

A study of the effects of ammonium salts on chemical bath deposited zinc sulfide thin films

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Abstract

We have obtained further insights into the CBD growth mechanisms of ZnS thin films using an aqueous medium containing an ammonium salt. At room temperature the optimum concentration of this salt has enabled us to increase the thickness of the film by more than 400%. The optical transmission below the band edge of our best film is also found to be excellent. © 1999 Elsevier Science S.A. All rights reserved.

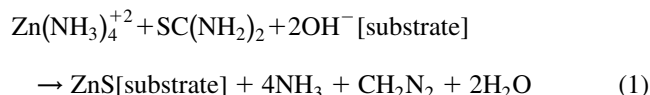
Keywords: Growth mechanism; Inorganic compounds; Sulphides; Zinc

1. Introduction

Zinc sulfide (ZnS), a II–VI compound, both in bulk and thin film forms, is receiving ever-increasing attention owing to its potential uses [1–3] in a wide variety of applications. However, the deposition of high quality ZnS thin film over a large area is required if it is to be effectively used in electroluminescent devices and solar cells. Of all the deposition methods, chemical bath deposition (CBD) is the least costly low temperature technique capable of producing films that meet the above requirements.

CBD has been used over the years to deposit chalcogenide material thin films: mainly CdS [3], CdSe [4], PbS [5], and has up until recently been found unsuitable [3] to grow ZnS/Cd_{1-x}Zn_xS films. Generally, in a CBD process, ammonia (NH₃) is used as a complexing agent to bind the metallic ions so as to minimize the precipitation of the corresponding bulk compounds. However, in the case of ZnS, for example, the zinc tetrammine ([Zn(NH₃)₄]²⁺) complex ions which should normally undergo an heterogeneous reaction, according to the global reaction Eq. (1) (the details of these growth mechanisms is similar to that of CdS described elsewhere [6,7]), with thiourea (SC(NH₂)₂), the chalcogen precursor, on the substrate in the basic aqueous solution to form ZnS films has a very high stability constant. This high stability constant prevents either the adsorption of [Zn(NH₃)₄]²⁺ onto the substrate or the relaxation of the Zn–NH₃ bond of the adsorbed complex thereby stopping the subsequent heterogeneous reaction with SC(NH₂)₂. This

leads to little or no film growth.



Recently, Dona [8] et al. reported that the deposition of ZnS thin films by CBD is possible with the use of NH₃ and hydrazine (N₂H₄) as complexing agents. In the present paper we confirm this finding and report that the thickness of the deposited film is increased if the deposition is carried out at room temperature in the presence of an ammonium salt. We also present an analytical framework that explains our results and provides further insight into ZnS growth mechanisms in CBD. Furthermore, we show how to improve the quality of the deposited ZnS film by using a combination of growth temperatures. Some characterization results of the CBD grown ZnS film are also presented.

2. Experimental

The reagents used for these studies are zinc sulfate heptahydrate (ZnSO₄·7H₂O), ammonium sulfate ((NH₄)₂SO₄), thiourea (SC(NH₂)₂), 14.3 N ammonium hydroxide (NH₄OH), and 85%, or 100% hydrazine monohydrate (N₂H₄·H₂O). These chemicals are of analytical grade. The experimental solution of the desired concentrations of various reagents is prepared by adding first the required mass of ZnSO₄·7H₂O and (NH₄)₂SO₄ into the beaker containing stirred deionized water at 85 or 21°C (room temperature) with the cleaned substrate retained with a Teflon holder. The volume of deionized water ranged

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Table 1

Saturation thickness of CBD grown ZnS thin films. Growth conditions: $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.0075 \text{ M}$, $[\text{SC}(\text{NH}_2)_2] = 0.0075 \text{ M}$, concentration of $(\text{NH}_4)_2\text{SO}_4$ buffer when used is 0.05 M , concentrations of NH_3 and N_2H_4 when used separately or together are 0.44 M and 1.08 M , respectively.

Sample #	T ($^\circ\text{C}$)	$(\text{NH}_4)_2\text{SO}_4$	Complexing agent	Thickness (\AA)
ZnS1	85	Without	NH_3	Negligible
ZnS2AH	21	Without	NH_3	Negligible
ZnS3AH	21	Without	N_2H_4	Negligible
ZnS52AH	85	Without	$\text{NH}_3, \text{N}_2\text{H}_4$	200
ZnS53H	21	Without	$\text{NH}_3, \text{N}_2\text{H}_4$	400
ZnS34H	21	With	$\text{NH}_3, \text{N}_2\text{H}_4$	935

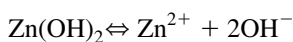
from 100–250 ml. The substrate is either quartz glass or Sn_2O coated soda lime glass. The procedures for cleaning the substrate are described in our previous work [6]. When this mixture is completely dissolved, the required volume of NH_4OH is added followed by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The predissolved $\text{SC}(\text{NH}_2)_2$ in about 5–10 ml of deionized water is then added to start the deposition. The reaction bath is covered with a serran wrap to minimize the escape of NH_3 and N_2H_4 . The growth process was carried out in a fume hood. For the deposition of thicker and higher quality films, the initial coating is deposited at 85°C for about 10–15 min and the subsequent layer deposited at 21°C using the optimum growth conditions.

The thickness was measured with an alphastep profilemeter. Optical characterization was carried out with a UV–Vis spectrophotometer.

3. Results and discussions

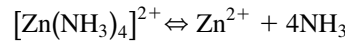
Table 1 shows the saturation thickness of ZnS grown thin films. We note that at any temperature when NH_3 and N_2H_4 are used separately we have a negligible growth. For NH_3 , this may be due to the high stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ as discussed in the introduction. For N_2H_4 , on the other hand, we have a low stability constant, hence a high Zn^{2+} concentration. As a result, the Zn^{2+} and the S^{2-} concentration product is greater than the solubility product of ZnS at the onset of the reaction, and precipitation instead of a heterogeneous reaction takes place.

Now, the film growth observed when both NH_3 and N_2H_4 are used, could be due to the change in the saturation level of the zinc-amine complex. Moreover, the increase in the thickness of the film from 200 \AA , when no buffer is used at 85°C , to 935 \AA , when the buffer is used at room temperature, may be due to a homogeneous reaction reduction. All these observations can further be understood by considering the graphical solution of the following equations [8,9]:



with

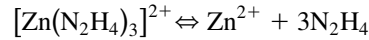
$$[\text{Zn}^{2+}][\text{OH}^-]^2 = 4.5 \times 10^{-17} \quad (2)$$



with

$$[\text{Zn}^{2+}][\text{NH}_3]^4 / [\text{Zn}(\text{NH}_3)_4^{2+}] = 10^{-8.9} \quad (3)$$

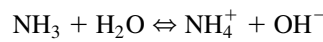
and



with

$$[\text{Zn}^{2+}][\text{N}_2\text{H}_4]^3 / [\text{Zn}(\text{N}_2\text{H}_4)_3^{2+}] = 10^{-5.5} \quad (4)$$

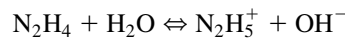
But the base hydrolysis [10] of NH_3 , and N_2H_4 are



where

$$[\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3] = 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

and [11]



where

$$[\text{N}_2\text{H}_5^+][\text{OH}^-] / [\text{N}_2\text{H}_4] = 8.5 \times 10^{-7} \text{ at } 25^\circ\text{C} \text{ respectively.}$$

Assuming [12]

$$[\text{NH}_4^+] = [\text{OH}^-], [\text{NH}_4\text{OH}] = [\text{NH}_3], [\text{N}_2\text{H}_5^+] = [\text{OH}^-]$$

and

$$[\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}] = [\text{N}_2\text{H}_4]$$

the latter equations become

$$[\text{OH}^-]^2 / [\text{NH}_3] = 1.8 \times 10^{-5} \quad (5)$$

$$[\text{OH}^-]^2 / [\text{N}_2\text{H}_4] = 8.5 \times 10^{-7} \quad (6)$$

Eqs. (5) and (6) and the fact that $[\text{H}^+][\text{OH}^-] = 10^{-14}$ at 25°C enable us to rewrite Eqs. (2)–(4), respectively, as follows

$$\text{pH} = 0.5p[\text{Zn}^{2+}] + 5.827 \quad (7)$$

$$\text{pH} = 10.52 + (1/8)p[\text{Zn}^{2+}] - (1/8)p[\text{Zn}(\text{NH}_3)_4^{2+}] \quad (8)$$

$$\text{pH} = 10.05 + (1/6)p[\text{Zn}^{2+}] - (1/6)p[\text{Zn}(\text{N}_2\text{H}_4)_3^{2+}] \quad (9)$$

Here, $[\text{Zn}^{2+}]$ is our independent variable. We, therefore, need to find $[\text{Zn}(\text{NH}_3)_4^{2+}]$ and $[\text{Zn}(\text{N}_2\text{H}_4)_3^{2+}]$ in terms of $[\text{Zn}^{2+}]$.

Coupling Eqs. (3) and (4) with [7]

$$C_{\text{salt}} = \alpha[\text{Zn}^{2+}]$$

Where, C_{salt} is the total concentration of zinc salt introduced into the reaction bath, and α is the overall complexation coefficient; and assuming

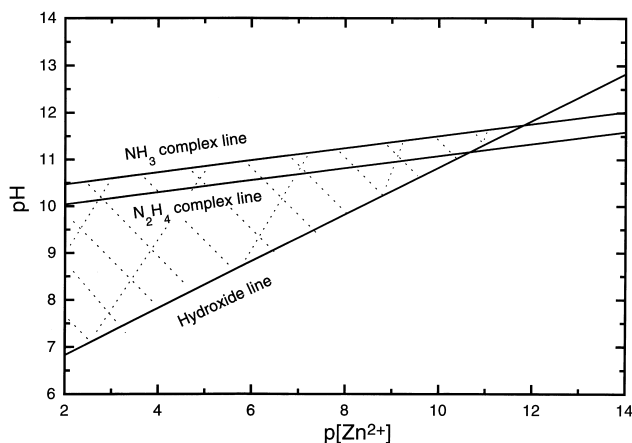


Fig. 1. Plot of pH of the reaction bath at 25°C containing $[\text{Zn}(\text{NH}_3)_4]^{2+}$ (NH_3 complex), $[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+}$ (N_2H_4 complex) and $\text{Zn}(\text{OH})_2$ (hydroxide) versus $p[\text{Zn}^{2+}]$. Concentration of Zn^{2+} precursor (C_{salt}) used in the computation is 0.0075 M and the selected value of β is 2.4.

$$[\text{Zn}(\text{NH}_3)_4]^{2+} + [\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+} = C_{\text{salt}}$$

for

$$[\text{NH}_4\text{OH}^+][\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}] \gg C_{\text{salt}}$$

we derive

$$[\text{Zn}(\text{NH}_3)_4]^{2+} = C_{\text{salt}} / (1 + 10^{-3.4} \beta^3 / [\text{NH}_3]) \quad (10)$$

$$[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+} = C_{\text{salt}} / (1 + 10^{3.4} [\text{NH}_3] / \beta^3) \quad (11)$$

where, $\beta = [\text{N}_2\text{H}_4] / [\text{NH}_3]$. From Eqs. (3) and (10) for a given $[\text{Zn}^{2+}]$ present in the reaction bath the corresponding $[\text{NH}_3]$ introduced in the same bath as NH_4OH is given by

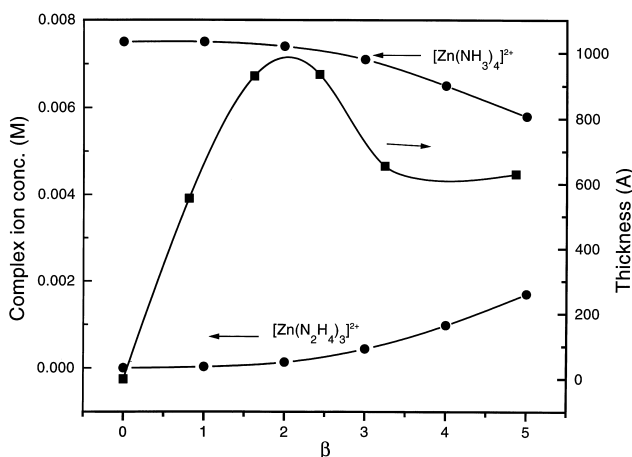


Fig. 2. Effect of $\beta = [\text{N}_2\text{H}_4] / [\text{NH}_3]$ on (●) the calculated concentrations of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+}$ and (■) the measured ZnS thin film saturation thickness. The complex concentrations calculated using Eq. 10 and Eq. 11 for $T = 25^\circ\text{C}$, $C_{\text{salt}} = [\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.0075$ M and $[\text{NH}_3] = [\text{NH}_4\text{OH}]$ fixed at 0.44 M. Film growth conditions: $T = 21^\circ\text{C}$, $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.0075$ M, $[\text{SC}(\text{NH}_2)_2] = 0.0075$ M, $[(\text{NH}_4)_2\text{SO}_4] = 0.05$ M and $[\text{NH}_4\text{OH}] = 0.44$ M; time of deposition is 18 h.

$$[\text{NH}_3]^4 + 10^{-3.4} \beta^3 [\text{NH}_3]^3 - 10^{-8.9} C_{\text{salt}} / [\text{Zn}^{2+}] = 0$$

where, the real positive roots are needed for a chosen C_{salt} and β to completely determine the numerical values of Eqs. (8)–(11).

On the other hand, the overall pH of the reaction bath, according to Eqs. (3), (4) and (7), is

$$\text{pH} = -0.5A + 5.827 \quad (12)$$

where

$$A = 1/2 \left(-7 \log_{10} [\text{NH}_3] - 3 \log_{10} \beta + \log_{10} [\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+} + \log_{10} [\text{Zn}(\text{NH}_3)_4]^{2+} - 14.4 \right)$$

The pH value in Eq. (12) agrees with what has been experimentally determined in the absence of ammonium salt at room temperature.

The plots of pH against $p[\text{Zn}^{2+}]$ (at constant C_{salt} and β) in Eq. 7–9 give straight lines called the hydroxide, ammonia complex, and hydrazine complex lines, respectively as shown in Fig. 1. There is $\text{Zn}(\text{OH})_2$ in the solution, only, if the overall pH of the reaction bath lies above the hydroxide line. And $[\text{Zn}(\text{NH}_3)_4]^{2+}$ or $[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+}$ is present in the solution if the overall pH is below the corresponding complex line. It has been previously demonstrated and experimentally confirmed by Kitaev [12] et al. and Kaur [10] et al. using a similar approach for CdS that film growth is possible if the complex and the hydroxide of the metal are simultaneously present in the reaction bath. Thus, in this case, the region of interest where it is thermodynamically possible to grow a film is in the shaded region. However, the further the pH of the solution is from the hydroxide line the higher the concentration of $\text{Zn}(\text{OH})_2$ colloids in the bath and the greater the tendency of causing the $\text{CS}(\text{NH}_2)_2$ to directly hydrolyze on these colloids to form a ZnS precipitate. But for a given $[\text{NH}_3]$ introduced into the reaction bath, the overall pH can be increased by increasing the temperature or decreased by the presence of an ammonium salt (buffer). In the study represented by Table 1, the concentration of NH_3 used is 0.44 M and this corresponds to $p[\text{Zn}^{2+}] = 9.6$. At 85°C the overall pH, 11.1, was found to be much closer to the complex lines, and owing to significant homogeneous reactions we ended up with a thinner film. At 21°C , when no buffer is used, a somewhat thicker film has to do with reduction in the overall pH (10.9) and, hence, a reduction in the homogeneous reaction. In the presence of a buffer at room temperature, the very thick film results from the overall pH, (10.5), i.e. perhaps, very close to the hydroxide line. This may mean that very few $\text{Zn}(\text{OH})_2$ colloids are present in the bulk of the reaction bath; and they appear to be confined to the surface of the substrate and the wall of the container where they help to cause a heterogeneous reaction, as described implicitly by Eq. (1), to predominantly take place.

For further insight into the growth of ZnS when NH_3 and N_2H_4 are used together, we consider Fig. 2. This shows the

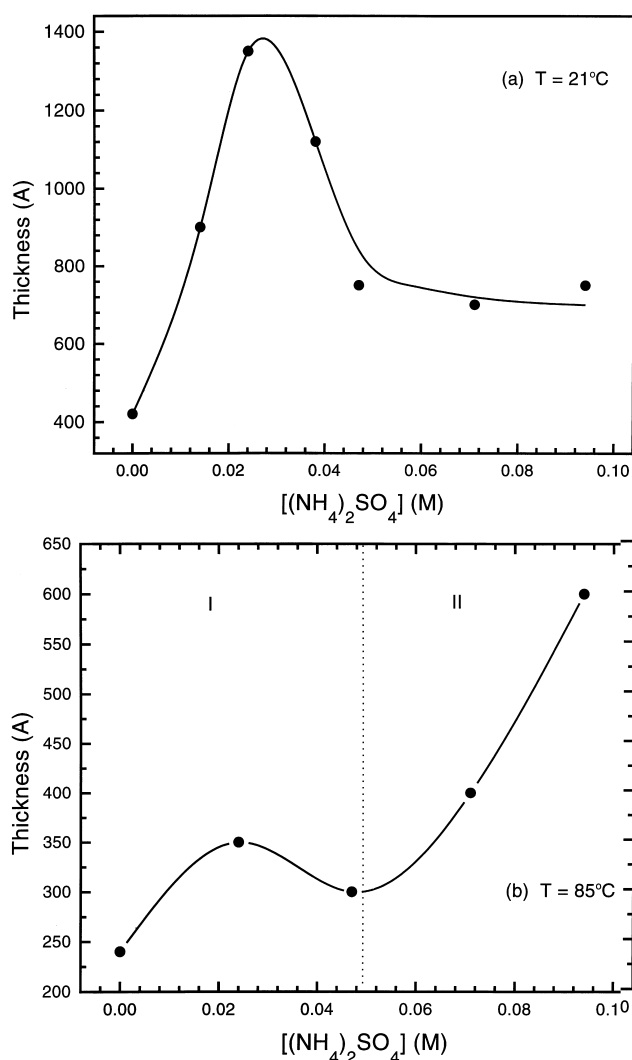


Fig. 3. Dependence of the ZnS film thickness on $[(\text{NH}_4)_2\text{SO}_4]$ at (a) 21°C and (b) 85°C . In both cases $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.009 \text{ M}$, $[\text{SC}(\text{NH}_2)_2] = 0.009 \text{ M}$, $[\text{NH}_4\text{OH}] = 0.5 \text{ M}$ and $\beta = 2$. Time of deposition is 12 h at 21°C and 2 h at 85°C .

calculated complex ions concentration (using Eq. (10) and Eq. (11) as a function of the concentration ratio (β) of hydrazine to ammonia introduced into the reaction bath. Here, the ammonia concentration is fixed at 0.44 M , $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.0075 \text{ M}$, and $T = 25^\circ\text{C}$. Fig. 2 also shows the plot of film thickness against β for the same concentrations of NH_3 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with $[\text{SC}(\text{NH}_2)_2] = 0.0075 \text{ M}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.05 \text{ M}$, and $T = 21^\circ\text{C}$. We observe that for the growth conditions used the optimum film thickness corresponds to $\beta = 2$. That at this value of β the concentration of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ changed only slightly shows that this complex plays a much bigger role in the growth of the ZnS film than $[\text{Zn}(\text{N}_2\text{H}_4)_3]^{2+}$ which has a negligible concentration. But, with the stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ being too high, it may mean that the presence of hydrazine helps part of this complex to exist as $[\text{Zn}(\text{NH}_3)_3]^{2+}$. This latter has a moderate stability

constant [13] (3.26×10^6) and is likely to be the major Zn precursor in the film growth. The low activation energy [8] (21 KJ/mol) previously reported, and the growth of the film at room temperature even in the presence of an ammonium salt confirms this fact. This assertion is born from the knowledge [6] that CBD grown CdS with an 85 KJ/mol activation energy [7], and a 10^7 stability constant for $[\text{Cd}(\text{NH}_3)_4]^{2+}$ (the major Cd precursor) is almost impossible to grow at room temperature if the ratio of $[\text{Cd}^{2+}]/[\text{NH}_4^+]$ introduced into the reaction bath is similar to that used in the present case for ZnS.

Now, NH_4OH introduced into the reaction bath plays a dual role as depicted by the base hydrolysis of NH_3 (previously quoted, and named here Eq. (13) for clarity).



First, it supplies NH_3 to bind Zn^{2+} into $[\text{Zn}(\text{NH}_3)_3]^{2+}$ or $[\text{Zn}(\text{NH}_3)_4]^{2+}$ that we have just quoted to be essential for the growth of the film. Secondly, it provides OH^- that hydrolyzes the sulfide precursor, $\text{SC}(\text{NH}_2)_2$, as follows



Ideally, $[\text{NH}_3]$ must be high enough to bind most of the Zn^{2+} as a complex ion and $[\text{OH}^-]$ low enough that reaction (14) takes place mostly on the substrate so that $[\text{S}^{2-}]$ in the reaction bath is very low. This ideal growth condition ensures that the ionic concentration product of Zn^{2+} and S^{2-} in the bulk of the bath is less than the solubility product of ZnS to prevent or minimize precipitation and facilitates a predominant heterogeneous growth of the high quality film. We have already established in the previous paragraphs that the presence of $(\text{NH}_4)_2\text{SO}_4$ reduces $[\text{OH}^-]$ and the homogeneous reaction and results in a net gain in film thickness. This, therefore, points to the fact that this salt brings the bath close to this ideal growth condition, owing, possibly, to a common ion effect [7,14]. The foundation of this effect lies in the fact that ammonium ions (NH_4^+) coming from the ammonium salt encourages Eq. (13) to proceed predominantly to the left making more NH_3 available. Excess NH_3 , on the other hand, tilts reaction (3) to the left and binds more Zn^{2+} in the form of a complex. In addition the backward reaction in Eq. (13) lowers the OH^- concentration as required. However, too high a concentration may also be detrimental to the process, as this may deplete the bath of OH^- crucial for the film growth as shown in Eq. (1). Therefore, there is a need to find an optimum $(\text{NH}_4)_2\text{SO}_4$ concentration.

Fig. 3a,b show the dependence of the ZnS film thickness on $[(\text{NH}_4)_2\text{SO}_4]$ at 21 and 85°C , respectively. In both cases $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.009 \text{ M}$, $[\text{SC}(\text{NH}_2)_2] = 0.009 \text{ M}$, and $[\text{NH}_4\text{OH}] = 0.5 \text{ M}$ with $\beta = 2$. Within the range of concentrations of ammonium salt used all film grown at room temperature (21°C) appear to be uniform and specularly reflecting. Also, as seen in Fig. 3a, the thickness of the film, increases rapidly with an increase in $[(\text{NH}_4)_2\text{SO}_4]$,

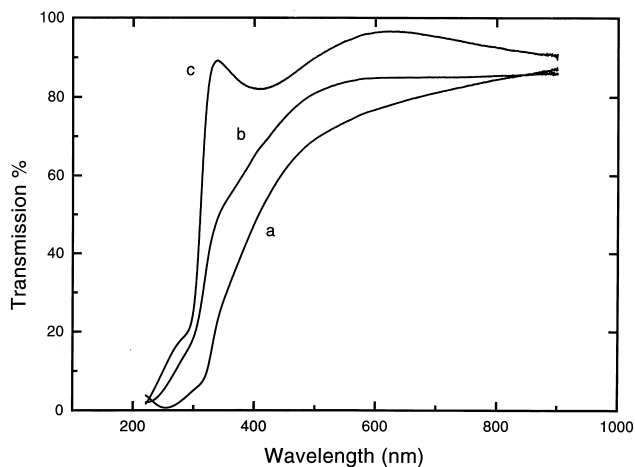


Fig. 4. Optical transmission spectra of CBD grown ZnS thin films. (a) $[\text{NH}_4\text{OH}] = 0.9 \text{ M}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.094 \text{ M}$, $T = 85^\circ\text{C}$ and film thickness is $0.12 \mu\text{m}$ after three dips of 1 h duration each. (b) $[\text{NH}_4\text{OH}] = 0.7 \text{ M}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.094 \text{ M}$, $T = 85^\circ\text{C}$ and film thickness is $0.11 \mu\text{m}$ after three dips of 1 h duration each. (c) $[\text{NH}_4\text{OH}] = 0.5 \text{ M}$, $[(\text{NH}_4)_2\text{SO}_4] = 0.025 \text{ M}$, the first dip carried out at 85°C for about 10 min and additional three dips of 6 h duration each at 21°C ; total film thickness is $0.34 \mu\text{m}$. $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] = 0.009 \text{ M}$, $[\text{SC}(\text{NH}_2)_2] = 0.009 \text{ M}$ and $\beta = 2$ in all three cases.

peaking at $0.14 \mu\text{m}$ around 0.025 M , and falls rapidly subsequently then gradually thereafter. For these growth conditions we therefore take 0.025 M as the optimum $[(\text{NH}_4)_2\text{SO}_4]$.

For the growth at 85°C , Fig. 3b is divided into two regions, (I) and (II). The thickness of the film in (I) appears to peak at about the same concentration of $(\text{NH}_4)_2\text{SO}_4$ as in Fig. 3a, and it increases with the increase in concentration of this same reagent in (II). Also, the films in region (I) are uniform and specularly reflecting, however, those in region (II) are not uniform and in addition have an island of uncovered glass about the center of the substrate. The size of the island appears to increase with an increase in $[(\text{NH}_4)_2\text{SO}_4]$. The observed phenomena in region (II) may be characteristic of a very low concentration of OH^- .

To illustrate this observation, we propose that in CBD

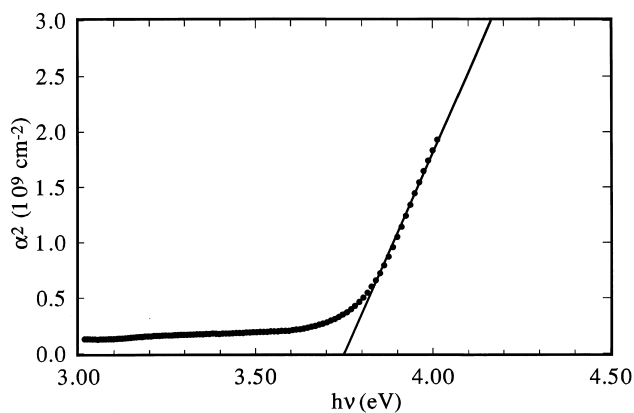


Fig. 5. Plot of α^2 versus $h\nu$ for the film of Fig. 4c.

growth of ZnS films it is OH^- that is first adsorbed onto the substrate followed by a zinc amine complex which then reacts with OH^- to form $\text{Zn}(\text{OH})_2$. Here, $\text{Zn}(\text{OH})_2$ serves as a nucleus on which $\text{SC}(\text{NH}_2)_2$ is adsorbed and hydrolyzed to form a ZnS molecule attached to the substrate. This growth process may be thought of as taking place one monolayer after another on the substrate; with the growth on an existing ZnS layer possibly being easier than on a bare substrate. Thus, in region (II) the initial OH^- , nuclei, or ZnS layer has partially covered the substrate from the edge inward, due primarily to low $[\text{OH}^-]$. The subsequent layers owing to reasons already advanced have, perhaps, followed the growth pattern of the initial layer resulting in the uncovered central portion of the glass. In the higher concentration of $(\text{NH}_4)_2\text{SO}_4$ studied this behavior does not arise at 21°C because the homogeneous reaction [6,7] that generally takes place at a faster rate than the heterogeneous reaction is diffusion limited; implying that at low temperature the former reaction slows down allowing available OH^- to be more involved in the film growth.

To check the validity of the low $[\text{OH}^-]$ argument for the bath at 85°C with $[(\text{NH}_4)_2\text{SO}_4] = 0.094 \text{ M}$ the concentration of NH_4OH is increased to 0.9 M . The grown film is found to be uniform with a milky appearance and no island. The elimination of the island due to increased $[\text{OH}^-]$ seems to justify our proposed model, which may be crucial for the future simulation of chemical bath depositions of ZnS film. We note that films deposited in region (I) of Fig. 3b and at 21°C are colorless, the milky appearance here, however, is likely due to adsorbed colloids produced by excess homogeneous reactions as expected. Colloids are generally known to degrade [6,15] the quality of the film. This fact is obvious from the transmission spectrum, Fig. 4a, of a $0.12 \mu\text{m}$ thick film deposited on quartz glass under this same growth condition. Here, the absorption edge appears broad and the transmission in the visible region, 600 nm for example, is about 75%. However, in Fig. 4b where $[\text{NH}_4\text{OH}]$ is reduced to 0.7 M and the homogeneous reaction is slightly reduced, the absorption edge of the film ($0.11 \mu\text{m}$ thick) becomes relatively sharpened and the transmission at 600 nm is found to increase to 85%, thus affirming our argument.

Fig. 4c shows the typical optical transmission spectrum of CBD grown ZnS films using the optimum growth condition of Fig. 3a. To eliminate the adherence problem associated with the growth of thicker films at room temperature the initial coating of this film is carried out at 85°C for about 10 min. The thickness of the film after three more coatings, of about 6 h duration each, is $0.34 \mu\text{m}$. Below the band edge, the overall optical transmission of this film is excellent compared to the previous films, indicating that minimal colloids adsorption or the accompanying light scattering have taken place. Besides, the transmission at 600 nm is almost 100%. We also observe that the absorption about the band edge is sharp indicating that ZnS has a direct band gap as expected. Consequently, the data from Fig. 4c used to plot α^2 versus photon energy, $h\nu$, as shown in Fig. 5,

yields a value of 3.9 eV as the bandgap of the CBD grown ZnS film. This value differs slightly from 3.75 eV obtained by Dona and Herrero [8] for the film grown at 75°C. Though other films grown at 85°C using optimum growth condition have band edges that agrees with this latter value, annealing generally lowers the bandgap of all films, independent of growth temperature, to a value that is lower or close to 3.75 eV. Further studies on the dependence of bandgap on growth and annealing temperatures are underway.

4. Conclusion

Using our optimum growth condition at room temperature in the presence of ammonium salt we have increased the thickness of ZnS films by more than 400% compared to that of the film deposited in a non-buffered medium at 85°C. The thickness of large bandgap film required for solar cell applications is about [6] 0.1 μm and that required for electroluminescent devices is less than or equal [16] to 0.5 μm . It is, therefore, obvious that CBD will be one of the low cost growth processes that has the potential of lowering the cost of these devices in the near future.

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