International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 4, Issue 9
September 2017

Study of Optical Properties of Nanocrystalline ZnS Thin Films Fabricated by CBD Technique

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ABSTRACT

Nanocrystalline Zinc Sulphide (ZnS) thin films with PolyvinylAlcohol (PVA) matrixwere synthesized by deposition on glass substrates by Chemical Bath Deposition (CBD) technique. The structural characterization was done by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV spectroscopy. The particle size was found to vary from 6.0 – 27nm. The compositional analysis of ZnS thin film was done by Energy Dispersive Analysis Of X Rays (EDAX)which indicate the absence of impurity in the films.The surface of the particles is hexagonalin structure. The energy band gap obtained from the result of UV spectroscopy is in the range 3.8 – 3.9eV.

Keywords: ***Nanostructure, ZnS, CBD, XRD, SEM, UV- spectroscopy.***

INTRODUCTION

Zinc Sulphide (ZnS) which is a typical n- type semiconductor, is the member of the family of II- VI semiconductors [1,2]. Zinc Sulphide exhibits two different crystal structures i.e. zinc blende and wurtzite structures and at room temperature, both structures have the same direct energy band gap of 3.6 eV in bulk state. It refractive index is 2.25 at 632 nm, and effective dielectric constant is 9 at 1 MHz. It also has wide wavelength pass band (0.4 - 13µm). It finds application in solar control coatings, antireflection coatings for heterojunction solar cells for light emitting diode, photovoltaic cells and blue shift light emitting diode. Some of the methods used for fabrication of ZnS thin films includeelectrodeposition [3], pulsed laser deposition [4], spray pyrolysis [5], chemical vapour deposition [6], molecular beam epitaxy [7], and chemical bath deposition [8]. The CBD technique has the advantages of low cost, low deposition temperature, easy coating of large surfaces with smooth and uniform layers. In this paper surface morphology and optical properties of the ZnS thin film synthesized by deposition on glass substrates by CBD technique was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV- spectroscopy respectively.

EXPERIMENTAL DETAILS

The process for fabrication of polyvinyl alcohol (PVA) capped nanocrystalline ZnS thin film on glass substrate by CBD technique is as follows. The glass substrates were firstcleaned with liquid detergent and washed thoroughly in distilled water and then immersed in concentrated nitric acid for five minutes. Finally, they were ultrasonically cleaned in acetone for 15 minutes before deposition.

The matrix solutions of Zinc acetate solution of six different molarities (0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M) with an aqueous solution (2wt%) of polyvinyl alcohol (PVA) are prepared and the same is stirred at 70°C for 2 hours. The ammonia solution is added drop by drop to the precursor solutions to maintain its pH value at 9.8. Then the same is mixed with equimolar solution of Thiourea and the mixture is stirred slowly until its color changes to milky. Using a suitable substrate holder, the ultrasonically cleaned glass substrates were immersed vertically in the resulting solution for 3hr at 50°C and then cooled down to room temperature and kept for 24hr to deposit of ZnS thin films.

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The chemical reactions that takes place during the deposition of ZnS thin film is [9]:

$$Zn(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow \quad ZnS \downarrow + 4NH_3 + CH_2N_2 + 2H_2O.$$

The asdeposited ZnS thin films on the glass substrate were taken out and washed thoroughly in distilled water several time and dried in air and then placed in a desiccator.

RESULT AND DISCUSSION

XRD Study

The structural characterization of the nanocrystalline was done by XRD. The X-ray diffraction (XRD) patterns of the ZnS thin films deposited for different molarities (0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M) were recorded with an X-ray diffractometer using CuKa radiation of wavelength, λ = 1.5406 Á . The XRD pattern of ZnS thin film of 0.3 M is shown in figure 1. All the XRD patterns have wurtzite structure as confirmed by standard JCPDS data No. 00-039-1363. The crystallite sizes of ZnS is calculated by using Scherrer's formula

$$D = \frac{K\lambda}{\beta C \quad \theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where K is a constant (= 0.94), β is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. The size of the ZnS crystals is found to vary in the range 6 - 27 nm which is comparatively much small as reported by earlier workers [10,11].

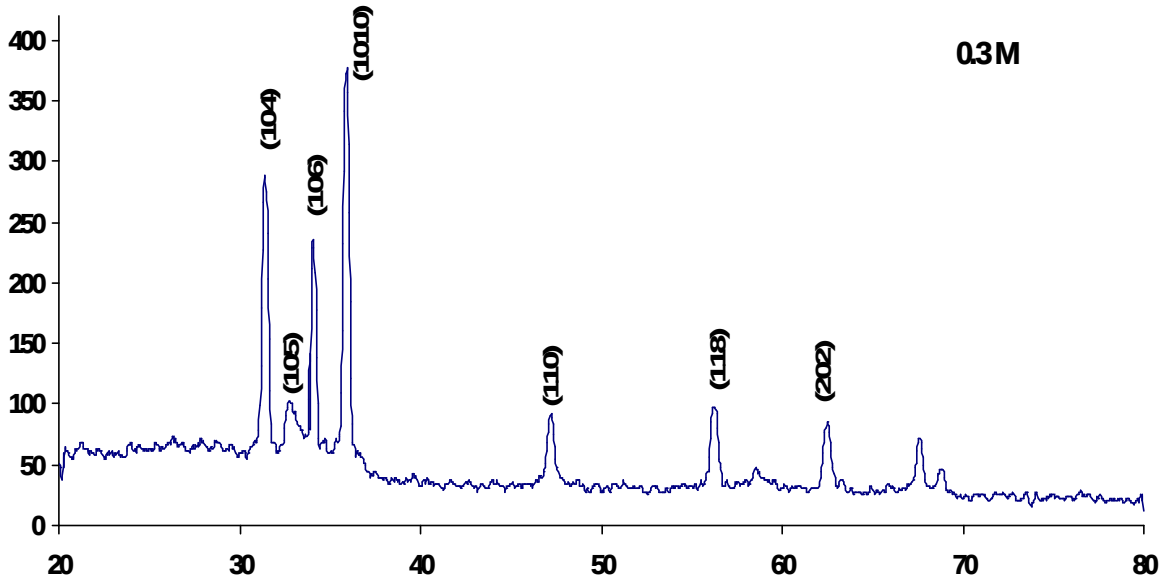

Figure 1. The XRD pattern of as-deposited ZnS of 0.3M

EDAX Analysis:

The EDAX analysis indicates that the products consist of Zinc andSulphur elements. The Silicon and Oxygen signals appear from the glass substrate. The percentage of the compositional elements present in the ZnS thin film of 0.3 M is presented in table 1 which shows that the prepared ZnS nanoparticles is almost free from impurities

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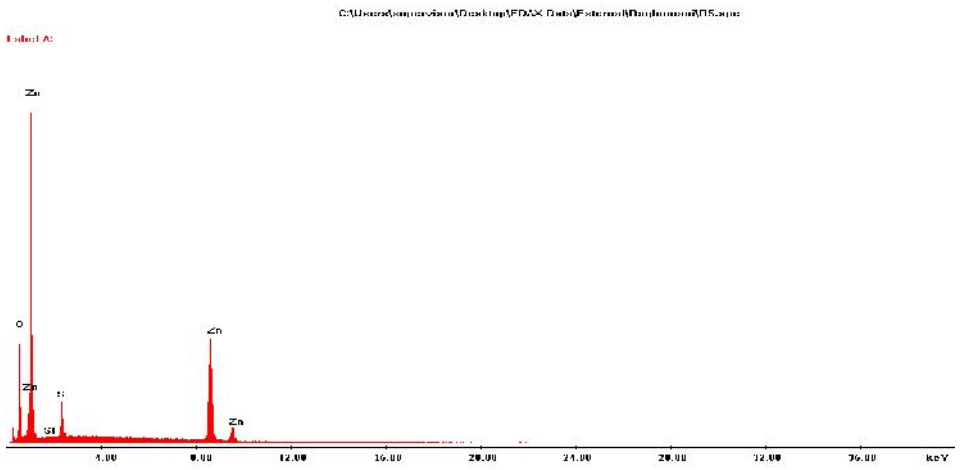

Figure 2.EDAX spectrum of ZnS thin film of 0.3 M.

Table 1.Percentage of the compositional elements present in the ZnS thin films of 0.3 M.

Molarity	Element	Weight%	Atomic%	[Zn]/[S]
.03 M	Zn S	68.07 4.91	36.19 5.32	6.802

SEM Study

The surface morphology of ZnS thin films on glass substrate was examined by scanning electron microscopy (SEM). Figure 3 shows the SEM image of ZnS nanocrystallites of 0.3 M. The as-deposited film shows flower like structure of nano size ZnS particles in the range ~ 25 – 50 nm. Bigger structures are also observed due to the formation of agglomeration of small size nanorods

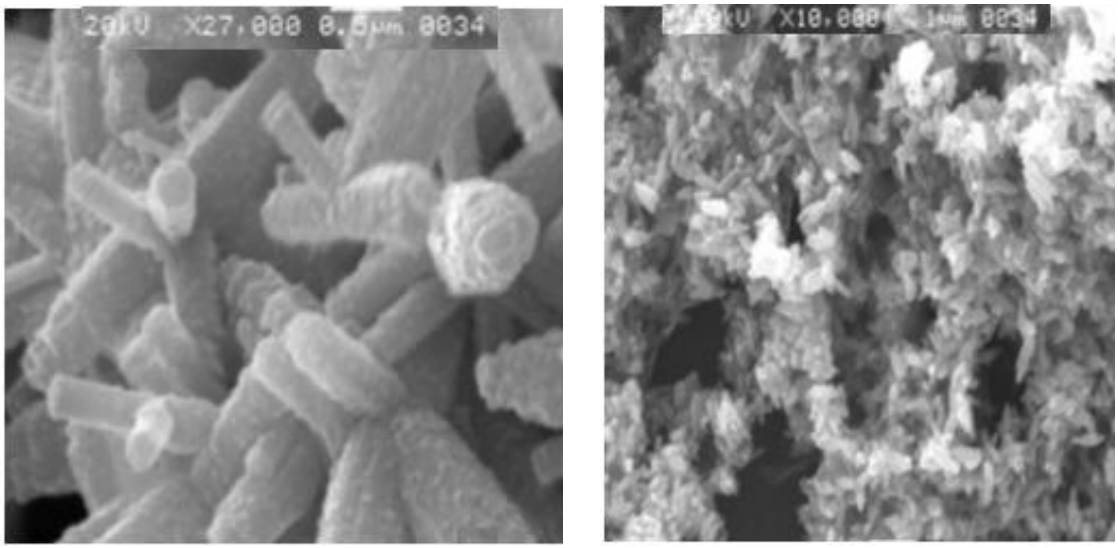

Figure 3. SEM surface morphology of ZnS thin film of 0.3 M.

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Optical properties

The optical properties of the ZnS thin film is determined from the absorbance measurement in the range 300 – 800 nm. Figure 4 shows the absorption spectra of ZnS thin films for different molarities. The absorption coefficient α associated with the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using the relation [12, 13]

$$\alpha = 2.3026\ A / t \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The absorption coefficient of direct band gap semiconductor is given by [14].

$$\alpha = c\ (h\nu - E_g)^{1/2} / h\nu \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

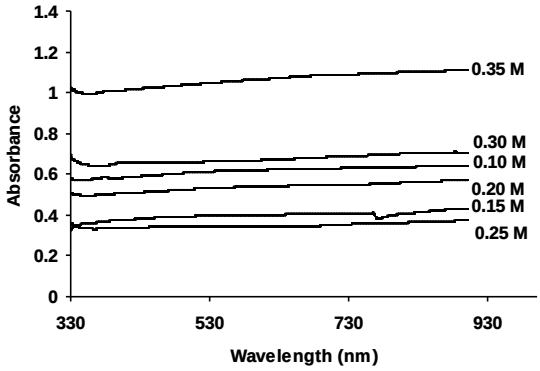

Figure 4. UV absorption spectra of ZnS thin films for different molarities

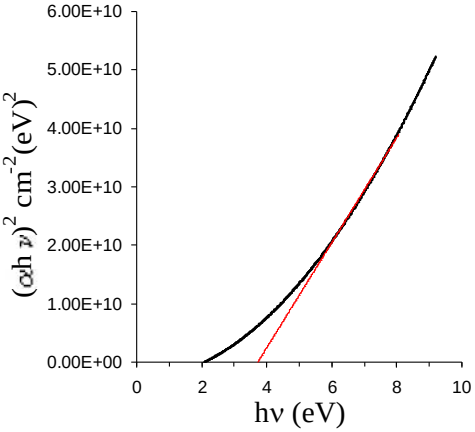

Figure 5.Plot of $h\nu \sim (.\alpha h\nu)^2$ of ZnS thin film on glass substrate at room temperature.

where α is absorption coefficient, c a constant, hνrepresents incident photon energy and $E_g$is the band gap. The graph between $h\nu \sim (\alpha h\nu)^2$ is plotted and shown in Figure 5. The intercepts of the extrapolated straight line at the $(\alpha h\nu)^2 = 0$ axis gives the value of the E_g of the material. The values of E_g is found to vary from 3.8 to 3.9 eV.

CONCLUSION

The nanocrystalline ZnS thin films capped with PVA were fabricated by chemical bath deposition (CBD) method on glass substrates. The nanostructure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), EDAX andUV spectroscopy. From XRD result the particle size are found to vary from 6 nm – 27 nm. The EDAX analysis shows the absence of impurity in the films. SEM result shows the presence of flower like structure of nano sized ZnS particles in the range ~ 25 – 50 nm. The study of UV spectroscopy indicates the variation of energy band gap in the range 3.8 – 3.9eV

ACKNOWLEDGMENT

The authors are thankful to UGC, NERO for financial assistant in the form of Minor Research Project. The authors also thankful to Department of Chemistry, Manipur University, Canchipur, Imphal for allowing to take the UV spectroscopy facility; Department of Physics, Manipur University Canchipur, Imphal for allowing to take SEM measurements, EDAX and XRD facilities.

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