temperature is one of the most important considerations affecting the physical properties such as the electrical and optical properties of thin films (Metin et al., 2009).

In this paper we report on the optical band-gap of CdS (0.5 M and 0.15 M) thin films, prepared by the chemical bath deposition technique. The effect of thermal annealing on the optical band-gap of these films is also discussed.

MATERIALS AND METHODS

Two different sets of films were prepared under varied conditions and concentrations of their ions sources (Cd$^{2+}$ from cadmium nitrate, S$^{2-}$ from thiourea) and Na$_2$EDTA as a complexing agent. The substrate (commercial glass slide) was washed with detergent, rinsed in distilled water, soaked in nitric acid, degreased in ethyl alcohol and then rinsed in distilled water. 50ml of Cd(NO$_3$)$_2$$\cdot$4H$_2$O solution was measured using 50ml pipette into a 600ml beaker.

75ml of 0.01 M Na$_2$EDTA was added to the solution, the pH adjusted to 11 with ammonia solution, and 50ml of 0.05M thiourea added. The previously cleaned substrate was then immersed horizontally in the solution with the help of a thread.

The beaker containing the mixture was placed in a water bath set at 70°C, for 120 minutes. The substrate was removed from the solution and dipped in distilled water to remove soluble impurities and dried in air. The procedure was repeated for several more slides. The 0.015 M CdS thin film was prepared using the same procedure described above, except that the concentration of thiourea was changed to 0.015M.

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

A UV mini Schimazu UV –VIS Spectrophotometer was used to determine the optical absorbance of the films as a function of wavelength at room temperature over the wavelength range 200 – 600 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. The samples were then thermally annealed for thirty (30) minutes, at temperatures of 100°C, and 200°C, after which the absorbance of the films were again recorded.
RESULTS AND DISCUSSION

The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. In order to determine the optical band gap of the films, the absorbance spectra of the films were recorded at room temperature.

A typical absorbance curve for 0.5 M CdS is shown in figure 1. It can be observed that above the 300 nm wavelength, the absorbance of the samples (as deposited, annealed at 100°C and 200°C) lie between 0.6 and 2.0, with the annealed samples having lower absorbance readings.

The slightly higher absorbance readings in the as deposited films can be attributed to the presence of lattice defects and dislocations (Kale and Lokande, 2005). These defects give rise to localized electronic levels which are in the band gap (Singh, 2003). These band gap electronic levels are also available for photon absorption. The defects like the dislocation density and strain in the films decrease as a result of annealing. This might be attributed to the improvement in crystallinity in the films with increasing annealing temperature (Melin et al., 2009). Thus annealing the samples at 100°C and 200°C, for 30 minutes, could lead to minimizing structural imperfections in the prepared thin films resulting in fewer states within the band gap available for photon absorption. Hence, lower absorbance readings.

Absorption spectra shows a sharp increase when the energy of the incident photons equals the energy band gap. This enhanced absorbance is observed at the 300 nm wavelength for all three samples.

A typical absorbance curve for 0.15 M CdS is shown in figure 2. The absorbance curve for all the samples are quite similar, with the absorbance for the as deposited samples almost the same as the annealed samples. This might be due to very little structural imperfections in the thin films. The absorbance of these films above the 300 nm wavelength is relatively lower, between 0 and 0.5. The absorption spectra also show a sharp increase in the vicinity of the 300 nm wavelength. Comparing the absorbance curve for the two different concentrations of CdS it appears that the sample with 0.15 M
CdS is more crystalline than that with 0.5 M CdS.

**Optical Band Gap**
The absorption coefficient, $\alpha$, of the thin films is calculated from the absorbance spectrum by using the expression;

$$\alpha = \frac{2.303A}{d} \quad (1)$$

Where $A$, is the absorbance, and $d$, is the thickness of the film.

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

$$\alpha h\nu = B \left( h\nu - E_g \right)^{1/2} \quad (2)$$

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.

The band gap of 0.5 M CdS in figure 3, shows an increase from 2.02 eV, as deposited to 2.12 eV and 2.24 eV after annealing at 100°C and 200°C, whilst that of 0.15 M CdS in figure 4, increased from 2.02 eV as deposited to 2.04 eV and 2.06 eV after annealing at 100°C and 200°C. Davis and Mott (1971) reported that the presence of high density of localized states in the band structure is responsible for lower energy band gap, hence as the annealing temperature increases, the density of localized states decreases so the band gap increases (Singh et al., 2006). The range of values for the band gap obtained in this work are consistent with other published results such as results of Pathan et al., (2004), who reported band gap values of between 2.17 eV to 2.24 eV.

The results of annealing depend significantly on its kinetics: the rate of heating and cooling and the time of exposure at a given tempera-
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Fig. 3: A graph of $(\alpha h \nu)^2$ plotted as a function of the photon energy, $h \nu$, for 0.5 M CdS 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 0.15 M CdS 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.
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The results reported in this work are thus different from that of other authors, reporting on the effects of thermal annealing on CdS films deposited by CBD. However since the temperatures for the annealing process were far lower (100°C to 200°C) than those used by other authors, this seems to suggest that annealing of thin films at lower temperatures result in the tempering of the thin films by removal of impurities, lattice defects and dislocations. Again this observation seem to suggest that there is a progressive increase of the band gap energy with increasing temperature until a transition temperature is reached, beyond which the band gap energy begins to decrease with further increase in temperature. For instance, Melin et al. (2009), have reported that the band gap energy of the as deposited films is 2.42 eV and systematically decreases to 2.28 eV for films annealed at 823 K (550°C). This had also been reported by Prabahar and Dhanam (2005). According to Melin et al. (2009), at high temperatures (823 K or 550°C), the film is degraded in terms of optical absorption in the forbidden region.

Haider et al. (2008) also annealed the CdS films at 300°C to 500°C, with increments of 50°C. They observed that the annealed samples showed a relative decrease in the band gap with both annealing temperature and time. These results are consistent with other published results, such as, George at al. (1995), who attributed this decrease in the band gap in the annealed samples to the grain size growth and composition changes taking place in the samples by CdO identified by XRD.

CONCLUSION

From the results obtained we can conclude that annealing of the CdS thin films at lower temperatures (100°C and 200°C) results in an increase in the optical band gap of the films. This increase may be attributed to the removal of impurities, lattice defects and dislocations in the films thereby improving crystallinity. The values obtained for the band gaps compare favorably well with values obtained from literature.

REFERENCES


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