

Optical and Structural Properties of CdS Thin Films Synthesized by CBD using Different Complexing Agents for Photovoltaic Application

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Abstract—CdS thin film, one of the most promising window layer candidates for solar cells have been successfully deposited using Chemical Bath Deposition (CBD) on glass substrates. In order to have a better control on the quality of the deposited films three different complexing agents TEA, Ammonia, and Ammonia+EDTA were used during the growth of the CdS thin films. The as-deposited films were characterized by using XRD, SEM, EDAX, UV-VIS spectroscopy and PL. The transmission spectra of the deposited films show a maximum transparency of 70-80% at wavelength ~ 500 -530 nm. The optical band gap of the as-deposited films was found to be in the range of (2.8-3.5 eV). The XRD pattern of the three samples confirms that the films were polycrystalline in nature showing peaks for both hexagonal and cubic crystals. The SEM Images of the grown films shows a bunch of scattered particles with sizes less than 0.1 micron and their conglomerates up to 3 μ m. The PL studies of the as-deposited films show a broad spectrum along with distinct luminescent red band near 1.5 eV showing crystallographic defects and deficiency of S^{2-} . A green luminescence band near 532 nm was also observed in the PL spectra showing the existence of Cd interstitials.

Keywords: CdS, CBD, Complexing Agents, Band Gap, Crystallographic Defects.

1. INTRODUCTION

In recent years, there is an increasing interest in developing the thin film solar cells as one of the alternative energy sources because of their environmental friendly nature. II-VI semiconductor thin films have been extensively investigated due to their low production cost [1] and potential application in various photovoltaic and optoelectronic applications [2-7]. Cadmium Sulphide (CdS) is the most widely studied Chalcogenide with band gap of 2.4 eV (in bulk) [8] and can exist in cubic or hexagonal forms. The application of CdS for their ability to absorb the blue portion of the solar spectrum as window layer in high efficiency heterojunction thin film solar cells has recently draws lot of attention towards this material [9].

Different methods have been used for the deposition of CdS thin films such as sputtering [10], vacuum evaporation [11], spray pyrolysis [12], electrodeposition [13], molecular beam epitaxy [14] and chemical bath deposition [15,16]. Among these various techniques CBD is simple method with economical advantages and capability of uniform, adherent and large area deposition [17,18]. In CBD the control of film thickness and deposition rate can be done by varying the solution p^H , temperature and reagent concentrations. The photoelectronic properties of CdS thin films are greatly influenced by both native and foreign imperfections. Impurities are generally added in the lattice during the film preparation which can cause considerable change in electrical and optical properties without causing a major change in crystal structure [19]. Most CBD reactions are carried out in alkaline solution. To prevent the precipitation of metal hydroxides, a complexing agent is added. The complexing agent also reduces the concentration of free metal ions, which helps to prevent rapid bulk precipitation of the desired product. While a complexing agent is added to the Cd salt, it forms some Cd-complex species, which upon dissociation give a very small amount of Cd^{2+} ions [20].

The objective of the present work is to study the effect of TEA (sample1), Ammonia (sample2), and Ammonia + EDTA (sample 3) as complexing agents for the deposition of CdS thin films on glass substrates by chemical bath deposition and its impact on structural and optical properties of the films for photovoltaic application. The structural and optical properties of the films were characterized with the help of SEM, XRD, EDX, PL and UV-Vis spectroscopy.

2. EXPERIMENTAL DETAILS

2.1. Preparation of the substrate

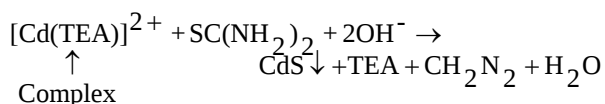
The CdS films were deposited on optically plane glass micro slides cut in to suitable size of ~ 3 cm x 2.5 cm. The glass

slides were cleaned in an ultrasonic bath by degreasing them with teepol followed by immersion in dilute nitric acid solution for about 1 hour. After taking out from the acid solution the glass slides were finally rinsed with distilled water and dried in a chamber by blowing hot air.

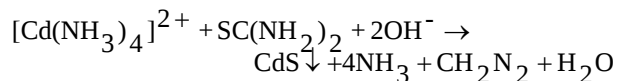
2.2. Synthesis of CdS and deposition of CdS thin film

The CdS thin films were deposited on glass substrate by CBD using the chemical precursors cadmium sulfate (CdSO_4) as a source of Cd^{2+} ion, Thiourea [$\text{CS}(\text{NH}_2)_2$] as a source of S^{2-} ion and (1) TEA (2) Ammonia (3) Ammonia + ethylenediamine-tetraacetic acid (EDTA) as complexing agent. 100 ml 0.25M cadmium sulfate and thiourea solution is prepared by dissolving CdSO_4 and [$\text{CS}(\text{NH}_2)_2$] salt respectively in deionized water under magnetic stirring.

For synthesis of CdS with triethanolamine (TEA) [$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$] as complexing agent, 25 ml of CdSO_4 solution prepared was taken in a beaker and about 4 ml of TEA solution was added to it drop by drop to maintain a PH 10 under magnetic stirring. After stirring for about 20-30 minutes 25 ml of thiourea solution was added to the mixture at room temperature. As the reaction precedes the color of the initially transparent solution become yellowish and at this point the cleaned glass substrates were immersed vertically in to the CBD solution with the help of substrate holder. The set up was then left overnight in a dark place at room temperature. Finally the deposited CdS thin films were cleaned in an ultrasonic bath with distilled water. The possible chemical reaction with TEA as complexing agent is as follows-



The same procedures were adopted for synthesis of CdS thin films by using Ammonia (NH_3) and Ammonia + (EDTA) [$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$] as complexing agents except that in case of ammonia about 10.5 ml of ammonia solution was added drop by drop to the 25 ml CdSO_4 solution in order to keep P^{H} at 10 and make the solution transparent under stirring. Where as in case of ammonia + EDTA as complexing agent, 25 ml, 0.125 M EDTA solution and subsequently 7 ml of ammonia was added to the 25 ml CdSO_4 solution drop by drop to maintain the P^{H} at 10. The possible chemical reaction with ammonia as complexing agent is as follows-



While the strong complexing agent (ammonia + EDTA) is used, the Cd^{2+} ions first forms complex with EDTA as $[\text{Cd}(\text{EDTA})]^{2+}$ which then slowly dissociates to release Cd^{2+} ions. The Cd^{2+} ions thus released again forms complex with ammonia and finally CdS gets deposited on glass substrates as described above.

2.3. Characterization Detail

The crystalline phases of CdS thin films were investigated with Rigaku Miniflex X-ray diffractometer facilitated with intense $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The scanning was done at a step size of 0.05° and at continuous scanning rate of $1^\circ/\text{min}$. For elemental compositions of the samples Energy dispersive X-ray analyses (EDX) of the deposited films were studied and for surface morphology of the films SEM pictures were taken at an operating voltage of 20kV with a JEOL JSM (Model 6390LV) scanning electron microscope (SEM) equipped with INCAx-Sight (Oxford instruments) EDX detector. For the optical properties of the films UV-vis absorption spectra were obtained in Shimadzu UV-Visible Spectrophotometer (UV-2600) in the wavelength range 200 to 1100 nm at a medium scanning rate by subtracting the absorption of the glass substrate which was taken as reference. Photoluminescence spectra were examined in a Horiba Jobin Yvon, FluoroMax-4 spectrofluorometer at excitation wavelength of 325 nm.

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction (XRD) analysis

The X-ray diffraction pattern of the as-deposited CdS thin films with TEA (sample 1), Ammonia (sample 2), and Ammonia + EDTA (sample 3) as complexing agents is as shown in the Fig. 1. The diffraction spectrum of the samples shows that the films are polycrystalline in nature showing a mixed phase of cubic and hexagonal structures (JCPDS 65-3414, 80-0019, 89-2944). However they shows a preferential orientation towards hexagonal structures. Similar type of polycrystalline behavior of the chemically deposited CdS thin films were reported by many authors [21-23]. According to Kaur et al. [23], the structure of chemically grown CdS is dominated by the deposition mechanism used. CdS film deposited with ammonia + EDTA as complexing agent shows a better degree of crystallinity than the other two samples.

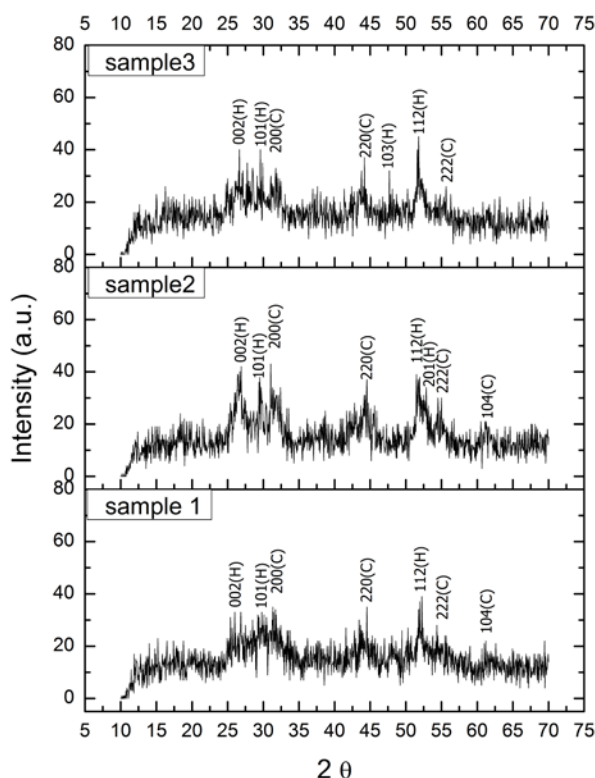


Fig. 1: XRD pattern of the three samples

3.2. SEM analysis

SEM is a useful technique to study the surface morphology of the films as it gives microscopic information of the surface. The SEM images (Fig. 2) reveals that the deposited films are rough and has quite a lot colloidal particles or clusters. Among all the three samples the sample 3 with ammonia+EDTA shows a slight better surface morphology. The Images of the grown films shows a bunch of scattered particles with sizes less than 0.1 micron and their conglomerates up to 3 μm .

It was reported that the deposition of CdS thin film by CBD takes place via competition between two different processes i.e., clusters-by-clusters deposition via CdS colloidal particles formed in the solution, and ions-by-ions deposition via metastable complex comprising Cd and S agents [24]. If the effective concentrations of Cd^{2+} and S^{2-} are high than that of CdS particles then ions-by-ions deposition is dominant in CBD process otherwise the clusters-by-clusters deposition become dominant. The clusters-by-clusters deposition is highly undesirable which yields in powdery and non-adherent films whereas the ions-by-ions deposition leads to uniform films. In future we will extend our study by controlling the different reaction parameters during CBD process to have uniform deposition of the films.

Fig.2. SEM image of the three samples

3.3. Energy dispersive X-ray analyses (EDX)

Fig. 3 shows the energy dispersive X-ray spectra of the deposited films. They show the presence of Cd and S in the films with their percent of composition in the inset of it. One can clearly observe the deficiency of S^{2-} in the deposited films. The other peaks present in the EDX spectra may be due the presence of other impurities.

3.4. UV-Vis Spectroscopic study

Study of materials by means of optical absorption and transmission provides a simple method for explaining some features related to band structure of the materials. The wavelength dependence of optical absorbance and transmittance in the UV-Visible region of the as-deposited thin films are shown in Fig. 4. The films show an optical transmittance of 70-80 % in the 600-800 nm range which is high enough for photovoltaic application. The absorption spectra also reveal the occurrence of sharp absorption edges at wavelengths 411 nm (sample 1), 476 nm (sample 2) and 461 nm (sample 3). Sample 1 with TEA shows a better transmission in visible region.

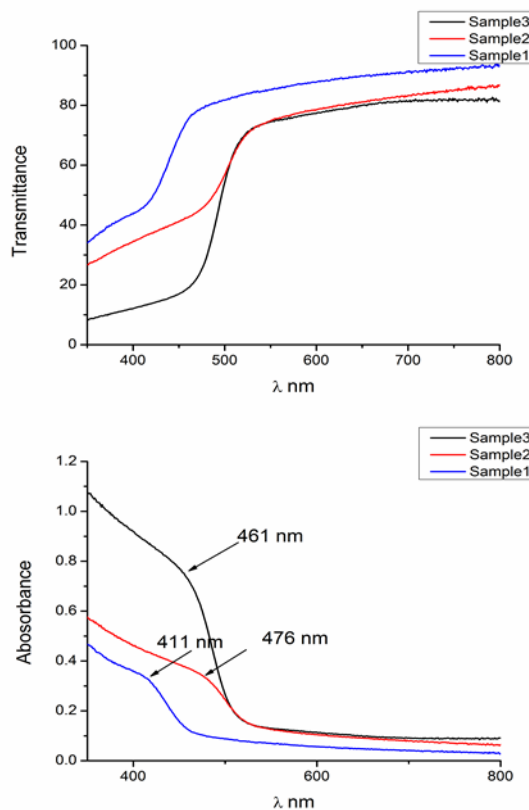


Fig. 4: Transmission and absorption spectra of the CdS films deposited with different complexing agents

The band gaps (E_g) of the films were measured using Tauc relation [25] given by

$$\propto h\nu = K(h\nu - E_g)^m$$

where $h\nu$ is the photon energy, K is a constant and m is a power factor which assumes values $\frac{1}{2}$, 2, 1.5, and 3 for allowed direct, allowed indirect, forbidden direct and indirect transitions respectively. The absorption coefficient (α) can be calculated from the optical transmittance

spectra using the following equation

$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right)$, where t is the thickness and T is the optical transmittance. The extrapolation of the straight line portions of the $(\alpha h\nu)^2$ vs $h\nu$ plots for zero absorption coefficient value gives a measure of the direct energy band gap (E_g) value. Fig. 5 shows the $(\alpha h\nu)^2$ vs $h\nu$ plots for the as-deposited CdS films. The band gap energies of the films were found to be 3.5, 2.82 and 2.84 eV respectively. The shift in the observed values from the band gap value of bulk CdS may be due to the variation of the film stoichiometry, grain size, presence of impurities etc. More detailed analysis is necessary to confirm this fact.

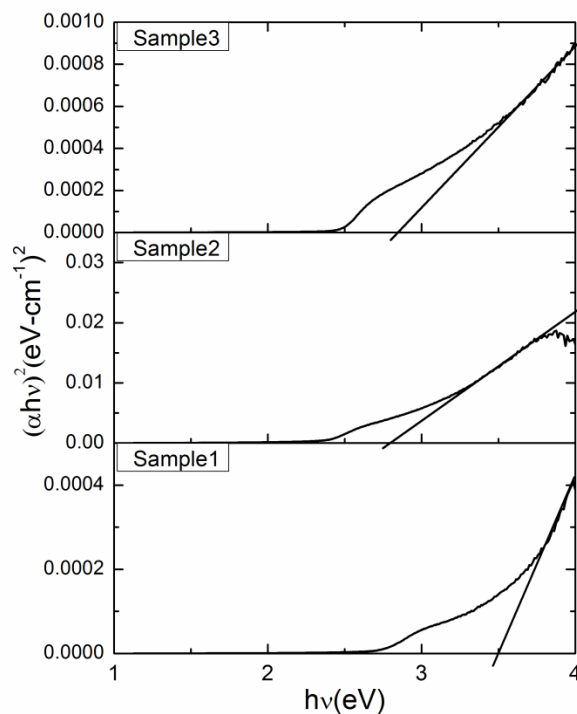


Fig. 5: $(\alpha h\nu)^2$ vs $h\nu$ plot for band gap calculation

3.5 Photoluminescence (PL) study

Photoluminescence analysis of the CdS deposited over glass substrate was performed to analyze the occurrence of the defects in the crystal. The photoluminescence (PL) spectra of the CdS films deposited at different substrate temperatures, as shown in Fig. 6, was measured at room temperature in which

the excitation wavelength of 325 nm is chosen for all samples and recorded in a wavelength range 400-850 nm. It is found that the group of peaks centered on 700 nm and 820 nm forms the dominant red band in CBD-CdS films. Red luminescence in polycrystalline CdS films was reported by many authors [26,27,28]. It is believed that the red luminescence is caused by transitions of electrons trapped in surface states to the valence band [29] and results in the accumulation of crystallographic defects in CdS films grown at low deposition temperatures. In general, the red emission band is associated with the involvement of sulfur vacancies in radiative recombination [29]. The existence of less significant yellow and green luminescence bands in the PL spectra may be attributed to the formation of deep donor Cd states. The small green luminescence band observed for all samples at 532 nm is due to the transition from donor states near conduction band to the valance band i.e due to donor acceptor transition. The broad PL spectra also confirm the S vacancies. These vacancies act as a trap for excited electrons and can extract electrons from valence band.

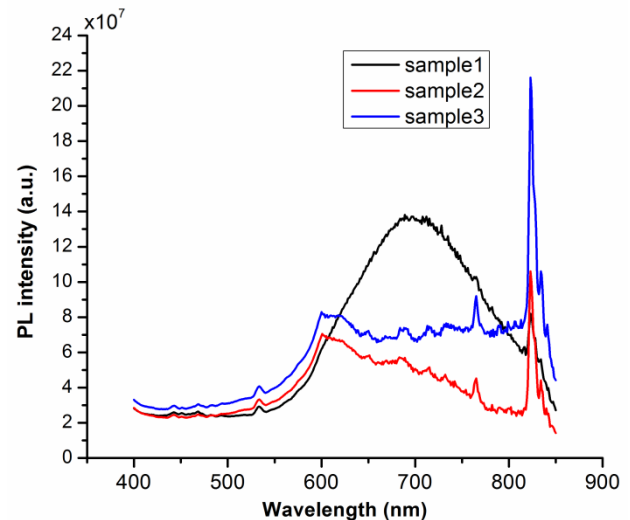


Fig. 5: PL spectra of the CdS thin films

4. CONCLUSION

CdS films were deposited on glass substrates at room temperature by chemical bath deposition with TEA, ammonia, and ammonia + EDTA as complexing agents. The XRD spectrum of the as-deposited films indicates the polycrystalline behavior with mixed cubic and hexagonal phases of CdS in the deposit. The EDX study confirms the presence of Cd and S in the deposited films. From the percentage composition it was confirmed that the films were sulfur deficit. The same was supported by our PL studies showing dominant red luminescence band. From the UV-Vis spectroscopic study, the optical band gap energy of the deposited films was found in the range of 2.8-3.5 eV, which is greater than the 2.4 eV value for bulk CdS. This difference

may be due to the defects in the crystal structure, grain size, presence of impurity sites etc. in the as-deposited films. The same fact was supported by the observed absorption edges in the absorption spectra. With an observed transparency of 70-80 % in the visible range and band gap values, the films are suitable for use as a window layer in photovoltaic devices. Though from our present study no concrete statement can be drawn about the suitability of the complexing agent, but the study reveals that films formed with TEA and ammonia + EDTA as complexing agent showed better result than with ammonia only. Further the film with TEA showed a greater transparency.

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