Front. Chem. China 2008, 3(1): 18–22
DOI 10.1007/s11458-008-0009-0

RESEARCH ARTICLE

Xiangdong ZHOU, Ziheng LI, Zhiyou LI, Shuang XU

Preparation and formation mechanism of CdS nano-films via chemical bath deposition

Abstract CdS semiconductor nano-films were grown on ITO glass substrates by means of chemical bath deposition (CBD), with $Cd(NO_3)_2$ as Cd ion and $(NH_2)_2CS$ as S ion sources. The concentration of Cd ions, deposition temperature, deposition time and post-treatment temperature have an impact on the formation of CdS nano-films. UV-vis absorption spectrum and atomic force microscope (AFM) images indicated that the change of concentration and post-treatment temperature may adjust the band-gap of CdS to obtain stable, homogeneous and compact films. Formation mechanism of the crystal nucleus and CdS film was also discussed. Active sites on the surface of ITO are critical to the formation of the crystal nucleus and a uniform and compact CdS nano-film. The active site and crystal nucleus are formed due to the comprehensive effect of electricity, thermodynamics and chemistry.

Keywords CdS nano-film, chemical bath deposition (CBD), uniform and compact film, active site, crystal nucleus

1 Introduction

Current research on semiconductors is focused on the properties of quantum dots which have a large band gap due to the quantum size effect and exhibit strong size-dependent optical and electrical properties. In complex assemblies, the use of these dots has created many opportunities for new research and the fundamental properties of semiconductor change as a function of size. For instance, the band-gap could be tuned between 4.9–2.4 eV as varying the size of CdS [1]. Chemical bath deposition (CBD) could yield stable, homogeneous and compact films. This is an inexpensive and convenient method for large area preparation of films at low temperatures (20–95°C) [2]. The influences of the volume ratio of the Cd ion source to the S ion source, type of cadmium salt, buffer solutions, and post-treatment temperature and atmosphere on the properties of the films have been studied [3–8]. In the CBD process, the quality of the film is decided directly by substrate and reaction conditions. Thus, making the CdS in the solution grow rather than deposit on the substrate is a concern. Ideally, the CdS is expected to grow on the substrate in the preparation of a CdS thin film using CBD. An active site may take place/be set up/prepared by proper treating methods which are diverse from each other depending on the nature of substrate, to favor the combination of Cd ion or S ion with the substrate. Of course, further studies are required to interpret the exact mechanism for the formation of a CdS film. The reactions for the formation of the film can be written as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+}$$

$$(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$

$$Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS\downarrow + 4NH_3\uparrow$$

In this report, we prepared homogeneous and compact CdS nano-films and systematically described the effects of deposition temperature, deposition time and post-treatment temperature. The concentration of the reactant solution was 1–5 mmol/L, the pH value was 10 and the volume ratio

Translated from *Journal of Jilin University* (*Science Edition*), 2007, 45(1): 116–120 [译自: 吉林大学学报 (自然科学版)]

Xiangdong ZHOU, Ziheng LI (✉), Zhiyou LI, Shuang XU
College of Physics, Jilin University, Changchun 130021, China
E-mail: liziheng@jlu.edu.cn

Ziheng LI
National Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

of S ion source to Cd ion source was 2.5:1. On the basis of the experimental results, a possible mechanism was proposed to elucidate the formation of a CdS nano-film. The active site on the surface of the ITO glass and the formation of a crystal nucleus are of importance to form homogeneous and compact CdS nano-film.

2 Experimental

2.1 Preparation of reaction solution

In a typical procedure, 0.3 mL KOH solution (0.1 mol/L), 1.9 mL $(NH_2)_2CS$ solution (1.0 mol/L), 2.0 mL CH_3COONH_4 solution (0.1 mol/L), 2.0 mL ammonia solution (25%), 5.0 mL triethanolamine aqueous solution (the volume ratio of H_2O to TEA was 1:1) and 17.3 mL distilled water were mixed under magnetic stirring (called solution A hereafter). 2.0 mL of solution A, 8.0 mL distilled water, and 5.0 mL triethanolamine were used to prepare CdS thin films. Here, the concentration of Cd ions in the mixed solution was 3.3 mmol/L, the concentration ratio of S ion source to Cd ion source was 2.5:1, and the pH value was 10. It was the typical solution in this paper unless otherwise stated. The pH of the solution was kept constant at 10 by varying the volume of KOH solution and ammonia solution when different concentrations of solution A, distilled water and triethanolamine solution were mixed.

2.2 Characterization and analysis of CdS nano-film

An indium-tin oxide (ITO)-coated glass was used as the substrate. It was ultrasonically cleaned subsequently in acetone and ethanol, and finally dried by infrared lamp. The ITO glass was immersed in the solution within a round-bottom flask in a water bath. The bath temperature was increased to 356 K. After the deposition, a homogeneous CdS film was obtained on the ITO glass. Finally, the obtained ITO glass was dried in an oven for heat treatment.

Morphologies of CBD-CdS thin films on glass substrates had been observed by AFM (Auto Probe CP Research, USA). UV–visible absorption spectra (UV-vis) were recorded on a Varian100 spectrometer at room temperature.

3 Results and discussion

3.1 Influence of the deposition temperature on the CdS film

Figure 1 shows the UV-visible absorption spectra of CdS film produced at different conditions. Figs. 1(a), 1(b), and 1(c) show the absorption spectra of CdS films deposited for 24 h at room temperature, deposition for 20 min at 356 K, and after heat-treatment at 573 K, respectively. The effect of deposition temperature on the CdS film quality was investigated. It can be seen from Fig. 1 that no deposition yielded at room temperature, but the deposition appeared at 356 K on the ITO-coated glass and the absorption spectrum showed a blue-shift from 503.1 nm to 444.3 nm after heat treatment. The CdS crystal integrated more densely and the absorption peak became stronger significantly after heat treatment.

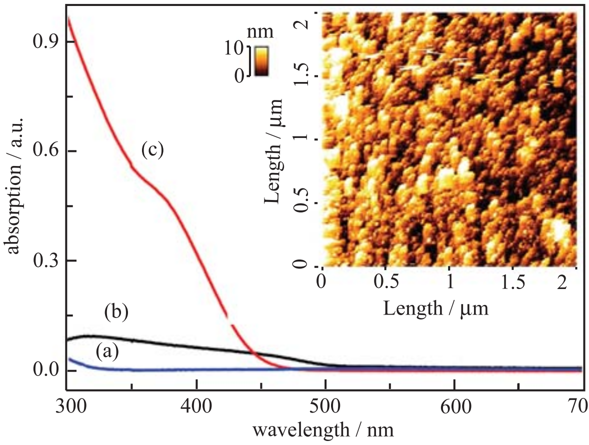

Fig. 1 Absorption spectra of CdS film deposited for 24 h at room temperature (a) , deposited for 20 min at 356 K (b), post-treatment at 573 K (c).
AFM image of CdS film was shown in inset.

The effect of post-treatment on the surface morphology of the samples was shown in the inset of Fig. 1. A compact film as thick as 80 nm and composed of protuberances 30 nm in size was observed. The UV-visible absorption peak blue shifted obviously after heat treatment, indicating that the films showed a sound crystalline structure and the CdS crystals merged compactly.

3.2 Influence of the concentration of Cd ion on the CdS film

Figure 2 shows the absorption spectra of CdS films deposited for 20 min at 356 K, then heat treated for 30 min at 573 K. The concentrations of Cd ion were 3.3 mmol/L (curve a) and 1.9 mmol/L (curve b), respectively. It can be found from Fig. 2 that decreasing the concentration of Cd ion favors the formation of CdS film.

It was observed that the film could be formed after deposition for 60 min from the solution with higher concentration of Cd ions, but no film could be found even if the deposition time was increased up to 100 min in the solution with a lower concentration of Cd ions. Under higher ion concentration, CdS nano-clusters were

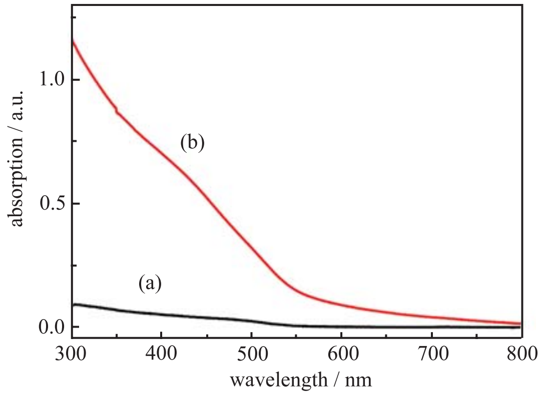

Fig. 2 Absorption spectra of CdS films deposited for 20 min at 356 K then post-treated for 30 min at 573 K Cd^{2+} concentrations were 3.3 mmol/L (a) and 1.9 mmol/L (b), respectively.

easily produced and coalesced to form large colloidal particles, leading to a continuous coating of CdS colloidal particles on the substrate. Controlling Cd ion concentration thus plays a vital role in the preparation of CdS film.

3.3 Influence of the deposition time on the CdS film

Fig. 3 shows the UV–vis absorption spectra of CdS films deposited at different reaction times at 356K. The inset shows variation of the edge of the band-gap with reaction time. A red shift of the band-gap indicated that the CdS films had larger thickness with increasing reaction time. A blue shift appeared after deposition of 40 min, and almost no change took place after 50 min. It can be seen from the inset that deposition time has little influence on the band-gap of CdS films.

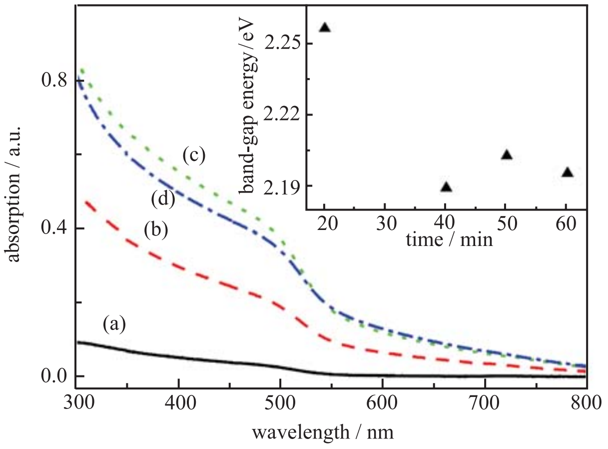

Fig. 3 Absorption spectra of CdS films. Curves (a), (b), (c), (d) denote CdS films deposited for 20, 40, 50 and 60 min, respectively; Band-gap energy dependence on deposition time for CdS is shown in inset.

3.4 Influence of post-treatment temperature on the CdS film

Figure 4 shows the variation of band-gap energy of CdS film depending on post-treatment temperature. One can see from the figure that the band-gap energy of CdS film decreased with the increase of annealing temperature. It was important to note that the band-gap energy of the CdS film reached the minimum value when the annealing temperature was 623 K, then the band-gap energy increased with increasing annealing temperature. This indicated that the band-gap of CdS film could be adjusted by the annealing temperature significantly. Allen [9] and co-workers thought that the variation of band-gap of CdS film was attributed to thermal diffusion and interaction of electron- phonon by calculation.

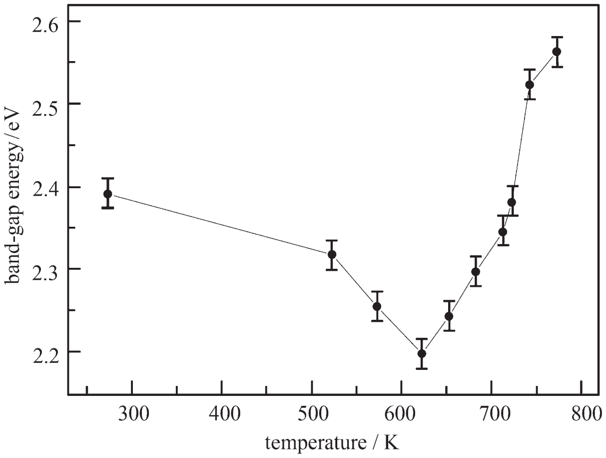

Fig. 4 Band-gap energy dependence on post-annealing temperature for CdS film

Generally, band-gap of the material was decided by structure and particle size. It was known that phase transition should also be reflected in the band-gap variation. The phase transition of CdS film from the cubic to the hexagonal phase had been observed when annealing. The band-gap attained the minimum value at the phase transition temperature. The band-gap had been observed at 573 K in ref. [5], which was lower than our case due to the different preparation methods. When the thermal annealing temperature was lower than the phase transition temperature, the band-gap decreased gradually with temperature due to the quantum size effect. When the thermal annealing temperature was higher than the transition temperature, the band-gap increased with temperature due to the phase transition from the metastable cubic phase to the stable hexagonal phase and a gradual improvement in crystalline quality in the CdS film (see Figs. 1b, 1c).

3.5 Mechanism on formation of nano-CdS film

The solubility product of CdS is small ($K\text{sp} = 1.4 \times 10^{-29}$), and hence the formation of CdS needs the following conditions:

(1) The concentrations of $Cd(NO_3)_2$ and $(NH_2)_2CS$ must be low in favor of the formation of a CdS film instead of a CdS precipitate.

(2) A perfect CdS film can be prepared only at a certain temperature ($> 80°C$).

(3) Adding a buffer solution to maintain the pH values of the solution at 9–10. The alkaline environment provided by the buffer solution is necessary for $(NH_2)_2CS$ to release S^{2-} and the Cd^{2+} to exist as $Cd(NH_3)_4{}^{2+}$, to guarantee that the reaction is carried out uniformly and slowly.

In our experiments, deposited CdS films remained uncontrollable in spite of observing the above deposition parameters. It was found that for films prepared from chemical bath, substrate roughness seemed to play an important role on the structural and optical properties of the films [10]. It was noteworthy that CdS films deposited on SnO_2 substrate with high roughness showed an even more compact and smooth surface than that on glass and ITO substrates. The effects of operation sequence on structural and optical properties of the films were investigated. ITO-coated glass was washed by acetone and ethanol under ultrasonic bath, dried under infrared lamp, and then immediately immersed in the reaction solution. Finally, homogeneous and compact CdS film could be prepared on ITO-coated glass. However, coarse CdS film could be obtained when the ITO-coated glass was immersed in the reaction solution after being air-dried at room temperature. Moreover, putting the ITO-coated glass in the reaction solution after it had reached 80°C prevented the development of a homogeneous and compact CdS film. The correct procedure was drying ITO-coated glass under the infrared lamp, immediately immersing it in the reaction solution, and then slowly increasing the temperature of the reaction solution to 80°C. In this case, homogeneous and compact CdS films could be fabricated even though the reaction solution was not stirred.

When the reaction solution was heated to 80°C before immersing the substrate, a mass of nuclei was formed, and powdery films were obtained by the cluster-by-cluster mechanism through the attraction and aggregation of CdS clusters precipitated in bulk solutions. The pre-heated ITO-coated glass substrate had a large surface tension and surface heat energy. When the dried ITO-coated glass was put into a cool reaction solution quickly, a temperature difference was produced between the glass surface and interior. There was a homogeneous nucleation throughout the substrate surface during the initial CdS growth process by the reaction of $Cd(NH_3)_4{}^{2+}$ and S^{2-}. The final CdS film was formed by keeping the reaction temperature at 80°C for a certain time. It is worth mentioning that the work function of the ITO-coated glass was 4.8 eV – an indication of electronegativity that enabled $Cd(NH_3)_4{}^{2+}$ to hold the active site on the glass substrate completely.

On the basis of the above results and discussion, the formation mechanism of CdS film was established as follows:

The first step: formation of solid CdS phase in the aqueous medium:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+}$$

$$(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$

The second step: perfect crystalline nuclei appeared on the substrate in the early stage of CdS deposition under the effects of electricity, thermodynamics, dynamics and chemistry factors which coalesced to form the final CdS film. Fig. 5 shows the formation process of CdS film.

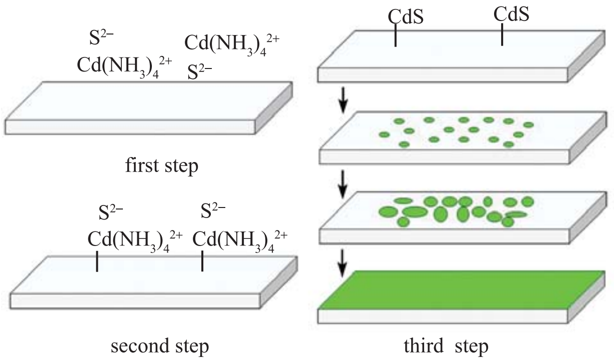

Fig. 5 Sketch map of process of forming CdS film

The third step: the crystalline nuclei deposited on the substrate, which was grown and coalesced with NH_3 released from $Cd(NH_3)_2$ and S^{2-}, combined to form the final CdS film. The reaction was described as follows:

$$Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS\downarrow + 4NH_3\uparrow$$

4 Conclusions

In summary, homogeneous and compact CdS semiconductor nano-films were grown on ITO glass substrates by means of chemical bath deposition (CBD) with $Cd(NO_3)_2$ as Cd ion and $(NH_2)_2CS$ as S ion sources. The experiments indicated that deposition temperature played a vital role in the formation of CdS film. Furthermore, deposition temperature had a distinct influence on the variation of the film's band-gap, while deposition time had little influence. The crystallinity of CdS was improved through heat treatment, and a shift of the edge of the band-gap appeared. In the meantime, the formation mechanism of nano-CdS film had been discussed based on the experiment results. Operation sequence and pre-treatment of the substrate were critical to the formation of active sites and crystal nuclei on the surface of ITO glass. The formation of the crystal nucleus resulted from the interaction between factors of electricity, thermodynamics, dynamics and chemistry.

Acknowledgements We gratefully acknowledge the Chinese Postdoctoral Foundation for financial support for this research.

References

1. Rao A P, Pajonk G M, Rao V, Effect of pH, aging, and drying on the size of CdS nanocrystallites, monolithicity, and transparency of nanocrystalline CdS-Doped silica xerogels. J Mater Syn Proce, 2001, 9: 11–18
2. Vigil O, Rodrìguez Y, Zelaya-Angel O, Vàzquez-Lòpez C, Morales-Acevedo A, Vàzquez-Luna J G, Properties of CdS thin films chemically deposited in the presence of a magnetic field. Thin Solid Films, 1998, 322: 329–333
3. Yamaguchi K, Yoshida T, Sugiura T, Minoura H, A novel approach for CdS thin-film deposition: electrochemically induced atom-by-atom growth of CdS thin films from acidic chemical bath. J Phys Chem B, 1998, 102: 9677–9686
4. Ichimaura M, Goto F, Arai E, Structural and optical characterization of CdS films grown by photochemical deposition. J Appl Phys, 1999, 85: 7411–7417
5. Lozada-Morales R, Zelaya-Angel O, Torres-Delgado G, On the yellow-band emission in CdS films. Appl Phys A, 2001, 73: 61–65
6. Oliva A I, Solís-Canto O, Castro-Rodríguez R, Quintana P, Formation of the band gap energy on CdS thin films growth by two different techniques. Thin Solid Films, 2001, 391: 28–35
7. Martínez M A, Guillén C, Herrero J, Morphological and structural studies of CBD-CdS thin films by microscopy and diffraction techniques. Appl Surf Sci, 1998, 136: 8–16
8. Yang J, Tian H Z, Wang C X, Fabrication of high-quality transparent ZnO/Diamond heterojunction. Journal of Jilin University (Science Edition), 2006, 4(3): 460–464 (in Chineses)
9. Allen P B, Cardona M, Theory of the temperature dependence of the direct gap of germanium. Phys Rev B, 1981, 23(4): 1495–1505
10. Zhang H, Yang D R, Ma X Y, Que D L, CdS thin films fabricated by chemical bath deposition. Acta Energiae Solaris Sinica, 2003, 24(1): 1–4 (in Chineses)