Influence of Preparative Parameters on Growth of CdS Thin Film for Photovoltaic Applications

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***Abstract*- Cadmium sulfide (CdS) thin films have been deposited by low cost chemical bath deposition technique (CBDT). The various preparative parameters such as speed of rotation, deposition time, deposition temperature, pH of bath, film thickness, growth rate, etc. have been studied. Prepared thin films were characterized by x-ray diffraction (XRD) and scanning electron microscope (SEM). All the films show pure cubic structure with nanometer grain size. The grain size obtained is in the range of 2.87nm to 3.75nm. The grain size obtained from XRD matches with the grain size obtained from SEM. All the physical conditions were kept constant while growing the films.**

Keywords: **Thin films, chemical bath deposition, cadmium sulfide, photovoltaic.**

I. INTRODUCTION

Cadmium sulfide (CdS) is an important II-VI semiconductor with a wide band gap which is suitable for applications in solar cell, solar selective coatings, UV light emitting diode, photocatalysis and phosphors in flat panel displays, photo detectors, laser diodes, etc. CdS is one of the most promising materials for hetero-junction thin film solar cells [1-4]. Wide bandgap CdS (Eg = 2.42eV) has been used extensively as a window layer with Cu_2S/CdTe/$CuInSe_2$ with efficiency 14-16%. Keeping these aspects in view, more attention is being given in producing good quality CdS thin films for comprehensive studies and their various applications.

Spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition and chemical bath deposition (CBD) are widely used techniques for deposition of thin films. Particularly CBD is attractive as a low cost and simple compared with other new and sophisticated methods. Also it is a controllable chemical reaction at close to room temperature. Another advantage of the CBD method with respect to the other techniques is that films can be deposited on different kinds, shapes and sizes of substrates [5-8].

In this work, various preparative parameters have been studied for the development of good quality CdS thin films. Also the structural and morphological characterization was reported, which is very important in many scientific, technological and industrial applications in the field of optoelectronic devices specially, photovoltaic applications.

II. EXPERIMENTAL DETAILS

The starting materials used for the preparation of CdS films of varying thicknesses were cadmium sulphate ($CdSO_4$) as a Cd^{2+} ion source and thiourea [$SC(NH_2)_2$] as an S^{2-} ion source. An alkaline solution of ammonia was used as a complexing agent. All the chemicals used were of analytical reagent grade. The process involving a controllable chemical reaction at a low rate, by adjusting the pH (between 8 & 10) and temperature (between 30ºC & 90ºC) of the working solution allows maintaining the stoichiometry constant for any ratio of anions and cations. After deposition the substrates were removed from the chemical bath and cleaned in DI water. The experimental arrangement consists of a special substrate holder, high torque motor, hot plate, temperature controller and magnetic stirrer to promote ion-by-ion heterogeneous growth on the substrate.

Commercial glass slides are used as substrate. Cleaning of substrate is important in deposition of thin films, cleaning steps and growth procedure is reported elsewhere[9-10,23]. The crystallographic structure of films was analyzed with a diffractometer (EXPERT-PRO) by using Cu-Kα lines (λ= 1.542Å). 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 (SEM).

The obtained thin films are optically semi-transparent, adherent and homogenous. The color of the film is yellowish, and it becomes yellowish – orange for higher deposition time.

III. RESULTS AND DISCUSSION

A. Influence of preparative parameters on growth rate

1) *Influence of speed of rotation:* Rotation of substrate may help to increase the deposition of CdS molecules on the substrates affecting the quality of the film. It was found that, the films formed on the stationary or low speed of substrates (40-

2) 50rpm) were porous, powdery, thick and non-uniform. Whereas at intermediate speed (70-80rpm) films were smooth, specularly reflecting, adhesive and uniform [5,11].

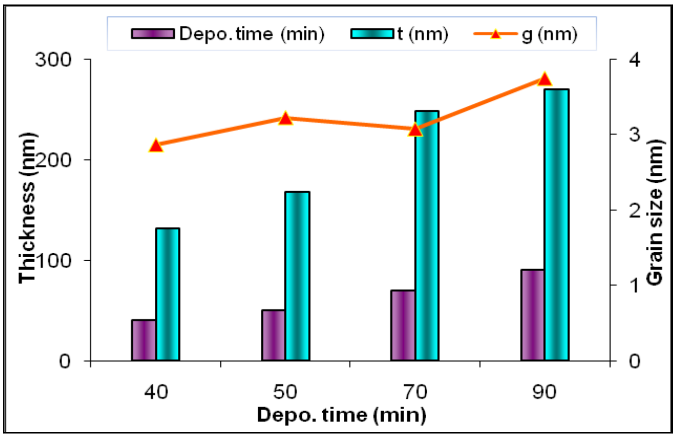

Fig. 1 Variation in film thickness & grain size with deposition time for CdS film

3) *Influence of deposition time on Film thickness:* Fig.1 shows the variation in film thickness and grain size with deposition time for the as-deposited CdS thin film. The plot shows that the thickness of film increases with deposition time. Here, the deposition process clearly shows two different growth phases: quasi linear phase and saturation phase. At the initial stage of deposition process the growth rate is high; it may be due to the high concentration of Cd^{2+} and S^{2-} ions available in the solution. As the time goes, more and more CdS is formed on the substrate and the solution becomes deficient in ions, giving lower rate of deposition and film attains terminal thickness. These results are in good agreement with the results observed by many researchers. [13-15].

The deposition time is optimized by measuring the thickness and growth rate of the deposited film for each 10 minutes during the process. It is observed that the film thickness increases up to the time 40-50 minutes; called the quasi linear phase, then the thickness remains nearly constant, known as saturation phase. The average growth rate obtained is 3.24nm/min.

4) *Influence of deposition time/film thickness on g*rain size: The variation of grain size with the film thickness is also shown in figure 1. The grain size of as-deposited nano-crystalline CdS films was estimated from XRD using Debye-Scherres's formula. It shows, as the film thickness was changed from 132 nm to 272 nm, the grain size was changed from 2.87 nm to 3.75 nm and the growth rate varies between 3.30nm/min and 3.02nm/min. Which is due to the presence of two different growth phases as quasi linear phase and saturation phase, concluded that with the longer deposition time; the increment in the grain size was less marked leading to average grain size. This indicates that for longer deposition time, a re-crystallization process takes place and not properly a grain growth [16-17]. The observed variation in film thickness, grain size and growth rate with deposition time is tabulated in table 1.

Table 1 Variation in film thickness, grain size and growth rate with deposition time.

Depo. time (min)	t (nm)	g (nm)	Growth rate (nm/min)
40	132	2.87	3.30
50	178	3.23	3.56
70	214	3.28	3.06
90	272	3.75	3.02

5) *Influence of deposition temperature on film thickness:* Fig. 2 shows the variation of film thickness with deposition time at different temperatures between 30^0C and 90^0C. It shows an increase in film thickness with the temperature except the case of 90^0C. Here, rise in the film thickness with the temperature may be due to the dissociation of the Cd complexes (i.e. ammonia and thiourea) and increase in the hydrolysis of thiourea $[SC(NH_2)_2]$ as the temperature increases [17-19].

This study reveals that the optimum temperature of chemical bath for growth of CdS films was 70±2^{0}C. It can be seen from fig. 2 that the average growth rate is high at 70+2^{0}C in comparison with other temperatures. The growth rate for lower temperatures is slow/less, whereas at 90^{0}C the growth rate is initially high, but it falls down/rapidly as the deposition time increases. This decrease in film thickness at higher temperature could be due to the decrease in ammonia concentration due to its high evaporation rate at higher temperature. The average growth rate at 70±2^{0}C is high (3.2 nm/min) and it is slow at room temperature (0.76 nm/min).

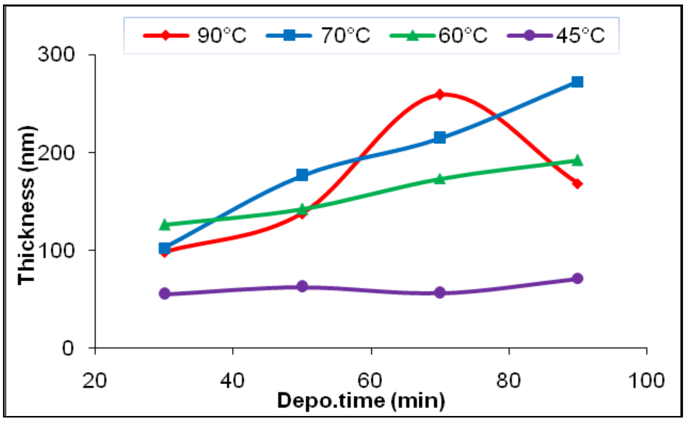

Fig. 2 Variation of film thickness with deposition time at different temperatures.

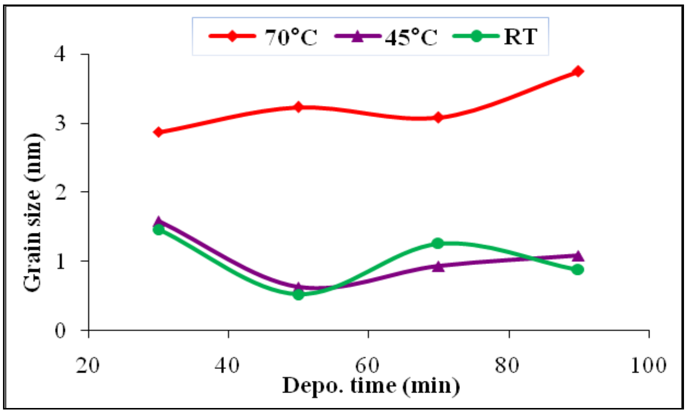

Fig. 3 shows the variation of grain size with deposition time at different temperatures.

6) Influence of deposition temperature on grain size: Fig. 3 shows the variation of grain size with deposition time at different temperatures. It clearly indicates the grain size of the film deposited at optimal temperature (70±2^{0}C) varies from 2.87nm to 3.75nm as the temperature varies from 30^{0}C to 90^{0}C. It shows the variation is uniform with larger grains, which helps to form a homogeneous, constant thickness buffer layer for solar cells.

Whereas at lower temperature degree of super saturation is higher and therefore the CdS thickness and grain size tend to decrease. It can be seen from fig 3, the average grain size at higher temperature is > 3.23 nm and it is ~ 1nm at lower temperatures [2].

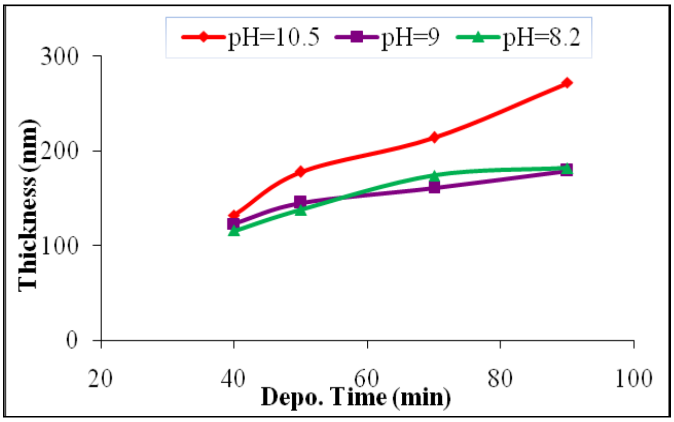

Fig.4 Variation of film thickness with the deposition time at different pH values.

*7) Influence of pH on film thickness:*Fig. 4 shows the variation of film thickness with the deposition time at different pH values. It clearly indicates the film thickness increases linearly with the pH value. It is also found that for low pH, the Cd^{2+} ion concentration in solution is more due to less complexation of Cd^{2+} ions and the homogeneous process takes place at slow rate resulting in a lower thickness. At high pH the Cd^{2+} ion concentration is less due to higher complexation but S^{2-} ion concentration is more that gives higher deposition rate [16-18, 22].

8) Influence of pH on grain size: Fig. 5 shows the variation of grain size with deposition time at different pH values. It is observed that the grain size increases linearly with film thickness or the deposition time, the grain size is larger at pH=10.5, which is the optimized value for chemical bath deposited CdS films. This increase in grain size improves the quality of film. However, for lower pH values, the grain size obtained is very low. The growth rate at optimal value of pH varies uniformly from 3.3nm/min to 3.0nm/min, which is good result for the development of homogeneous and uniform deposition of thin films. For lower pH the growth rate varies from 2.9nm/min to 2.0nm/min [16-18].

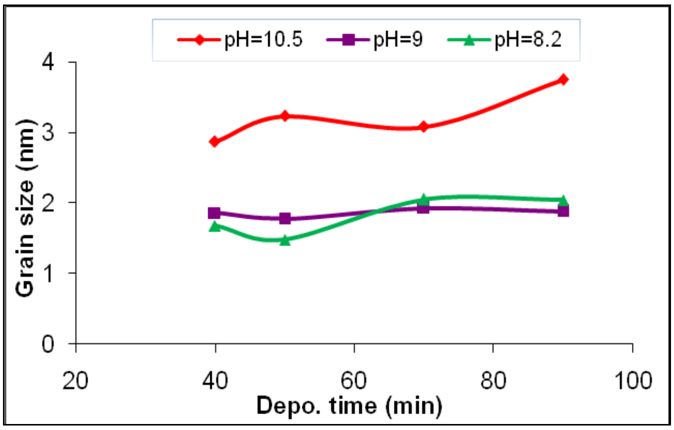

Fig. 5 shows the variation of grain size with deposition time at different pH values.

B. *Influence of preparative parameters on structural properties of CdS thin films*

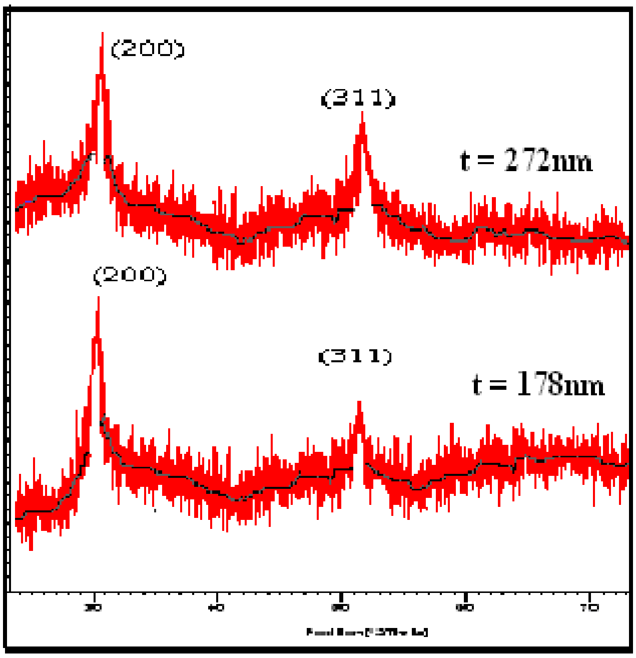

Fig. 6 XRD pattern of CdS films for thicknesses 178nm and 272nm.

Fig. 6 shows the XRD pattern of CdS films for different film thicknesses. The CdS film shows two dominant crystalline peaks (200) and (311). A comparison of the peak position (2θ values) of the JCPDS XRD spectra data for CdS suggests that the as-deposited CdS films have the cubic structure with the X-ray diffraction peaks corresponding to (200) and (311) peaks.

The average grain size (g) has been obtained from the XRD patterns using Debye-Scherrer's formula[10-11],

$$g = K\lambda / \beta \cos\theta \quad \ldots (1)$$

Where,

K = constant taken to be 0.94; λ = wavelength of x-ray used (1.542Å)
β = FWHM of the peak and θ = Bragg's angle

C. Influence of preparative parameters on morphology of CdS films

The surface morphology of CdS films at different magnitude and thickness are shown in fig. 7 analyzed by SEM technique. The SEM micrograph shows, some of the as-deposited films are not uniform throughout all the regions, but are without any void; pinhole or cracks and that they cover the substrates well. Small nano-sized grains engaged in a fibrous-like structure with smoother films are observed. The grain size obtained from SEM matches with the grain size obtained by XRD.

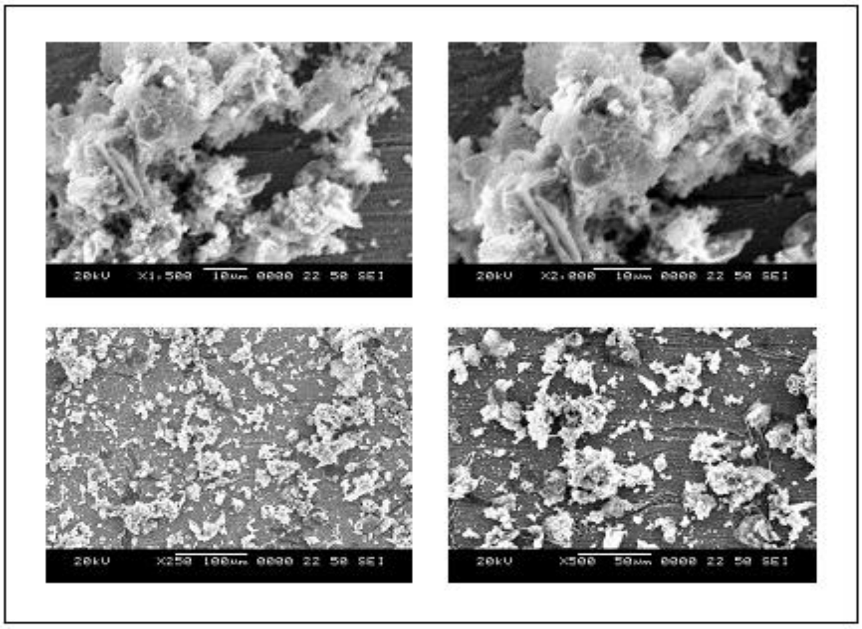

Fig. 7 SEM images of CdS films at different magnitude and thickness.

IV. CONCLUSIONS

The preparative parameters have been optimized for the growth of good quality, nanocrystalline CdS thin films. It is observed that the film thickness varies between 132 nm and 272 nm, the grain size between 2.87 nm and 3.75 nm and the growth rate varies between 3.30nm/min and 3.02nm/min. This study reveals the presence of two different growth phases as quasi linear phase and saturation phase. The structural and morphological study shows pure cubic structured, smoother and well adhered nanocrystalline films useful for various optoelectronic and photovoltaic applications.

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