

## GROWTH CHARACTERIZATION OF CdZnS THIN FILM PREPARED BY CHEMICAL BATH DEPOSITION

GUOZHI JIA <sup>A)</sup>, NA WANG, LEI GONG, XUENING FEI

*Tianjin Institute of Urban Construction, Tianjin 300384, P. R. China*

Ternary semiconductor CdZnS films were prepared by chemical bath deposition (CBD). Effect of  $Zn^{2+}$  concentration and deposition time on the forming characterization of CdZnS films are investigated by the optical transmission spectra. 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  $Cd_{1-x}Zn_xS$  thin film when  $Zn^{2+}$  concentration is low, while the integrated rate of  $Zn^{2+}$  into the film only increase with the increase of  $Zn^{2+}$  concentration. Effect of the deposition time on forming process of the CdZnS film was also discussed. The result shows that the rate of  $Cd^{2+}$  integrated into CdZnS system is rapider than the rate of  $Zn^{2+}$  during the growth process of CdZnS thin films with the increasing of the deposition time.

(Received September 6, 2009; accepted September 29, 2009)

*Keywords:* CdZnS; Chemical bath deposition; Optical properties

### 1. Introduction

Recently, there has been considerable interest in the fabrication of ternary semiconductor nano-microstructure thin film since these structures offer the prospect of high performance semiconductor laser diodes[1], photovoltaic and photoconducting devices [2]. The replacements of CdS with the higher energy gap ternary  $Cd_{1-x}Zn_xS$  can lead to a decrease in window absorption loss and decrease the lattice mismatching with the CuInGaSe chalcopyrite semiconductor [3]. Among the various preparation techniques of CdZnS films, 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 [5]. 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, 5, 6] The optical transmission spectra is an important tool for studying the composite film. It can be used to analyzed the optical characterization and determination the optical constants of film.

In this paper, ternary semiconductor CdZnS films were prepared by chemical bath deposition. Effect of  $Zn^{2+}$  concentration and deposition time on the forming characterization of CdZnS films are investigated by the optical transmission spectra. Here mainly discussed that the influence mechanism of  $Zn^{2+}$  concentration on forming CdZnS films during the different range of Zn/Cd ratio.

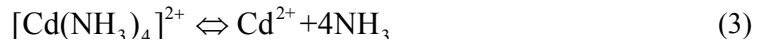
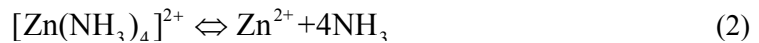
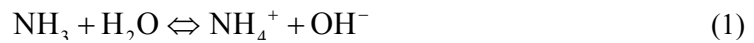
### 2. Experiments

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,  $3.64 \times 10^{-3}$ 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, 7] The mixture ratio  $x$  ( $x = \text{ZnSO}_4 / [\text{CdCl}_2 + \text{ZnSO}_4]$ ) was varied from 0.1 to 0.9, where the concentration of  $\text{CdCl}_2$  remains  $3.64 \times 10^{-3} \text{M}$  in all experiment in order to investigate the influence of  $\text{Zn}^{2+}$  concentration on the growth characteristic of film. The solution was stirred for few minutes and heated. The  $3.64 \times 10^{-3} \text{M}$  thiourea solution and the cleaned glass substrate was inclined vertically to the walls of beaker for 2h after the solution reached a required temperature, 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. The UV-vis absorption spectra of the samples were recorded on a New Century T6 photospectrometer.

### 3. Results and discussion

The growth of ZnS film is considered as the cluster-by-cluster mode, the particles formed agglomerates of the ZnS nanocrystallites, at the same time, the film was grown by accumulation of the building units of ZnS. As for the CdS, the growth of film can mainly be considered as the atom-by-atom mode,  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  can be adsorbed on the substrate and reacted with  $\text{S}^{2-}$  to form CdS film, which can accelerate the process of reaction. When the  $\text{Zn}^{2+}$  was added into the solution for preparing of CdS thin film, the growth process of CdZnS thin film can be influenced by the concentration of  $\text{Zn}^{2+}$ . In case of  $\text{NH}_3$  as complexing agents, the  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  exist predominantly in the form of ion complex. The rates of ZnS and CdS formation are determined by the concentration of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  provided by  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ , and the concentration of  $\text{S}^{2-}$  from the hydrolysis of  $\text{SC}(\text{NH}_2)_2$ , respectively. The general reaction can be expressed as



The stability constant ( $\kappa$ ) of the metal ammonia complex ions can be one of the decisive factors of the growth rate. For  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , the value  $\kappa$  is about  $10^{8.9}$ , while for  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ , the value  $\kappa$  is only  $10^{6.9}$ , thus,  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  is more stable than  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  in an alkaline solution.

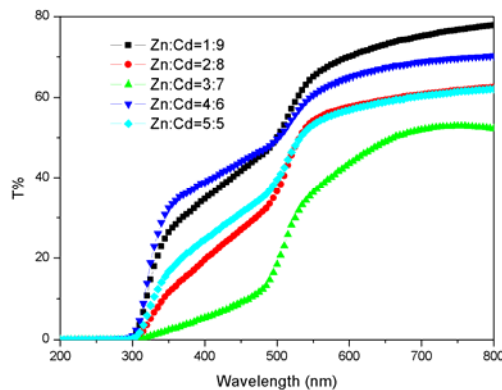


Fig.1 Optical transmission spectrum of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  thin film with different Zn and Cd ratio:

(a)1:9, (b)2:8, (c)3:7, (d)4:6, (e)5:5.

Fig. 1 shows the optical transmission spectra 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 the  $Zn^{2+}$  ion concentration. 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. The transmittances lying between the pure CdS and ZnS thin films in 300-500 nm range prove that was formed by CBD technique.

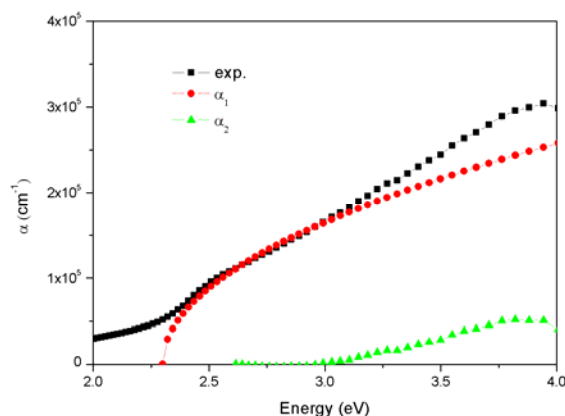


Fig. 2. The experimental of the absorption coefficient and the calculated values of  $\alpha_{CdS}$  and  $\alpha_{CdZnS}$  for the sample of  $Zn^{2+}$  and  $Cd^{2+}$  ratio as 1:9.

The relationship between the absorption coefficient  $\alpha$  and the transmittance spectra can be expressed as

$$\alpha = -\frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (8)$$

where  $d$  is the thickness of the film and  $T$  is the transmittance from the transmittance spectra. The absorption spectrum can be analyzed according to the reported earlier about the multilayered system.[7, 8] The relationship of the absorption coefficient and the incident photon energy are given by the following equation:

$$\alpha_{CdS} = A_1 (h\nu - E_{gCdS})^n \quad (9)$$

$$\alpha_{CdZnS} = A_2 (h\nu - E_{gCdZnS})^n \quad (10)$$

Where  $\alpha_{CdS}$  and  $\alpha_{CdZnS}$  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. Fig. 2 shows the variation of the typical absorption coefficient of CdS and CdZnS bilayers film with the incident photon energy for the Zn: Cd ratio as 1:9. The absorption coefficient increases with the increase of the incident beam energy for all samples. This may be due to the large absorption coefficient for different thin film composition. It can be further found that two transition points are located at about 2.4 eV and 3.1 eV, which respectively corresponded to the absorption of CdS and CdZnS grains.

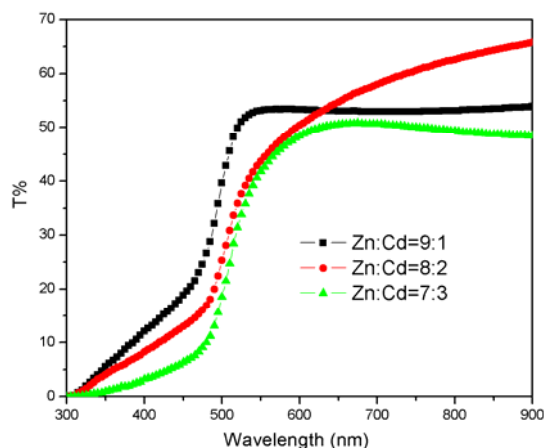


Fig. 3 shows the optical transmission spectra of CdZnS thin films prepared at the large  $Zn^{2+}$  concentration for different Zn: Cd ratio at the high  $Zn^{2+}$  concentration range.

Fig. 3 shows the optical transmission spectra of CdZnS thin films prepared at the large  $Zn^{2+}$  concentration for different Zn: Cd ratio at the high  $Zn^{2+}$  concentration range. It is observed a blue-shift of the transmittance curves toward the shorter wavelength region with increasing  $Zn^{2+}$  concentration, which can be due to increase of Zn content in CdZnS thin films. Obviously, effect of  $Zn^{2+}$  concentration on the optical properties of film is very important when  $Zn^{2+}$  concentration is higher than  $Cd^{2+}$  concentration. The influencing process can be single, mainly be the integrated rate of  $Zn^{2+}$  into the film compared with the result of fig. 1.

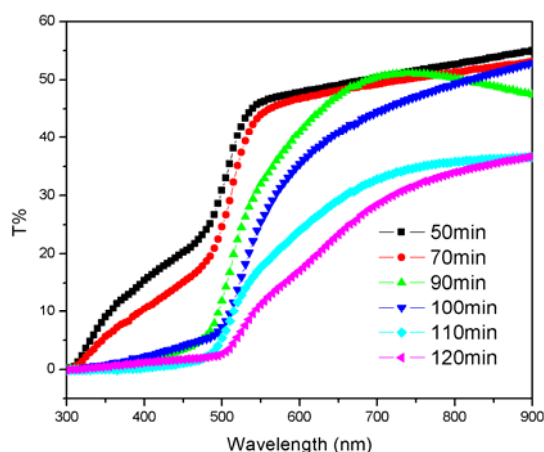


Fig.4 Optical transmission spectrum of  $Cd_xZn_{1-x}S$  thin film prepared by CBD at different deposition time for Zn and Cd ratio as 5:5.

In order to have a deeper insight into the reaction process and physics mechanism of CdZnS thin film forming by CBD. Fig. 4 shows the optical transmission spectra of CdZnS thin films with different growth time at the fixed Zn: Cd ratio (5:5). It can be seen that the transmission intensity decreases with the increasing of the deposition time. It is also observed a red-shift of the transmittance curves toward the longer wavelength region with the increasing of the deposition time, which proved that the rate of  $Cd^{2+}$  integrated into CdZnS system is rapider than the rate of  $Zn^{2+}$  during the growth process of CdZnS thin films. Thus, it can be difficult that the CdZnS thin film with the high Zn content was prepared by CBD without the help means when the  $NH_3$  is used as the only complexing agents.

#### 4. Conclusion

Ternary semiconductor CdZnS films were prepared by chemical bath deposition (CBD). Effect of  $Zn^{2+}$  concentration and deposition time on the forming characterization of CdZnS films are investigated by the optical transmission spectra. 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  $Cd_{1-x}Zn_xS$  thin film when  $Zn^{2+}$  concentration is low. The rate of  $Cd^{2+}$  integrated into CdZnS system is more rapid than the rate of  $Zn^{2+}$  formation during the growth process of CdZnS thin films with the increasing of the deposition time.

#### Acknowledgments

This work has been supported in part by the Natural Science Foundation of Tianjin (09JCYBJC04100) and the Science and Technology Plan Projects of the Ministry of Construction of China (2008-KT-11).

#### References

- [1] V.I. Kozlovskii, D.A. Sannikov, D.E. Sviridov, *Bulletin of the Lebedev Physics Institute* **35**, 35 (2008).
- [2] N. Naghavi, C. Hubert, A. Etcheberry, V. Bermudez, D. Hariskos, M. Powalla, D. Lincot, *Progress in Photovoltaics* **17**, 1 (2009).
- [3] N. Gaewdang, T. Gaewdang, *Materials Letters* **59**, 3577 (2005).
- [4] B. Kumar, P. Vasekar, S.A. Pethe, N.G. Dhere, G.I. Koishiyev, *Thin Solid Films* **517**, 2295 (2009).
- [5] J. Song, S.S. Li, L. Chen, R. Noufi, T.J. Anderson, O.D. Crisalle, *Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion (IEEE Cat. No. 06CH37747)* (2006) 4 pp.|CD.
- [6] W.C. Song, J.H. Lee, *Journal of the Korean Physical Society* **54**, 1660 (2009).
- [7] J.M. Dona, J. Herrero, *Thin Solid Films* **268**, 5 (1995).
- [8] S.S. Ou, O.M. Stafsudd, B.M. Basol, *Journal of Applied Physics* **55**, 3769 (1984).