Effects of temperature on the morphology and optical properties of ZnS thin films deposited by chemical bath

P.E. Martín-Várguez, O. Ceh, I. J. González-Panzo, S. Tec-Yam, R. Patiño, and A. I. Oliva
Centro de Investigación y de Estudios Avanzados del IPN, Unidad Mérida.
Departamento de Física Aplicada. Km 6 Antigua Carretera a Progreso, A.P. 73-
Cordemex, 97310 Mérida Yucatán
E-mail: oceh@mda.cinvestav.mx

Abstract. Zinc sulphide thin films were deposited on Corning glass substrates by the chemical bath deposition technique at different temperatures. The influence of the bath temperature and deposition time on the morphological and optical properties of the ZnS films are herein investigated. ZnS films were deposited by changing the bath-temperature from 50 ºC to 90 ºC, and deposition times from 60 to 160 min. Thin and transparent films were obtained with thicknesses from 10 to 90 nm with the increment of the bath temperature, meanwhile the band gap energy $E_g$ values diminishes from 4.15 to 3.4 eV. The quality of the ZnS film surfaces was also influenced by increasing the bath temperature, as showed by the reduced grain size and the increase of roughness, obtained from atomic force microscopy images. ZnS films of good optical quality were obtained at 90 ºC with a mean value of $E_g=3.56\pm0.03$ eV.

1. Introduction
Due to its suitable optical properties, zinc sulphide (ZnS) emerges as an attractive semiconductor material for electronic and solar applications. ZnS thin films are commonly used as optical filter due to its appropriate band gap energy value of $E_g = 3.68$ eV at room temperature [1-3]. They can also be used as buffer layer or as antireflective coating [4] for improving the efficiency of thin film solar cells. Efficiencies above 18 % have been reported for ZnS/Cu(In,Ga)Se$_2$ (CIGS) thin film solar cells [5]. Cadmium sulphide (CdS) has been typically used as buffer layer on CIGS thin solar cells to protect the Cu(In,Ga)Se$_2$ junction from possible damage during the zinc oxide (ZnO) sputtering deposition, which would cause unwanted modifications to the surface of the CIGS absorber. The efficiency of the CdS/CIGS solar cells drops at short wavelengths due to optical absorption losses from the CdS layer. The solar absorption can be improved by replacing the CdS film with other semiconducting material with a wider energy band gap. Because of its appropriate optical characteristics, ZnS arises as a good candidate for being used as a buffer layer in solar cell applications. The ZnS higher band gap energy (3.68 eV) [6] compared to that one of the CdS (2.42 eV) makes the ZnS wavelength range of transparency wider (above 330 nm) than the CdS one (above 520 nm) [8], increasing then the amount of sunlight on the photovoltaic conversion process. In addition, replacing CdS with ZnS is environmentally attractive by its non-toxicity. The effects of the chemical bath temperature on the ZnS rate of growth and of annealing temperature on the structural properties ZnS films have been studied [9,10]. In this work, ZnS thin films were deposited on glass substrates by the chemical bath deposition (CBD) technique varying the bath temperature and the deposition time, in order to study the influence of such parameters on the ZnS morphological and their optical properties.
2. Theory

The solubility product value of ZnS at 25 ºC has been reported as \( K_{sp} = 10^{-24.7} \) [11]. As a consequence, ZnS precipitation may take place even at very low ion concentrations of Zn\(^{2+}\) and S\(^{-2}\). Controlling the free Zn\(^{2+}\) concentration, becomes an important issue in order to achieve such low-concentration precipitations. The use of a suitable complexing agent, promotes the releasing of low concentrations of Zn ions. In this work NH\(_3\) is proposed as the complexing agent. The following chemical reactions are proposed as the mechanism for the formation of ZnS films:

\[
\begin{align*}
\text{NH}_4^+ + \text{OH}^- & \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \quad (1) \\
\text{Zn}^{2+} + 4\text{NH}_3 & \leftrightarrow [\text{Zn(NH}_3)_4]^{2+} \quad (2) \\
\text{SC(NH}_2)_2 + 2\text{OH}^- & \leftrightarrow \text{S}^{2-} + \text{H}_2\text{NCN} + 2\text{H}_2\text{O} \quad (3) \\
[\text{Zn(NH}_3)_4]^{2+} + \text{S}^{2-} & \rightarrow \text{ZnS (s)} + 4\text{NH}_3 \quad (4)
\end{align*}
\]

Given that, the ZnS present a direct band gap energy \( E_g \), its value can be estimated from the relation:

\[
\alpha^2(h\nu) = A(h\nu - E_g) \quad (5)
\]

where \( \alpha \) is the absorption coefficient, \( h \) the Planck’s constant, \( \nu \) the incident light frequency, and \( A \) is a constant which depends on the type of material. Thus, the \( E_g \) value can be estimated as the \( h\nu \) value obtained at the intersection with the x-axis (\( \alpha^2 = 0 \)) from the \( \alpha^2 \) vs \( h\nu \) plot.

3. Experimental

ZnS thin films were deposited on Corning glass substrates (10 x 25 mm\(^2\)). Substrates were sequentially cleaned with soap, trichloroethylene, acetone, isopropyl alcohol, and de-ionized water, and dried with air as a last step. Teflon sample-holders were used to vertically support the substrates within the bath. The chemical bath was composed by the following analytical grade reagents: 80 ml of 0.02 M ZnCl\(_2\), 80 ml of 0.20 M SC(NH\(_2\))\(_2\), 80 ml of 1.50 M NH\(_4\)NO\(_3\), and 200 ml of 0.90 M KOH. A glass beaker was used as a container for the films deposition. In order to control the bath temperature during the heating process, a hot plate with an adapted proportional-integral-differential (PID) feedback system was used, with variations of \( \pm 0.5 \) ºC. Five groups of ZnS samples at different temperature (each) were obtained by changing the bath temperature from 50 ºC to 90 ºC in steps of 10 ºC. For each bath temperature, five samples were deposited with different deposition time ranging from 60 min to 140 min. For the chemical bath preparation, ZnCl\(_2\), KOH, and NH\(_4\)NO\(_3\) reagents were subsequently poured (in this order) to the glass beaker and magnetically stirred and heated until the work temperature was reached. Once such a temperature was reached, the solution of SC(NH\(_2\))\(_2\) was finally added to the container, and the ZnS deposition process took place. During the deposition process, a nearly constant pH=11.9 was measured. After the defined-deposition time has passed, each sample was taken out from the bath, and ultrasonically cleaned to eliminate surface residues. Deposited ZnS films were optically characterized with a StellarNet EPP-2000 spectrophotometer to measure the band gap energy. Atomic force microscopy (AFM) images were obtained with an AMBIOS Universal SPM equipment to analyse the surface morphology, and thickness was measured by the Dektak 8 profilometer.

4. Results

The ZnS films deposited by CBD on glass substrates presented low thickness values (10 to 90 nm), good transparency, and good adherence to the substrates. Figure 1 shows a group of representative AFM images of ZnS films deposited at 90 ºC and different deposition times. Small differences on the surface morphology can be observed. The rms-roughness and grain size values estimated from the AFM images as a function of deposition time and bath temperature are showed in Figures 2 and 3. From Figure 2, it is observed that the roughness value increases with the increase of both deposition time and bath temperature. The grain size do not show a very clear tendency with deposition time (Figure 3), but at high temperatures, seems to diminish the average values of grain size, as observed with AFM. Higher roughness and grain size values are commonly associated with the increment of
film thickness (i.e. deposition time) until a saturation region is reached. However, some chemical compounds different to ZnS could co-precipitate at low temperatures.

**Figure 1.** AFM images (1x1 μm²) of ZnS/glass films deposited at 90 °C: a) 60 min, b) 75 min, c) 90 min, d) 105 min, and e) 120 min, as deposition time.

**Figure 2.** Roughness value vs deposition time of ZnS films deposited at different bath temperatures.

**Figure 3.** Grain size vs deposition time of ZnS films deposited at different bath temperatures.

Figure 4 shows the α² versus energy plot of the five samples of ZnS films deposited at 90 °C and different deposition times. An increase of the absorbance coefficient with the increase of deposition time can be clearly observed which is directly related with the thickness of the films. A mean value of the band gap energy E_g = (3.56 ± 0.03) eV was estimated for all the films deposited at 90 °C, a slightly lower value than the 3.68 eV value reported in the literature [12].

**Figure 4.** α² vs energy plot for ZnS films deposited at 90 °C and different deposition times. The band gap energy value is reported for each case. A sequential formation of the absorption edge with deposition time is observed.

**Figure 5.** α² vs energy plot for ZnS films deposited during 140 min at different temperatures. The formation of the absorption edge can be appreciated by increasing the bath temperature.
This difference could be associated with defects both on the film stoichiometry and on the crystalline structure during deposition. Figure 5 shows the $\alpha^2$ vs energy plot of the ZnS films deposited during 120 min at different temperatures. Inset in Figure 5 corresponds to the thinnest ZnS films deposited at lower temperatures which presented the lowest absorbance values. An important increase in absorbance intensity is observed with the increase of the bath temperature. A formation of the absorption edge of the ZnS films is observed when the bath temperature increases. Thus, the band gap energy value can be clearly determined from this edge. By increasing the bath temperature, the chemical reaction is accelerated, which makes lower the time deposition required to obtain determined thickness due to the rapid exhaustion of the chemical bath. Thus, the bath temperature strongly influences on the obtained optical properties of the ZnS films, as can be concluded from the presented results. Profilometry measurements were carried out on the ZnS films through an intentionally formed step with a HCl-10% solution on a corner. Reported thickness values varied from 10 to 90 nm, being the higher values for the films deposited at higher temperatures. Experimental data for ZnS films properties obtained for different temperatures and 120 min as deposition time, are reported in Table I.

### Table I. Experimental values obtained from ZnS films deposited at different temperatures and 120 min as deposition time.

| Deposition temperature (°C) | Grain size (nm) | Roughness rms (nm) | Band gap energy (eV) | Thickness (nm) |
|-----------------------------|----------------|--------------------|---------------------|----------------|
| 50                          | 82             | 1.4                | 4.11                | 11             |
| 60                          | 87             | 7.5                | 3.80                | 12             |
| 70                          | 96             | 8.0                | 3.62                | 24             |
| 80                          | 98             | 7.1                | 3.53                | 31             |
| 90                          | 64             | 8.9                | 3.59                | 86             |

5. Conclusions
ZnS thin films were deposited on glass substrates by chemical bath deposition at bath temperatures ranging from 50 to 90 °C and deposition times ranging from 60 to 160 min. Better ZnS films, thicker transparent, and with a band gap energy value close to ZnS, were obtained for films deposited at 90 °C as bath temperature. A mean value of $E_g = 3.56 \pm 0.03$ eV was obtained for the group of these better ZnS films. The temperature of the bath was found to have a strong influence on the surface quality (roughness), the grain size, and the gap energy obtained.

References
[1] Ben T, Kamoun N, Kanzari M, and Bennaceur R 2006 Thin Solid Films 500 4
[2] Ben T, Kamoun N, and Guasch C 2008 Appl. Surf. Sci. 254 5039
[3] Ge Y H, Shi W M, Xu J, Y H Qiu and. Wei GP 2005 Proc. 15th International Photovoltaic Science and Engineering Conference Shanghai, China October 10-15 p. 262
[4] Gangopadhyay U, Kim K, Dhungel S K, Saha H, and Yi J 2007 Advances in OptoElectronics, vol. 2007, Article ID 18619
[5] Contreras M A, Nakada T, Hongo M, Pudov A O, and Sites J R. 2003 Proc. 3rd World Conference of Photovoltaic Energy Conversion. Osaka Japan May 11-18 p. 570
[6] Göde F, Gümüş C, and Zor M 2007 J. Cryst. Growth 299 136.
[7] Arenas O L, Nair M T S, and Nair P K. 1997 Semicond. Sci. Technol. 12 1323
[8] Negami T, Aoygi T, and Satoh T 2002 Proc. 29th IEEE, PVSC, New Orleans, p. 656
[9] Liu Q, Guobing M, and Jianping A 2008 Applied Surface Science 254 5711
[10] Roy P, Ota J R, and Srivastava S K 2006 Thin Solid Films 515 1912
[11] Cotton F A, and Wilkinson G 1980 Advanced Inorganic Chemistry (Wiley-Interscience New York)
[12] Nadeem M Y, and Ahmed W 1999 Turk J. Phys. 24 651