VNU Journal of Science, Mathematics - Physics 24 (2008) 119-123

# Growth of CdS thin films by chemical bath deposition technique

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Received 29 April 2008; received in revised form 04 September 2008

**Abstract.** The structural, morphological and optical properties of CBD deposited CdS thin films have been studied by varying the processing parameters and the Cd/S ratio of the starting precursors in order to better understand the growth conditions. The films were characterized by X-ray diffraction, SEM, Raman, and photoluminescence spectroscopy. XRD patterns show that as-deposited CdS films were polycrystalline. The grain size are increasing with increasing the Cd/S ratio and/or the deposition time. The fact that the symmetry-dependent Raman bands of the CdS thin films under investigation did not appear indicates the poor preferential orientation of as-deposited CdS crystallites, which is in accordance with the measured XRD pattern.
*Keywords:* CdS thin film; chemical bath deposition.

## 1. Introduction

Chalcogenide semiconductor thin films are being intensively investigated for low-cost photovoltaic and optoelectronic applications [1,2]. Cadmium sulfide is commonly used as n-type semiconducting layer for heterojunction thin films solar cells. Multilayered CdS films can be employed in the manufacture of the optoelectronic devices.

The deposition of CdS film has been explored by various techniques, such as thermal evaporation [3], sputtering [4], molecular beam epitaxy [5], spray pyrolysis [6], chemical bath deposition [7]. Chemical bath deposition is a method of growing thin films of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 100°C. It has been identified as a low process suitable for the preparation of large area thin films [8]. In this study, we report the preparation of CdS thin films onto microscope glass slides by CBD method. The structural, morphological and optical properties of the as-prepared films are investigated under various processing conditions.

## 2. Experimental detail

### *2.1. Synthesis*

Reagents used for the deposition include cadmium sulfate $CdSO_4$, ammonia water $NH_4OH$ and thiourea $CS(NH_2)_2$. All reagents are of analytical grade and used without further purification. The

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glass substrates were soaked in 5% HF solution, left then for 20 minutes under ultrasonic duty in isopropyl alcohol, washed with distilled water and finally dried in the air.

The typical procedure for the film growth is described as follows. Drop by and by 25 % $NH_4OH$ into a 100 ml beaker containing 25 ml of 1M $CdSO_4$ solution until the initially formed white precipitate is completely dissolved. The clean substrates are mounted vertically in the bath beaker in such a way that an approximately 5 mm thick layer of deposition bath separates the substrates each other and the wall of the bath. 25 ml of 1M $CS(NH_2)_2$ then is poured into the mixtures. Finally, the distilled water is gradually added to make the volume up to 100 ml. The deposition is made at 60°C under magnetic stirring for all samples. To vary the composition of the films, different concentrates of the $CdSO_4$ and thiourea are used.

The CdS formation is detailed in the following series of chemical reactions:

$$CdSO_4 + NH_4OH \leftrightarrow Cd(OH)_2 + (NH_4)_2SO_4$$

$$Cd(OH)_2 + 4NH_4OH \leftrightarrow Cd(NH_3)_4^{2+} + 2OH^- + 4H_2O$$

$$H_2N-\overset{\overset{S}{|}}{C}-H_2N \leftrightarrow H_2N-\overset{\overset{SH}{|}}{C}=NH$$

$$H_2N-\overset{\overset{S}{|}}{C}=H_2N+OH^- \leftrightarrow H_2N-\overset{\overset{OH}{|}}{C}=NH+SH^-$$

$$Cd(NH_3)_4^{2+} + SH^- = CdS\downarrow + NH_4^+ + 3NH_3$$

CdS thin films formed on the substrates are optically transparent, adherent, homogeneous and yellowish in colour without any powdered precipitation.

After deposition, the substrate were removed from the chemical bath, cleaned thoroughly in distilled water and dried in the air at room temperature. The deposition time is chosen to be 2 h for the bath containing 25 ml of 1M $CdSO_4$ solution and 9 h for the bath with 3 ml of 1M $CdSO_4$ solution.

### *2.2. Characterization*

The X-ray diffraction (XRD) patterns of the as-deposited CdS thin film were recorded in a D5005 Brucker X-ray diffractometer with $CuK_\alpha$ radiation $\lambda$ = 1.54056°A, operated at 40 kV and 40 mA. The scanning speed was 0.030 °/s in the $2\theta$ range from 5° to 65°. The scanning electron microscopy (SEM) images of the obtained CdS thin films were taken on a JEOL5410. The Raman spectroscopy measurements were made a LABRAM-1B (Jobin Yvon Spex) using 180 grooves/mm diffraction grating, D 0.3 filter and a He-Ne laser of the wavelength 632,817 nm as a light source. The photoluminescence spectra at room temperature of the investigated samples were measured on a FPL-322 spectrofluorometer (Jobin Yvon Spex) using a Xenon400 lamp as the excitation light source.

## 3. Results and discussion

### *3.1. X-ray Diffraction (XRD) Analysis*

The typical diffractogram of the as-deposited CdS thin films is shown in Fig. 1. XRD analysis indicated that the film are polycrystalline with less pronounced orientation along a c-axis ((002) direction) perpendicular to the substrate plan. The degree of the preferential orientation may be increasing with the post-deposition annealing temperature. Although the (002) orientation is not very

pronounced, in comparison with [9] (inset in Fig. 1), the obtained CdS thin film have only the cubic structure (zincblende type). One can see the observed diffraction peaks at the $2\theta$ values of 26.5, 30.8, 43.9, and 52.1° correspond to reflections from (111), (200), (220), and (311) planes of cubic CdS [10].

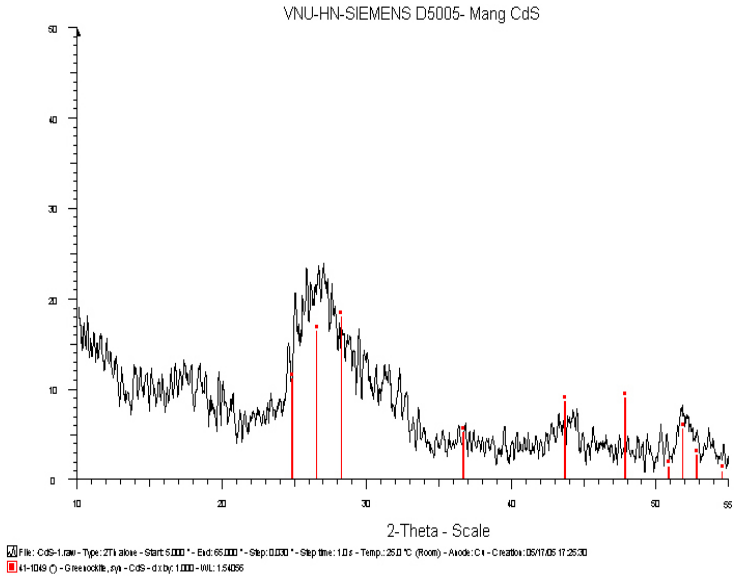


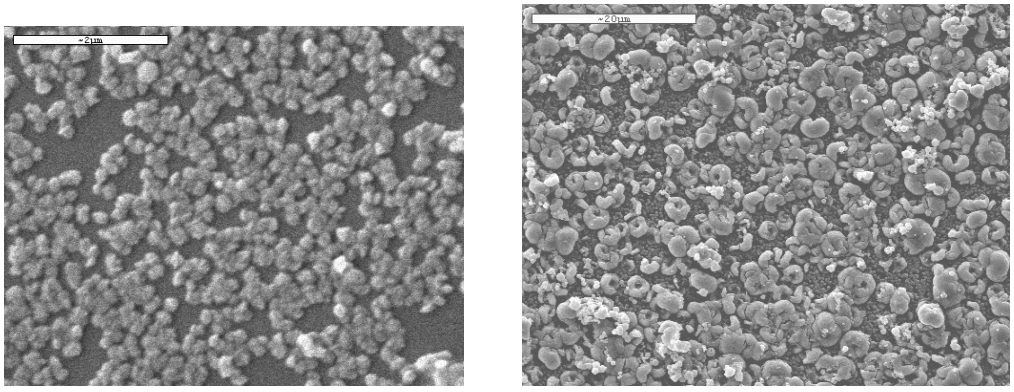

Fig. 1. Typical X-ray diffractogram of CdS thin films as grown. Inset shows XRD pattern of the CdS thin films reported in [9].

Table 1. Standard ASTM card for CdS [10]

| $2\theta$ | d($A^0$) | hkl |
|---|---|---|
| 24.828 | 3.580 | 100 |
| 26.449 | 3.360 | 002 $\alpha$ - CdS |
| 28.216 | 3.159 | 101 |
| 36.648 | - | 102 |
| 43.735 | 2.067 | 110 $\alpha$ - CdS |
| 51.875 | 1.761 | 112 $\beta$ - CdS |

*3.2. Scanning Electron Microscopy (SEM) Imaging*

To study the homogeneity of the films and to compare one with another, the surface investigations in the SEM imaging were performed. The most homogeneous film (Fig. 2a) were obtained in the bath with 3 ml of 1M $CdSO_4$ solution for 9 h. In this case, the slow deposition rate led to the small uniform grain size and shape and the good adhesion to the substrate. On the films deposited in the bath containing 25 ml of 1M $CdSO_4$ solution for 2 h (Fig. 2b), one can see many scattered particles about 2 microns in diameter and their conglomerates up to 4 $\mu$m. The heterogeneity increase with increasing the Cd/S ration in the bath due to the violent precipitation.



(a) (b)

Fig. 2. SEM images of CdS thin films prepared in the bath with 3 ml of 1M $CdSO_4$ solution for 9h (a) and with 25 ml of 1M $CdSO_4$ solution for 2h (b).

*3.3. Raman spectroscopy*

The typical Raman spectrum of the as-prepared CdS thin films is displayed in Fig. 3. The related researches [6] show that Raman spectra of CdS thin films strongly depends on the film grain size and thickness. One can see only a relatively large band centered at ca. 300 $cm^{-1}$. This peak can be identified as the first overtone of the longitudinal optical phonons (1LO) by comparing with CdS Raman spectra obtained in [10]. The fact that the characteristic Raman bands at 500$cm^{-1}$ and 1100$cm^{-1}$ corresponding to the symmetry-dependent normal oscillations did not appear indicates the poor preferential orientation of as-deposited CdS crystallite, which is in accordance with the XRD pattern shown in Fig. 1.

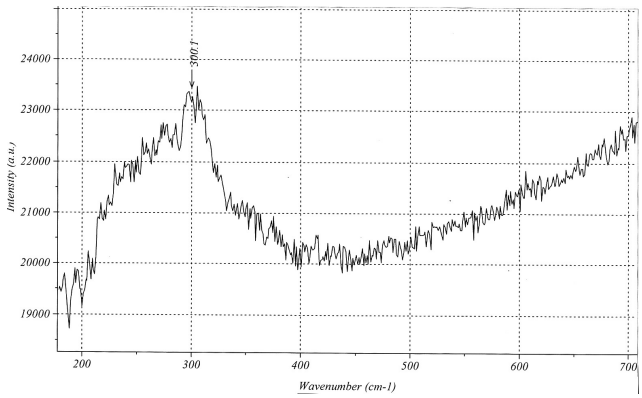



Fig. 3. Typical Raman spectrum of the as-prepared CdS thin films.

*3.4. Photoluminescence spectra*

Preliminary investigations show that photoluminescence (PL) spectra of the obtained CdS thin films have two distinct bands at ca. 465 nm and ca. 549 nm, respectively. The measured PL excitation spectra corresponding to the two emission bands allows to fix the excitation wavelength at ca. 369 nm suitable to the CdS thin films under consideration. The typical PL spectrum is presented in Fig. 4.

As reported in [6], the PL spectra of thin films growth by the spray pyrolysis technique consist of a characteristic red band centered at about 698 nm. The apparition of this red band may be assigned to the excess of $Cd^{2+}$ which leads to increase the defect quantity in the films, while the chemical bath deposited CdS thin films reported in [4] has the PL band around 1.72 eV (the red band) due to sulfur vacancies, without the corresponding exciton band. Yet, in any cases, the PL spectra of the CdS thin film under investigation has no red emission band. One might say that the obtained films are more or less stoichiometric. However, the Energy Dissipative X-ray (EDX) characterization is to be investigate for further detailed information in this regard.

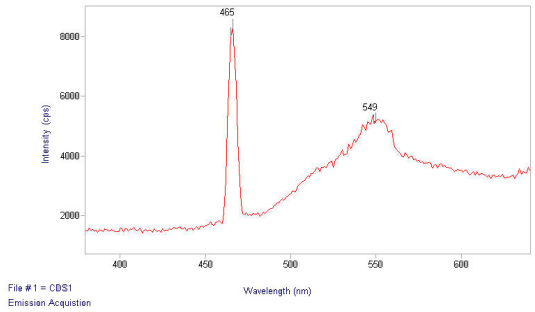



Fig. 4. Typical photoluminescence spectrum of the as-prepared CdS thin films.

## 4. Conclusions

In this work, we show a route to the deposition of CdS thin film on glass substrates using CBD technique from heated solutions with various cadmium concentrations. The system of precursors consists of cadmium sulfate and thiourea in basic ammonia water. The as-deposited films have been characterized by XRD, SEM and optical spectroscopic methods (Raman and PL). The films are of cubic (zincblende) type polycrystalline, stoichiometric but not very highly (002)-oriented. The influence of the Cd concentrations on the films morphology is also reported. The obtained results can be useful for the started point for synthesis and processing of multilayers films solar cells applications. Further investigation to determine electrical properties of the films are in progress.

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