Influence of deposition temperature on CdS thin films by polyol method*

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Abstract: CdS thin films were successfully deposited onto glass substrates for the first time by the polyol method using cadmium acetate, thiourea and diethylene glycol as the raw materials. The effects of the deposition temperature from 120 to 200 ℃ in steps of 20 ℃ on the structure, morphology and optical properties of the resultant films were investigated. It was found that the crystallinity was improved and the value of the surface average roughness was decreased with increasing the deposition temperature. The average grain sizes of the CdS thin films were 77.16 and 76.61 nm at 140 and 180 ℃, respectively. All samples showed excellent transmittance and the band gaps were found to reduce from 2.55 to 2.45 eV with the increase of the deposition temperature, which was attributed to the improvement of crystallinity.

Key words: CdS film; polyol method; deposition temperature; microstructure; optical properties
DOI: 10.1088/1674-4926/35/8/083003 **EEACC:** 2520

1. Introduction

Cadmium sulfide (CdS) is an important chalcogenide semiconductor with a direct band gap energy of 2.42 eV, which falls in the visible spectrum region, and with a large absorption coefficient of 4×10^4 cm^{-1} at room temperature[1, 2]. Therefore, it is used as the buffer layer in Cu(In,Ga)Se_2 (CIGS) solar cells and the window layer in CdTe solar cells[3, 4]. Moreover, CdS also has potential applications in light-emitting diodes[5], photoconductors[6], sensors[7, 8] and photo-electrocatalysis devices[9] due to its high absorption coefficient, low resistivity and easy ohmic contact.

CdS thin film deposition has already attracted great attention to develop synthesis techniques with the advantages of green, low cost and easy fabrication on a large scale. Various techniques such as chemical bath deposition (CBD)[10−12], chemical vapor deposition[13], electrodeposition[14], molecular beam epitaxy[15], a successive ionic layer adsorption and reaction (SILAR) method[16] and spray pyrolysis[17], have been reported for the preparation of CdS thin films. Most of the aforementioned methods are effective. However, there are few reports about the synthesis of CdS thin films by the polyol method.

It is well known that diethylene glycol (DEG) has excellent water solubility, biocompatible lubricity, and thermal stability; furthermore, many researchers have reported the preparation of nanomaterials using DEG, exploiting its non-toxic, nonirritating and moisturizing properties. For example, Feldmann[18] used DEG in the preparation of nanoscale MS particles (M = Zn, Cd, Hg), Quan Zewei[19] used DEG as a reductant to synthesize PbS crystals, and Sorachon Yoriya[20] has fabricated TiO_2 nanotube in DEG/HF electrolyte.

The aim of this study is to confirm the effect of deposition temperature on the structure, morphology and optical properties of CdS thin film by the polyol method. The thin films were deposited in high-boiling polyol (DEG, bp 246 ℃) solution by a chemical reaction between dissolved precursors composed of cadmium salt as a source of Cd and thiourea as a source of S. The polyol itself was used for a stabilizer, limiting particle growth and prohibiting agglomeration[21]. Highly crystalline sulfides were yielded as a result of the application of high temperatures (≥120 ℃). Moreover, the polyol method is a simple, single-step process for preparing nanostructured powders and films[22]; it can avoid powder aggregation and fulfill surface modification of particles to effectively inhibit their secondary aggregation[23].

2. Experimental

CdS thin films were prepared by the simple polyol method in which cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$), thiourea ($NH_2CSNH_2$) and diethylene glycol (DEG, $HO(CH_2)_2O(CH_2)_2OH$) were used. All chemicals used in this investigation were AR grade and without any further purification.

CdS thin films were deposited on microscope glass substrates of $40 \times 25 \times 1$ mm^3 dimension through the polyol method. Prior to deposition, all glass substrates were ultrasonically cleaned with 30% nitric acid, deionized water and ethanol for 20 min, respectively. 0.01 mol/L cadmium acetate and 0.01 mol/L thiourea were dissolved into diethylene glycol as the deposition solution. The glass substrates were vertically immersed into the solution and agitation was needed during film deposition. The deposition time was maintained at 40 min when the color of the solution turned yellowish at different

* Project supported by the High-Tech Research and Development Program of China (No. 2009AA03Z427).
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Received 9 January 2014, revised manuscript received 10 March 2014

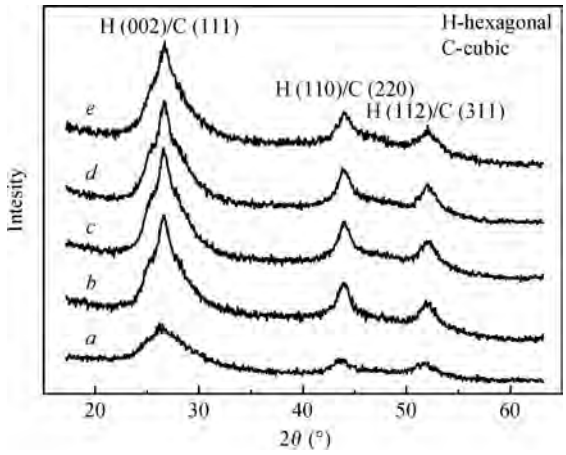

Fig. 1. X-ray diffraction patterns of CdS thin films grown at different temperatures. *a*: 120 ℃. *b*: 140 ℃. *c*: 160 ℃. *d*: 180 ℃. *e*: 200 ℃.

temperatures (120, 140, 160, 180, and 200 ℃). After deposition, the substrates were washed ultrasonically in ethanol for 15 s to remove the loosely adhered CdS particles and organic impurities on the films. Finally, the samples were dried in air. The chemistry of CdS thin film formation by the polyol method was complicated and has not been reported until now.

The crystal phase of the films was determined by X-ray diffraction (XRD, Panalytical X'pert PRO, Netherlands), using Cu Ka radiation. The morphology of the films was observed through scanning electron microscopy (SEM, Fei Quanta 200, USA) and atomic force microscopy (AFM, CSPM4000, China). Additionally, the optical property of the film was examined by a UV–vis 2550 spectrophotometer (Shimadzu 2550, Japan) ranging from 300 nm to 800 nm.

3. Results and discussion

3.1. Structural characterization of CdS thin films

Figure 1 shows the X-ray diffraction spectra of the CdS thin films deposited at the different temperatures. The diffraction peaks at 2θ positions of 26.6°, 43.9° and 52.0° can be assigned to the planes (002), (110) and (112) of the hexagonal wurtzite structure (JCPDS, 41-1049) or planes (111), (220) and (311) of the cubic zinc blende structure (JCPDS, 10-0454). However, it is difficult to conclude whether the films are purely hexagonal or purely cubic or a mixture of two phases due to only three characteristic peaks presented; vacuum evaporation[24] and chemical bath deposition[25] obtained the same results. The whole XRD spectra exhibits a broad peak located in the low diffraction angles, which suggests that the films are formed with a smaller mean grain size[10]. It is also noted that the intensity of the diffraction peaks increases with the increasing of the deposition temperature from 120 to 140 ℃, but the intensity of the diffraction peaks does not change significantly by further increasing the deposition temperature from 140 to 200 ℃. This indicates that the deposition temperature plays a role in the degree of crystallinity. From the XRD pattern, the mean grain sizes are estimated according to the Scherer formula:

$$d = \frac{0.94\lambda}{B\cos\theta}, \quad (1)$$

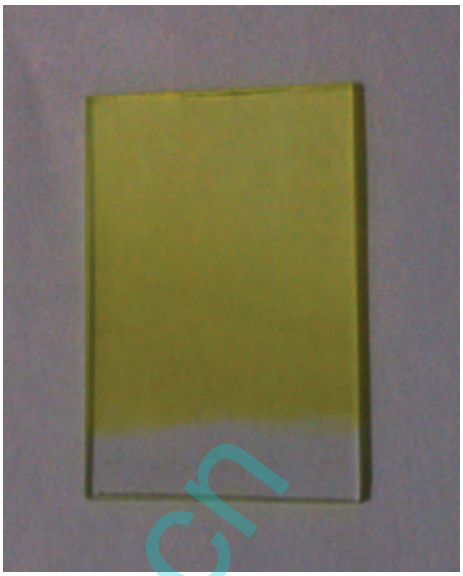

Fig. 2. (Color online) The photo of CdS thin film.

where d, λ, θ, and B are the mean grain size, the X-ray wavelength of 0.154 nm, the Bragg diffraction angle, and the FWHM of the diffraction peak of CdS (111) plane at 26.6°, respectively. The average grain sizes are 7.8, 12.4, 17.8, 12.4, and 15.5 nm corresponding to the five samples (from 120 to 200 ℃), respectively.

3.2. The morphology of CdS thin films

Figure 2 shows the photo of CdS thin films deposited at 180 ℃. To the naked eye, it can be observed that the film is yellow, uniform, complete and well-adhered to the substrate. The microtopography of CdS films is later observed through SEM and AFM. Figure 3 shows the SEM morphology of the CdS thin films deposited at 120, 140, 160, 180, and 200 ℃, respectively. It is found that when the deposition temperature is 120 or 140 ℃, the film displays a rougher, inhomogeneous surface with some overgrowth grains. When the deposition temperature rises to 160–200 ℃, the surface becomes much smoother. It indicates that the deposition temperature is a crucial factor affecting the morphology of the CdS films.

In order to further find out the structure and the grain size of CdS thin films, an AFM morphology study is carried out and the films deposited at temperature of 140 and 180 ℃ are chosen. Typical contact mode AFM images are shown in Fig. 4. The employed surfaces morphology at the micro scale shows the relatively uniform, dense and homogeneous circular grains distribution over the substrates. It is seen that the grain boundaries of CdS films can be distinguished clearly, so the grain size of the films could be estimated by Nano Measurer 1.2.5 Software (Fudan University) from AFM images[26]. It can be seen that the substrate is covered with granular structures of different sizes, mainly ranging from 50 to 90 nm (see Fig. 5) and the average grain sizes of CdS nanoparticles are about 77.16 and 76.61 nm, the values are similar to the results obtained by the CBD method[11]. The grain size observed by the AFM is larger than that by the Scherrer relation, which might be attributed to the agglomeration of small size grains, called polygonizations of the crystallites[27].

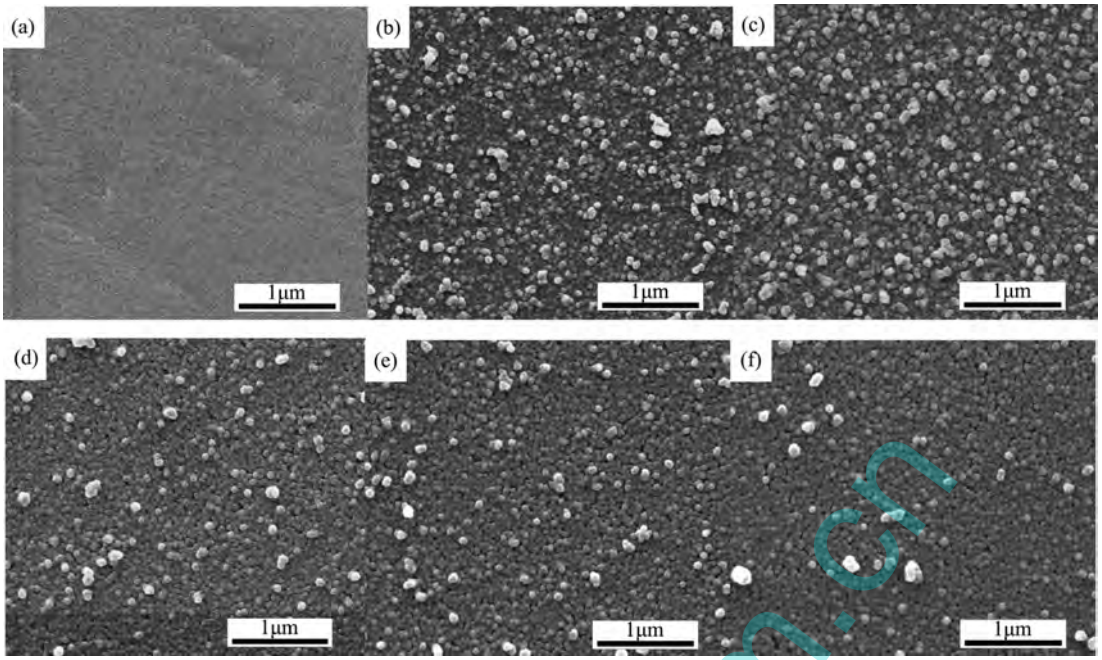

Fig. 3. SEM micrographs of CdS thin films grown at different temperatures. (a) Glass substrate. (b) 120 ℃. (c) 140 ℃. (d) 160 ℃. (e) 180 ℃. (f) 200 ℃.

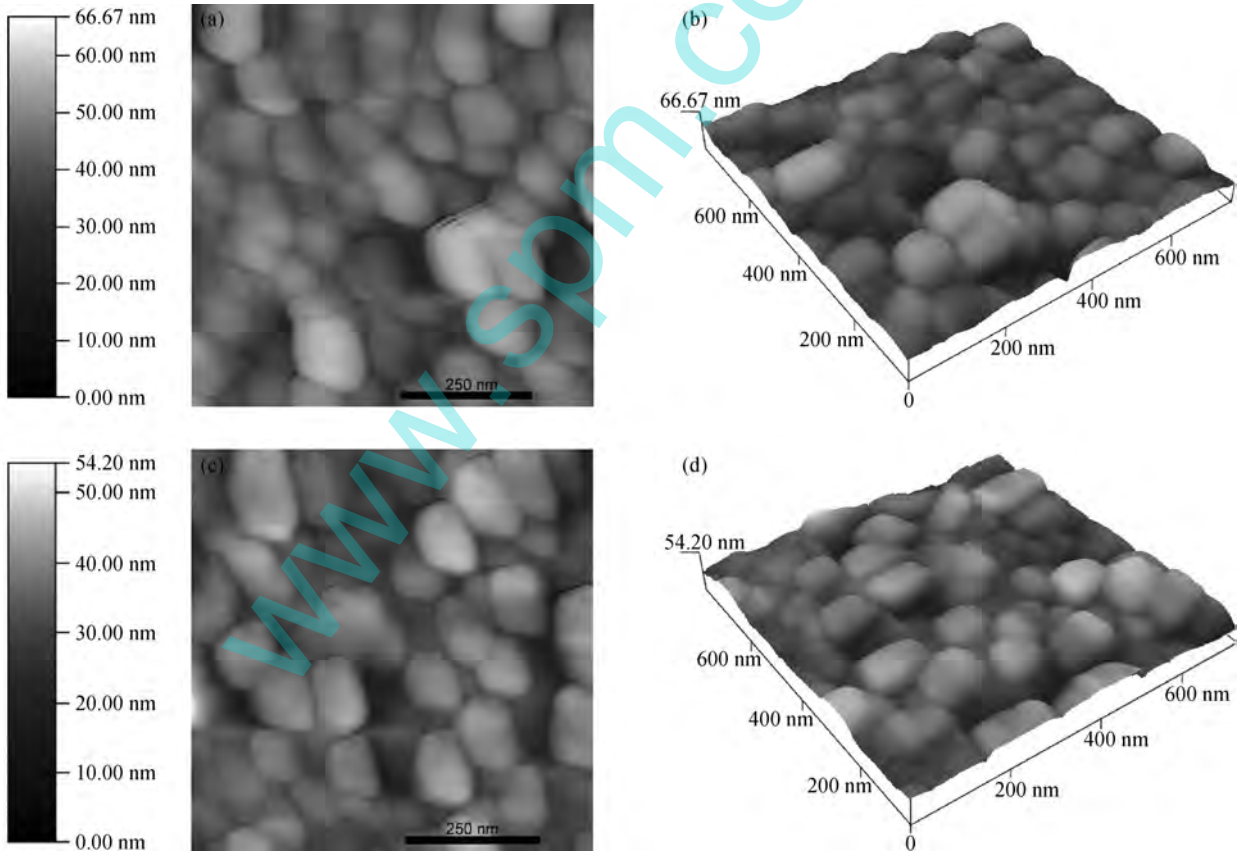

Fig. 4. AFM micrographs of CdS thin films grown at different temperatures. (a) 2D AFM at 140 ℃. (b) 3D AFM at 140 ℃. (c) 2D AFM at 180 ℃. (d) 3D AFM at 180 ℃.

The surface topology, values of average roughness (Ra) and root mean squared (RMS) roughness are analyzed and presented in Table 1; the values are lower than the result obtained by electrodeposition[14]. The table indicates that the surface of the sample has relatively smaller roughness values at higher deposition temperatures, which agrees with the results of the SEM. This trend is found by many authors[11, 28]. However, the real reason is unclear, but we deduce that at higher depo-

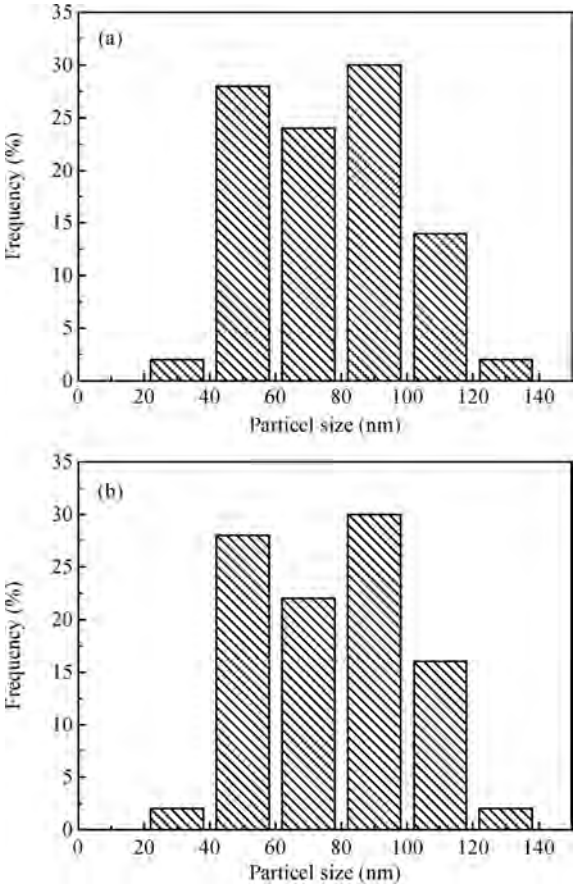

Fig. 5. The histogram of size distribution of CdS thin films grown at different temperatures. (a) 140 ℃. (b) 180 ℃.

Table 1. Surface topology and values of average roughness (Ra) and root mean squared (RMS) roughness.

Deposition temperature (℃)	Average height (nm)	Ra (nm)	RMS (nm)
140	28.0	4.60	5.94
180	22.1	4.38	5.43

sition temperatures, due to the high rate of the chemical reaction and ion diffusion to the grains, the surface grains grow rapidly to coalesce with each other to shape a continuous film. On the other hand, higher deposition temperatures may lead to a slight annealing effect, which results in the smoother surface compared to films deposited at lower temperatures.

3.3. Optical properties of CdS thin films

Optical properties of CdS films are measured with UV–vis spectrophotometer. Figure 6 shows the optical transmittance spectra of CdS thin films deposited at different temperatures in the wavelength range of 300–800 nm. It can be found that the CdS thin films present a higher transmission in the longer wavelength range and the average transmission in the wavelength range 300–800 nm is 81.3%, 66.9%, 69.1%, 68.0%, and 74.3% from 120 to 200 ℃, respectively. The absorption edge is between 470 nm and 510 nm for all films and exhibits slightly a red shift with the increase of deposition temperature. This indicates that the deposition temperature can indeed affect the

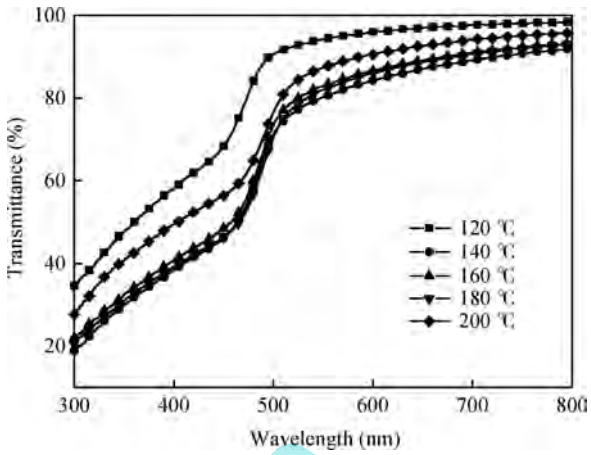

Fig. 6. Optical transmittance of CdS thin films grown at different temperatures.

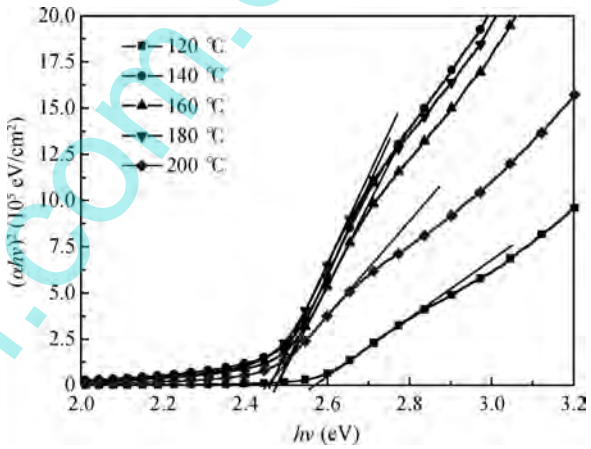

Fig. 7. Optical band gap calculations of CdS thin films grown at different temperatures.

band gap value of CdS thin films.

The optical band gap of CdS thin films can be estimated from the plot of $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, as shown in Fig. 7, according to the Tauc formula for a direct band-gap semiconductor:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \tag{2}$$

where α is the absorption coefficient, A is a constant, E_g is the optical gap energy, ν is the frequency of the incident photon, and h is the Planck constant. The optical gaps of the deposited film are 2.55, 2.46, 2.46, 2.45, and 2.45 eV by increasing the deposition temperature from 120 to 200 ℃, respectively, which are slightly larger than the value of 2.42 eV for single crystal CdS. The increase of band-gap energy is possibly due to the structural defects presented in CdS thin films prepared by the polyol method. The values are similar to the results obtained by the CBD method[11, 27] but higher than those obtained by the SILAR method[16]. It can be clearly seen that the optical band gap of the films reduced from 2.55 to 2.45 eV with increasing the deposition temperature, which is attributed to the improvement of crystallinity[29, 30], and agrees with the XRD results.

4. Conclusions

In this study, we have presented an easy and low cost synthetic process of CdS films in the polyhydric alcohol solution and prepared a set of samples with various deposition temperatures in the same solution. The crystal structure, morphology, and optical properties of CdS films depend strongly on the deposition temperature. With the increasing deposition temperature, the crystallinity of the samples was improved and the surface of CdS thin films becomes smoother. At 140 and 180 ℃, the average grain sizes of CdS thin films are about 77.16 and 76.61 nm, and the values of Ra and RMS are 4.6 nm and 5.94 nm, and 4.38 nm and 5.43 nm, respectively. These values are relatively small, which might be due to the films at the micro scale being relatively smooth and uniform. Films that are fabricated at different temperatures from 120 to 200 ℃ show good transmittance. The band gaps reduce from 2.55 to 2.45 eV with the increase of deposition temperature. Although the exact formation mechanism of the CdS thin films is unclear, we think that temperature is an important factor in determining not only the phase composition but also the morphology and optical properties of the CdS thin films. Some correlative studies are needed to know the exact mechanism.

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