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Study of the Effect of Film Thickness on Structure and Optical Properties of Nanostructured ZnS Thin Films Deposited by Spray Technique

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The sprayed ZnS thin films were deposited on a glass substrate at 400 °C using ultrasonic spray chemical technique (SPC). In this work, we have studied the effect of film thickness on structure and optical properties of nanostructured ZnS thin films. XRD analysis of ZnS thin films, which confirmed a hexagonal structure of ZnS with good crystallinity, has revealed that the crystallite size maximum of 45.3 nm was obtained with 577 nm. This is confirmed by the polycrystalline films at high film thickness. As for the optical properties, ZnS thin films have a good transparency in the visible region; the band gap energy of all deposited films was varied from 3.9 to 4.1 eV. At lower film thickness, the ZnS thin films become less disorder and fewer defects that are related to the Urbach energy, which was obtained of the order of 0.19 eV at 360 nm. However, it is noted that the variation of the extinction coefficient k follows the same trend, which indicates that the minimum value was obtained for ZnS film deposited with 360 nm. The best variation of refractive index was also obtained for 360 nm.

Keywords: ZnS, Thin films, Film thickness, Ultrasonic spray method.

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1. INTRODUCTION

Based on the latest researches on the investigation of new materials to be used in solar cell applications, various nanostructured materials composed of binary semiconductor compounds, such as In_2O_3, ZnO, Cu_2O, SnO_2 and CdO, have been investigated for several applications [1, 2]. Naturally, ZnS, which belongs to II-VI compound semiconductors, has been under extensive research in recent years because of its wide technological applications [3]. Among these materials, ZnS has potential applications in optoelectronic and piezoelectric devices; it has a high transparency and good conductivity, as well as chemical and mechanical stability [4]. ZnS has been intensively studied as a promising material for solar cells because of its wide band gap (3.5-3.8 eV) and high stability that are similar to ZnO [5].

Nanocrystalline ZnS thin films can be produced by several techniques such as reactive evaporation, molecular beam epitaxy (MBE), magnetron sputtering technique, pulsed laser deposition (PLD), spray pyrolysis, sol-gel process, chemical vapor deposition, and electrochemical deposition [6, 7]. Among these techniques, ultrasonic spray method may be the most convenient technique because of its simplicity, low cost, easy to add doping materials and promising for high rate and mass production capability of uniform large area coatings in industrial applications [8]. For review and the development of ZnS nanomaterials by the same method, which can be used in various applications in photovoltaics, for this reason we will discuss some researches, which were studied on ZnS thin films. Recently, M. Adelifard et al. [9] have studied the synthesis and characterization of nanostructural CuS-ZnS binary compound thin films prepared by spray pyrolysis. They have found that all the studied samples have a degenerate *p*-type conductivity with a carrier density of about 10^{21} cm^{-3}, which is in agreement with the reflectance spectra on the basis of plasma oscillations. However, K. Ben Bacha et al. [10], which have studied the structural, morphological and optical properties of sprayed ZnS thin films on various substrate natures, have found that the ZnS films prepared by spray pyrolysis technique are a promising candidate for the optical domain that is used as a reflector of its high refractive index (2.55-2.71) and photovoltaic devices. The above discussion has been about ZnS, but the same works have investigated the performance by different researches [11].

The object of this work is to present an original research for photovoltaic applications, which was performed by chemical spray pyrolysis of ZnS thin films on glass substrate as a function of film thickness. The crystalline structure, optical and electrical properties of ZnS films were studied.

2. EXPERIMENTAL DETAILS

ZnS thin films were elaborated by spray ultrasonic method on glass substrate at 450 °C. ZnS thin films were deposited at two different ZnS molarities with 3 and 8 min of deposition time. The solution was prepared by dissolving amount in range of 0.05-0.1 M of zinc acetate dehydrated, $Zn(CH_3COO)_2.2H_2O$ in isopropanol, then 0.1 M solution of thiourea was added as a stabilizer, the mixture solution was stirred and heated at 25-50 °C for 3 h to yield a clear and transparency solution.

The crystal phase and crystalline orientation of the thin films were determined by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with CuKα radiation ($\lambda = 1.541$ Å), the analysis of the samples was scanned from 30° to 55°. A scanning electron microscope (SEM, JSM-6700F) equipped with EDX was used to examine both morphology and elemental composition of the samples. The surface morphology was characterized using AFM A.100 APE Research (Italy) with resolution of 256 × 256 pxl of atomic force microscope. The optical transmission spectra of the films were measured in the range of 300-800 nm using a double-beam Lambda 35UV/visible spectrophotometer. All spectra were measured at room temperature in air.

3. RESULTS AND DISCUSSION

The crystalline quality of ZnS thin films was carried out by analyzing the XRD patterns shown in Fig. 1. The ZnS thin films were obtained at various film thicknesses 360, 428 and 577 nm. As can be seen, four diffraction peaks were observed at 28.68, 31.80, 45.47 and 56.50° corresponding to (008), (104), (1010) and (118) phases, respectively. The XRD are in agreement with hexagonal structure of ZnS (JCPDS: 39-1363) [12]. For 360 nm, it was obtained that (104) peak has higher intensity than the preferred orientation with (104) plane (Fig. 1). On the other hand, the film deposited with 428 nm has a high crystalline quality, however, the film deposited with 577 nm has one diffraction peak, which was (104) plane, indicating an improvement in (104) peak intensity compared to other films, revealing that the films are nanocrystalline and a preferred orientation with (104) plane is perpendicular to the substrate.

The lattice constants a and c are calculated from peak positions according to the following equation [13]. As a result of calculations, the lattice parameters are equal to 3.8 Å and 4.88 Å determined by

$$\frac{1}{d^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}, \tag{1}$$

where a, c are the lattice parameters, h, k, l are the Miller indices of the planes, d_{hkl} is the interplanar spacing.

In order to attain the detailed structure information, the grain sizes G of (111) and (200) planes were calculated according to the Scherrer equation [14]:

$$G=\frac{0.9\lambda}{\beta\cos\theta}, \tag{2}$$

where G is the crystallite size, λ is the X-ray wavelength ($\lambda = 1.5406$ Å), β is the full width at half-maximum (FWHM), and θ is the Bragg angle of the diffraction peaks, the variations are shown in Table 1. Fig. 2 shows the variation of crystallite sizes of ZnS thin films as a function of film thickness. As shown, the crystallite size increased with increasing film thickness up to the maximum value and was 45.3 nm for film thickness of 577 nm (Table 1) indicating that the films have nanocrystalline structure. As we can see, both the particle size and Zn concentration correlate very well.

The surface morphology of deposited ZnS thin films was studied with SEM as presented in Fig. 3a-c, which show the evaluation of film thickness on surface morphology at 577, 428 and 360 nm, respectively. We can see a hexagonal shape of the ZnS, which is in agreement with the wurtzite hexagonal phase found by XRD. When the film thickness increased to 577 nm (Fig. 3a), the nanostructure became a polycrystalline ZnS thin film due

Table 1 – Results of the grain size of ZnS thin films from XRD

Molarity (M)	Deposition time (min)	FWHM (°)	Grain size (nm)	Film thickness (nm)
0.05	3	0.27	30.2	360
0.05	8	0.25	32.6	428
0.1	8	0.18	45.3	577

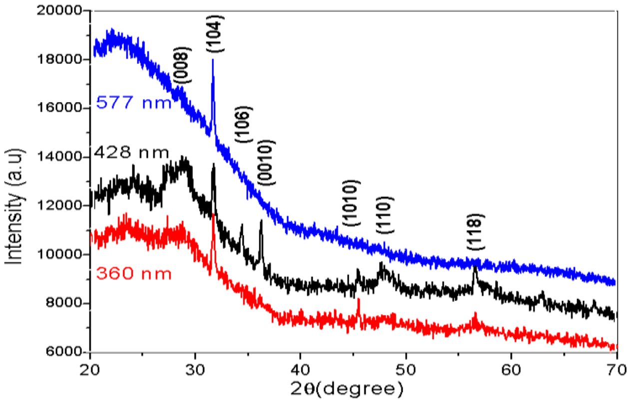

Fig. 1 – XRD spectra of ZnS thin films prepared with various films thickness

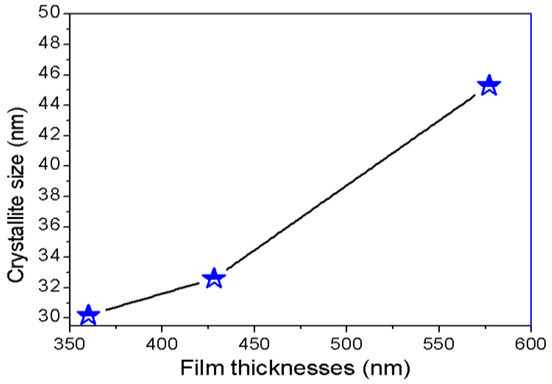

Fig. 2 – Variation of crystallite size of ZnS thin films prepared at different film thickness

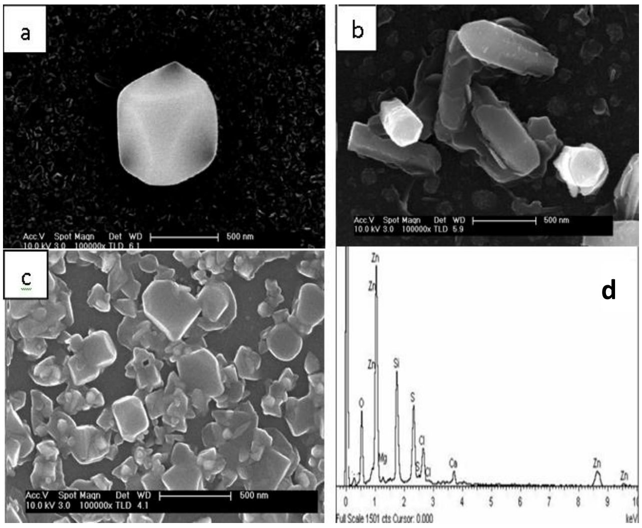

Fig. 3 – SEM micrograph spectrum analysis of ZnS thin films deposited with 577, 428 and 360 nm of film thickness, respectively (a, b, c); EDX of deposited ZnS thin films at 360 nm (d)

to the increase in the number of crystalline forms but not clearly well. It was evident that the film thickness had a significant influence on the surface morphology of ZnS films. Typical EDS spectrum is presented in Fig. 2d for the ZnS thin film which was deposited with film thickness of 360 nm. As can be seen, films are composed of S, O, Zn and Si (Table 2). The Si peaks originate from the substrate; however, the presence of other peaks originates from the glass substrate.

The surface topography was studied by atomic force microscopy (AFM) as shown in Fig. 4, which presents two- and three-dimensional AFM images of ZnS thin films deposited on glass substrate with scanning area of 2 × 2 μm^2. As shown, the ZnS samples consist of smaller and larger grain size, when the grain size increases with increasing film thickness and the surface becomes more homogenous when film thickness rises. The roughness of ZnS thin films was estimated from the arithmetic average of the absolute values of the surface height deviations. The values of the surface roughness are 3.9, 4.9 and 5 nm for 360, 428 and 577 nm of film thickness, respectively. Therefore, as can be seen, they are in agreement with the SEM results.

Table 2 – Composition of ZnS thin films

Molarity (M)	Deposition time (min)	Zn (%)	S (%)	S/Zn
0.05	3	45.1	54.8	1.21
0.05	8	53.2	46.8	0.87
0.1	8	51.8	48.1	0.92

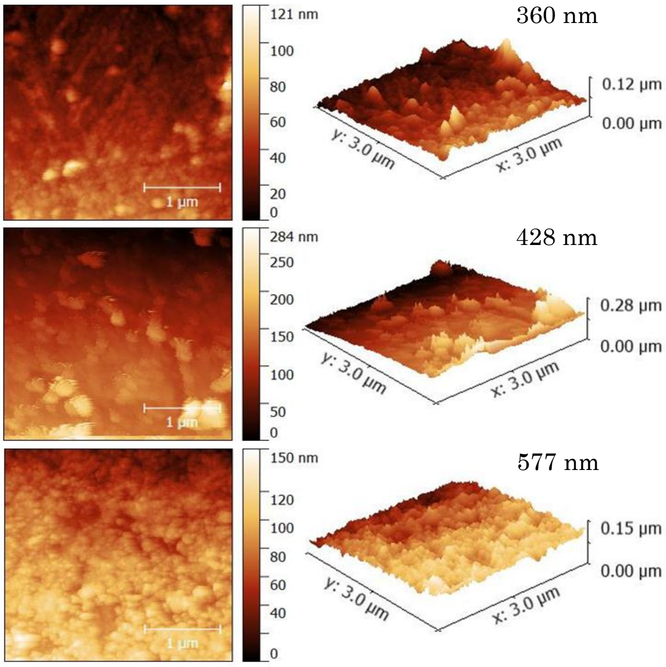

Fig. 4 – 2D and 3D AFM images of ZnS thin films deposited at various film thickness

The optical properties of ZnS thin films deposited at different film thickness were studied by measuring the transmittance in the wavelength region 200 to 800 nm. Fig. 5 presents the transmittance variation. As can be seen, the transmittance decreases with increasing film thickness, and it was decreased from 80 % to 50 % in the visible region. Probably it is due to the crystallite size (Fig. 2) or increasing surface roughness that caused losses in light scatter (Fig. 4).

The optical gap energy was calculated from the Tauc formula [15], which is given by the following relation:

$$(Ah\upsilon)^2 = C(h\upsilon - E_g)\,, \qquad (3)$$

where C is a constant, $h\upsilon$ is the incident wavelength, A is the absorption coefficient, E_g is the optical band gap.

Fig. 6a shows the estimation method of optical band gap of ZnS thin films deposited at different film thickness of 360, 428 and 577 nm. Besides, we have concluded the Urbach tail energy (E_u), which is related to the disorder in the film network, as it is expressed by [15]:

$$A = A_0\, exp\left(\frac{h\upsilon}{E_u}\right), \qquad (4)$$

where A_0 is a constant, $h\upsilon$ is the photon energy, E_u is the Urbach energy, Fig. 6b, shows the estimation method of Urbach energy of ZnS thin films deposited at different film thickness of 360, 428 and 577 nm.

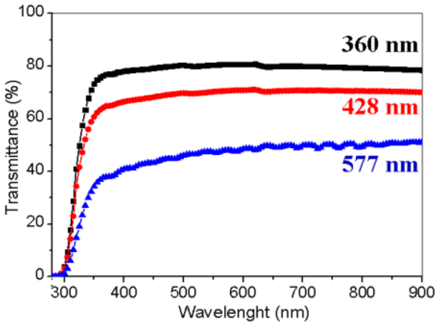

Fig. 5 – Optical transmission spectra of ZnS thin films prepared at different film thickness

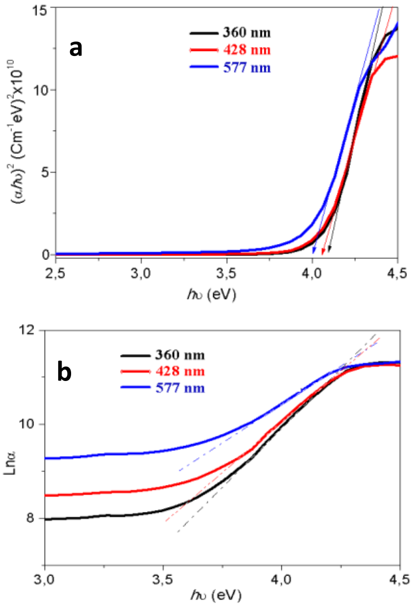

Fig. 6 – Band gap of ZnS thin films prepared at different film thickness (a); Urbach energy of ZnS thin films prepared at different film thickness (b)

Table 3 – Optical properties of ZnS thin films deposited at different conditions

Molarity M	deposition time (min)	E_g (eV)	E_u (eV)	n
0.05	3	4.097	0.198	1.948
0.05	8	4.053	0.233	2.231
0.1	8	3.994	0.306	2.625

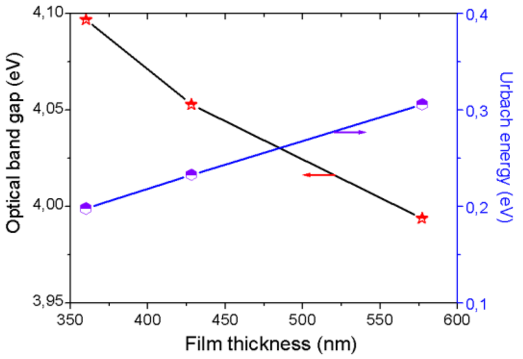

Fig. 7 – Variation of band gap and Urbach energy of ZnS thin films prepared at different film thickness

Fig. 7 shows the variation of optical band gap and Urbach energy of ZnS thin films deposited with various film thickness. As can be seen, all deposited films have a band gap of about 4 eV that is 4.097, 4.053 and 3.994 eV for film thickness of 360, 428 and 577 nm, respectively. These results are slightly shifted and similar to the previously reported values in the references [16, 17]. Offor et al. [17] have used distilled water as a solvent and have found the same results but using Zn concentration four times higher than ours. Compared with cubic phase prepared by spray ultrasonic, which is given in the range 3.2-3.6 eV, our optical gap energy for the wurtzite structure is a little higher which is confirmed by the theoretical value [18]. This large gap energy makes it a good material for heterojunction solar cells because of the increase in the transmitted light ratio. However, the Urbach energy increased with increasing the film thickness from 360 to 577 nm, which indicates that the defects have been decreased at high film thickness. This phenomenon can be explained by an increase in the optical gap energy (Table 3), explained by the Burstein-Moss effect, which causes the widen energy band (blue shift). On the other hand, it can be caused by the Fermi level merges into the conduction band with an increase in the carrier concentration. This can be explained by increase of the crystallite size (Table 1).

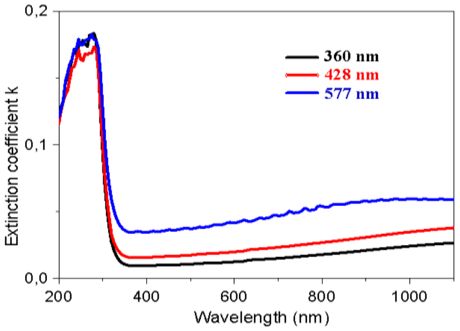

Fig. 8 – Variations with wavelength of the extinction coefficient (k) of ZnS thin films at various film thickness

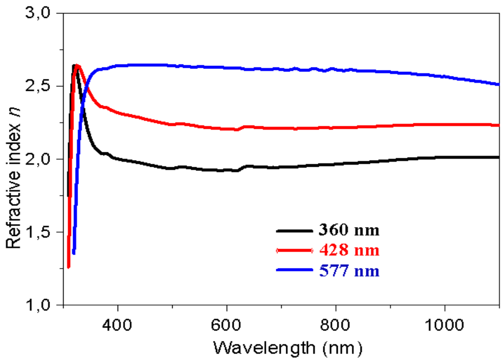

Fig. 9 – The relation between the refractive index and wavelength for ZnS thin films at different film thickness

For further information about optical properties of ZnS thin films, the extinction coefficient k can be determined by the optical absorption coefficient α, which is defined by [19]:

$$k = \frac{\alpha\lambda}{4\pi}. \tag{5}$$

Fig. 8 shows the variation of extinction coefficient (k) with wavelength of ZnS thin films with various film thickness. It is noted that, both k follow the same trend, where it indicates that the minimum value was obtained for ZnS film deposited with 360 nm. Refractive index is an important parameter for characterization of optical materials design and it includes valuable information for higher efficiency optical materials. In this work, the refractive index (n) can be calculated by using the following formula [20]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - K^2}, \tag{6}$$

where R is the reflectance and K is the extinction coefficient of ZnS thin films.

The variation of refractive index as a function of wavelength for spectrum range 300-1100 nm of ZnS thin films is shown in Fig. 9. It can be seen that the refractive index values of ZnS thin films are constant in the visible region, the mean values are presented in Table 3. The results show that the refractive index values of prepared films have values in the range of 1.9-2.6. The best variation of refractive index was obtained with 360 nm.

4. CONCLUSIONS

In summary, high-quality transparent ZnS thin films were grown on glass substrates at room temperature by ultrasonic spray chemical technique. The influence of film thickness (360, 428 and 577 nm) on structural, microstructural and optical properties was investigated. The following results were obtained.

- From XRD analysis of ZnS thin films, which confirmed a hexagonal structure of ZnS with good crystallinity, it was found that the crystallite size maximum of 45.3 nm was obtained with 577 nm. This confirms the preparation of polycrystalline films at high film thickness.
- As for the optical properties, ZnS thin films have a good transparency in the visible region, the band gap energy of all deposited films varied in the range 3.9 to 4.1 eV. At lower film thickness, the ZnS thin films become less disorder and fewer defects, which are related to the Urbach energy, which was obtained of the order of 0.19 eV at 360 nm.
- However, it is noted that the variation of extinction coefficient *k* follows the same trend, where it indicates that the minimum value was obtained for ZnS film deposited with 360 nm. The best variation of refractive index was obtained with 360 nm.
- The best estimated structure and optical characterization are achieved in deposited ZnS film with 360 nm.

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Вивчення впливу товщини плівки на структуру та оптичні властивості наноструктурованих тонких плівок ZnS, нанесених методом розпилення

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Тонкі плівки ZnS осаджували на скляну підкладку при температурі 400 °C за допомогою ультразвукової хімічної методики розпилення. У роботі ми вивчили вплив товщини плівки на структуру та оптичні властивості наноструктурованих тонких плівок ZnS. XRD аналіз тонких плівок ZnS, який підтвердив гексагональну структуру ZnS, виявив, що максимальний розмір кристалітів 45,3 нм був отриманий при товщині плівки 577 нм. Це підтверджують полікристалічні плівки з великою товщиною. Що стосується оптичних властивостей, то тонкі плівки ZnS мають хорошу прозорість у видимій області; енергія забороненої зони для усіх нанесених плівок змінювалася від 3,9 до 4,1 еВ. При меншій товщині тонкі плівки ZnS стають менш невпорядкованими і мають менше дефектів, пов'язаних з енергією Урбаха 0,19 еВ при 360 нм. Однак зазначається, що коливання коефіцієнта екстинції *k* слідують тією ж тенденцією, що вказує на те, що мінімальна величина отримана для плівки ZnS, осадженої при 360 нм. Найкраща зміна показника заломлення також була отримана для товщини 360 нм.

Ключові слова: ZnS, Тонкі плівки, Товщина плівки, Ультразвуковий метод розпилення.