

Theoretical Survey on Cadmium Sulfide Thin Films for Solar Cell Applications†

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Cadmium sulfide thin films are one of the most promising materials due to its photo conducting nature and suitable band gap (2.42 eV). It has been used for several types of thin film solar cells. In this paper we present some new investigation made on cadmium sulfide thin films used, we can change the compound as well as the concentration will be changed. The films thickness was in the range (102-120) nm and most film's thickness decreased while Zn concentration in solution increased. The transmittance of films increased as Zn concentration increased. All films, however, have high transmittance of 65-86 % the wavelength region (500-900 nm). This material has many applications and from these applications we are interested in photovoltaic applications.

Key Words: Band gap, Cadmium sulfide, Photovoltaic.

INTRODUCTION

In recent years, a significant interest is associated with the A_{II}-B_{VI} semiconductor compounds, due to their novel properties and large area of applications. Various nanostructures made out from A_{II}-B_{VI} semiconductor compounds have been made, such as nanowires, nanorods, nanotubes, nanobelts, etc., with wide range of applications, especially in electronics and optoelectronics devices, where the techniques for the manipulation of the electrical and optical properties, doping and free carriers transport properties are intensely discussed¹⁻¹⁰.

Among these semiconductor compounds, CdS is one of the widely studied materials¹⁻¹¹. This material has many applications and from these applications we are interested in photovoltaic applications, in particular in manufacturing high efficiencies heterojunction CdS/CdTe solar cells¹¹. A substantial number of experimental efforts have been made so far in order to improve the efficiencies of these experimental cells. However the efficiencies for the solar energy conversion are still relatively low, despite the theoretical calculations that suggests a maximum achievable efficiency of 30 % for CdTe solar cells.

The increased interest for this kind of solar cells is also due to their use in space technologies, where a considerable amount of work has been done in characterizing various properties of CdS/CdTe photovoltaic cells after their irradiation

with different ionizing radiations. Previously Cd_{1-x}Zn_xS thin film optimization process¹², thin film with low Zn content¹³ and their film optical characterization¹⁴ have been prepared via chemical bath deposition (CBD) by Kasim Uthman ISAH, Caijuan Tian and M.A. Mahdi, respectively.

EXPERIMENTAL

General procedure: Cd_{1-x}Zn_xS thin films were deposited on Menzel-Glazer glass slides. The chemicals used were 0.015 M cadmium acetate, 0.015 M zinc acetate and 0.05 M thiourea. The concentration of ammonium acetate used as buffer was varied from 0.1-0.6 M in steps of 0.1, while ammonia solution concentration was varied from 0.4-1.2 M in steps of 0.2. The temperature was also varied from 55- 85 °C while keeping the ammonium acetate and ammonium hydroxide constant. The measurements were taken from the near ultraviolet (300 nm) to the near infrared (900 nm) regions².

The depositions were performed with CdCl₂, ZnCl₂ and thiourea concentrations varying from 0.001 to 0.06 mol/L, ammonia concentrations in the range of 0.072 to 0.179 mol/L and pH values between 8.5 and 10.5 to obtain the optimum growth conditions of the Cd_{1-x}Zn_xS thin films¹³ (Tables 1-3).

Thin films of cdZnS were deposited from the solution by using high purity start materials (Sigma-Adrich) cadmium acetate as a Cd²⁺ ions source, zinc acetate as a Zn²⁺ ions source,

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TABLE-1
THIN FILMS PREPARATION PARAMETERS

Molarities mol in 5 mL					
S. No.	Samples	Cadmium acetate	Zinc acetate	Thiourea	Film thickness (nm)
1	S1	0.04	0.0	0.04	120
2	S2	0.04	0.02	0.04	116
3	S3	0.04	0.03	0.04	117
4	S4	0.02	0.04	0.04	113
5	S5	0.00	0.04	0.04	102

TABLE-2
FILM THICKNESS AND AMMONIA HYDROXIDE CONCENTRATION

S. No.	Film thickness (nm)	Ammonia hydroxide concentration (M)
1	50	0.4
2	125	0.6
3	300	0.8
4	100	1.0

TABLE-3
FILM THICKNESS AND AMMONIA ACETATE CONCENTRATION

S. No.	Film thickness (nm)	Ammonium acetate Concentration (M)
1	50	0.1
2	125	0.2
3	282	0.3
4	120	0.4
5	100	0.5

thiourea as a S^{2-} ions source in an alkaline solution of ammonia and ammonium acetate as a buffer solution. The temperature fixed at $800\text{ }^{\circ}\text{C}^{14}$.

RESULTS AND DISCUSSION

Optimization: Fig. 1 show the dependence of deposited $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film thickness on $[\text{NH}_3]$ introduced into the reaction bath as ammonium hydroxide NH_3OH from a concentration of 0.4-1.0 M. The reagent concentrations are $[\text{Cd}(\text{CH}_3\text{COO})_2] = [\text{Zn}(\text{CH}_3\text{COO})_2] = 0.015$, $[\text{CH}_3\text{COONHH}_4] = 0.3$ and $[\text{SC}(\text{NH}_2)_2] = 0.05$ M. $[\text{NH}_3]$ is varied from 0.4 to 1.0 M in steps of 0.2. The film thickness is negligible at 0.4 M $[\text{NH}_3]$ and increases with increasing $[\text{NH}_3]$ and peaks at a concentration of 0.8 M ammonia and subsequently decreases at higher $[\text{NH}_3]^{12}$.

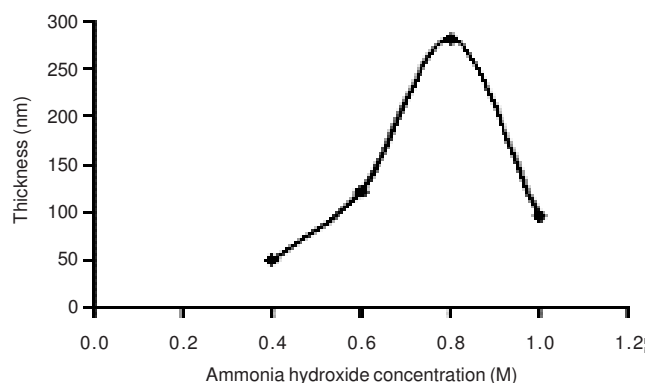


Fig. 1. Influence of ammonia concentration on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film thickness

The variation of deposited film thickness as a function of ammonium acetate concentration is shown in Fig. 2. Five concentration of the ammonium salt (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 M) were considered at a temperature of $75\text{ }^{\circ}\text{C}$ and a pH varying from 9.2-9.7. The figure shows a gradual increase in film thickness with increasing ammonium acetate. Concentration, with the film thickness peaking at a concentration of 0.3 M and a thickness of 282 nm. Higher concentration of ammonium acetate shows a decrease in film optimal thickness of 282 nm at 0.3 M ammonium acetate concentration to a film thickness of 170 nm at an ammonium acetate concentration of 0.6 M. This observation is consistent¹².

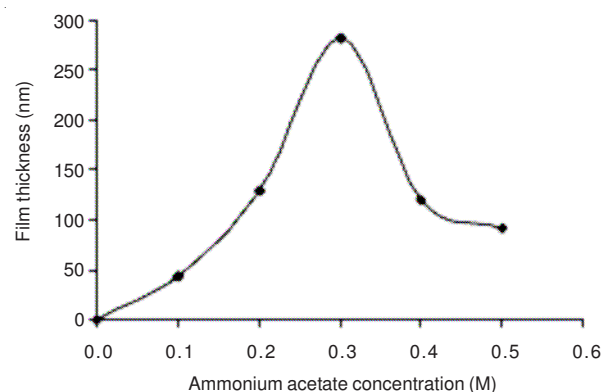


Fig. 2. Influence of ammonium acetate concentration on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film thickness

Various temperatures from 45 to $85\text{ }^{\circ}\text{C}$ in steps of $10\text{ }^{\circ}\text{C}$ were used in the co-depositing $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ to obtain the optimal temperature. Fig. 3 shows an increase in film thickness as the temperature increases from 45 to $75\text{ }^{\circ}\text{C}$ and drops at $85\text{ }^{\circ}\text{C}$. The rise in the film thickness may be due to the increase in the hydrolysis of thiourea as the temperature increases¹⁵. This provides the S^{2-} necessary for the metal chalcogenide formation. Also the kinetic energy of the ions in solution is higher at higher temperature, which brings about increased interaction between them and subsequent deposition at volume nucleation centers of the substrate¹⁶.

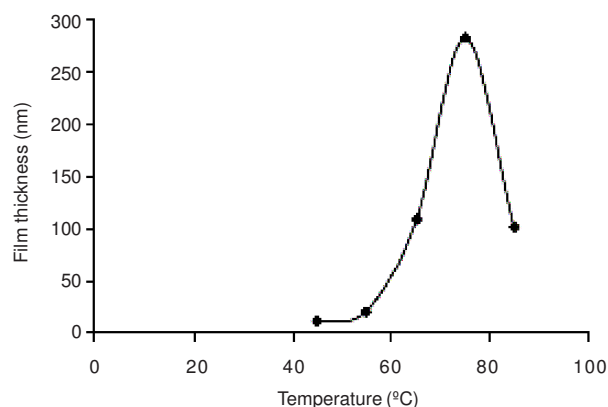


Fig. 3. $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ film thickness dependence on bath temperature

At pH value 8.5, only a single strong $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ (002) peak can be detected (Fig. 4). However, as the pH value increases, the intensity of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ (002) peak decreases and peaks

of ZnS and ZnO also emerge in these patterns. This is probably caused by the excessive ammonia which leads to the reactions of $\text{Zn}(\text{NH}_3)_4^{2+}$ and OH^- and that may be responsible for the accentuation of ZnO peak when the pH value increases to 9.5. When the pH value reaches up to 10, on the contrary, all the peaks are weakened¹³.

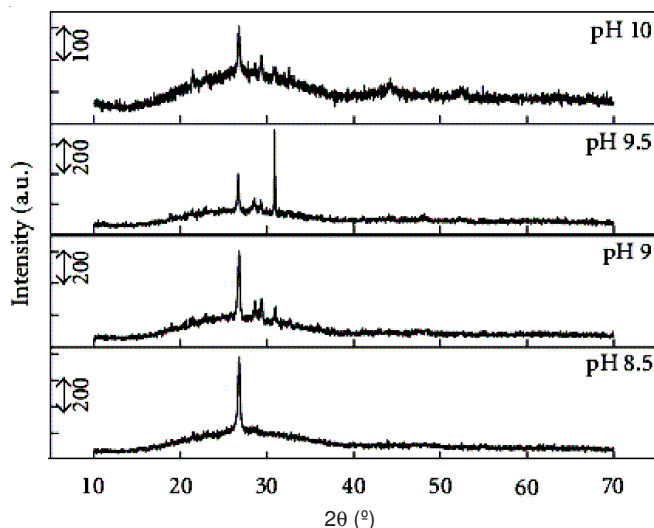


Fig. 4. XRD patterns of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at different pH values

We investigated XRD patterns (not shown there) of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at different temperatures. As the bath temperature increases from 60 to 90 °C, the intensity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ (002) firstly becomes strong and then weakens. Also, peaks other than $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ cannot be detected in the thin films deposited at 70 °C. Therefore, the optimal bath temperature to preparing $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films by chemical bath deposition is 70 °C¹³.

The optical transmittance spectra of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films recorded in the wavelength range 300-800 nm. The wavelength dependence of optical transmittance of the investigated films deposited at different Cd and Zn source molarities. The film's optical transmittances of 65-85 % in the 600-800 nm range which is high enough for solar cell applications. The Zn^{2+} concentration is increased and Cd^{2+} concentration decreased in the solution, the films became more transparent in wavelength longer than 500 nm and the curves shifted towards low wavelength³.

Conclusion

Optimum film thickness was obtained for ammonium acetate concentration of 0.3 and 0.8 M ammonium hydroxide. These concentrations tend to minimize homogeneous reaction leading to improved film quality and thickness maximization, in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared by using chemical bath deposition (CBD) method. Films thickness decreased with increasing in Zn concentration, so the transmission may increase. Depending on Cd and Zn ions source molar concentration, the values of the direct optical band gaps changed from 2.42 eV for CdS to 3.7 eV for ZnS. The $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films may be assumed as an ideal alternative material to CdS and ZnS since its composition can be simply controlled.

REFERENCES

1. S. Chun, K.S. Han, J.S. Lee, H.J. Lim, H. Lee and D. Kim, *Curr. Appl. Phys.*, **10**, S196 (2010).
2. K. Ravichandran and P. Philominathan, *Appl. Surf. Sci.*, **255**, 5736 (2009).
3. A. Rotaru, A.M. Kropidlowska, C. Constantinescu, N. Scarisoreanu, M. Dumitru, M. Strankowski, P. Rotaru, V. Ion, C. Vasiliu, B. Becker and M. Dinescu, *Appl. Surf. Sci.*, **255**, 6786 (2009).
4. A.S. Khomane, *J. Alloys Comp.*, **496**, 508 (2010).
5. N.S. Das, P.K. Ghosh, M.K. Mitra and K.K. Chattopadhyay, *Physica E*, **42**, 2097 (2010).
6. H. Xie, C. Tian, W. Li, L. Feng, J. Zhang, L. Wu, Y. Cai, Z. Lei and Y. Yang, *Appl. Surf. Sci.*, **257**, 1623 (2010).
7. A.A. Yadav, M.A. Barote and E.U. Masumdar, *Solid State Sci.*, **12**, 1173 (2010).
8. J. Schaffner, E. Feldmeier, A. Swirschuk, H.J. Schimper, A. Klein and W. Jaegermann, *Thin Solid Films*, **519**, 7556 (2011).
9. M.C. Baykul and A. Balcioglu, *Microelectron. Eng.*, **51-52**, 703 (2000).
10. M. Ghenescu, L. Ion, I. Enculescu, C. Tazlaoanu, V.A. Antohe, M. Sima, M. Enculescu, E. Matei, R. Neumann, O. Ghenescu, V. Covlea and S. Antohe, *Physica E*, **40**, 2485 (2008).
11. O. Toma, S. Iftimie, C. Besleaga, T.L. Mitran, V. Ghenescu, O. Porumb, A. Toderas, M. Radu, L. Ion and S. Antohe, *Chalcogenide Lett.*, **8**, 747 (2011).
12. K.U. Isah, N. Hariharan and A. Oberafo, *Leonardo J. Sci.*, **7**, 111 (2008).
13. C.J. Tian, J.J. Gao, W. Li, L.H. Feng, J.Q. Zhang and L.L. Wu, *Int. J. Photoener.*, **2012**, Article ID 549382 (2012).
14. M.A. Mahdi and S.K.J. Al-Ani, *Int. J. Nanoelectron. Mater.*, **5**, 11 (2012).
15. G. Sasikala, P. Thilakan and C. Subramanian, *Sol. Ener. Mater. Sol. Cells*, **62**, 275 (2000).
16. R.C. Kainthla, D.K. Pandya and K.L. Chopra, *J. Electrochem. Soc.*, **127**, 277 (1980).