

Chemical bath deposited nanocrystalline ZnS thin films: a spectroscopic study

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Thin films of Zinc sulfide (ZnS) have been prepared on glass substrates by chemical bath deposition (CBD) technique. The preparative parameters and spectroscopic properties of deposited films were investigated for the photovoltaic applications. The physical conditions were kept identical while growing all the samples. The as-deposited ZnS films were characterized by XRD, SEM and Spectrophotometer. All the films have pure cubic (Zinc-blende) structure. The grain size of ZnS films has been found to be in the range of 3.5 to 4.6 nm as the thickness changes from 63 nm to 124 nm. The films have 65-80% transmittance, 8-15% absorbance and ~4% reflectance towards the VIS-Near IR region. The band gap varies in between 3.52 eV to 3.78 eV.

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1. Introduction

Coal, oil and gas are at present the main sources of energy, will exhaust in near future. Sun is a huge source of energy that can be converted into electrical energy using solar cells and this is the best alternative option.

Zinc sulfide (ZnS) is an important II-VI semiconductor material with a wide direct band gap $E_g = 3.54$ eV. Consequently, it is a potentially important material to be used as an antireflection coating for hetero-junction solar cells. ZnS is also applicable for a variety of other applications such as electro-luminescent devices, detectors and many other optoelectronic devices [1].

Spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition and chemical bath deposition (CBD) are widely used techniques for deposition of thin films. Particularly the CBD technique is easy, inexpensive and convenient method for large area preparation of thin films, at close to room temperature. Also it is a controllable chemical reaction. Another advantage of the CBD method with respect to the other techniques is that, films can be deposited on different kinds, shapes and sizes of substrates [2-5].

In this work, we were prepared nano-crystalline ZnS thin films using zinc acetate, ammonia and thiourea with various thicknesses and deposition time. Some spectroscopic properties of as-deposited ZnS thin films were reported. The objective is to provide the comprehensive study of spectroscopic properties of ZnS thin films.

2. Experimental details

The ZnS films were fabricated by the controlled CBD technique using aqueous solutions of 0.08 M zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$, 0.15 M thiourea $\text{SC}(\text{NH}_2)_2$ was added in 100-120 ml of de-ionized water. Complexing agent

ammonia was added slowly to adjust the pH (between 9 and 10). The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at $70 \pm 2^\circ\text{C}$ for various deposition times. Zinc acetate used as zinc precursors, which slowly releases the Zn^{++} ions. Thiourea releases S^{--} ions by means of an alkaline hydrolysis process. The substrate used is commercial glass slide. Cleaning of substrate is important in deposition of thin films, cleaning steps and growth procedure is reported elsewhere [5-8].

The crystallographic structure of films was analyzed with a diffractometer (EXPERT-PRO) by using Cu-K α lines ($\lambda = 1.542\text{\AA}$). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). The optical absorption and transmission spectra for a range of samples of ZnS thin films of various thicknesses were obtained in UV-VIS-NIR region using Perkin-Elmer UV-VIS lambda-35 spectrometer in the wavelength range 100-1000 nm with uncoated glass slide as the reference [15].

3. Results and discussion

The physical conditions were kept identical while growing all the samples. All the measurements were done at room temperature for the films deposited by chemical route. The thickness of the films was determined by weight-difference method.

3.1 Study of preparative parameters

Table 1 shows the summary of deposition time, film thickness, grain size obtained from XRD and lattice constant for various samples. The variation of film thickness and grain size with deposition time is shown in Fig. 1.

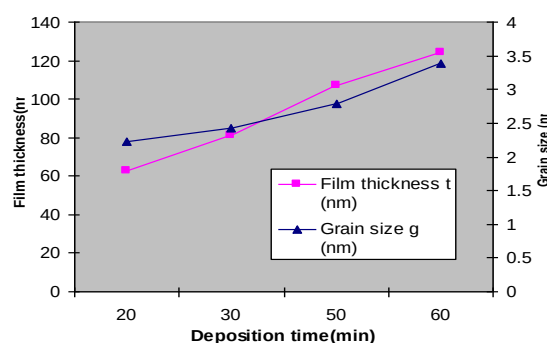


Fig. 1. Variation of film thickness and grain size with deposition time.

Table 1. A summary of deposition time, film thickness, grain size from XRD and lattice constant for various samples.

Sample	Deposition time (min)	Film thickness t (nm)	Grain size (XRD) g (nm)	Lattice constant (nm)	Band gap (eV)
A1	20	63	2.220	0.5434	3.68
A2	30	81	2.428	0.5415	3.78
A3	50	107	2.780	0.5402	3.56
A4	60	124	3.390	0.5398	3.52

3.2 XRD studies

Fig. 2 shows the XRD patterns of ZnS nanoparticles showing reflections from (111), (200) and (311) planes, indicating the formation of ZnS nano particles having pure cubic (zinc-blende) structure (JCPDS XRD spectra data for ZnS). The lattice parameter have been calculated which is in agreement with the standard data (0.542 nm) [Table 1].

The average size of grain (g) has been obtained from the XRD patterns using Debye-Scherrer's formula, [10,15]

$$g = K\lambda / \beta \cos\theta \quad (1)$$

Where,

- K = constant taken to be 0.94,
- λ = wavelength of X-ray used (1.542Å),
- β = FWHM of the peak and
- θ = Bragg's angle.

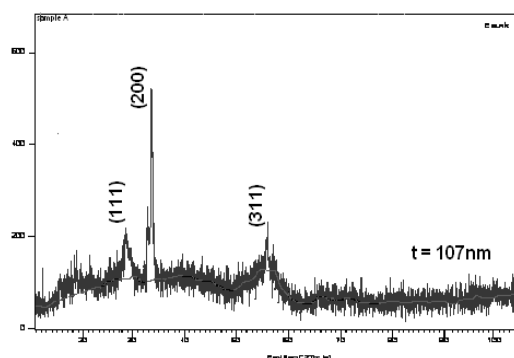


Fig. 2. XRD pattern of ZnS nano-crystalline film.

The peak broadening (111) and (311) in the XRD patterns clearly indicates the formation of ZnS nano-crystals of very small size. The grain sizes were found to be within the range from 2.2 to 3.3 nm as the film thickness were changed from 63 nm to 124 nm. Table 1 shows the grain size for different thicknesses.

3.3 SEM analysis

Fig. 3 shows scanning electron micrographs (SEM) of ZnS nano-crystalline films at different magnifications. It is an excellent technique for the study of surface morphology of thin films. From the SEM images, it is observed that the 'as-deposited' films are not uniform throughout, but are continuous without any cracks and the substrate is well covered. The fibrous like structure was observed with nano sized grains of ZnS. The grain size obtained from SEM matches with the grain size obtained from XRD.

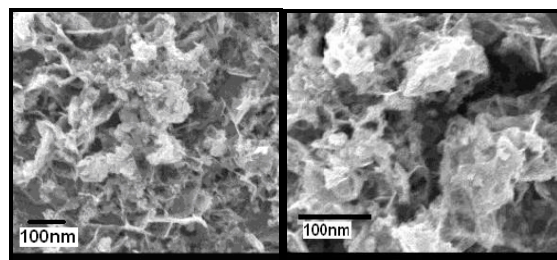


Fig. 3. SEM of ZnS nanocrystalline films at different magnifications.

3.4 Spectroscopic studies

Fig. 4 shows the optical transmission spectra of ZnS thin films for various thicknesses. All the films show 65–85% transmission for wavelengths longer than 400 nm. It is observed that the transmission in case of least thickness films is better than other three. The sharp rise in transmission is an identification of good crystallinity of films. It is observed that a (red) shift towards longer wavelengths directly depends on the increasing of the deposition time/ film thickness. These results suggest that the decrease of film thickness slightly increases the optical band-gap of ZnS films and it may be due to the small size of the polycrystalline ZnS films. Similar behavior in the transmission spectra of ZnS films prepared by other technique have been reported elsewhere [6, 12].

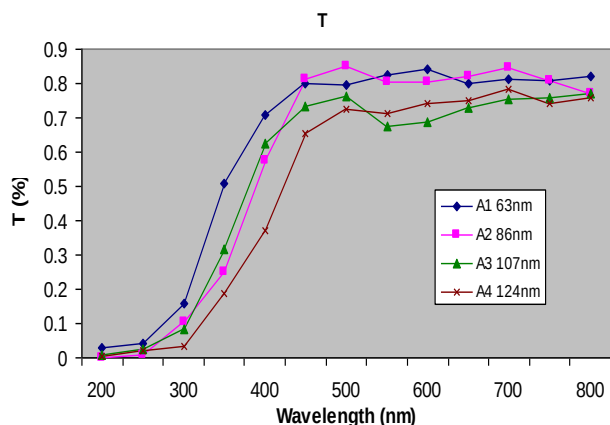


Fig. 4. Optical transmission spectra of ZnS nano crystalline films for various thicknesses.

The absorption spectra indicates the low absorbance from ~500 nm onwards, however absorbance is high in the UV region. From the absorbance data, the absorption coefficient α was calculated using Lamberts law [11],

$$\ln(I_0/I_t) = 2.303 A \\ = 2.303 \log 1/T = \alpha t \quad (2)$$

Where, I_0 and I_t are the intensity of incident and transmitted light respectively. A the absorbance, T the optical transmission and t the film thickness.

The absorption coefficient α was found to follow the relation, [12]

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (3)$$

The band gap E_g was determined from each film by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis at $\alpha = 0$. The band gap energy E_g obtained for each thickness is different. It was observed that the band gap is least for higher thickness (3.52 eV) and is highest for lower thickness (3.78 eV) which is due to the increase in grain size. The band gap of other two films is intermediate. Fig. 5 shows

all band gap values observed are closest to the band gap of single crystal ZnS (3.54 eV) [10-13].

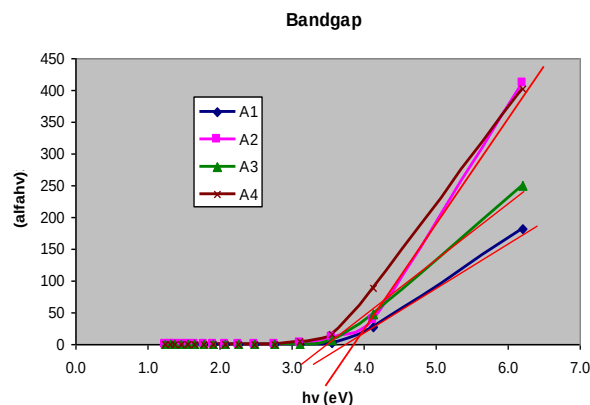


Fig. 5. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for all ZnS nano-crystalline films.

4. Conclusions

ZnS thin films prepared by CBD technique for various thicknesses have been characterized using optical measurements as T-R-A spectra, optical band gap energy as well as thickness, structure, surface morphology. The obtained films were not uniform but continuous without cracks, with nano sized grains. The films have better transmission in VIS-NIR region. The optical band gap was found to be in the range of 3.52 eV to 3.78 eV, as the thickness varies from 63 nm to 124 nm. The films were found to be cubic (zinc-blende) in structure.

All the films exhibit high transmittance (65–85%), low absorbance and low reflectance in the region from ~500 nm onwards. This makes the films suitable for use as an antireflection coating for hetero-junction solar cells and optoelectronic applications.

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