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Effect of Deposition Parameters on Properties of Nanostructure Chalcogenide Thin Films for Photovoltaic Applications

S. S. Kawar

Shri. Dr. R. G. Rathod Arts & Science College, Murtizapur, Dist. Akola, 444107, India.

Abstract : We deposited chalcogenide thin films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited films were investigated by XRD, SEM, FTIR and UV-VIS Spectrophotometer. It is found that, the average grain size of the films is 08 to 130nm and 08 to 113nm. The band gap is also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the films. We observed that, the influence of the deposition parameters on the properties of thin films includes the deposition temperature, deposition time and reagent concentration and pH of the solution dependence of the film thickness, grain size and energy band gap. The change in deposition parameters affects the band gap of thin films. It is also clear that the growth rate increases as the film thickness and grain size increases while band gap decreases.
Keywords: Deposition Parameters, Nanostructure Chalcogenide, Thin Films, Photovoltaic Applications.

Introduction:

Cadmium Sulfide and Zinc Sulfide is compound semiconductors with a wide range of potential applications. This material has existed in cubic or hexagonal forms and is wide- direct-band gap semiconductors. The CdS and ZnS is an excellent material used with the semiconductor cadmium telluride to fabricate solar cells given its optimal band gap energy (2.42eV) for optical windows, while great importance in the optoelectronic applications and a diverse range of applications for thin films of this semiconductor including as waveguides, heterojunction devices and in thin-film electroluminescent displays in which it is the most commonly used host material[1]. Applications in optoelectronic methods or photovoltaic devices is another area receiving attention , In CdS based solar cells, the use of wider band gap materials such as ZnS or CdZnS could lead to decreases in window absorption losses and improvements in the short circuit current of the cells[1-5].

In this work we report the preparation of the CdS and ZnS chalcogenide thin films having a nanometer grain size by using Chemical Bath Deposition (CBD) Technique and study the effect of deposition parameters on the properties of thin films. The CBD is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin film at close to room temperature.

The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process. Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates[1-5].

Experimental:

Thin films of CdS were deposited from a solution of analytical grade $CdSO_4$ (Cadmium Sulphate) a Cd^{++} ion source and Thiourea as a S^{--} ion source in an alkaline solution of Ammonia. Commercial glass slides, used as substrates, were cleaned in acetone and methanol ultrasonically, and finally, again washed with methanol ultrasonically before use. After cleaning the glass slides were kept vertically in a closed beaker with the help of a special holder which is attached to AC Motor having a constant speed of 60 r.p.m. We have double distilled water in a beaker and then added $CdSO_4$ of particular molarity as a Cd^{++} ion source slowly under Magnetic stirring. Add liquid Ammonia slowly to the solution for adjusting the pH of solution which is measured on pH meter, providing the temperature to the solution by means of heating coil. Add Thiourea (SC $(NH_2)_2$) of particular molarity as a S^{--} ion source was slowly poured into the solution only when the appropriate temperature i.e. 60°C was reached. Finally the temperature was kept constant with the help of a temperature controller in the range 70°C to 72°C. The time for the deposition was varied from 10 to 60 Min. after achieving constant temperature. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and finally dried in air. The same procedure is repeated for different time durations[6].

The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-Kα lines (λ= 1.54 Å). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM - 6400 Scanning Electron Microscope. IR spectra of representative sample 0.1M was recorded with the FTIR-8400S (SHIMADZU, Japan). The absorbance vs the wavelength was recorded with the UV-VIS spectrometer (Perkin Elmer: Lambda 35) in the wavelength range 200–600 nm for a different molarities[6]. Also we were changing the different parameters such as Time, Molarities, pH and Temperature and observed the effects of deposition parameters on the properties of thin films.

Result and discussion:

Film Structure Studies:

The X-ray diffractogram of CdS films show broadened diffraction profiles (figure 1). It is observed that XRD patterns show a preferred orientation along (002) plane. The grain size of the nanocrystalline films is estimated using the Scherrer formula[9],

$$D = K\lambda/\beta 2\theta \cos\theta$$

where K is a constant taken to be 0·94, λ the wavelength of X-ray used (λ = 1·54 Å) and β2θ the full width at half maximum of (002) peak of XRD pattern, Bragg angle, 2θ, is around 26·5°. The grain sizes were found to be within the range 08 to 113nm.

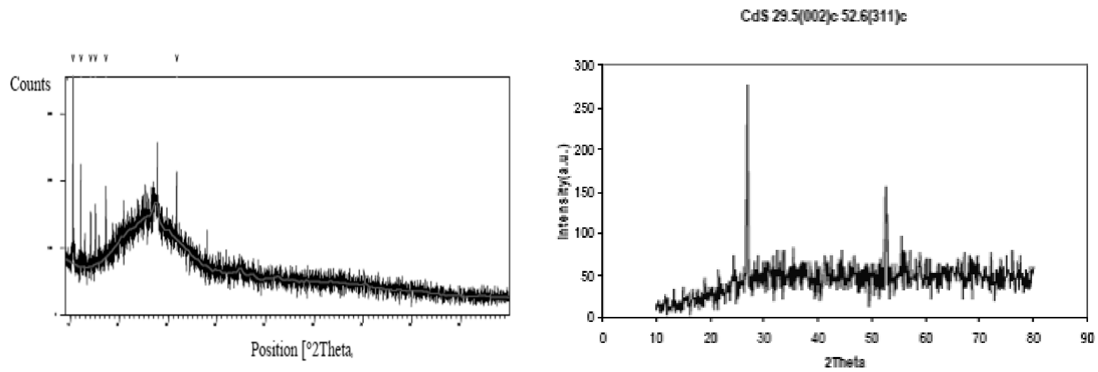

Figure1: XRD of CdS Nanocrystalline Film

SEM Studies:

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 2 shows the surface morphology of CdS thin films deposited at 345K temperature observed by SEM. From the micrographs, it is observed that the 'as-deposited' films are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. From the figure, we clearly observe the small nanosized grains engaged in a fibrous- like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. From these images, it can be seen that the grain sizes of the films are not uniform. Therefore, from Figure 2, we estimated the grain sizes from different grains within the films and found to be about 08 to 130 nm.

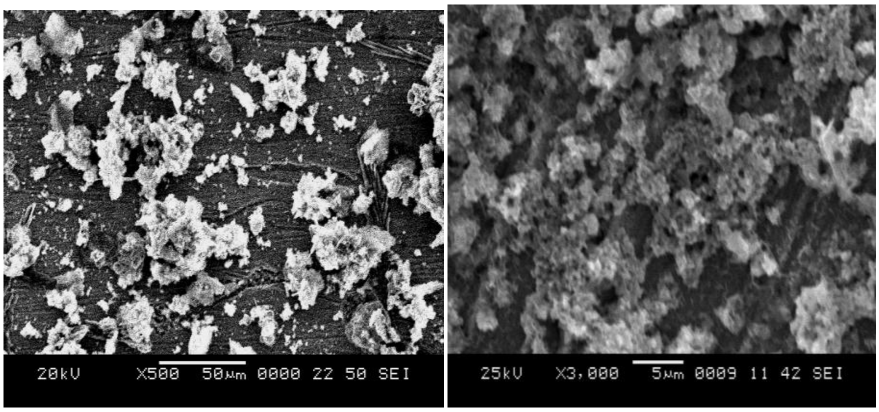

Figure2: (a) and (b) SEM of CdS nanocrystalline films at different magnitudes.

Effect of deposition temperature:

Effect of deposition temperature on grain size:

Figure 3 shows the variation of Grain Size as a function of film thickness at different deposition Temperature. Figure shows an increase in Grain Size as the film thickness increases at the temperature increases from 323^0K to 345^0K. Grain size variation with thickness of CdS films determined from the full width at half maximum of most intense X-ray diffraction peak using Scherrer formula.

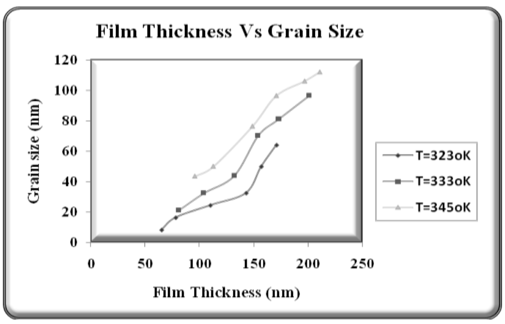

Figure 3: variation of Grain Size as a function of Film Thickness at different Deposition Temperature.

The chemical deposition of CdS at low temperature is based on the slow release of free Cd^{2+}. The CdS formed homogeneously throughout the solution grows into clusters where they aggregate into layers. At higher temperatures, the thermal dissociation of the complex and anion is increased and the rate of release of S^{2-} from thiourea is more and growth of cluster occurs. Thus, at higher temperature the CdS film thickness increases and corresponding the large grains are obtained[7]. At low temperature, degree of super saturation is higher and therefore the CdS film thickness and grain size tend to decrease. It can be seen from the figure the grain size increases from 8.11 to 112nm. The maximum film thickness 211nm and the grain size 112nm obtained at the highest temperature 345^0K.

Effect of deposition temperature on energy band gap:

Energy Gap variation with thickness of CdS films determined from the UV-VIS Spectroscopy study. To study the influence of deposition temperature on the energy band gap of CdS films, the deposition temperature was maintained at 323, 333 and 353°K.

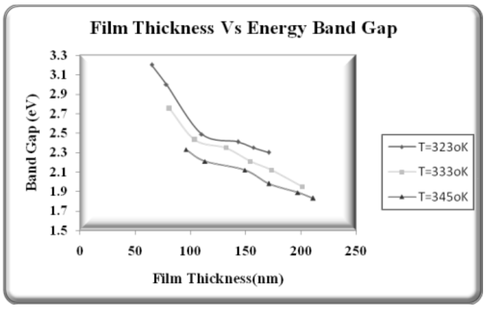

Figure 4: Variation of Energy Gap as a function of Film Thickness at different Deposition Temperature.

Figure 4 shows the variation of band Gap as a function of film thickness at different deposition Temperature. Figure shows a decrease in Band Gap as the temperature increases from 323^0K to 345^0K. As the deposition temperature is increased, the crystallite size of CdS films is increased resulting in to decrease in band gap[7,8]. The energy band gap decreases from 3.2 to 1.83eV when the temperature increases from 323 to 345°K. The average Energy gap of CdS 2.42eV is obtained from the UV-VIS study.

Effect of pH:

The morphology of film is often determined by the preparation methodology and the growth process relating to materials. The growth mechanism of CdS films by Chemical bath deposition (CBD) has been discussed by different authors. It is reported that the reaction rate often takes an important role on the morphology conversion in sulfide deposition. It is reported that the reaction rate and deposition rate of CdS are determined by parameters such as the proportion of the chelating agent, metal ions and the pH of the solution. Several legends have been utilized in the deposition of CdS, such as NH_3, triethanolamine, ethylenediamine, ethylenediaminetetraacetic acid, nitrilotriacetic acid (NTA), cyano-complex, citrato-complex, and more recently tartaric acid. However the usage of NH_3 was reported from last forty years. NH_3 act as a complexing agent as well as pH enhancer to the Cd salt solution. It is used to control the hydrolysis of the Cd^{2+} and S^{2-} in the solution. The Cd^{2+} exists predominantly in the form of ion complex $Cd(NH_3)^{2+}$, in the presence of sufficient NH_3. The rate of CdS formation is determined by the concentration of Cd^{2+} provided by $Cd(NH_3)^{2+}$ and the concentration of S^{2-} from the hydrolysis of $SC(NH_2)_2$. The overall reaction can be expressed in equation,

$$Cd(NH_3)_4^{2+} + S{=}C(NH_2)_2 \rightarrow CdS\,(s) + CH_2N{\equiv}N + 2NH_4 + 2NH_3. \quad (1)$$

Herein, the reaction rate which takes a crucial role in the property and morphology of CdS films is determined by the decomposing rate of the complex ions and the virtual concentration of free reactant ions.

So here we studied the effect of variation of legend concentration [pH] of the solution on the properties of samples like Film Thickness, Grain Size, Energy Band Gap and Deposition Rate etc. For this experiment, different concentrations of legends [NH_3] were added to the chemical bath, keeping all other parameters constant.

Effect of pH on Film Thickness:

To study the influence of pH on the film thickness of CdS films, the legend concentrations NH_3 is varied between 0.4 to 1M i.e. the pH is varied between 8, 9.5 and 11. Figure 5 shows the variation of Film Thickness as a function of deposition time at different legend concentration [pH] of the solution. It is clear from the figure that the Film thickness increases linearly with legend concentration [pH].

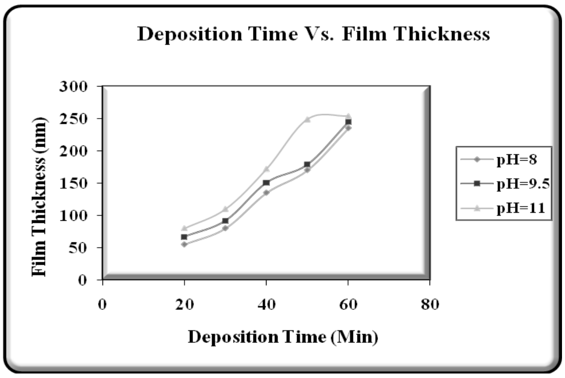

Figure 5: Variation of Film Thickness as a function of Deposition Time at different Legend Concentration [pH]

It is found that for low NH_3 concentration, the OH concentration is low, the Cd^{2+} ion concentration in the solution is more due to less complexation of Cd^{2+} ions, and the homogeneous process takes place at slow rate resulting in a lower terminal thickness. At high NH_3 concentration, availability of Cd^{2+} ions is low due to higher complexation, but S^{2-} ion concentration is more that gives higher deposition rate.

Effect of pH on Grain Size:

To study the influence of pH on the Grain size of CdS films, the legend concentrations NH_3 is varied between 0.4 to 1M i.e. the pH is varied between 8, 9.5 and 11. Figure 6 shows that the variation of grain size as a function of film thickness at different legend concentration [pH] of the solution.

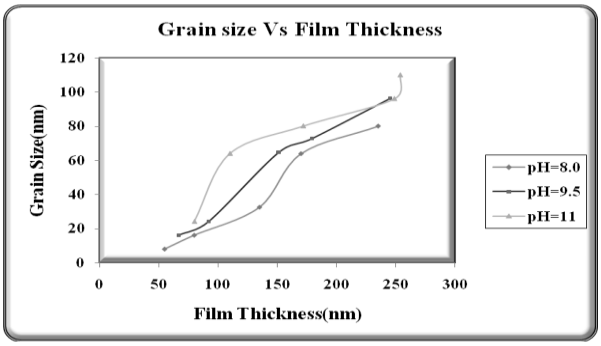

Figure 6: Variation of Grain Size as a function of Film Thickness at different Legend Concentration [pH]

It is clear from the figure that the grain size increases linearly with film thickness at pH of the solution from 16 to 110nm. The grain size of the crystallite (diameter D) was determined from the full width at half maximum (β) of the XRD planes and peaks by using the Scherrer formula.

It's worth noting that where the film thickness is maximum, the grain size is maximum. This may be attributed to lattice strain in films. The average grain size, in general, increases with increasing film thickness which in turn reduces the strain in the film (smaller the grain size more the stress in films). This actually agrees with our observation (Figure 6) i.e. where grain size increases when the thickness of the film increases.

Effect of pH on Energy Band Gap:

To study the influence of pH on the Energy Gap of CdS films, the legend concentrations NH_3 is varied between 0.4 and 1M i.e. the pH is varied between 8, 9.5 and 11. Figure 7 shows the variation of Energy Band Gap as a function of film thickness at different legend concentration [pH] of the solution.

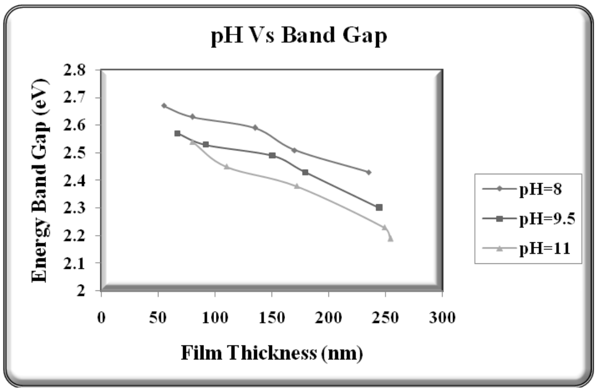

Figure 7: Variation of Energy Band Gap as a function of Film Thickness at different Legend Concentration [pH]

It is clear from the figure that the Energy gap decreases linearly with increasing film thickness at pH of the solution from 2.67 to 2.19 eV. The Energy Band Gap of the Samples was determined from the UV-VIS spectroscopy study and the absorption coefficient α (cm^{-1}). The average Energy gap is 2.45eV.

It's worth noting that where the film thickness is maximum, the grain size is maximum. This may be attributed to lattice strain in films. Rakhshani and Al-Azab [18] reported that such stress in CdS films causes a relative change in optical band gap $\Delta Eg/Eg$ that is proportional to the extent of strain in film (the more stress the higher Eg). They reported an inverse relationship between Eg and grain size. This actually agrees with our observation (figure 7) where band gap is maximum when thickness is minimum and minimum when thickness is maximum.

Conclusion:

The influence of the deposition parameters on the properties of thin films includes the deposition temperature, deposition time, reagent concentration and pH of the solution dependence of the film thickness, grain size and energy band gap. From the present study, it is observed that, the grain size and energy gap changes with deposition temperature. As the deposition temperature increases, the film thickness and grain size increases while the band gap decreases. Therefore it may be conclude that the growth rate depends on the deposition temperature. It is found that, the film thickness changes with deposition time, from the analysis of the study it is clear that, as the deposition time increases, the film thickness and grain size increases while the band gap decreases. After the study of effect of pH of the solution on the properties of samples like film thickness, grain size, optical band gap and deposition rate, it is observed that as the pH of the solution increases the film thickness and grain size increases while band gap decreases.

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