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THEORITICAL SURVEY ON CADMIUM SULFIDE THIN FILMS FOR SOLAR CELL APPLICATIONS

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ABSTRACT

CdS (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 (CdS) 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 wave length region (500-900 nm). This material has many applications and from these applications we are interested in photovoltaic applications.

Keywords: Band gap, Cadmium Sulfide, Photovoltaic.

1. 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 discussed [8-17].

Among these semiconductor compounds, CdS is one of the widely studied materials [1] [8– 17]. 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 cells [1].

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 process[2], thin film with low Zn content[4] and their film optical characterization [3] have been prepared via CBD (Chemical Bath Deposition) by Kasim uthman ISAH, Caijuan Tian and M.A.Mahdi respectively. We have analyzed all these three papers and reported our findings in result and discussion section.

2. EXPERIMENTAL DETAILS

A. General procedure

 $Cd_{1-x}Zn_{x}S$ thin films were deposited on Menzelglazer glass slides. The chemicals used were 0.015M cadmium acetate (Cd (CH₃COO) $_2$), 0.015M zinc acetate (Zn (CH_3COO)) and 0.05M thiourea (SC $(NH₂)₂$). The concentration of ammonium acetate (NH4CH3COO) used as buffer has varied from 0.1- 0.6M in steps of 0.1, while ammonia solution (NH3OH) concentration has varied from 0.4-1.2M in steps of 0.2. The temperature also varied from 55- 85°C [2].

The depositions were performed with $CdCl₂$, $ZnCl₂$, and $SC(NH₂)₂$ 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 [4].

Thin films of CdZnS were deposited from the materials (Sigma-Aldrich) cadmium acetate [Cd $(CH_3 (COO)$ ₂] as a Cd²⁺ ions source, zinc acetate [Zn] $(CH_3 (COO)$ ₂] as a Zn^{2+} ions source, thiourea [SC $(NH₂)₂$] as a S⁻² ions source in an alkaline solution of ammonia $[NH_3]$ and ammonium acetate $[NH_4 (CH3)$ COO)] as a buffer solution. The temperature fixed at 800^oC [3].

TABLE: 1 THIN FILMS PREPARATION PARAMETERS

Molarities mol in 5 ml						
S.	Sampl	Cadmi	Zinc	Thiour	Film	
N	es	um	acet	ea	thickness	
\mathbf{o}		acetate	ate		(nm)	
1.	S ₁	0.04	0.0	0.04	120	
2.	S ₂	0.04	0.02	0.04	116	
3.	S ₃	0.04	0.03	0.04	117	
4.	S ₄	0.02	0.04	0.04	113	
5.	S ₅	0.00	0.04	0.04	102	

3. RESULTS AND DISCUSSION

Optimization: Figure:1- Shows the dependence of deposited Cd $_{1-X}Zn_XS$ film thickness on [NH3] introduced into the reaction bath as ammonium hydroxide NH₃OH from a concentration of 0.4 – 1.0M.The reagent concentrations such as $[Cd(CH_3COO)_2] = [Zn(CH_3COO)_2] = 0.015,$ $[NH_4CH_3OO] = 0.3$ and $[SC(NH_2)_2] = 0.05M$. $[NH_3]$ has varied from 0.4 to 1.0M in steps of 0.2. The film thickness is negligible at $0.4M$ [NH₃] and increases with increasing [NH3] and Peaks at a concentration of 0.8M ammonia, and subsequently decreases at higher $[NH_3]$.

At low [NH₃] there is insufficient NH₃ to bind the Cd^{2+} and Zn^{2+} into there tetrramine complexes, Cd 2+ $(NH_3)_4$ ²⁺ and Zn $(NH_3)_4$ ²⁺ . As $[NH_3]$ increases heterogeneous reaction which favour atom-by-atom deposition predominates. At $[NH_3]$ in the neighborhood of 0.8M, there is optimum NH needed 3 to bind Cd²⁺ and Zn^{2+} into there tetraamine complex ions required for atom-by-atom deposition. At concentrations higher than 0.8M, the film, thickness decreases. This is due to the over stabilization of the tetramines complexes at very high ammonia concentration which subsequently reduce the growth rate [2].

Figure. 1 Influence of ammonia concentration on Cd1-XZnxS film thickness

TABLE: 2 A SUMMARY OF FILM THICKNESS, AMMONIA HYDROXIDE CONCENTRATION

S.N Ω	Film Thickness (nm)	Ammonia hydroxide concentration (M)
	50	0.4
2.	125	0.6
3.	300	0.8

The variation of deposited film thickness as a function of ammonium acetate concentration in shown in figure 2. Five concentration of the ammonium salt (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6M) where considered at a temperature of 75°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 0.3M and a thickness of 282nm. Higher concentration of ammonium acetate shows a decrease in film optimal thickness of 282nm at 0.3M ammonium acetate concentration to a film thickness of 170nm at an ammonium acetate concentration of 0.6M. This observation is consistent [2].

Ammonium acetate concentration (M)

Figure. 2 Influence of ammonium acetate concentration on Cd \prod_{1-x} **Zn** \sum_{x} **film thickness**

TABLE: 3
A SUMMARY OF FILM THICKNESS.
AMMONIA ACETATE CONCENTRATION

Various temperatures from 45° C to 85° C in steps of 10°C were used in the co-depositing Cd Zn S to $1-x$ x obtain the optimal temperature. Fig. 3 show an increase in film thickness as the temperature increases from 45 \degree C to 75 C and drops at 85 \degree C. The $\bar{0}$ rise in the film thickness may be due to the increase in the hydrolysis of SC (NH_2) as the temperature increases [18]. This provides the S necessary for the $\overline{2}$ 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 substrate [19].

Figure. 3 Cd1-XZnxS film thickness dependence on bath temperature

Figure: 4-The pH value is 8.5, only a single strong Cd1*−x*Zn*x*S (002) peak can be detected. However, as the pH value increases, the intensity of the Cd1*−x*Zn*x*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 Zn(NH3)^{2+} 4 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 10.0, on the contrary, all the peaks are weakened [4].

Figure. 4 XRD patterns of Cd_1 **,** XZn_XS **thin films prepared at different pH values.**

We investigate XRD patterns (not shown there) of Cd1-XZn*x*S thin films prepared at different temperatures. As the bath temperature increases from 60⁰C to 90⁰C, the intensity of Cd1-XZn*x*S (002) firstly becomes strong and then weakens. Also, peaks other than Cd1*−x*Zn*x*S cannot be detected in the thin films deposited at 70°C. Therefore, the optimal bath temperature to preparing Cd1*−x*Zn*x*S thin films by CBD is 70⁰C [4].

 From table 1, it can be noted that for the three top samples, the films thickness decreased with increasing zinc acetate molarities and at a fixed ratio of cadmium molarities. Due the low Zn (OH) ² solubility in water, Zn concentration in thin films will be less. Due to the different solubility values between Cd (OH) $_2$ and Zn (OH) $_2$, the thickness of CdS thin films (S1) are higher than ZnS thin films (S5) as the same ions source concentration.

The optical transmittance spectra of Cd1*−x*Zn*x*S thin films recorded in the wavelength range 300- 800nm. 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 500nm and the curves shifted towards low wavelength [3].

4. CONCLUSIONS

Optimum film thickness was obtained for ammonium acetate concentration of 0.3M and 0.8M ammonium hydroxide. These concentrations tend to minimize homogeneous reaction leading to improved film quality and thickness maximization, in $Cd₁$ $x \, Zn_x S$ 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 2.42eV for CdS to 3.7 eV for ZnS. Cd_{1−x}Zn_xS thin films may be assumed as ideal alternative material to CdS and ZnS since its composition can be simply controlled.

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