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Properties of CdS Chemically Deposited thin films on the Effect of Ammonia Concentration

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Abstract : *The effect of ammonia concentration on electrical properties, optical properties and structural properties of chemical bath deposited (CBD) Cadmium sulphide (CdS) thin films has been revealed. The films were prepared by using cadmium acetate as cadmium ion (Cd^{2+}) source, thiourea as sulphur ion (S^{2-}) source and ammonia as the complexing agent. Ammonia concentration was changed from 0.1 M – 3.0 M. Ammonia concentration at 2.0 M uniform, dense and continuously coated films were obtained. Not only typical cadmium-pure but also unusual sulphur deficiency phenomena were observed for CBD CdS thin films. In the present investigation, the carrier concentration varied form $1.831X10^6cm^{-3}$ to $1.026X10^6cm^{-3}$ when ammonia concentration is changed from 0.5M to 2.5 M. The direct band gap energy at 0.5M is 1.92eV while at 2.5M is 2.65eV. The surface morphology of as deposited thin films is almost smooth and no grains were observed clearly at low molar concentration and predominant grains at the concentration of ammonia is 2.0M. By estimated Cd:S ratio value is found to be 1.04 by using EDAX. The thin film deposited at 2.0M concentration shows the highest degree crystallinity. The formation mechanism of the films with various ammonia concentrations is discussed.*

Keywords: *Ammonia effect, CBD-CdS thin films, Optical studies, SEM, XRD*

I. Introduction

A number of physical and chemical methods were employed for the fabrication of hetero-junction semiconductor thin films [1]. A wide variety of microstructures and consequently properties can be obtained by simply varying the deposition conditions during the growth of the thin film. Also, the thin film properties are strongly dependent on the method of **deposition,** the **substrate materials**, **temperature, rate of deposition** and the **background pressure**. The application and properties of the given material determine the most suitable technique for the preparation of thin films of the material. The different materials for the window layer, active layer and transparent conducting electrodes for solar cells were prepared and characterised. Various deposition techniques were employed for the deposition of these materials in thin film form and the structural and optical properties of these films were studied using different characterisation tools [2]. Among them chemical bath deposited (CBD) thin films have been reported in1960's – 1990's. Recent attention in chemical solution deposition of CdS nanocrystals, nanotubes etc [3]. In this deposition, high quality thin films of CdS were prepared effectively. CdS is a direct band gap of 2.42 eV II – IV semiconductor compound at room temperature and it has been studied for many years for various optoelectronic applications. Some applications of CdS thin films including photo detectors, piezoelectric transducers, bolo meters, solar cells, etc. [4]. CdS is one of the most investigated thin films for photovoltaic application in the last five decades. Literature gives that CdS exist in two crystalline forms [5] namely hexagonal phase and cubic phase . It is possible to grow CdS thin films in both these phases. Extensive researches have been done on the deposition and characterization of CdS semiconducting thin films due to their potential applications [6]. Direct band gap CdS thin films have been the subject of intensive research because of its intermediate band gap, high absorption coefficient, electron affinity, low resistivity, easy ohmic contact and finally the structure.

Deposition of CdS is based on the slow release of Cd^{2+} ions and S^{2-} ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrate suitably mounted in the bath. The slow release of Cd^{2+} is achieved by adding a complexing agent to the Cd salt. The S^{2-} ions are supplied by the decomposition of thiourea. It is observed that under a critical concentration ratio of species in solution, nanocrystalline CdS can be deposited [7]. Over the years, different cadmium sources have been used in this process, such as cadmium sulphate, cadmium acetate, cadmium iodide/nitrate, and cadmium chloride [6, 7]. The effect of Cd source on the film properties has drawn attention for some times. Kitaev *et al.* found that when $CdCl_2$ was used as a Cd source the CdS film thickness was moderate and higher than $CdSO_4$ or $Cd(NO_3)_2$ were used [8]. Similar results were obtained when Ortega-Borges and Lincot [9] studied the CdS growth rate dependence. Actually, CdTe is one of the most important semi conductors because of the direct band gap energy (1.45 eV), and the high conversion efficiency of solar light in electricity. This is normally prepared by sublimation, by heating CdTe powder of high purity at 700°C and deposited on a substrate at 500°C [10]. However, CdTe does not grow stoichiometrically, having slight Cd vacancies deficiency, consequently growing as p-doped [11]. Thus, a natural n-doped material is required as a partner to achieve a good junction with high efficiency in solar conversion. CdS thin films grown as n-type semiconductor due to the donor centres formed during deposition. CdS is normally prepared by a low cost and low temperature technique: the Chemical Bath Deposition (CBD).

CdS polycrystalline films possess a direct band gap of 2.42-2.45 eV at room temperature. Hani et al studied the effect of cadmium sources on film optical/electrical properties as well as film thickness, composition and crystal structure [12]. The literature also revealed that the influence of thiourea concentration and found that the growth rate was faster when the quantity of thiourea is much greater than cadmium chloride concentration in the solution. Moreover, the literature also reported the influence of ammonia concentration on CdS thin film thickness [13]. Several reports mentioned a modified CBD process for fabrication of large sized ZnS or CdS thin films [14]. Application of substrate vibration reduced the formation and residence gas bubbles on the glass substrates during CBD of ZnS or CdS, resulting in the growth of smooth, uniform and compact thin films with a quality high enough for use in large sized solar cells. In our work with Chemical Bath Deposition (CBD) of CdS, it was observed that the ammonia concentration in the CBD solution also played an important role in the characterization of CdS thin films. In this work, we investigated the influence of ammonia concentration on the electrical, optical and structural properties of CdS thin films. We present the results of the CdS thin films using UV-Vis absorption, X-ray diffraction, Scanning Electron Microscope (SEM), and Energy Dispersive X-ray Spectroscopy (EDAX). The detailed study on the effect of ammonia concentration on the physical properties of CBD-CdS thin films is mentioned.

II. Experimental Details

In the present work, the experimental setup for the fabrication of CdS thin films by CBD consists of magnetic stirrer and an aqueous solution used for preparation of Cd and S ions. The thin films were growing on 25.4 mm X 76.2 mm X 1.5 mm microscope glass slides. Before the deposition, the glass substrates were cleaned in an ultrasonic cleaner using acetone and alcohol and they were soaked in a chromic acid cleaning solution for 20 min. Further, they were cleaned ultrasonically in an isopropyl alcohol. Finally, they were washed in deionised water and dried by flowing with dry nitrogen for 30 min. The initial pH was adjusted with pH meter until to obtain the pH=10.0 value. For this present work, cadmium acetate is the cadmium source and ammonium acetate serves as a buffer. Ammonia is the complexing agent and thiourea is the source of sulphur.

The temperature of the mixer was maintained at constant temperature, 70°C and also all these processes were carried out at this temperature only. The growth of CdS film occurs either by ion-by-ion condensation of Cd and S ions on the substrate surface or by the adsorption of colloidal particles of CdS [15]. The glass substrates were cleaned thoroughly and inserted in the deposition cell containing the required amount of de-ionized water. As-grown CdS layers are hard and look **yellowish, shiny** and have a **smooth surface**. The last steps were washing in deionised water and air drying. The glass slides are taken out from the solution after end of the film deposition. The prepared slides were rinsed with 10% ammonia solution, ultrasonically cleaned with deionised water for a few minutes to remove the white and adherent precipitates during deposition and blown dry nitrogen gas. The prepared thin films were examined and characterised by means of UV-Vis absorption spectrophotometer, SEM and XRD.

III. Results And Discussion

Chemical Bath Deposition (CBD) of high quality CdS thin films are based on the chemical precipitation of CdS in bath. The precipitation control can be achieved by controlling the free cadmium metal ions concentration; generally ammonia is used as a complexing agent. The cadmium salt produces free cadmium ions (Cd^{2+}) through a dissociation reaction. The cadmium ions then complexing with ammonia form the dominant tetra-amino-cadmium complex ion $Cd(NH_3)_4^{2+}$. On the surface, the $Cd(NH_3)_4^{2+}$ ions react with hydroxide ions to form the absorbed dihydroxo-diamino-cadmium complex. This complex then reacts with thiourea to form the absorbed metastable complex $[Cd(OH)_2(NH_3)_2SC(NH_2)_2]$. Finally, CdS is formed and a new surface site is generated through decomposition of the absorbed metastable complex [16]. The reaction of this process is given below:

$$Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow CdS + CH_2N_2 + 2H_2O + 4\ NH_3 \qquad (1)$$

Table 1: Concentration and volumes of reactants in the CBD deposition bath

Exp. No.	$Cd(CH_3COO)_2\ 2H_2O$ 30 ml (M)	$(NH_4)_2(CH_3COO)_2\ 2H_2O$ 30 ml (M)	$SC(NH_2)_2$ 20 ml (M)	$NH_3\ H_2O$ 26 ml (M)
1.	0.004	0.04	0.05	0.1
2.	0.004	0.04	0.05	0.25
3.	0.004	0.04	0.05	0.5
4.	0.004	0.04	0.05	1.0
5.	0.004	0.04	0.05	1.25
6.	0.004	0.04	0.05	1.5
7.	0.004	0.04	0.05	2.0
8.	0.004	0.04	0.05	2.5
9.	0.004	0.04	0.05	3.0

The Table 1 gives the concentration of ammonia and volumes of reactants to form the CdS thin films in the CBD bath. In the table, experiments 1 and 9 did not have any deposition. In the experiments 2-8, the film growth rate shows behaviour of super saturation. The observation made in the first 20 min was that the fastest growth obtained in experiment 4 with ammonia concentration 1.0 M. It is observed that the growth decreases with the increase of the concentration of ammonia from 1.0 M. In the experiment 8, the deposition is quite slow when compared to experiment 3. Exp. 3-8 show the growth rates of depositions which gives the thickness, super saturation of film deposition surface, uniformity of film colour and grain geometry among all the tests. During CBD deposition, the temperature is kept constant at 70° C and it was observed that the growth increases with the increase of the concentration of ammonia and decrease of the concentration of thiourea [16]. Unlike other deposition methods, the growth rate in the CBD technique cannot be kept constant during film deposition. Fig. 1 shows the growth rate decay with the increase of the ammonia concentration and this is one of the parameters that influence the characterization of polycrystalline thin films.

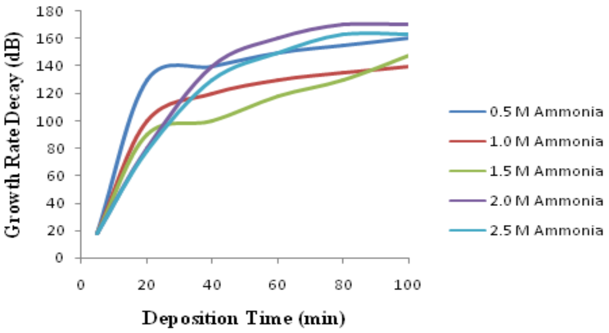

Figure1. Variation of the growth rate Vs deposition time

The result shown in Fig.1 is consistent with that reported by Q Q Liu *et al* [17]. They studied the dependence of film growth rate as a function of ammonia concentration from 0.5 M to 1.0 M and found that the film growth rate was peaked at 1.5 M of concentration of ammonia. Their work also showed that the ammonia concentration of 0.6 M was sufficient to bind Cd^{2+} into cadmium tetra amine complex ions $Cd(NH_3)_4^{2+}$ needed for slow growth rate as described in Eq. (1). On the other hand, when ammonia concentration is sufficiently low, the product of $[Cd^{2+}]$ and $[OH^-]$ was greater than the solubility product of $Cd(OH)_2$ (1.2×10^{-14}) given in the Eq.(2):

$$Cd^{2+} + OH^- \leftrightarrow Cd(OH)_2 \qquad (2)$$

The ammonia concentration varied from 0.1 to 3.0 M. When 0.1 M of ammonia was added to the solution for the first experiment as shown in Table 1, no film was formed on the substrate even after a deposition time of over 3 hrs. In experiments 2-9, the ammonia concentration was increased from 0.25 to 3.0 M, and films were obtained on the glass substrate and the colour of the film changed from **light yellow to deep yellow (Fig.2a)**. However, when the ammonia concentration was equal to or exceeds 2.5 M, nothing was deposited on the substrates except much yellow powder was produced in the bath after CBD deposition.

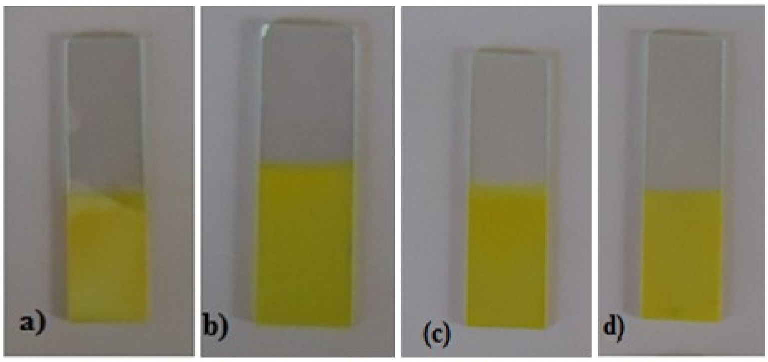

Figure 2. Deposited CdS Thin Films a) 0.5M b) 1.0M c) 1.5M d) 2.0M

Type of conductivity of the thin films, mobility and carrier concentration of the as-doped films is determined by using Hall Effect experiment. The Hall coefficient was calculated for all the investigated samples. The sign is negative and charge carriers are due to electrons. Therefore, the results showed that the prepared thin films of CdS had negative (n-type) conductivity. From the observations, it is observed that the Hall coefficient is found to be increased from 340.8 cm^3/Coulomb to 608.4 cm^3/Coulomb as the ammonia concentration is increased from 0.5 to 2.0 M and constant at 2.5 M. The mobility of the CdS thin films is calculated from the Hall coefficient [18]. It is found to be increased from 1.363 cm^2/V-S to 4.58 cm^2/V-S as the concentration is increased from 0.5 to 2.0 M, and at 2.5 M concentration the mobility is also same i.e., 4.58 cm^2/V-S. It is observed that the carrier concentration decreases with the increase of ammonia concentration. The carrier concentration at 0.5 M is 1.8316X10^{16} cm^{-3} and at 2.5 M is 1.026 X10^{16} cm^{-3}. This is because the S: Cd ratio increases in the same order. The excess content of Cd means that either interstitial Cd ions or S vacancies exist in the film, act as donor and results in decrease in the carrier concentration of the films [19].

The optical band gap energy and absorption coefficient (α) of the chalcogenides thin films was determined using UV-VIS spectrophotometer in the wavelength range of 350 to 850 nm at room temperature. In the present work, the photons of selected wavelength are directed at the sample, and the relative transmission of various photons observed.

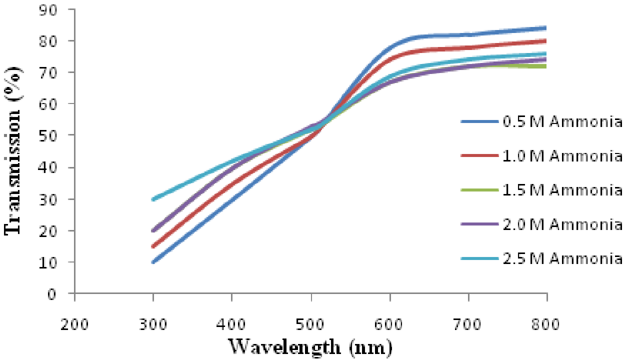

Figure 3. Transmittance spectra of CdS films

Fig. 3 shows the optical transmission spectra of CdS thin films at different ammonia concentrations in the wavelength range of 350 to 850 nm. All the films have a high transmission in the wavelength range of above 550 nm. The percentage of transmittance was about 70% at near IR region.

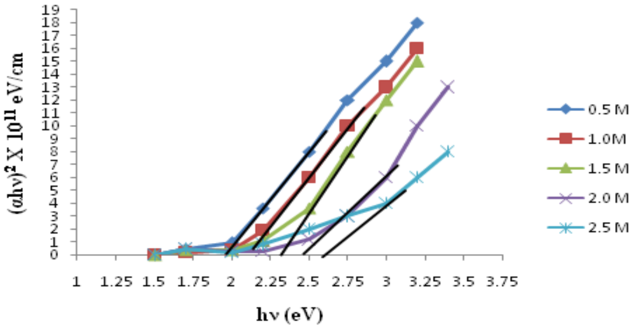

Figure 4. $(\alpha h\upsilon)^2$ **Vs** $(h\upsilon)$ **plots of CdS films**

The optical band gap energy (E_g) of the CdS thin films have been determined by extrapolating the linear portion of the curves of $(\alpha h\nu)^2$ Vs $(h\nu)$ as shown in Fig. 4. From the figure, it is observed that all the films have direct band gap values of 1.92 eV to 2.65 eV for the films of ammonia concentration in the range of 0.5 M to 2.5 M. These values are found to be smaller than the values reported previously which were in the range of 2.42 eV to 2.62 eV [20]. The deviation of the energy gap values from the standard bulk value of 2.42 eV is due to the use of greatly wide range of ammonia concentration in the present CBD process [21,23]. Hence, the CdS thin films can be considered to be good for use as visible transmitting thin films since the range of band gap for visible transmitting film is 1.5 to 3.0 eV.

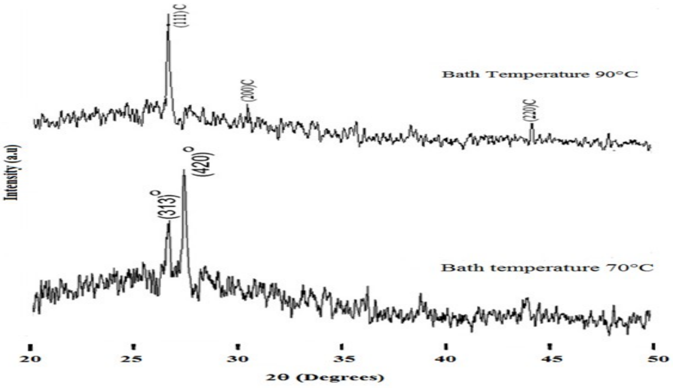

Figure 5. X-ray diffraction pattern for the CdS thin films with the temperature 70°C

Fig. 5 shows the XRD patterns for CdS thin film with the bath temperature 70°C and 90°C. The observation was that at bath temperature 70°C consists of a primitive lattice structure with the orthorhombic phases and this is matched with the JCPDS reference No. 47-1179 [22]. From the fig. 5, a peak from orthorhombic structure, wurtzite, was observed at 26.81° corresponding to the (3 1 3) reflection and 27.42° corresponding to the (4 2 0) reflection. When temperature is changed from 70°C to 90°C, the angle of reflections shifted and orthorhombic phases have changed into cubic phases. The observed major reflection for the film with bath temperature 90°C is identified as per the standard JCPDS card No. 89-0440 (cubic-C). 2θ values of diffraction peaks observed are 26.56°, 30.59° and 43.73° which corresponding to reflections from (1 1 1), (2 0 0) and (2 2 0) planes of cubic (zincblende) CdS, respectively. The sudden change in phase from orthorhombic to cubic is due to the reduction of sulphur content in high temperature.

Fig. 6 displays SEM images of CdS thin films recorded at different concentrations of ammonia. It is observed that the surface morphology of as-deposited films is almost smooth and no grains are observed clearly at low molar concentration (Fig.6.a). The size of the grain in the deposited films has been observed with the increase in the concentration of ammonia. Thus, the change in the surface features and the improvement in the

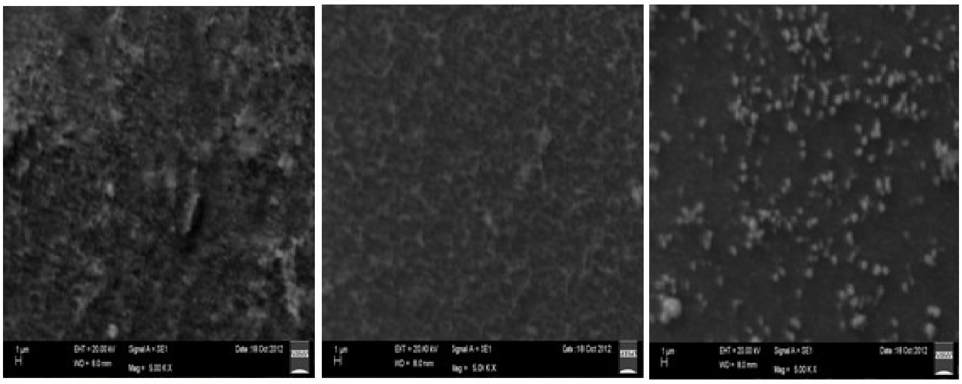

Figure 6. SEM images a) 0.5M b) 1.0 M c) 2.0 M

Grain growth are clearly noticed from the SEM images of the film deposited at a higher concentration. The films deposited at 2.0 M concentration of ammonia are having predominant grains (Fig. 6. c). The developments of uniformly distributed roughly spherical grains grown perpendicular to the surface of the substances are observed for the films at 2.0 M. It is noticed that the film surface is pin-hole free texture without any micro cracks [24]. The estimated average grain size is observed to be increasing with the increase of the concentration of ammonia. The estimated mean size of the grain at molar concentration is about 0.4 µm .

In the present work, the compositional analysis of the films were carried out by Energy dispersive analysis of X-ray (EDAX) spectroscopy using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. The EDAX spectra of CdS thin films doped at different ammonia concentration are shown in Fig. 7.

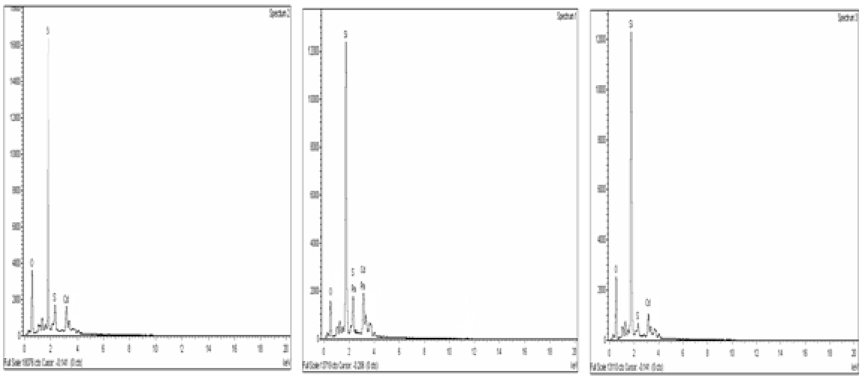

Figure 7. EDAX spectra a) 0.5 M b) 1.0 M c) 2.0 M

The EDAX spectrum displays the characteristic peaks corresponding to the binding energy state of Cd and Oxygen ions. No other impurity peaks are detected in the spectrum which is an indication of the chemical purity of the sample. The estimated Cd to S ratio value is found to be 1.04 (Cd:S = 50.04:49.96). No, detectable change in the computational changes are observed during the increase of ammonia concentration. Since the films are deposited on Silicon substrate, a predominant peak corresponding to silicon is observed in the spectra. For our calculation, we have not uniformly considered these Si peaks [24].

IV. Conclusion

The energy gap of as-doped CdS thin films in the present study shows that the energy gap is decreased from 2.7497 eV to 2.2122 eV when concentration is increased from 0.5M to 2.0M and becomes constant above 2.0M. The deviation of these values from the standard bulk value of 2.37 eV is explained on the basis of the small grain size. The difference between E_g values of our samples and the earlier reports can be attributed to various grain sizes of thin film due to the use of the greatly wide range of ammonia concentration in our CBD process. The Hall coefficient is a characteristic of the material from which the conductor is made. Also, the Hall coefficient depends on the type of the charge carriers that constitute the current. The Hall coefficient was calculated for investigating all samples. The sign is ***negative*** and charge carriers are due to ***electrons***. Therefore, the results showed that the prepared thin films of CdS had negative (n-type) conductivity. It is observed that all the films have direct band gap values of 1.92 eV to 2.65 eV for the films with ammonia concentration in the range of 0.5 M to 2.5 M. These values are found to be smaller than the values reported previously which were in the range of 2.42 eV to 2.62 eV. The deviation of the energy gap values from the standard bulk value of 2.42 eV is due to the use of greatly wide range of ammonia concentration in the present CBD process. Hence the CdS thin films can be considered to be good for use as visible transmitting thin films since the range of band gap for visible transmitting film is 1.5 to 3.0 eV. It is observed that the surface morphology of as deposited films is almost smooth and no grains are observed clearly at low molar concentration. The size of the grain in the deposited films has been observed in the increase of concentration of ammonia. Also, the films deposited at 2.0 M concentration of ammonia are having predominant grains. The EDAX spectrum displays the characteristic peaks corresponding to the binding energy state of Cd and Oxygen ions. No other impurity peaks are detected in the spectrum which is an indication of the chemical purity of the sample. The estimated Cd to S ratio value is found to be 1.04 (Cd:S = 50.04:49.96). No, detectable change in the computational changes were observed during the increase of ammonia concentration.

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