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# CHARACTERIZATION OF CHEMICALLY DEPOSITED CADMIUM SULFIDE THIN FILMS

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Cadmium sulfide (CdS) thin films have been deposited on glass/conducting glass substrates using low-cost chemical bath deposition method. The deposited films have been characterized using various techniques in order to optimize growth parameters. It has been confirmed by X-ray diffraction measurement that the deposited layers are mainly consisting of CdS phase. The PEC measurements indicate that the deposited CdS layer is $n$-type in electrical conduction, and optical absorbance measurements show that the band gap is 2.42 eV for as-deposited film and 2.27 eV upon heat treatment for one hour in air ambient. Both atomic force microscopy and scanning electron microscopy measurements indicate the formation of pinhole free and smooth surface of CdS films of nanosized grains. The electrical resistivity is also observed in the order of $104^4$ $\Omega$ cm and decreases as temperature increases.

*Keywords*: Chemically bath deposited CdS; film growth; structural and optical properties.

## 1. Introduction

In recent years, research has done on into the area of preparation and characterization of cadmium sulfide (CdS) thin films. CdS is an important II–IV semiconductor compound, which has a wide energy gap, a good transparency in region of visible light, and excellent photoconductive property. It has been used in a lot of applications including electronic and optoelectronic devices such as solar cells,[1,2] photoconductor, and diode laser.[3] Being an $n$-type semiconductor material, it has been observed that CdS is an excellent heterojunction solar cell partner of $p$-type narrow band gap semiconductor materials like CdTe or $CuInSe_2$, where CdS layer

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is used as the window material. Thin films of CdS can be prepared by different techniques such as chemical bath deposition (CBD),[2,4–6] electrodeposition,[7] laser ablation,[8] sputtering,[9] vacuum evaporation,[10] etc. Among these various techniques, CBD is the most efficient method because it is a simple and low-cost method that produces uniform, adherent, and reproducible large area thin films. Moreover, CBD gives the best photoconductivity and morphological properties such as roughness and pinhole density when compared to films processed by other techniques.[11] Using a CBD-CdS as a buffer layer, efficiency exceeding 17% has been achieved in $CuInSe_2$ based thin film.[5]

In this report, we investigated chemically deposited CdS films onto the fluorinated tin oxide (FTO)-coated glass substrate from an aqueous alkaline medium using thiourea as a sulfur ion source. The characterization of the film including structural, compositional, optical, electrical, etc. is presented. The aim of this work is to use $n$-type CdS window materials in CdTe or $CuInSe_2$-based solar cell structures. The results will be presented in this paper using observed experimental data.

## 2. Experimental Details

### 2.1. *Substrate preparation*

Poor adhesion and nonuniform films are common problems when depositing films onto smooth surface. So in the deposition of thin film, substrate cleaning is very important since the contaminated surface provides nucleation sites facilitating the growth which results in nonuniform film growth. Before depositing CdS layers, FTO/glass substrates were boiled using soapy distilled water for around 20 min and then rinsed with distilled water. To eliminate grease and other oily substances, substrates were rinsed with acetone, and then boiled in distilled water for about 20 min, and finally dried in air prior to film deposition.

### 2.2. *Deposition of CdS thin films*

The deposition of CdS layers was carried out on FTO-coated glass substrates. The chemicals used for the preparation of thin film were analytical grade of purity more than 99.9%. A typical bath contains 0.02 M $CdCl_2$, 0.07 M $NH_4Cl$, and 0.14 M thiourea and dissolved in distilled water. Ammonia solution was used to adjust the pH value of the bath to 10.7. The substrates were kept vertically in the bath containing reaction mixture. The solution was maintained under constant magnetic stirring during the deposition at a temperature of 263 K and deposition was allowed for 40 min. At the end of the deposition process, the films were taken out from the bath and immediately cleaned in hot distilled water and finally dried in blowing air. After complete drying, the films were annealed at 673 K for 1 h in air ambient in order to enhance their structural property. The thickness of the film was found to be approximately 0.36 $\mu$m.

### 2.3. *Characterization techniques*

Photoelectrochemical (PEC) cell was used for determining electrical conductivity type of CdS layers where a CdS/NaCl electrolyte (solid/liquid) junction was illuminated by white light. The optical absorption spectra were estimated in the wavelength range 400–1100 nm using a UV-1201V spectrophotometer, Shimadzu, Japan. The thickness of the film was determined using data pack in spectrophotometer. The crystallography study of chemically deposited CdS film was examined using Philip PW-3040 X'Pert PRO X-ray diffractometer using Cu $K_\alpha$ radiation ($\lambda_\alpha = 1.54056$ Å) in the $2\theta$ ranges from 20°–90° operated at 40 kV and 30 mA. Scanning electron microscopy (SEM) (Model S-3400N Hitachi, Japan) has been studied in order to obtain the microstructure of the film attached with an energy dispersive X-ray analysis (EDXA) analyzer for quantitative measurement of the sample stoichiometry. The atomic force microscopy (AFM) was used to study the surface morphology and surface roughness of the film using Nanoscope III (Digital Instruments) scanning probe microscope. The dc electrical resistivity was measured using a two-probe method in the temperature range 273–373 K. A laboratory dc power supply (Topward-3303D, China), and digital multimeter (Fluke 15B, China) were used for measurement. The area of the film was defined (1.44 $\text{cm}^2$) and aluminum coating with silver paste was applied to ensure good ohmic contacts to the film. The CdS layers were etched in a dilute $NaOH+Na_2S_2O_3$ solution to remove any contaminants from the surface, prior to aluminum coating.

## 3. Results and Discussions

### 3.1. *Growth mechanism of CdS*

The deposition of CdS film takes place in an aqueous alkaline bath containing cadmium salt along with complexing agent $NH_4OH$ that allows controlling $Cd^{2+}$ concentration. The process based on magnetic stirring is applied to promote slow release of $Cd^{2+}$ and $S^{2-}$ ions into solution which then grow on an ion-by-ion basis on the substrate mounted in the solution. When the ionic product of $Cd^{2+}$ and $S^{2-}$ exceeds the solubility product of $K_{\text{sp}} = 7.1 \times 10^{-28}$ of CdS then the deposition occurs.[12]

The main chemical reaction from the cadmium side is as follows[13]:

$$NH_4{}^{+} + OH^{-} \leftrightarrow NH_3 + H_2O\,, \tag{1}$$

$$Cd^{2+} + 4NH_3 \leftrightarrow Cd(NH_3)_4{}^{2+}\,. \tag{2}$$

The presence of ammonium salt, however, promotes the forward reaction in Eq. (1). This then reduces the pH or $OH^-$ concentration in the reaction and then insoluble $Cd(OH)_2$ species is formed. Since the product of $[Cd^{2+}]$ and $[OH^-]$ is greater than the solubility product of $Cd(OH)_2$, ($K_{\text{sp}} = 10.2 \times 10^{-14}$)[12] in excess of $NH_3$ concentration, this gives rise to the formation of the complex cadmium tetraamine complex ion $Cd(NH_3)_4{}^{2+}$ shown in Eq. (2). As the ammonia complex undergoes thermal decomposition, $Cd^{2+}$ ions are released in the bath. At the same time, thiourea hydrolysis in the alkaline solution to give $S^{2-}$ ions as

$$(NH_2)CS + OH^- \leftrightarrow SH^- + H_2O + H_2CN_2\,, \tag{3}$$

$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O\,. \tag{4}$$

The formation of CdS films can take place from the bath containing $Cd^{2+}$ and $S^{2-}$ ions as

$$Cd(NH_3)_4{}^{2+} + S^{2-} \leftrightarrow CdS + 4NH_3\,.$$

The appearance of dense yellowish precipitation in the solution seems to indicate that the film formation comes from the adsorption and aggregation of the colloidal particles formed in the solution.

### 3.2. *Electrical conductivity type*

The PEC cell was used to identify the electrical conductivity type of CdS layers. PEC cell was made in NaCl solution in which two electrodes were partially immersed. One electrode is CdS-deposited FTO and the other is a pure carbon rod and these electrodes were externally connected to a digital voltmeter. Figure 1 shows a typical set-up for PEC cell measurement. The CdS-deposited FTO forms a solid/liquid Schottky junction at CdS/NaCl solution. The voltage under dark and illuminated condition was measured in order to estimate the open circuit voltage. Few hundred millivolts is an indication of the formation of a good Schottky junction at the CdS/NaCl junction. The polarity of the voltage indicates the determination of conductivity type of CdS layer. Table 1 shows the obtained results of both as-deposited and annealed CdS samples. It is clear from the result that both as-deposited and annealed CdS samples are $n$-type in electrical conductivity and upon annealing in air enhance the conversion efficiency.

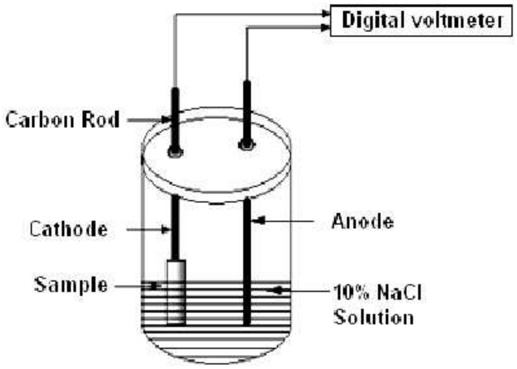

Fig. 1. Experimental set-up for Photoelectrochemical (PEC) cell measurement.

Table 1. The summary of typical PEC measurements for as-deposited and annealed CdS layers grown on FTO substrates.

| Sample | $V_{\text{dark}}$ (mV) | $V_{\text{light}}$ (mV) | $\Delta V$ (mV) | Comments |
|---|---|---|---|---|
| As-deposited 1 | −230 | −531 | −301 | *n*-type |
| As-deposited 2 | −210 | −483 | −273 | *n*-type |
| As-deposited 3 | −216 | −485 | −269 | *n*-type |
| Annealed 1 | −235 | −570 | −335 | *n*-type |
| Annealed 2 | −220 | −520 | −300 | *n*-type |
| Annealed 3 | −230 | −530 | −300 | *n*-type |

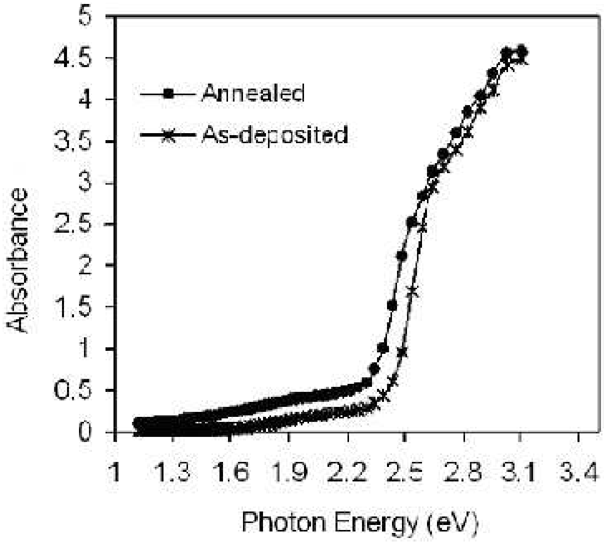

Fig. 2. Variation of absorbance of CdS thin film (for both as-deposited and annealed) with photon energy.

### 3.3. *Optical absorption spectra*

Optical absorption spectra were recorded for both as-deposited and annealed CdS layers in the wavelength range 400–1100 nm. Using absorption data, the band gap energy ($E_g$) of the CdS film was estimated by plotting $A^2$ against the photon energy ($h\nu$) as shown in Fig. 2. The linear nature of the plot indicates that CdS is a direct band gap material. Extrapolating the linear portion gives the value of direct band gap. The band gap energy ($E_g$) of as-deposited thin film was found to be 2.42 eV, which is equal to the bulk (standard) value for hexagonal CdS at room temperature.[2,5,14,15] Annealing the sample at 673 K for 1 h in air caused a decrease in band gap to be 2.27 eV. This band gap shift is also clearly indicated by the yellow color appearance for as-deposited layers and orange color appearance for annealed one. The shifting of band gap can be due to change in film thickness, grain sizes or even the presence of different phases upon annealing.[2,5,15,16]

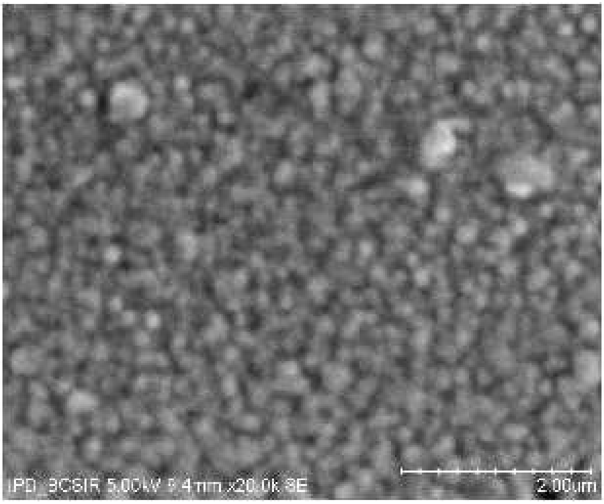

Fig. 3. The SEM image of as-deposited CdS thin film (20,000×).

## 3.4. *Morphological study*

### 3.4.1. *Scanning electron microscopy (SEM)*

A micro-structural study of CdS thin film is performed using the SEM. Figure 3 shows the SEM image of as-deposited CdS film on FTO-coated glass substrate. SEM image shows that the substrate is well covered with the deposited material without cracks and pinholes. The approximate average cluster sizes were estimated from different clusters within the film and are found to be about 150–300 nm, which consist of a number of nanosized grains.

### 3.4.2. *Atomic force microscopy (AFM)*

AFM is a convenient technique to study the surface morphology of thin film. Figure 4 shows the AFM image of as-deposited CdS thin film where micrograph was scanned for $(5 \times 5)$ $\mu\text{m}^2$ region. The surfaces of the films are observed without any void, pinhole, or cracks, and they cover the substrates well, which is supported from SEM image. The surface topology shows the clusters composed of nanoparticles of different sizes. The average cluster size of as-deposited CdS film varies from 150–300 nm, which agrees well with the SEM studies. The rms surface roughness of CdS film is measured to be 16.43 nm.

## 3.5. *Structural characterization*

CdS thin film can grow with cubic ($\beta$-CdS, Hawleyite) and hexagonal ($\alpha$-CdS, Greenokite) forms and also polytype forms. Rieke and Bentjen suggested that predominantly cubic forms of CBD-CdS films were deposited at room temperature on

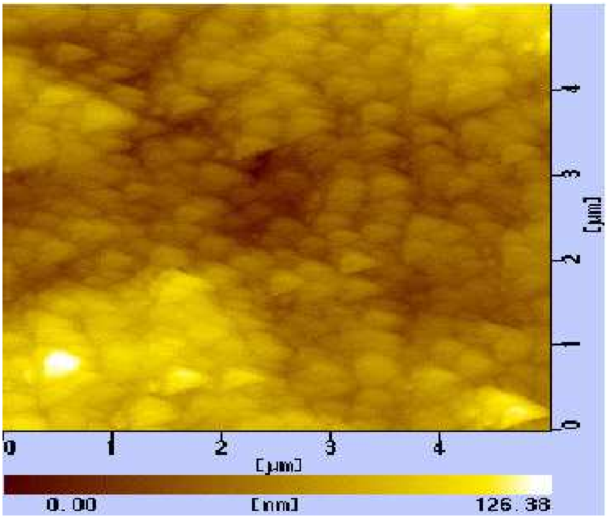

Fig. 4. The AFM image of as-deposited CdS film with scan area of $(5 \times 5)$ $\mu$m$^2$.

silicon substrates using the ammonia-thiourea system.[17] In contrast, Lincot *et al.* found that the initial layers formed from a similar system (but on carbon films supported on copper or gold grids at 333 K) were composed of well-defined crystallites of hexagonal of the order of 10 nm in size.[18] However, they also observed smaller colloidal particles formed in the solution (3–6 nm), which had a mixed hexagonal/cubic structure. Similarly, Chu *et al.* reported that the deposited films of CdS onto $SnO_2$ were polytypic, and only somewhat crystalline films were obtained on glass substrate.[19] Hence, X-ray diffraction (XRD) measurements of CdS thin films have been carried out in order to investigate the crystal structure. Figure 5 shows the XRD pattern for as-deposited CdS film. The manifestation of sharp peak associated to stable hexagonal phase of CdS reveals the polycrystalline nature of the film. The intense diffraction peak at $2\theta = 26.6^\circ$, which coincides with the (002) diffraction line of the CdS hexagonal crystalline phase.[20] A diffraction peak for the cubic phase also at $2\theta = 26.6^\circ$ corresponds to the (111) plane,[21] which causes ambiguity. However, the peaks, which should be absent in the hexagonal CdS spectrum, but having a large intensity for hexagonal phase,[2] are observed for as-grown films, enabling us to consider that CBD grown CdS films have a hexagonal phase. Due to the fact that most intense peaks of cubic and hexagonal phase coincide in the diffraction angle within 1%, the interpretation of XRD spectra became a difficult task. However, with the increase of substrate temperature, the appearance of hexagonal phase increases.[6] The crystallite size ($D$) was calculated using the Scherrer's formula $D = 0.94\ \lambda/\beta \cos\theta$, where $\lambda$ (1.54056 Å) is the X-ray wavelength, $\theta$ is the Braggs angle, and $\beta$ is the full width at half maximum (FWHM) of the diffraction peak in radians. The calculated value of $D$ and FWHM are given in Table 2. The average crystalline size was calculated by resolving (002) peak for hexagonal phase.

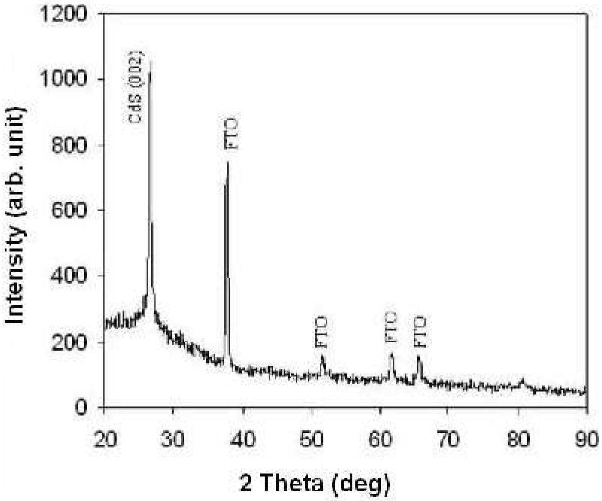

Fig. 5. The X-ray diffraction pattern of CdS thin film.

Table 2. The summary of XRD data and calculated structural parameters of CdS film.

| Sample | Plane of reflection ($hkl$) | $2\theta$ (deg) | d-spacing (Å) | FWHM (deg) | Crystalline size ($D$) (nm) | Micro-strain ($\varepsilon$) $10^{-4}$ lin$^{-2}$ m$^{-4}$ | Dislocation density ($\delta$) $10^{14}$ lin/m$^2$ |
|---|---|---|---|---|---|---|---|
| CdS | 002 | 26.6 | 3.348 | 0.2558 | 33 | 8.2 | 9.2 |

The micro-strain and dislocation density have been calculated using the following relations[22] and their values are given in Table 2: micro-strain $(\varepsilon) = w\cos\theta/4$ and dislocation density $(\delta) = 1/D^2$, where $w$ is the FWHM and $D$ is the crystalline size.

### 3.6. *Compositional analysis*

EDXA has been performed for quantitative analysis of as-deposited CdS films (Table 3). Figure 6 shows a typical EDXA spectrum of CdS film and its relevant analysis. It shows the presence of Cd and S with Cd present slightly more than the stoichiometric ratio. Such excess of Cd seems to be typical of chemical bath deposited CdS thin film.[6] It can be due to coexistence of CdS with other Cd com-

Table 3. EDAX analysis of as-deposited CdS film.

| Elements | Atom % | Atom % error |
|---|---|---|
| Cd | 55.77 | +/ − 4.82 |
| S | 40.52 | +/ − 2.14 |
| O | 3.71 | +/ − 1.26 |

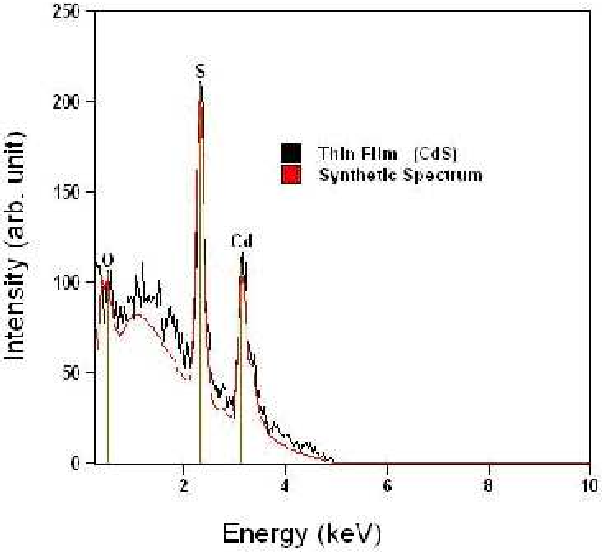

Fig. 6. A typical EDXA pattern of as-deposited CdS thin film.

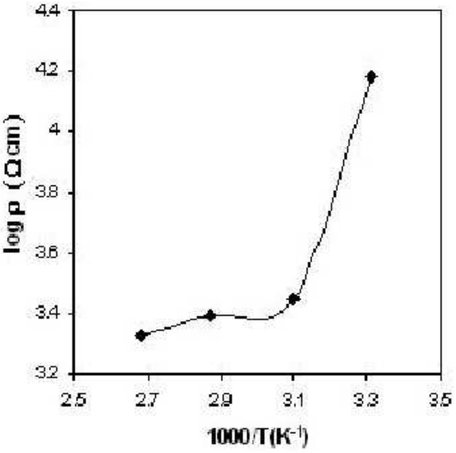

Fig. 7. Variation of resistivity of CdS thin film with temperature.

pounds, which are also intermediates or products of the CBD reaction.[6] O is also identified. This may be due to the presence of $Cd(OH)_2$ in the deposited film.

### 3.7. *Electrical resistivity measurement*

The electrical resistivity measurement by two-point probe method has been done within the temperature range of 302–402 K. The room temperature electrical resistivity of as-deposited CdS thin film is found in the order of $10^4$ $\Omega$ cm, which is decreased to $10^3$ $\Omega$ cm after increasing temperature. This value of resistivity for as-deposited CBD–CdS film agrees well with other published reports.[23] Figure 7 shows the change of room temperature resistivity with the increase of temperature. The decrease in electrical resistivity with increase in temperature may be due to improvement in crystallite size, decrease in (1) density of grainboundary intercrystallite, (2) grain boundary discontinuities, (3) defects such as pinholes, voids, etc.

## 4. Conclusion

CdS thin films have been deposited by CBD technique onto FTO-coated glass substrate at a temperature of 363 K. Conductivity types of CdS layers are of $n$-type, which is confirmed by PEC measurement. XRD studies show that the films are polycrystalline with the crystallite size 33 nm and have preferential orientation in the (002) direction and confirm a hexagonal structure. However, there might have been some contribution from the presence of cubic phase in the hexagonal phase. It is revealed from AFM and SEM studies that the FTO substrate is well covered with CdS thin film with the formation of large clusters of about 150–300 nm. The optical band gap of as-deposited CdS is 2.42 eV and reduces to 2.27 eV upon heat treatment together with a clear color change from yellow to orange. The electrical resistivity of as-deposited films is of the order of $10^4$ $\Omega$ cm and resistivity decreased as a result of increasing temperature.

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