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Effect of Annealing on Optical Properties of CdS Thin Films

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Abstract: *- Cadmium sulphide (CdS) thin films have been deposited by using Chemical Bath Deposition (CBD) Technique. Initially bath parameters such as deposition temperature, pH of the precursor, deposition time, molarities of the precursors were optimized for deposition of CdS thin films. The prepared CdS thin films were annealed at different temperatures (100, 200, 300, 400 ^{0}C). As deposited and annealed CdS thin films were characterized by Uv-Visible spectrophotometer. The effect of annealing temperature on interaction of light with deposited material was investigated.*

Keywords: *- Chemical Bath Deposition**,** CdS thin films, Optical properties, optical band gap*.

I. INTRODUCTION

In last few decades efforts have been devoted to preparing II-IV semiconductor thin films because of their wide range of application in the fabrication of solar cells and other optoelectronic devices. The CdS material is an important candidate used as a window layer in solar cell architecture [1]. In thin-film form, CdS can be combined with other layers for use in certain types of solar cells[2]. CdS was also one of the first semiconductor materials to be used for thin-film transistors (TFTs)[3].

Over the past few years, several deposition methods have been employed including radio-frequency sputtering [4], hydrothermal [5], SILAR [6] and chemical bath deposition method [7-9] to prepare cadmium sulphide thin films. Among various deposition methods, chemical bath deposition method has been identified as simple and low cost thin films deposition method with many advantages. Up-to-date, chemical bath deposition method has been successfully used to deposit various thin films including ZnSe [10], CdS, CdZnS[11,12], Ni4S3 [13] and As2S3 [14]. Chemical bath deposition method is based on the controlled precipitation from solution of a compound on a suitable substrate. CBD is a technique in which thin films are deposited on substrates immersed in dilute solutions containing metal ions and either sulfide or selenide ions. This process usually uses a chelating agent to control the release of metal ions and sulfide ions to produce the controlled homogeneous precipitation of the film on the solid substrate. CBD is well suited for producing large-area thin films and has many other advantages. Firstly, it does not require sophisticated instruments or other expensive equipment, such as a vacuum system, and the starting chemicals are commonly available and inexpensive. Secondly, low temperature deposition avoids oxidation and corrosion of metallic substrates and so various substrates can be used, including insulators, semiconductors and metals. Thirdly, the preparation parameters are easily controlled.

In the present paper Chemical Bath deposition technique was used for deposition of CdS thin films. The prepared CdS thin films were annealed at different temperatures in air. As deposited and annealed CdS films were characterized by using Uv-Visible spectrophotometer. Effect of annealing on optical properties was studied.

II. EXPERIMENTAL

i. Materials and Method: In order to prepare CdS thin films, cadmium chloride ($CdCl_2$), and thiourea (NH_2CSNH_2) were used as Cd^{+2} and S^{-2} ions respectively. The stock solutions of $CdCl_2$ (1M), and NH_2-CS-NH_2 (1M) were prepared. Five different baths were prepared each containing 10ml of 1M CdCl2, 10ml of 1M NH_2-CS-NH_2 , 2ml triethyleneamide (TEA) was added as a chelating agent with continuous stirring. pH of the precursors was adjusted to 10.5 by drop wise addition of Ammonia to slowed down the reaction. The above prepared chemical baths were kept in constant temperature bath, maintained at constant optimized temperature 45 ^{0}C. The glass substrates used for deposition of CdS films were previously cleaned, immersed in each bath. After optimized deposition time 12 hours the substrates were taken out of the baths. The deposited substrates were washed twice with doubly deionised water and dried in air. The uniform yellow colored films were deposited over substrates.

ii. Mechanism CdS Thin Film Formation: The method which is used to prepare cadmium Zinc sulphide (CdZnS) includes the reaction of Cd^{2+}, Zn^{2+} ions and S^{2-} ions were found in solution from thiourea is as:

$$(NH2)2\ CS + OH^- \leftrightarrow SH^- + CN_2H_2 + H_2O \quad \text{--------------1}$$

$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O \quad \text{--------------2}$$

Dissolving $CdCl_2$ in water made both cadmium ions available in the solution and formation of complexes of those ions as: In case of NH_3 as complexing agents, the Cd^{2+} exist predominantly in the form of ion complex. The ratesof CdS formation are determined by the concentration of Cd^{2+} provided by $[Cd(NH_3)_4]^{2+}$, and the concentration of S^{2-} from the hydrolysis of $SC(NH_2)_2$, respectively. The general reaction can be expressed as :

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
$$[Cd(NH_3)_4]^{2+} \leftrightarrow Cd^{2+} + 4\,NH_3$$
$$[Cd\,(NH_3)_4]^{2+} + S^{2-} + NH_3 \rightarrow CdS + \text{Remaining product.} \qquad \text{--------3}$$

The prepared CdS thin films were rinsed with deionized water to remove the loosely bound particles and dried in air. The film sample are numbered 1through 5. Film sample 1was kept as deposited, sample 2, 3, 4 and 5 were heated in air for100, 200, 300, 400 ^{0}C. The as deposited and annealed films are characterized by Uv-Visible spectroscopy.

III. RESULTS AND DISCUSSION

Deposited films were characterized by using systronics double beam 2201 spectrophotometer; the percentage absorption was plotted against wavelengths (nm) as shown in fig. 13. All the films show that absorption decreased with increase in wavelengths. The annealed CdS thin films show the significant blue shift of absorption edge as compared to the as-deposited CdS thin film. The film annealed at 400 0C exhibit significant blue shift as compared to other samples. It was reported that blue shifting of absorption edge indicates that the prepared film exhibit low absorption in the blue region which is the advantage for solar cell application [23]. The optical band gap [24] was obtained by using the relation(1).

$$\alpha = A\,(h\nu - E_g)^n / h\nu \qquad (1)$$

Where A is constant depending upon the transition probability, for direct allowed transition n=2, Eg is band gap energy and hυ is the photon energy. The band gap energy 'Eg' is determined by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ against hν to the energy axis at $\alpha = 0$. where α absorption Coefficient can be obtained from equation (1).

The figure shows 2. the plot of $(\alpha h\nu)^2$ as a function of photon energy hν. The variation of band gap is plotted as a function deposition temperature is shown in Fig 3.

The CdS is a wide band gap material and exhibits band gap of 2.42 eV in bulk form however the deposited films show higher band gap. The increase of band gap is related to particle size and quantum confinement effect which is the scope of the work. The band gap was found increased significantly from 3.63 to 3.8 eV on annealing. The variation of optical band gap with annealing temperature was presented in Fig. 3.

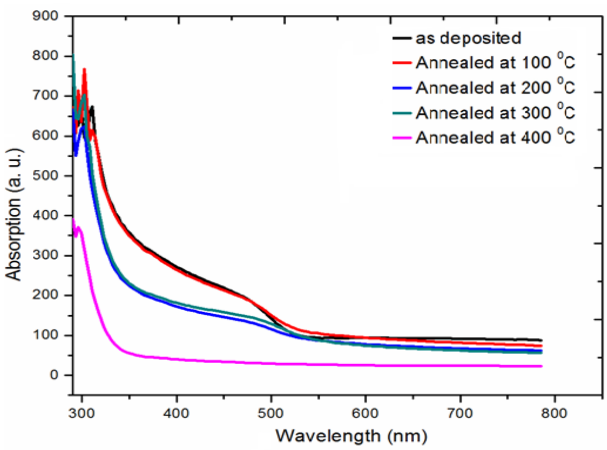

Fig. 1. Variation of absorption ploted verses wavelength in nm.

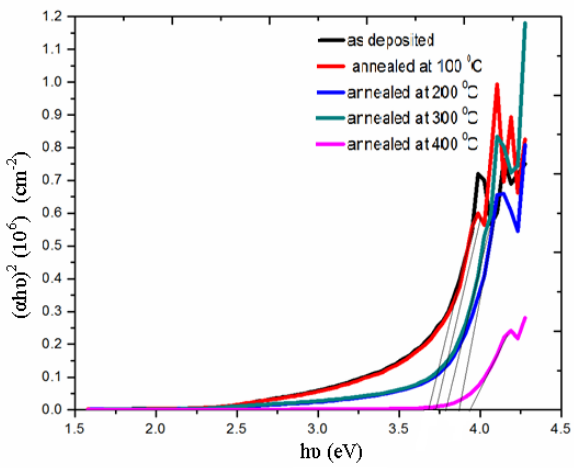

Fig. 2. Plot of $(\alpha h\upsilon)^2$ vs. photon energy (eV) .

Fig. 4 shows the plot of percentage transmittance verses wavelengths (nm). The significant increase in transmittance was observed with increasing the annealing temperature. The annealed films show higher transmittance as compared to as-deposited CdS thin films. The film sample annealed at 400 ^{0}C exhibit 64% transmittance in red and infrared region of the electromagnetic spectrum. The high transmittance and wide band gap are the important characteristics of solar cell devices. The study of optical properties of deposited CdS thin films concluded that the interaction of photon energy is related to structural changes of CdS material deposited on the substrate.

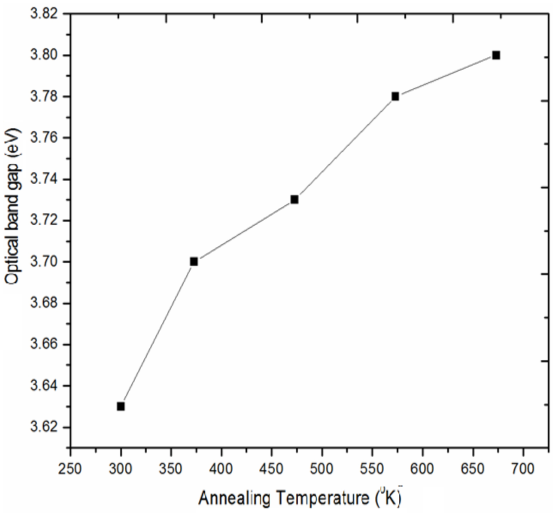

Fig. 3. Variation of optical band gap plotted vs. annealing

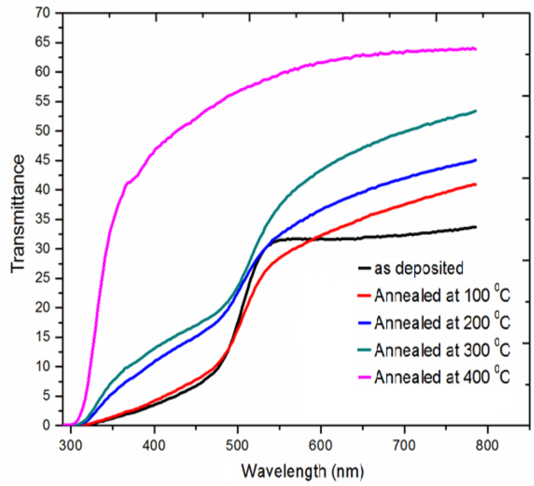

Fig. 4. Variation of percentage transmittance plotted vs wavelengths

IV. CONCLUSION

Thin uniform CdS thin films were deposited using Chemical Bath technique. The optical study show that annealed films exhibits significant blue shift of absorption edge as compared to as-deposited film. The increase in band gap and percentage transmittance on annealing concluded that interaction of light with matter related to the structural changes of deposited CdS material on annealing.

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