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EFFECT OF HYDRAZINE ON ZnS THIN FILMS OVER GLASS

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Thin Zinc sulphide films are deposited on glass using the chemical bath deposition technique. Zinc sulfate, hydrazine and thiourea at a pH~10.5 were used in the deposit of the ZnS thin films. The surface morphology was affected by the amount of hydrazine, which demonstrates a compact surface for 0.5 ml of hydrazine and atomic ratio of 1/1, showing a surface free of pinholes. The temperature variations show that at temperatures of 80 °C it had a better deposited. All deposited films exhibit a relatively high transparency in the range of 300 to 800 nm. The band gap varies from 3.62 to 4.21 eV.

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Keywords: Chemical bath deposition; ZnS thin films; Hydrazine

1. Introduction

ZnS thin films, with direct band gap and n-type conductivity, are considered promising candidates for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells [1,2]. It is a promising material for photovoltaic cells [3], optoelectronic device applications such as blue light emitting diodes [4]. Various techniques have been employed to prepare thin ZnS films, sputtering [5], metal-organic vapor phase epitaxy [6], successive ionic layer adsorption and reaction (SILAR) [7,8], atomic layer deposition (ALD) [9], spray pyrolysis [10], solvothermal [11], chemical vapor deposition (CVD) [12], and chemical bath deposition (CBD) [13-15].

The chemical bath deposition (CBD) is generally economical, simple, and is well known as a prevalent low-temperature aqueous technique for depositing large-area of semiconductors thin films. CBD is a technique in which thin films are deposited on substrates immersed in diluted solutions containing metal ions and the chalcogenide source [16]. This works reports the effect of temperature, hydrazine and the Zn/S ratio, on the optical properties and morphology of ZnS layers deposited on glass substrates.

2. Experimental

Thin ZnS films were deposited on commercial glass (25.4×76.2×1.5mm). The substrates were cleaned with acetone, isopropyl alcohol and deionized (DI) water, then finally dried in nitrogen. The ZnS thin films were prepared by mixing 2.5 ml ammonium hydroxide (NH_4OH), 4 ml of zinc sulfate ($ZnSO_4$), 4 ml of thiourea ($SC(NH_2)_2$) and 0.5, 1.25 and 2.5 ml of hydrazine (N_2H_4). The Zn/S ratio in the aqueous solution was changed from 1/1, 1/2 and 1/5. Finally, the necessary amount of deionized water was added to form a 25 ml solution in the reaction bath. All

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the reagents used were analytic grade and were purchased from Sigma-Aldrich. The temperatures of the deposition process were 25, 50 and 80 °C. After deposition, the ZnS films were first washed with methanol and then with DI water in an ultrasonic bath, being subsequently dried with nitrogen. The ZnS films were characterized, with their morphology being analyzed in a Zeiss SUPRA 40 SEM with an operating voltage of 15 kV. The optical properties of the thin films were measured at room temperature using a Cary 100 UV-Vis spectrophotometer.

3. Results and discussion

Fig, 1 shows SEM images obtained for ZnS thin films deposited at different Zn/S ratio on a glass substrate in order to study the surface morphology. In this work, the surface shows that the amount of hydrazine has a significant effect on the morphology of the ZnS film. The films have poor uniformity and were covered by relatively large particles when the amount of hydrazine was 0.5 ml, irregular grains are uniformly distributed on the surface at the Zn/S ratio of 1/1, as shown Figure 1. A slight increase of the grain size

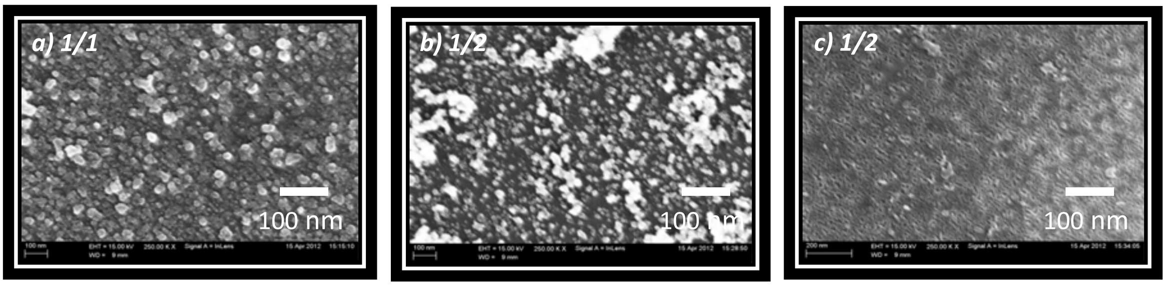

Fig. 1. Morphology of ZnS thin films at different Zn/S ratios with 0.5 ml of hydrazine.
follows as the amount of hydrazine increases, but this does not improve the surface roughness (Fig, 2).

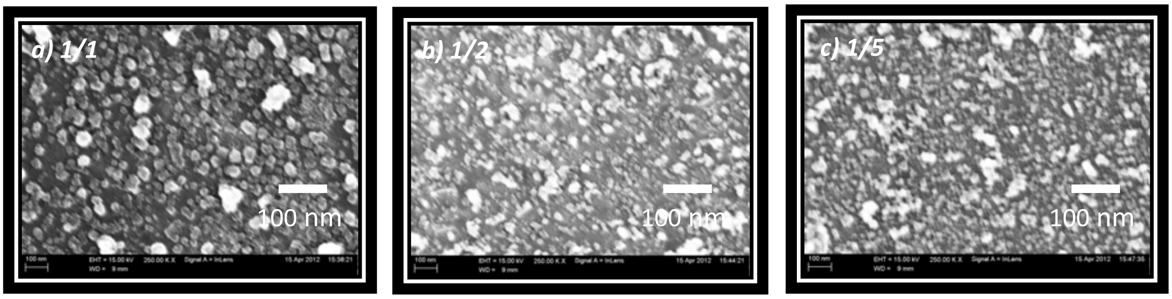

Fig. 2. Morphology of ZnS thin films at different Zn/S ratios with 1.25 ml of hydrazine.

The films obtained with 2.5 ml of hydrazine were continuously coated by large irregular shaped colloidal particles. The particle size in these films was 50 nm, this showed a clear dependence on the amount of hydrazine, as shown in Figure 3.

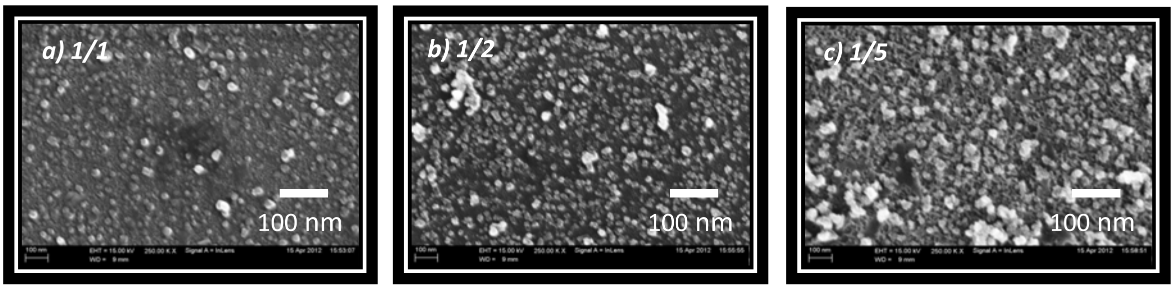

Fig. 3. SEM images of ZnS thin films with 2.5 ml of hydrazine.

On all deposited of ZnS thin films at room temperature, the films which showed a better deposit were at the Zn/S ratio of 1/1. Figure 4 shows the ZnS thin films deposited at the Zn/S ratio of 1/1, 0.5 ml hydrazine with various bath temperatures for 2h.

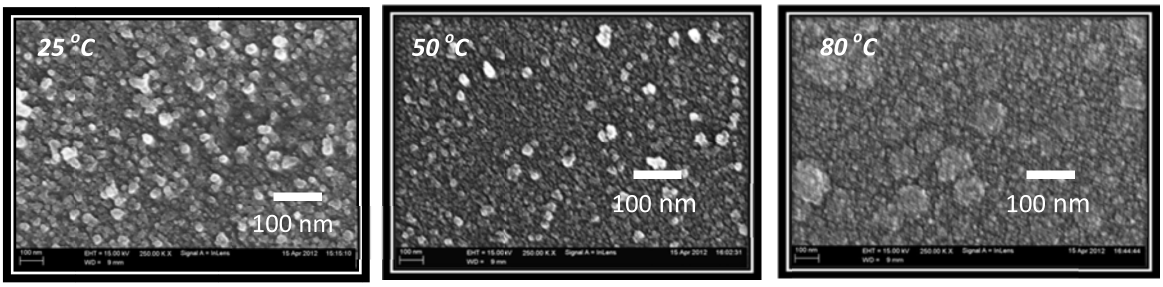

Fig. 4. SEM images of ZnS thin films with different temperatures.

It can be appreciated that ZnS thin films deposited at 25 °C are not homogenous and the formation of a small amount of ZnS clusters. When the deposition temperature is 80 °C, the films exhibit a homogeneous surface, free of pinholes and clusters. Figure 5a shows the variation of the optical transmittance in the UV-Visible range, of films deposited with different amount of hydrazine at room temperature. It can be seen that ZnS thin films have a high transmittance.

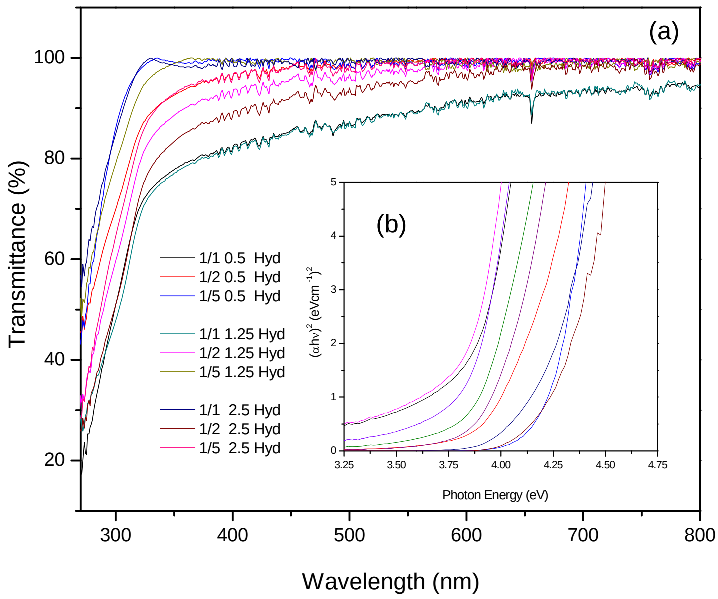

Fig. 5. Optical properties of ZnS thin films, (a) transmittance and (b) band gap at room temperature.

The deposited films exhibit a relatively high transparency ranged from 90 to 70% for wavelength greater than 300 nm. The optical band gap, Eg, was determined by Tauc relationship and was used as follows [17]. This was calculated from the UV-Vis spectra by plotting $(\alpha h\upsilon)^2$ vs. hυ on the x-axis, as shown in Figure 5b. The variation of the optical bang gap is a function of Zn/S ratio, where, the optical bang gap of the deposited film is incremented with increasing Zn/S ratio; it varies from 3.79 to 4.21 eV. Figure 6a shows the optical transmittance at 25 °C, 50 °C, and 80 °C for 2h. It can be observed that the transmittance of the films decreases rapidly with the increase at deposition temperature from 50 °C to 80 °C, which is mainly caused by reducing pinholes and increasing film thickness. For higher deposition temperature, the transmittance initially increases to 85%

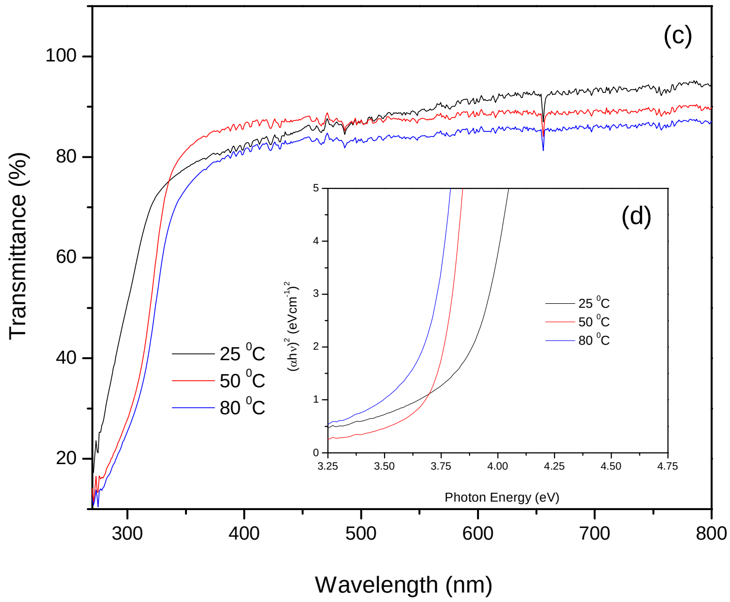

Fig. 6. Optical properties of ZnS thin films, (a) transmittance, (b) band gap and at different temperatures.

for the film deposited at 25 °C due to less light scattering by its smoothest surface. It decreases to about 80% at deposition temperatures above 80 °C, which may be due to lighter scattering on their rough surfaces [18]. The transmission is over 85% when the wavelength is larger than 400nm. The optical band gap of the ZnS films at different temperatures is found to decrease with temperature from 3.84 eV to 3.62 eV, as shown in Figure 6b. The deviation of these values from the standard bulk value of 3.7 eV [19] is explained on the basis of the small grain size. The difference between Eg values of the samples and the reports in the literature can be attributed to various grain sizes and morphologies of thin films due to the use of hydrazine in the deposit of the films.

4. Conclusions

Zinc sulphide thin films were prepared on glass substrates by the CBD technique. The morphological characterizations reveal that the effect of hydrazine is very large. The morphology, optical properties depend strongly of the amount of hydrazine. On all deposits of ZnS thin films at room temperature, the films that showed a better deposit were at the Zn/S ratio of 1/1. The effect of temperature demonstrated that ZnS films deposited at 80 °C showed a compact and smooth surface, and excellent transmission in visible high range. The band gaps Eg are found to decrease from 3.84 eV to 3.62 eV when the temperature increases, this is due to the vanishing of holes in the films.

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