Role of Thiourea in the Kinetic of Growth of the Chemical Bath Deposited ZnS Films

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ZnS films were deposited onto glass substrates by the chemical bath technique at temperatures from 60 to 90 °C. Zinc chloride, potassium hydroxide, ammonium nitrate, and thiourea were used as chemical components. According to the species distribution diagrams, the concentration of the chemical components were maintained constant except for thiourea whose concentration is required to decrease when the bath temperature increases, in order to maintain constant the \( \text{Zn(OH)}_2^-/\text{HS}^- \) ions concentration. To investigate the kinetic of growth of the ZnS films, their thicknesses were measured as a function of deposition time and bath temperature. The activation energy value estimated for the growing process was \( E_a = 44.9 \text{kJ/mol} \) which is typical for chemical reactions. The mean value of the bandgap energy of the films was 3.67 eV with optical transmittances up to 80% for all bath temperatures. The rms-roughness of the deposited films was observed to decrease when the bath temperature increases. Results of X-ray diffraction analysis on deposited films reveal a cubic (111) as preferential orientation. Additionally, SEM-EDS results of the ZnS films shows a stoichiometry ratio of \([\text{Zn}/\text{S}] = 0.4-0.6\) for all deposition times and bath temperatures.

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a thermodynamic analysis of the chemical bath for ZnS films deposition were discussed. In that work, different concentrations of the bath chemical reagents were studied at 80 °C as bath temperature for the ZnS films preparation. Thus, optimal concentrations and pH bath values were reported for depositing ZnS films with good qualities. The physicochemical analyzes reports the solubility plot and the speciation diagrams as a function of pH which result useful to obtain the optimal region were pH and the chemical concentrations at 80 °C produces the better ZnS films quality.

Based on the speciation diagrams, the present work focuses on the synthesis of the ZnS films by CBD technique when the bath temperatures range from 60 to 90 °C. For this purpose, the thiourea concentration and the deposition time were varied with bath temperature, meanwhile the concentration of the other chemical reagents remain constant. In the CBD technique is common to use bath temperatures in the range from 60 to 90 °C. For this reason, this range of temperature was chosen for studying the kinetic of growth of the CBD-ZnS films. The objective of this work is to study the role of thiourea in the growth kinetics of the CBD-ZnS films as a function of temperature by changing the thiourea concentration but maintaining similar the concentrations of the other chemical reagents. From the results, the activation energy of the chemical process was estimated. Additionally, the morphology, optical properties, stoichiometry and crystalline structure of the deposited ZnS films were investigated in order to observe differences in the films quality.

Chemical Formation of the ZnS

The chemical formation of the ZnS can be explained if the most probably chemical reactions of the different chemical reagents are considered. The chemical reagents used in this work are: ZnCl2, KOH, NH4NO3 and SC(NH2)2 in aqueous solution and the most representative chemical reactions are:

For thiourea decomposition,

\[
SC(NH_2)_2(aq) \leftrightarrow S^2(b) + H_2NCN(aq) + 2H^+(aq)
\]  

[1]

For zinc-aminocomplexes formation,

\[
Zn^{2+}(aq) + 4NH_3(aq) \leftrightarrow Zn(NH_3)_4^{2+}(aq)
\]  

[2]

For zinc-hydroxycomplexes formation,

\[
Zn^{2+}(aq) + 4OH^-(aq) \leftrightarrow Zn(OH)_4^{2+}(aq)
\]  

[3]

Precipitated zinc formation,

\[
ZnS(s) \leftrightarrow Zn^{2+}(aq) + S^{2-}(aq) \quad \text{or} \quad Zn(OH)_2(s) \leftrightarrow Zn^{2+}(aq) + 2OH^-(aq)
\]  

[4]

Other chemical species can be formed depending on the pH conditions but the chemical reactions 1 to 4 are the most interesting according to the speciation diagrams obtained as a function of bath temperature and chemical concentrations.

Experimental

Species distribution diagrams.— For the chemical bath, the fixed chemical reagents and their concentrations are: 80 mL of ZnCl2 [0.0194 M], 80 mL of NH4NO3 [0.847 M], and 200 mL of KOH [0.771 M]. Figure 1 shows the corresponding diagrams of the species distribution as a function of pH from 60 to 90 °C as bath temperature. The methodology for obtaining the speciation diagrams has been widely explained in Ref. 36. The species distribution diagrams were obtained, in this case, by maintaining the same relative concentration of the zinc-complex (Zn(OH)2+2) and bisulfide (HS-) ions present into the chemical bath in aqueous solution for the different bath temperatures. From diagrams, as the bath temperature decrease, the thiourea concentration requires to increase in order to maintain the same Zn(OH)2+2/HS- relative ions concentration. The desirable pH value determined for the speciation diagram for the chemical bath is marked with a vertical bar in Fig. 1.

In a preliminary work, the desirable pH value of the bath for obtaining high quality ZnS films was determined by the interception between the Zn(OH)3- and Zn(OH)2+2 curves. Otherwise, Zn(OH)2 can also be formed at higher pH values and/or no formation of ZnS is achieved at lower pH values, according to Equations 1 to 4. The species containing sulfur such as HS-, H2S and S2- from the thiourea decomposition are included in the species diagrams, being the last two ones of very low concentration. From Figure 1, the main ions at the desirable pH value are: HS-, Zn(OH)2+2, Zn(OH)3- and Zn(OH)2+2. Note that the desirable pH value reduces when the bath temperature increases.
Horizontal lines in Figure 1 indicate the same \( \text{Zn}(OH)_{2}^{2-}/\text{HS}^{-} \) relative ion concentrations for all bath temperatures. For this purpose, the required thiourea concentration in the chemical bath reduces when the temperature increases according to: \([0.547 \text{ M}], [0.348 \text{ M}], [0.216 \text{ M}]\) and \([0.134 \text{ M}]\) for 60, 70, 80 and 90\(^\circ\)C, respectively. The volume of each thiourea concentration was 80 mL for all the species distribution diagrams presented in Figure 1. The other chemical parameters of the bath were intentionally maintained constant for all the bath temperatures by means of fixed concentrations given at the desirable pH value (Fig. 1).

**Growth kinetics and growth mechanisms.**— Different routes for the chemical reactions and the growth mechanisms\(^{1,27-38}\) have been proposed for ZnS films deposition. However, the chemical routes depend on the kind of chemical reagents used for films formation. From Fig. 1, the \( \text{HS}^{-}, \text{Zn}(OH)_{2}^{-}\) and \( \text{Zn}(OH)_{3}^{2-}\) aqueous species at the desirable pH value can be directly related to the ZnS films deposition and growth through the following chemical reactions:

\[
\text{Zn}(OH)_{2}^{2-} + \text{HS}^{-} \rightarrow \text{ZnS} + 3 \text{OH}^{-} + \text{H}_{2}\text{O}
\]

\[
\text{Zn}(OH)_{3}^{2-} + \text{HS}^{-} \rightarrow \text{ZnS} + 2 \text{OH}^{-} + \text{H}_{2}\text{O}
\]

Equations 5 and 6 describe an ion by ion growth mechanism. Furthermore, if the pH value does not show important changes along the deposition time, a uniform growing of the ZnS films can be obtained, i.e. a well-controlled chemical reaction can be achieved.

On the other hand, the dependence with temperature of the growth rate for the ZnS films deposition can be expressed by the Arrhenius equation:

\[
k(T) = A \exp \left(-\frac{E_{a}}{RT}\right)
\]

where \(k(T)\) is the growth rate as a function of temperature, \(A\) is the pre-exponential factor, related with the initial concentration, \(E_{a}\) is the activation energy, and \(R\) is the universal constant of the ideal gases (\(R = 8.3145 \text{ J/mol K}\)). In the experimental conditions the following rate law equation can be considered:

\[
r = k(T)[\text{SC(NH}_{2}])^{a} [\text{K} \text{OH}]^{b} [\text{NH}_{3}]^{c} [\text{NO}_{3}^{-}]^{d} [\text{ZnCl}_{2}]^{e}
\]

Where \(r\) is the growth rate as a function of the reagent concentration; \(a, b, c, d\) and \(e\) are the reaction orders from each reagent concentration. The values of the reaction orders can be determined by observing the dependence of the growth rate with the concentration of each chemical reagent. From our experimental conditions the growth rate depends only on the SC(NH\(_2\))\(_2\) concentration which was varied according to the bath temperature. Thus, the \(r\) can be expressed as:

\[
r = A \cdot B [\text{SC(NH}_{2}])^{a} \exp \left(-\frac{E_{a}}{RT}\right)
\]

Where constant \(B\) includes all concentrations of the chemical reagents except for SC(NH\(_2\)). It was necessary to develop Eq. 9 because in our experimental conditions both SC(NH\(_2\))\(_2\) concentration and bath temperature were varied. The reaction order \(a\) and the activation energy \(E_{a}\) parameters of interest in this work, can be determined from a multiple linear regression model that will be explained later. Thus, bath temperatures from 60 to 90\(^\circ\)C for films deposition where investigated in order to determine the \(E_{a}\) value. For each chemical bath and temperature, groups of samples of ZnS films were deposited on glass substrates at different deposition times in order to measure the corresponding thickness and to estimate the rate of growth.

**Experimental.—** Corning glass slides were used as substrates for the CBD-ZnS films deposition. Before deposition, substrates were cleaned in four stages with soap and distilled water, trichloroethylene, acetone and isopropyl alcohol into an ultrasonic device during 5 min, and drying with air for each stage. For deposition, the cleaned substrates were supported by Teflon holders to avoid contamination. Groups of five samples were deposited for each bath temperature.

| Table I. Deposition times used for ZnS films deposition at different bath temperatures. |
|-----------------------------------|-----------------------------------|
| bath temperature (°C)             | deposition times (min)            |
|-----------------------------------|-----------------------------------|
| 60                                | 80                                | 160                              | 240                              | 320                              | 400                              |
| 70                                | 50                                | 100                              | 150                              | 200                              | 250                              |
| 80                                | 30                                | 60                               | 90                               | 120                              | 150                              |
| 90                                | 20                                | 40                               | 60                               | 80                               | 100                              |

The deposition times for each group of films for each bath temperature are listed in Table I. Higher bath temperatures require shorter deposition times. The magnetic agitation of the chemical solution was maintained similar in all experiments. The bath temperature was controlled with ±1\(^\circ\)C of precision with an electronic temperature controller and a hot-plate. The initial and final pH values were measured for each chemical bath in order to verify its stability during time deposition. CBD-ZnS films thicknesses were measured by a profilometer Dekatak 8 for determining the rate of growth. Also, ZnS films were characterized by atomic force microscopy (SPM, Ambios Universal) for their morphology and surface roughness, by UV-Vis spectrophotometry (Agilent 8453) for the absorbance/transmittance spectra and the bandgap energy determination, by X-ray diffraction technique (Siemens D-5000) for the crystalline structure, and by SEM-EDS analyzes with a scanning electron microscope (Philips XL-30) for the stoichiometry and microstructure.

**Results and Discussion**

**Growth rate and activation energy.**— Figure 2 shows scatter plots of the thicknesses measured on the deposited CBD-ZnS films as a function of deposition time for the different bath temperatures listed in Table I. The growth rate \(r\) for each bath temperature was estimated from a linear fitting and is included in Figure 2. Figure 2 also shows an increment of the induction time at the beginning of the growth when the bath temperature is reduced (the interception of \(r\) at \(y = 0\)).

Table II lists the corresponding rates of growth determined from Figure 2 for each bath temperature as well as the initial, final, and desirable pH value of each temperature studied. Table II shows the stability of the pH value achieved during deposition and its proximity to the desirable pH value for each bath temperature described in Fig. 1.

![Figure 2](image-url)
Table II. Rate of growth, r, and initial, final and desirable pH for the ZnS films deposited at different bath temperatures.

| bath temperature (°C) | rate of growth r (nm/min) | initial pH | final pH | desirable pH |
|-----------------------|--------------------------|------------|----------|--------------|
| 60                    | 0.549                    | 12.05      | 12.04    | 12.00        |
| 70                    | 0.893                    | 11.87      | 11.86    | 11.85        |
| 80                    | 1.332                    | 11.70      | 11.69    | 11.70        |
| 90                    | 2.076                    | 11.54      | 11.53    | 11.55        |

From Eq. 9, by taking the natural logarithm, \( \ln r = \ln (AB) + a\ln [\text{SC(NH}_2\text{)}_2] - E_a/RT \), a linear equation of the form \( y(x) = A_0 + A_1(x_1) + A_2(x_2) \) can be resolved by a multiple linear regression, being \( A_1 = a \) and \( A_2 = -E_a/RT \). Table III lists the corresponding data for calculating the activation energy \( E_a \) and the reaction order of \( \text{SC(NH}_2\text{)}_2 \). Solving the linear equation, values of \( E_a = 44.9 \text{ kJ/mol} \) and a reaction order of \( a \sim 0 \) were obtained. Different authors have discussed the relevance of the activation energy value for CBD-ZnS films, but the rate-determining step in the deposition process is discussed according to the activation energy value estimated. For example, Sundara et al. reported the effect of bath concentration and temperature on the growth of CBD-ZnS films. In their work, a low \( E_a \) value of \( \sim 10.46 \text{ kJ/mol} \) was reported and they suggest that the rate of growth is controlled predominantly by temperature rather than by chemical process. Doña and Herrero reported a kinetic study where they analyze the influence of the concentration of the chemical reagents and the deposition temperature on the growth and quality of the CBD-ZnS films. In their work, an \( E_a \) value of \( \sim 20.92 \text{ kJ/mol} \) was reported and interpreted such that the rate-determining step in the deposition process is not a chemical one. Additionally, Valdejo reported in the kinetic study of the Zn(OH)S films a value of \( E_a = 33.60 \text{ kJ/mol} \), proposing that this \( E_a \) value of the rate of growth could occur by a physical process. On the other hand, recent kinetic studies of CBD-ZnS(S,O,OH) buffer layers published by Hubert et al. reported an activation energy of about 59 kJ/mol where authors affirm that the growth process is controlled by chemical reactions. Other interesting mechanistic study of CBD-ZnS films reported an \( E_a \) value of 53.4 kJ/mol, where authors indicate that this high \( E_a \) value is typically expected for chemical reactions. Finally, Chen et al. studied the effect of the deposition variables on the properties of CBD-ZnS films, estimating an \( E_a \) value of 59.8 kJ/mol. As can be noted from the literature, different \( E_a \) values have been reported and consequently, different growth mechanisms can be proposed. We assume that our estimated \( E_a \) value is typical for chemical reactions and suggests that the rate-determining step in the deposition process is mainly controlled by chemical reactions. On the other hand, the reaction order value for \( \text{SC(NH}_2\text{)}_2 \) estimated here, affirm that the \( \text{SC(NH}_2\text{)}_2 \) concentrations depend on the bath temperature and do not affect the growing process of the CBD-ZnS films. The different \( \text{SC(NH}_2\text{)}_2 \) concentrations used here, permit to maintain constant the \( \text{Zn(OH)}_2^-/\text{HS}^- \) relative concentration in the chemical bath.

Table III. Obtained data after multiple linear regression to estimate the \( E_a \) value and the reaction order of \( \text{SC(NH}_2\text{)}_2 \).

| T(°C) | \( \text{ln}[\text{SC(NH}_2\text{)}_2] \) | \( \text{ln} r \) |
|-------|----------------------------------|----------------|
| 60    | 0.003                            | -2.30805       |
| 70    | 0.00291                          | -2.7603        |
| 80    | 0.00283                          | -3.23722       |
| 90    | 0.00275                          | -3.71466       |

Step iii) can be seeing only for the film deposited at 60 °C for 320 min, where the main ions were exhausted. Otherwise, SEM micrographs of the ZnS films help to observe the three steps of the film formation process through deposition time. Figure 3 shows a group of SEM micrographs corresponding to the growing conditions (temperature and deposition time) described in Table I, where: 3a) 60 °C (80 min), 3b) 70 °C (50 min), 3c) 80 °C (60 min), 3d) 60 °C (320 min), 3e) 70 °C (250 min), and 3f) 90 °C (100 min). The SEM images in Figures 3a and 3b show the surfaces of the initial ZnS formation during the induction time, i.e., at the beginning of deposition time for 60 and 70 °C as bath temperatures, where reduced population of small grains in the surface of substrate is observed. The growing process of films is shown in the SEM micrographs in Figures 3c and 3d, giving the uniformity of the grains observed on film surface at different bath temperatures. Reduced grains are clearly seen in the micrographs. Finally, saturation in growth of film can be seen in the SEM images in Figures 3e and 3f, as the surface of the ZnS films appears formed by bigger and diffused grains.

The growing process of the films observed in Figure 3 presents the formation of clusters on the surface, which is characteristic of this step. The observed clusters are marked with arrows in the micrographs in Figure 3. The clusters can be formed by the aggregation of involved aqueous ions during the film deposition and growth. By using the same \( Zn(OH)H_2^+ /HS^- \) concentration ratio, the desirable pH value was achieved to be constant during all the deposition time for different bath temperatures, i.e., a well-controlled chemical reaction were maintained during deposition and growth of the ZnS films. Thus, it is acceptable to assume a cluster mechanism for the deposition and growth of the ZnS films under the chemical conditions imposed in this work. According to our estimated activation energy value, at the initial ZnS film formation there exists an intermediate adsorption process of the involved aqueous ions in the chemical solution/substrate surface creating clusters and a thin ZnS film during the induction time. During the ZnS film growth process, the clusters of the involved ions may increase the adsorption process, resulting in heterogeneous catalysis in the chemical solution/substrate surface that increases the thickness of the film, such that the film acts as catalytic surface. Then, we assume that the growing process by clusters is controlled by the zinc-hydroxide ions interaction with the bisulfide ions in the frontier between the chemical solution/ZnS film surface and the substrate surface.

Bandgap energy and optical transmittance.— Figure 4a shows the \( \alpha \) vs energy (hv) plots obtained from the spectrophotometry measurements of the deposited ZnS films under conditions listed in Table I. In order to obtain the direct bandgap energy \( (E_g) \) of the deposited ZnS films, we use the relation \( \alpha^2 = A(hv - E_g) \), where \( A \) is the absorption coefficient, \( h \) the Planck’s constant, \( v \) the light frequency, and \( A \) is a constant. The bandgap energy of the films is determined from these plots through the intersection of the linear portion of the absorption curve with the energy axis at \( \alpha^2 = 0 \), as is shown in Figure 4a.

Figure 4a shows the behavior of the \( \alpha^2 \) vs energy plots for the ZnS films deposited at different bath temperatures. A mean value of \( E_g = 3.67 \text{ eV} \) was obtained for the films with higher deposition time, a very close value to the ZnS bulk. Similar values in the intensity of the \( \alpha^2 \)-axis mean similar thickness in films. However, the absorption edge improves with higher temperatures according to the Beer’s law. Thus, similar ZnS films on thickness and bandgap energy were deposited at different temperatures but varying the thiourea concentration through the species diagrams in order to maintain similar \( Zn(OH)H_2^+ /HS^- \) concentration. In a complementary mode, Figure 4b shows the transmittance vs wavelength plots obtained for the same ZnS films measured in Figure 4a. Optical transmittances up to 80% were obtained for ZnS films deposited at 80 and 90 °C. Lower bath temperatures reduce the transmittance at most wavelengths values. From Figure 4, similar ZnS films in the bandgap energy values and optical transmittances were obtained at different bath temperatures. Reduction in the optical transmittance with deposition time is explained by the increase of film thickness according to the Beer’s law.
Figure 3. SEM micrographs of the surface of the ZnS films deposited at different temperatures (times) conditions described in Table I: a) 60°C (80 min), b) 70°C (50 min), c) 80°C (60 min), d) 60°C (320 min), e) 70°C (250 min), and f) 90°C (100 min).

Figure 4. a) Plots of $\alpha^2$ vs energy to obtain the bandgap energy value; b) optical transmittance vs wavelength of the ZnS films deposited at different bath temperatures.
Films morphology. X-ray diffraction pattern and stoichiometry.—Figure 5 shows the $(1 \times 1 \mu m^2)$ AFM images from the surface of the deposited ZnS films. The AFM images correspond to the highest deposition time obtained at: a) 60°C, b) 70°C, c) 80°C and d) 90°C as bath temperature. Differences on the surface morphology of films can be clearly observed in the AFM images. As the bath temperature increases, the grain size diminishes, being 80 and 90°C the temperatures where small and well packed grains appear, maybe due to the higher rate of growth achieved. The reduction of the rms-roughness values (18.2, 14.3, 9.4 and 7.3 nm) measured from the AFM images when the bath temperature increases (60, 70, 80 and 90°C) confirms the high transparency with the increase of the bath temperature.

From the morphology results in Fig. 5, can be affirmed that high rates of growth produces well packing grains and uniform ZnS film surfaces. Figure 6 shows the X-ray diffraction patterns obtained from the ZnS films deposited at the different bath temperatures and higher deposition time. The crystalline orientation improves with the increase of bath temperature. A preferential peak with (111) orientation at $2\theta = 29.3^\circ$ corresponding for the cubic sphalerite structure can be observed in Figure 6 for all films. Two additional orientations of the cubic structure, (220) at $2\theta = 49^\circ$ and (311) at $2\theta = 57.4^\circ$ were obtained for the ZnS films deposited at 90°C, and the (100) orientation at $2\theta = 24.6^\circ$ for the films deposited at 80°C. These additional orientations were also obtained for the ZnS films deposited at 70 and 60°C. Only one (100) orientation corresponding to a zincite hexagonal structure ZnO at $2\theta = 31.2^\circ$ was observed at 60°C. This peak of ZnO (100) orientation can be explained by the reduced rate of film growth obtained at low temperatures; thus, low temperature during film deposition influences on the crystalline structure of the film. Additionally, an increment of temperature during the film formation results in a better crystalline ZnS structure.

EDS analysis on the ZnS films deposited at conditions described in Table I reveals the atomic concentrations of Zn and S. Figure 7 shows the stoichiometric [Zn/S] ratio measured on the films as a function of deposition time for the different bath temperatures. The atomic concentration [Zn/S] of the films for all the bath temperatures, ranged between 0.4 and 0.6, indicating that the ZnS films grow with excess of sulfur. Non important changes in the stoichiometric [Zn/S] ratio were observed for all deposition times and bath temperatures. Thus, the chemical conditions reported in Fig. 1 maintain constant the $\text{ZH}_2\text{O}^-/\text{HS}^-$ concentration at the desirable pH value for the different bath temperatures.

Conclusions

The role of thiourea in the kinetic of growth of the chemical bath deposited ZnS films was studied. Groups of ZnS films were deposited on glass substrates at bath temperatures from 60 to 90°C and different deposition times. Thicknesses of the deposited ZnS films and the rates of growth were measured at bath temperatures between 60 and 90°C. The chemical bath solution was formed by fixed concentrations of KOH, NH4NO3 and ZnCl2, and different SC(NH2)2 concentrations depending on the bath temperature. Our chemical conditions, estimated from the species distribution diagrams, maintain the $\text{ZH}_2\text{O}^-/\text{HS}^-$ relative concentration such that pH value of the bath remains constant for the different bath temperatures, producing similar qualities of the deposited ZnS films. The activation energy of the growing process...
estimated by the Arrhenius equation was \( E_a = 44.9 \) kJ/mol. This result indicates that the growth mechanism of the deposited ZnS films can be explained by a chemical process controlled by clusters formation in the substrate/ZnS film surface. The ZnS film formation is controlled by the interaction of the zinc-hydroxide ions with the bisulfide ions in the chemical solution. A similar bandgap energy value of 3.67 eV and transmittances up to 80% were obtained on the ZnS films for the different deposition times and bath temperatures. The high temperature during deposition have a strong influence on the morphology and on structural properties of the ZnS films, providing films with well-packaging grains and cubic crystalline structure, mainly at 80 and 90°C. Stoichiometric atomic ratio of [Zn/S] = 0.4-0.6 was measured in all deposited ZnS films.

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