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OPTICAL PROPERTIES AND FORMING MECHANISM OF CdZnS THIN FILM GROWN BY CHEMICAL BATH DEPOSITION

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Ternary semiconducting CdZnS films were prepared by chemical doping of CdS with different concentration of Zn ion in a chemical bath deposition (CBD). We have analyzed the optical transmission and absorption properties of samples prepared by chemical bath deposition. The competition mechanism of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 to form the complex plays a critical role in the formation of $Cd_xZn_{1-x}S$ thin film. In addition, the optical properties of the films with mixed phases were further investigated, The composition of CdZnS were determinated. Moreover, the influence of Zn^{2+} concentration on the forming mechanism of the CdZnS thin film was discussed. In general, Zn^{2+} plays a key role during the process of regulating the growth rate and forming the ternary semiconductor CdZnS films by CBD.

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1. Introduction

The growth of ternary semiconductor nano-microstructure thin film has been studied very extensively in recent years since these structures offer the prospect of high performance semiconductor laser diodes[1], photovoltaic and photoconducting devices[2]. The ternary compound Cadmium Zinc Sulphide ($Cd_xZn_{1-x}S$) have been mostly extensivley investigated as important candidate for wide band gap material. Moreover, the replacements of CdS with the higher energy gap ternary $Cd_xZn_{1-x}S$ have also led to a decrease in window absorption loss and decrease the lattice mismacthing with the CuInGaSe chalcopyrite semiconductor.[3] Althougth, the band gap of the binary compounds can be tunned by changing the particle size, the controllability of particle size can be the most problem during the fabrication of quantum dots thin film.[4] With comparison to the binary semiconductor nano-film, the band gap of CdxZn1-xS thin film was prone to be tunned by changing percentage content of the composition.

The various techniques have been adopted for the preparation of CdZnS films, such as vacuum evaporation,[5-7] reactive sputtering[8] and chemical solution spray [9-11]. Chemical bath deposition (CBD) is extremely attractive because of its advantageous features over other thin film deposition techniques, such as its simple, low temperature, low cost, low evaporation temperature and easy coating of large surfaces. This technology is based on controlled release of the metal ions(M^{2+}) and sulphide ions (S^{2-}) in an aqueous bath[2]. It is generally thought that the metal ions and sulphide ions were slowly released owing to the controllable of the complexing agents to form the thin film on the substrate. The controllable composition of the ternary semiconductor thin film can be difficultly realized due to the great difference between the growth characteristics of ZnS and one of CdS films. Only a few investigations have been focused on the influence of growth parameters on the optical properties of films prepared by CBD [2,12,13]. Song *et al*. showed that the grain size of CdZnS films was found to increase with increasing Zn-content in the solution, and further influence the optical properties of films[14]. Ng. Gaewdang *et al*. investigated that the effects of mixture ratio x ($x = Zn^{2+}/[Cd^{2+} + Zn^{2+}]$) on the surface morphology, structure, and transmission properties are analyzed[3]. It was found to produce a decrease in the grain size with the increase in mixture ratio in starting solution. The above investigations suggested that the

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concentration of Zn ions is the important factor to influence the size and optical properties of film during the CBD process. In contrast to the case of the binary semiconductor films, studies on growth mechanism of the ternary semiconductor film are more limited. As far as the ternary CdZnS semiconductor film prepared by CBD is concerned, a detail knowledge of the competition process of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 to forming the complex is therefore fundamental for the controllable composition of the ternary CdZnS thin film.

In this paper, CdZnS films were prepared by chemical doping of CdS with different concentration of Zn ion in a chemical bath. In this expertiment, the concentration of Cd^{2+}, not the concentration of [Cd^{2+} +Zn^{2+}], remains a fixed value. This renders it able to clearly understand the effect of the concentration of Zn ion on the growth mechanism of the CdZnS film. We have analyzed the optical transmission and absorption properties of samples prepared by CBD. This study shows Zn ions can regulate the growth rate of CdS. The competition mechanism of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 to forming the complex play a critical role in the forming of $Cd_xZn_{1-x}S$ thin film. In addition, the optical properties of the films with mixed phases were further investigated, the composition of CdZnS were determinated. Moreover, the influence of Zn^{2+} concentration on the forming mechanism of the CdZnS thin film was discussed.

2. Experimental

All reagents were used as received. Commercial glass (16mm×76mm) were thoroughly cleaned by detergent solution, acetone, ethanol washed, and deionized water. Aqueous solutions contain 0.396M ammonium nitrate, 0.357M KOH, 3.64×10^{-3}M $CdCl_2$ and different mole ratio $ZnSO_4$ for different experiments, and then all solutions were mixed in a beaker without further adjusting the pH. The experimental procedure for growing CdZnS thin films is the difference with described previously.[3,15] The mixture ratio x (x =Zn^{2+}/[Cd^{2+} +Zn^{2+}]) was varied from 0.5 to 0.9, where the concentration of $CdCl_2$ remains 3.64×10^{-3}M in all experiment in order to investigate the influence of Zn^{2+} concentration on the growth characteristic of film. The solution was stirred for few minutes and heated at 85℃. The 3.64×10^{-3}M thiourea solution and the cleaned glass substrate was inclined vertically to the walls of beaker for 2h after the solution reached a required temperature (85℃), The reaction solution was no stirred during the deposition process. The glass substrates were removed from the beaker after reaction, and washed in running tap water, and then dried in air before characterization.

Scanning electron microscopy (SEM, JSM-5600) was used to characterize the morphology of the films. The UV-VIS absorption spectra of the samples were recorded on a New Century T6 photospectrometer.

3. Results and discussion

Fig. 1 shows SEM images of the as-prepared ZnS and CdS films deposited on the glass by the CBD. The reactions both were carried out by using NH_3 as the complexing agent at 85℃ for 1h. It can be seen from figure 1(a) that only ZnS discrete grains are formed, the morphology of ZnS in the film can be attributed to the mechanism of ZnS thin film by CBD. As far as ZnS is concerned, the growth process of the thin film generally thought that the cluster-by-cluster growth is the main mechanism of the ZnS thin film. Therefore, the molar ratio of Zn ion and the complexing agent NH_3 directly affects the formation rate of ZnS aggregates, and the growth rate of thin film. In the experiment, the molar ratio of Zn and NH_3 is very low, about 1×10^{-3}, which can result in the low rate of film growth and forming ZnS discrete grains [16]. In the case of CdS, the atom-by-atom growth and the hydroxide cluster mechanism play main role during the growth process of the thin film by CBD. Tak, *et al*. [17] observed that single CdS particles are sparsely deposited at the initial stage and coalesce to create bigger ones. As shown in figure 1(b), a compact CdS film with large grain size was formed.

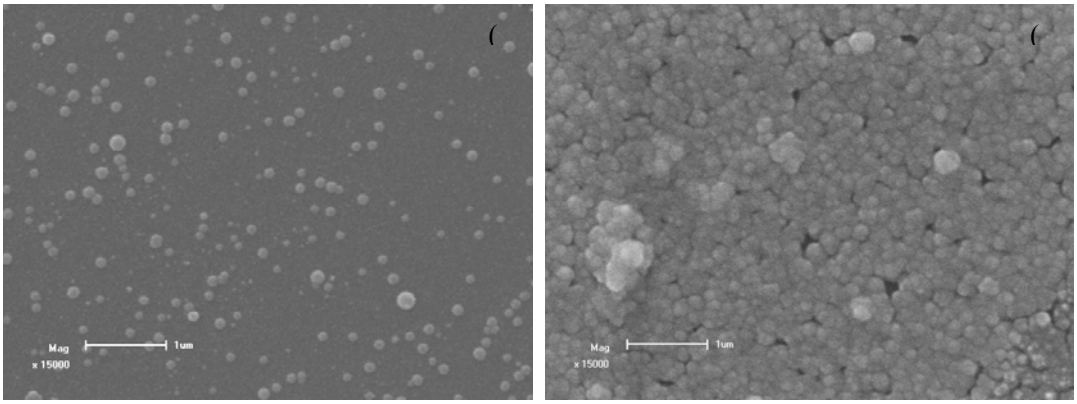

Fig.1 SEM images of the as-prepared ZnS (a) and CdS (b) films deposited on the glass by the CBD.

Fig. 2 shows the optical transmission spectrum recorded for the different Zn:Cd ratio of 1:9, 2:8, 3:7, 4:6, 5:5 in the range 200-800 nm. In the experiment, the mole concentration of only Zn^{2+} was changed. It is clearly seen that the transmittance properties of thin films were influenced by Zn:Cd molar ratios. The transmittance in the 300-500 nm range is obviously different with that in the 500-800 nm range. With increasing of Zn:Cd ratio from 1:9 to 3:7, the transmittance decreased firstly, increased as Zn:Cd ratio is 4:6, then decreased with the further increasing of Zn:Cd ratio to 5:5. The pure CdS thin film is with excellent transmittance in the 500-800 nm range, for pure ZnS thin film in the 300-800 nm range. By the analysis of transmittance properties in the 300-500nm range, it can difficultly draw a conclusion that the ternary semiconductor CdZnS thin films or the separate ZnS and CdS nano-grains were formed. The transmittances lying between the pure CdS and ZnS thin films in 300-500 nm range prove that the compound was formed by CBD technique.

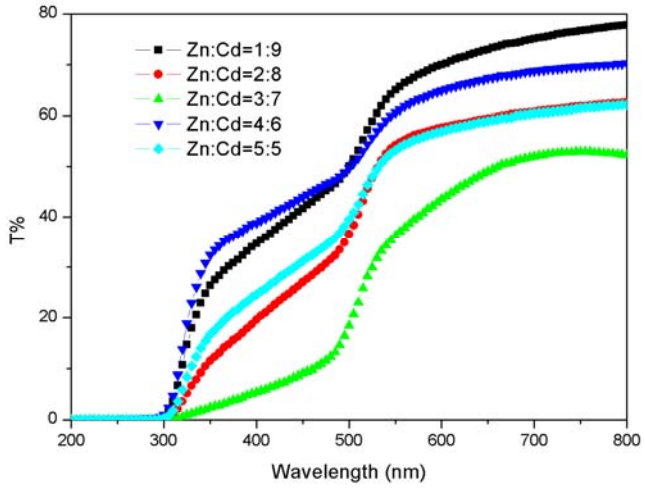

Fig. 2. Optical transmission spectrum of $Cd_xZn_{1-x}S$ thin film with different Zn and Cd ratio.

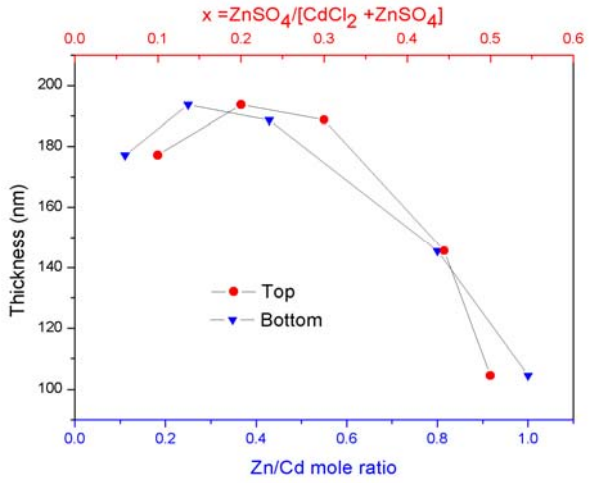

Fig. 3.The thickness of $Cd_xZn_{1-x}S$ thin film variation with different Zn and Cd ratio (bottom) and the mixture ratio x =$ZnSO_4$/[$CdCl_2$ +$ZnSO_4$] (top) obtained from the profilometer.

It is observed that the absorption edge of CdZnS shifted toward longer wavelength, but one of CdS toward shorter wavelength and their intensity increased with the increasing of Zn^{2+} concentration. The red shift of the absorption peak at about 310 nm suggested the formation of CdZnS, while the blue shift of the absorption peak at about 475nm should be due to the quantum-size effects for CdS. In fact, this Zn^{2+} concentration is responsible for determining the formation or not of the CdZnS onto the substrate surface.

In order to have a deeper insight into the reaction process and physics mechanism at the different energy regions, the thickness of thin film as a function of the nominal Cd^{2+} and Zn^{2+} mole ratios (bottom abscissa) and Zn^{2+} concentration (top abscissa) have been studied in figure 3. Interestingly, the thickness does not change monotonically with Zn/Cd mole ratio and the mixture ratio x increasing but first increases and then decreases. As the $ZnSO_4$ was further increased above a certain concentration, the thickness of film is decrease rapidly. It is interesting to mention also that the thickness of the thin films the thickness reached maximum when Zn/Cd mole ratio and the mixture ratio x was 0.25, 0.2, respectively, which can be ascribed to the different deposition characteristics for CdS and ZnS thin film.

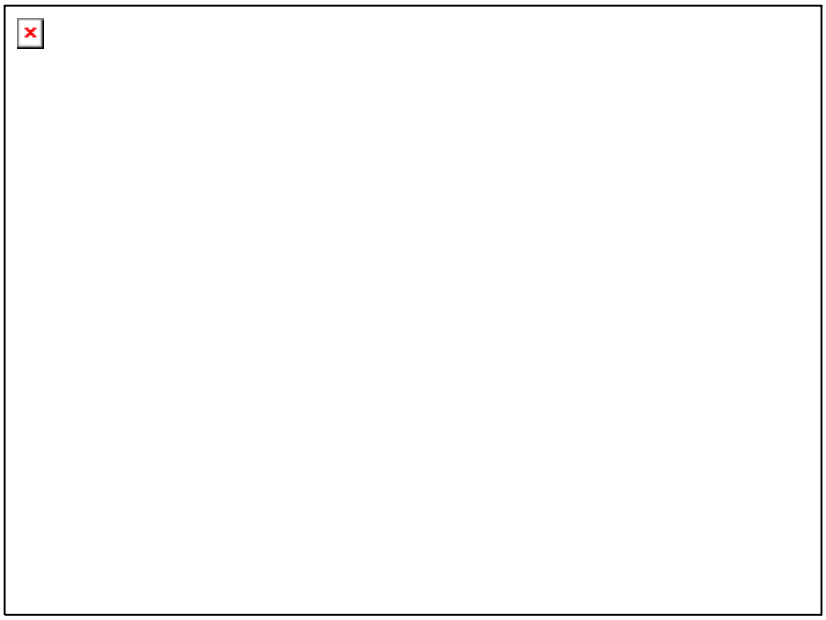

Fig. 4. The experimental of the absorption coefficient and the calculated values of α_{CdS} and α_{CdZnS} for the samples prepared with different Zn and Cd ratio: (a)1:9, (b)2:8, (c)3:7, (d)4:6, (e)5:5.

The absorption spectrum can be analyzed according to the reported earlier about the multilayered system.[15,18]. The relationship of the absorption coefficient and the incident photon energy is given by the following equation:

$$\alpha_{CdS} = A_1(h\nu - E_{gCdS})^n \quad (1)$$

$$\alpha_{CdZnS} = A_2(h\nu - E_{gCdZnS})^n \quad (2)$$

where α_{CdS} and α_{CdZnS} are the absorption coefficients of CdS and CdZnS, respectively, $h\nu$ is the energy of the incident photon, n is 0.5 for a direct transition semiconductor, E_{gCdS} and E_{gCdZnS} are bandgap energies of CdS and CdZnS, respectively, A_1 and A_2 are constants which are related to the effective masses associated with the bands. We suppose that the absorption process results from the direct transitions of pure CdS from 2.0 to 3.0 eV. Thus α_{CdS} can be calculated and extrapolated to the whole energy range according to the equation (1). While between 3.0 and 4.0eV, the absorption coefficient should be the sum of two processes: the direct transitions of CdS and of CdZnS. The absorption coefficient of CdZnS can be obtained by subtracting the pure CdS absorption coefficient from the total one. Fig. 4 shows the experimental data of the absorption coefficient and the calculated values of α_{CdS} and α_{CdZnS} for the samples prepared with different Zn and Cd mole ratio: (a)1:9, (b)2:8, (c)3:7, (d)4:6, (e)5:5. The extrapolation of straight-line portions of the plot to zero absorption coefficients gives the value of the energy gap from the calculated result of the CdZnS absorption coefficient. It can be seen that the band gaps of CdZnS part are very similar, about 3.1eV, indicating similar Zn contant of CdZnS thin film formed for different Cd and Zn ratio, which is agreement with the results of Dona *et al* [15]. However, it was clearly seen that the band gap of CdZnS increased to 3.2eV when the Zn/Cd mole ratio is increased as 1. This result indicates that the formation and composition of CdZnS film can be determined from the concentration of Zn^+. It can be due to the fact that aggregation of nanocrystallites get faster with increasing of the concentration of Zn^+.

Next, we consider the growth mechanism of CdZnS thin film by CBD. In case of NH_3 as complexing agents, the Cd^{2+} and Zn^{2+} exist predominantly in the form of ion complex. The rates of ZnS and CdS formation are determined by the concentration of Zn^{2+} and Cd^{2+} provided by $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$, and the concentration of S^{2-} from the hydrolysis of $SC(NH_2)^2$, respectively. The general reaction can be expressed as

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \quad (1)$$

$$[Zn(NH_3)_4]^{2+} \Leftrightarrow Zn^{2+} + 4NH_3 \quad (2)$$

$$[Cd(NH_3)_4]^{2+} \Leftrightarrow Cd^{2+} + 4NH_3 \quad (3)$$

$$(NH_2)CS + OH^- \Rightarrow CH_2N_2 + H_2O + HS^- \quad (4)$$

$$SH^- + OH^- \Rightarrow S^{2-} + H_2O \quad (5)$$

$$Zn^{2+} + S^{2-} \Rightarrow ZnS \quad (6)$$

$$Cd^{2+} + S^{2-} \Rightarrow CdS \quad (7)$$

The stability constant (κ) of the metal ammonia complex ions can be one of the decisive factors of the growth rate. For $[Zn(NH_3)_4]^{2+}$, the value κ is about $10^{8.9}$, while for $[Cd(NH_3)_4]^{2+}$, the

value κ is only $10^{6.9}$, thus, $[Zn(NH_3)_4]^{2+}$ is more stable than $[Cd(NH_3)_4]^{2+}$ in an alkaline solution. Here we maily consider the influence of the on the growth rate of CdS film on the transmission properties and the thickness of films because the growth rate of CdS was much larger than one of ZnS. With the mole concentration of Zn^{2+} increasing, the dissolved ammonia will form a zinc tetraamine complex with zinc ion (eqs 2), which can result in more cadmium ions were released from $[Cd(NH_3)_4]^{2+}$, then increasing the rate of CdS formation (eqs 3). If the concentration of Zn^{2+} is low, the influence of the hydroxide ion on CdS can very little. When the mole concentration of Zn^{2+} was further increased, the growth rate of CdS becomes low, which fact can be ascribed to the number of the sulfur ion released, decrease due to the hydroxide ion can decrease rapidly (eqs 1). In addition, the solubility product of CdS is more lower than that of ZnS, which can lead to the effect that the growth rate of CdS is more rapid than for ZnS. Therefore, the film should be the complex film composed of CdS and CdZnS. Moreover, the growth of ZnS film is considered as the cluster-by-cluster mode, on the one hand, the particles formed agglomerates of the ZnS nanocrystallites, on the other hand. Then the film is grown by accumulation of the building units of ZnS, which resulted in slowing the growth rate of ZnS films. As for the CdS, the growth of film can mainly be considered as the atom-by-atom mode, $[Cd(NH_3)_4]^{2+}$ can be adsorpted on the substrate and reacted with S^{2-} to form CdS film, which can accelerate the reaction process.

4. Conclusions

CdZnS films were prepared by chemical doping of CdS with different concentration of Zn ion in a chemical bath. In this expertiment, the concentration of Cd^{2+}, not the concentration of $[Cd^{2+} + Zn^{2+}]$, remains a fixed value. This renders it able to clearly understand the effect of the concentration of Zn ion on the growth mechanism of the CdZnS film. We have analyzed the optical transmission and absorption properties of samples prepared by CBD. This study shows Zn ions can regulate the growth rate of CdS. The competition mechanism of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 to form the complex, plays a critical role in the forming of $Cd_xZn_{1-x}S$ thin film. In addition, the optical properties of the films with mixed phases were further investigated. The composition of CdZnS were determined. In general, Zn^{2+} play a key role during the process of regulating the growth rate and forming the ternary semiconductor film CdZnS by CBD.

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