Optimization of Process Parameters of Chemical Bath Deposition of Cd$_{1-X}$Zn$_x$S Thin Film

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Abstract

Chemical bath deposition of Cd$_{1-x}$Zn$_x$S is achieved by the slow release of sulphide ions and the controlled release of cadmium and zinc ions in solution. However the difference in the solubility products of CdS and ZnS by several orders usually narrows the chalcogenide operating window, this coupled with the difference in their stability constant makes Cd$_{1-x}$Zn$_x$S CBD process very difficult. We report the deposition and optimization of the growth parameters that maximizes the thickness of the deposited film in alkaline solution. The film showed an optical transmittance of about 80%, a determine band gap of 2.49eV with a molar composition x of 0.09.

Keywords

Optimization; Cd$_{1-x}$Zn$_x$S; Optical Transmittance; Band Gap; Molar Composition.

Introduction

Ternary derivatives of CdS have generated a lot of research interest for applications in the field of optoelectronic devices. One such ternary compound is Cadmium Zinc Sulphide

(Cd$_{1-x}$Zn$_x$S) which is gaining prominence as good candidate for wide band gap material for photovoltaic ands photoconducting devices. Its band gap can be tailored from 2.42eV (CdS) to 3.7eV (ZnS). The addition of Zn to CdS enhances the open-circuit voltage and short-circuits current in heterojunction devices as a result of the decrease in the window absorption losses [1, 2].

Cd$_{1-x}$Zn$_x$S films have been deposited in various ways: Vacuum evaporation [3], metal organic chemical vapor deposition (MOCVD) [4], spray pyrolysis [5], successive ionic layer absorption and reaction (SILAR) [6] and chemical bath deposition [7]. Among these techniques CBD is favored because it is relatively simple, inexpensive and scalable technique for the deposition of high quality and large area films.

The CBD process is performed by slow release of S^{2-} and controlled free Zn^{2+} and Cd^{2+} ions in an alkaline solution. Thiourea (CS(NH$_2$)$_2$) and thioacethamide (CH$_3$CSNH$_2$) are two sulphiding agents commonly used. A chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. Apart from the formation of oxide in CdS deposition bath, the addition of Zn leads to more concerns, since the solubility product of CdS (ksp = 10^{-28}) and ZnS(ksp =10$^{-23.8}$) [8], are different by several orders of magnitude. The proper chalcogenide operating window is further narrowed and the process made more difficult due to the different stability constants of the Cd and Zn precursors [9].

As a result of these difficulties, some researchers have resorted to the use of multilayer processing [10]. Acidic bath deposition has also been investigated [11]. This has been based on the successive acidic bath deposition of ZnS, with the use of urea hydrolysis in the control of the pH. It is thus argued that if CdS could be successfully deposited from similar bath, the possibility of depositing the true ternary compound could be improved as the problem of the gross insolubility of Zinc hydroxyl specie would be reduced at low pH. Adherent orange-yellow films were obtained at a ph of 5.7 [11].

We report the alkaline deposition of Cd$_{1-x}$Zn$_x$S and the investigation of the various deposition parameters to obtain optimum film thickness.

Experimental

$Cd_{1-x}Zn_xS$ thin films were deposited on Menzel-glazer glass slides. The chemicals used were 0.015M cadmium acetate ($Cd(CH_3COO)_2$), 0.015M zinc acetate ($Zn(CH_3COO)_2$) and 0.05M thiourea ($SC(NH_2)_2$). The concentration of ammonium acetate (NH_4CH_3COO) used as buffer was varied from 0.1-0.6M in steps of 0.1, while ammonia solution (NH_3OH) concentration was varied from 0.4-1.2M in steps of 0.2. The temperature was also varied from 55- 85°C while keeping the ammonium acetate and ammonium hydroxide constant.

A 25ml beaker was used as container for the reacting chemicals; this was immersed in a water bath and heated to desired temperature with a hot plate. Cadmium acetate, Zinc acetate, ammonium acetate and thiourea were first mixed in the 25ml beaker and heated to desired temperature, ammonia solution was then added and substrates immersed vertically. The substrate had earlier been washed with detergent, rinsed in deionized water, soaked in nitric acid, degreased in ethyl alcohol and then rinsed in deionized water. The reacting bath was agitated throughout the period of deposition. The film thickness was measured using weight-difference-density consideration.

The normal incidence transmittance and absorbance spectrum of the film obtained at optimum deposition parameter was measured in the scanning mode using the double beam α-Helios UV- Vis spectrophotometer. The measurements were taken from the near ultraviolet (300nm) to the near infrared (900nm) regions. The measurements were taken under the parametric conditions of normal incidence, ambient temperature and uncoated Menzel Glazer glass slide as reference.

Result and Discussion

Optimization: Figure 1 Show the dependence of deposited $Cd^{1-x}Zn^xS$ film thickness on $[NH^3]$ introduced into the reaction bath as ammonium hydroxide NH^3OH from a concentration of 0.4 – 1.0M.The reagent concentrations are $[Cd(CH^3COO)^2]$ = $[Zn(CH^3COO)^2]$ = 0.015, $[NH^4CH^3OO]$ = 0.3 and $[SC(NH^2)^2]$ = 0.05M. $[NH^3]$ is varied from 0.4 to 1.0M in steps of 0.2. The film thickness is negligible at 0.4M $[NH^3]$ and increases with

increasing [NH₃] and Peaks at a concentration of 0.8M ammonia, and subsequently decreases at higher [NH₃].

At low [NH₃] there is insufficient NH₃ to bind the Cd^{2+} and Zn^{2+} into there tetrramine complexes, $Cd(NH_3)_4^{2+}$ and $Zn(NH_3)_4^{2+}$ [12, 13]. This leads to an excess of Cd^{2+}, Zn^{2+} and S^{2-} in deposition bath and favors homogenous nucleation of Cd₁₋ₓZnₓS colloids in solution with little film adhesion. As [NH₃] increases heterogeneous reaction which favour atom-by-atom deposition predominates. At [NH₃] in the neighborhood of 0.8M, there is optimum NH₃ needed to bind Cd^{2+} 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. Thus the observed decrease is film thickness beyond [NH₃] =0.8M. Therefore under the growth condition of $[Cd(CH_3COO)_2]$ = $[Zn(CH_3COO)_2]$ = 0,015M, $[SC(NH_2)_2]$ = 0.05M; $[NH_4CH_3COO]$ = 0.3M; 0.8M [NH₃] is observed to be the concentration that minimizes homogeneous reaction and favors atom-by-atom heterogeneous growth on substrate at Temperature of 75°C.
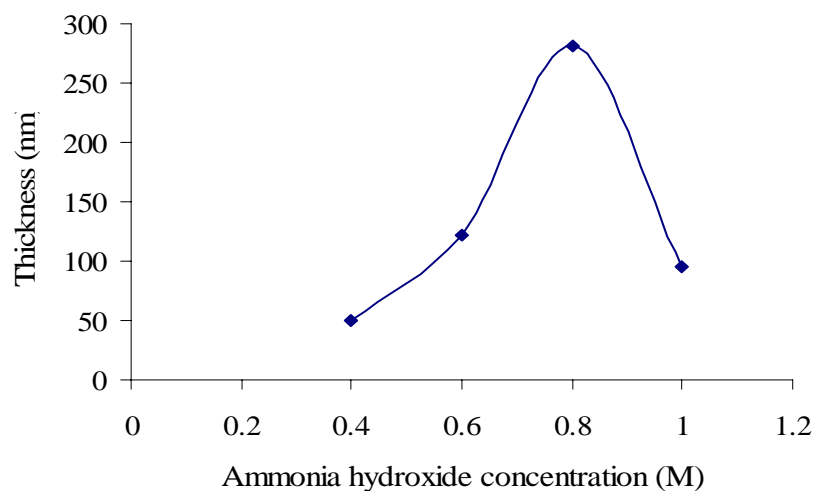

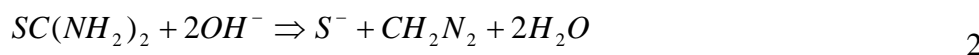*Fiure. 1. Influence of ammonia concentration on Cd¹⁻ˣZnˣS film thickness*

The variation of deposited film thickness as a function of ammonium acetate concentration is 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.

The action of ammonium salt has to be considered in relation to NH_4OH introduced into the reacting bath as NH_3 thus.

$$NH_3 + H_2O^+ \Leftrightarrow NH_4^+ + OH^- \qquad\qquad 1$$

This supplies the NH_3 needed to bind the Zn^{2+} and cd^{2+} into $[Zn(NH_3)_4]^{2-}$ and $[Cd(NH_3)_4]^{2-}$ and also provides OH^- that hydrolyzes the sulphide precursor $SC(NH_2)_2$ thus,

$$SC(NH_2)_2 + 2OH^- \Rightarrow S^- + CH_2N_2 + 2H_2O \qquad\qquad 2$$

The ammonium acetate provides the NH_4^+ and encourages equation 1 to tilt to the left, making more ammonia available for formation of tetraamine complexes.

For heterogeneous reaction required for thin film growth on substrate, $[NH_3]^+$ must be high enough to bind Zn^{2+} and Cd^{2+} as ion complexes and $[OH]^-$ low enough so that the hydrolysis of $SC(NH_2)_2$ according to equation 2 takes place on the substrate so that $[S^{2-}]$ is very low in reaction bath.

At low ammonium acetate concentration, there exists more OH^- in reaction bath that encourages excess of S^{2-} in reaction bath, with the formation of $Cd^{1-x}Zn^xS$ colloids in solution and hence the observation of lower film thickness at low ammonium salt concentration.

Too high a concentration of ammonium salt encourages backward reaction in equation 1 and depletes the bath of OH^- crucial for hydrolysis to occur according to equation 2 and thus the observed decrease in film thickness at higher ammonium salt concentration.
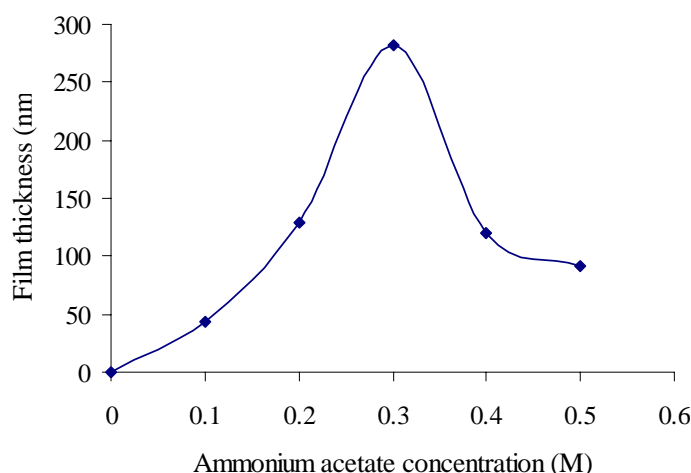
Figure 2. Influence of ammonium acetate concentration on Cd$_{1-x}$Zn$_x$S film thickness

The thickness dependence on temperature of the film is shown in figure 3. From the CBD kinetics deposition of ZnS, the Zn tetraamine complex can exist as $Zn(N^2H^4)_3{}^{2+}$ and as $Zn(NH^3)_4{}^{2+}$ [13]. $Zn(N^2H^4)_3{}^{2+}$ which though has a lower stability constant, is present only in low concentration as against $Zn(NH^3)_4{}^{2+}$ predominantly present in higher concentration but has a very high stability constant. The formation of ZnS from such a bath requires low activation energy of 21Kj/mol and thus favors low temperature deposition of about 21°C to ambient temperature [7]. CdS on the other hand forms a tetraamine complex mainly as $Cd(NH^3)_4{}^{2+}$ with an activation energy of 85Kj/mol [12, 14] almost impossible to grow at room temperature for a $[Cd^{2+}]/[NH^4{}^+]$ similar to $[Zn^{2+}]/[NH^4{}^+]$ ratio. Thus there co-deposition presents a challenge in terms of energy input into the system.

Various temperatures from 45^0C to 85^0C in steps of 10°C were used in the co-depositing Cd^{1-x}Zn^{x}S to obtain the optimal temperature. Fig. 3 show an increase in film thickness as the temperature increases from 45^0C to 75^0C and drops at 85°C. The rise in the film thickness may be due to the increase in the hydrolysis of $SC(NH^2)_2$ as the temperature increases [15]. 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 substrate [16].

The observed decrease in film thickness at temperatures above 75°C could be due to the decrease in ammonia concentration due to high evaporation rate at very high temperature.
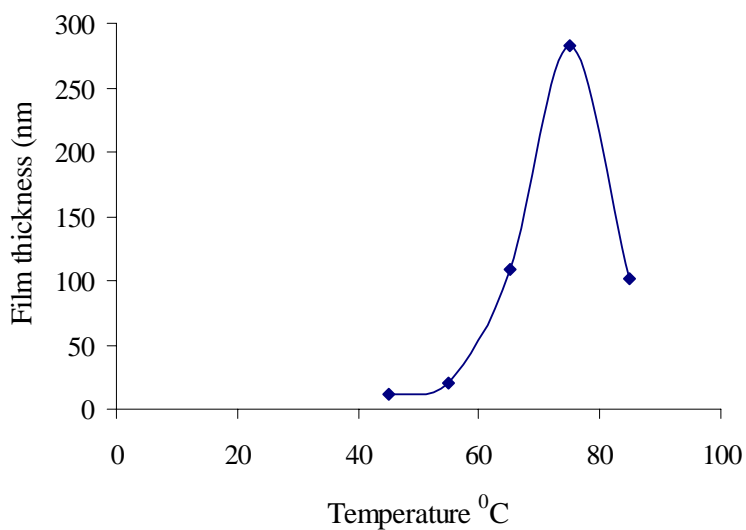

Figure 3. Cd$_{1-x}$Zn$_x$S film thickness dependence on bath temperature

Highly adherent specularly reflecting film of optimum thickness of 282nm was obtained at 0.3M ammonium acetate concentration, 0.8M ammonium hydroxide concentration and a temperature of 75°C.

Optical characterization: Measured values of transmittance (T), absorbance (A) and reflectance (R) spectra of the film as a function of wavelength (λ) are shown in figure 4, in the UV-Vis spectral range (300-900nm) of the film with the optimal thickness of 282nm. It shows a transmittance of 78-80% in the 510-900nm range.
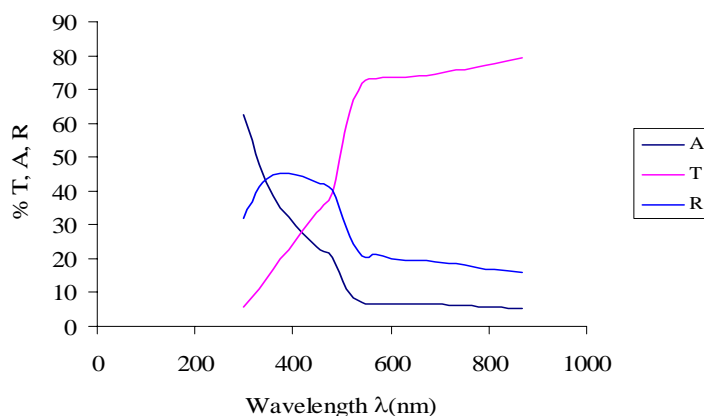

Fiure. 4. Transmittance (T), absorbance (A) and reflectance (R) spectra: T = 75°C, [NH^{3}OH] = 0.8M and [NH^{4}CH^{3}COO] = 0.3M

The plot of the square of the absorption coefficient α^2 versus the photon energy hυ is shown in Fig. 5.The shape of the curve indicates a direct transition and the broad nature of the curve shows the existence of more than one phase [8]. The absorption starting at about 2.4eV indicates the existence of a pure CdS phase. The band gap of the film Cd$_{1-x}$Zn$_x$S was determined as 2.49eV at the intercept of the extrapolation of α^2 to zero with the photon energy (hυ) axis in Fig. 5.

The composition of the ternary Cd$_{1-x}$Zn$_x$S was estimated from the Vegard's expression [11],

$$E_g(x) = 2.42 + 0.69x + 0.62x^2$$

E$_g$(x) is the band gap of the composition of the ternary Cd$_{1-x}$Zn$_x$S defined at x. The calculated value of x was 0.09. This is in reasonable agreement with the value of 0.11 obtained by Boyle et al [11].
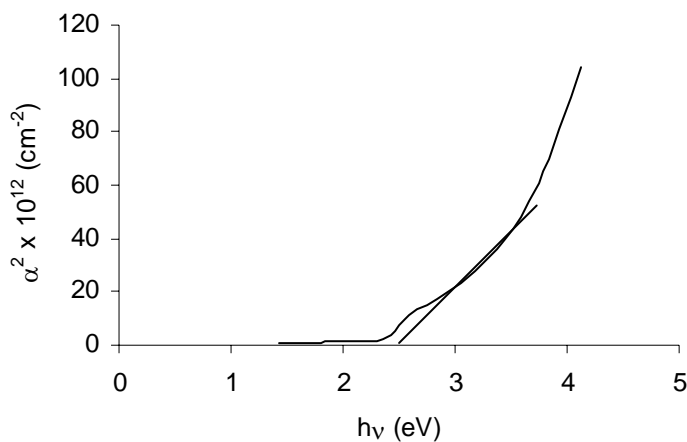

Figure 5. α^2 versus hυ: T =75 ^{0}C, [NH$_3$OH] = 0.8M and [NH$_4$CH$_3$COO]=0.3M

Conclusion

Cd$_{1-x}$Zn$_x$S films were deposited at a temperature of 75°C and a pH of between 9.2 and 9.7. 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. The film had a high enough long wavelength optical transmission for solar cell application, with a transmittance of about 80% at wavelength beyond the absorption edge for the optimum film thickness obtained. The film had a band gap of 2.49eV and the parameter x of the $Cd_{1-x}Zn_xS$ was determined as 0.09 from the band gap.

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