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Synthesis and Study of Nanocrystructured ZnS Thin Films by CBD

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Abstract: Nanocrystalline zinc sulphide (ZnS) thin films capped by polyvinyl alcohol (PVA) were fabricated by deposition on glass substrates by chemical bath deposition (CBD) method. Characterization of the nanostructure material was done by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV spectroscopy. Results show the particle size varies from 6.0 – 29 nm, the surface morphology of the particles are hexagonal in structure and the band gap is in the range 3.80 – 3.95 eV.

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

INTRODUCTION

Zinc sulphide (ZnS) is a typical n- type semiconductor belonging to the family of II- VI semiconductors [1]-[2] exhibiting two different crystal structures i.e. zinc blende and wurtzite structures. Both structures have the same direct energy band gap of 3.6 eV in bulk state at room temperature. It has high refractive index (2.25 at 632 nm), high effective dielectric constant (9 at 1 MHz) and wide wavelength pass band (0.4 - 13µm). ZnS can be used as solar control coatings, antireflection coatings for hetero junction solar cells for light emitting diode, photovoltaic cells and blue shift light emitting diode. Generally, different techniques such as electro deposition [3], pulsed laser deposition [4], spray pyrolysis [5], chemical vapor deposition [6], molecular beam epitaxial [7], and chemical bath deposition [8]-[9] have been used to synthesize ZnS thin films. In the present work, chemical bath deposition (CBD) technique is employed because of its advantages like low cost, low deposition temperature, easy coating of large surfaces with smooth and uniform layers. The present work aims to analyze the particle structure, surface morphology and optical properties of ZnS thin film by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV- spectroscopy.

EXPERIMENTAL

Fabrication of polyvinyl alcohol (PVA) capped nano crystalline ZnS thin film on glass substrate by CBD technique was performed by the following processes. Firstly, the glass substrates were cleaned by 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. Different molarities (0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M) of zinc acetate solution were added to an aqueous solution (2 wt %) of polyvinyl alcohol (PVA). Then the solution was stirred at 70°C for 2 hour for preparing different matrix solutions. The pH value of the solutions was maintained at 9.6 by adding ammonia solution drop by drop. Then the equimolar solution of Thiourea was added to each of matrix solutions. The color of the resulting solution was slowly turned in to milky. Six ultrasonically cleaned glass substrates were immersed vertically in the solution using a suitable substrate holder for 3h at 50°C and then cooled down to room temperature and kept for 24h to deposit of ZnS thin films. The chemical process for forming ZnS thin film is considered as follows [10]:

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

After deposition of ZnS thin films, the glass substrates were taken out and washed thoroughly in distilled water several time and dried in air and then placed in a dessicator.

RESULT AND DISCUSSION

Structural analysis

Structural characterization was done by XRD. The X-ray diffraction (XRD) patterns of the ZnS thin films deposited at different temperatures 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, $\lambda = 1.5406$ Å and are 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 are calculated by using Scherrer's formula of diffraction peak corresponding to a particular crystal plane.

$$D = K\lambda/\beta \cos\theta \qquad (1)$$

Where K is a constant (= 0.94), β is the full width at half maximum (FWHM) of the

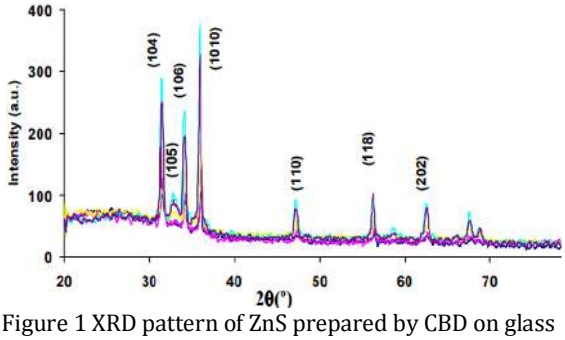

Figure 1 XRD pattern of ZnS prepared by CBD on glass substrate for different molarities (0.10, 0.15, 0.20, 0.25, 0.30 & 0.35 M).

From table 1, the size of the ZnS crystals are in the range 6 - 28 nm which is comparatively small as reported by earlier workers [11]-[12]. Structural parameters of as-deposited ZnS thin films are given in table 1. The thickness of ZnS film was measured by Gravimetric method using a sensitive microbalance

(Magnetic Analytical Balance, Wesnar Weighing Scales Ltd., Model MAB 182) using the relation:

$$t = M/\rho A \qquad (2)$$

where t is the thickness of film, M is the mass of the deposited film, ρ is the density of ZnS (= 4.1 g cm^{-3}) and A is the area of the film. The thickness of the film for different molarities is given in table.

Table 1: Structural parameters of as-deposited ZnS thin films (deposition time 24 h).

Molarity	Film Thickness (μm)	(hkl)	d spacing	Size (nm)
0.10	45.46	104	2.84	18.39
		106	2.62	26.77
		10	2.49	25.74
0.15	45.75	104	2.831	24.36
		105	2.702	3.834
		106	2.618	28.15
		10	2.488	23.86
0.20	49.82	104	2.84	20.16
		105	2.71	6.03
		106	2.63	27.56
		10	2.49	21.505
0.25	54.17	104	3.84	20.50
		105	2.72	20.92
		106	2.62	20.65
		10	2.49	20.76
0.30	85.49	104	2.85	26.97
		105	2.72	7.46
		106	2.63	27.24
		10	2.49	25.68
0.35	40.19	104	2.84	25.40
		105	2.71	6.47
		106	2.62	28.46
		10	2.49	25.22

SURFACE MORPHOLOGY

The surface morphology of ZnS thin films on glass substrate was examined by scanning electron microscopy (SEM). Figures (2a-2b) show the SEM image of ZnS nanocrystallites. 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.

EDAX ANALYSIS

Figure 3, shows the EDAX image of the particles for 0.3 M. The EDAX analysis indicates that the products consist of Zinc and Sulphur 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 2, showing that the prepared ZnS nanoparticles is almost free from impurities with ration Zn/S as 6.802.

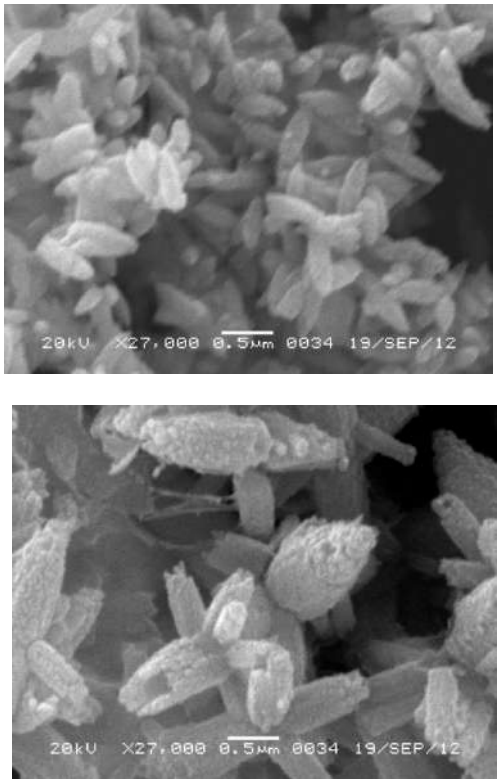

Figure 2 SEM micrograph of PVA capped ZnS nanocrystals on glass substrate for (a) 0.10M and (b) 0.35M.

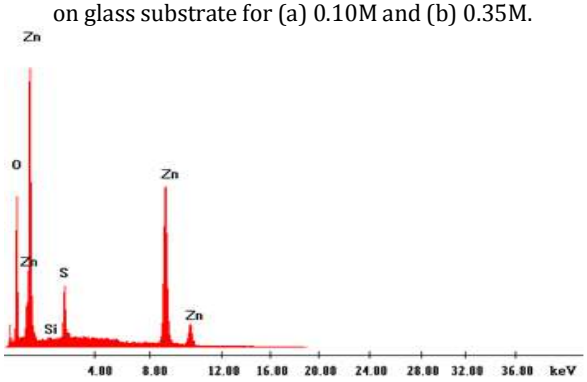

Figure 3 EDAX spectrum of ZnS thin film of 0.3 M.

Table 2 Percentage of the compositional elements presents in the ZnS thin films of 0.3 M.

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

OPTICAL PROPERTIES

The absorbance of the ZnS thin film is measured in the range 300 – 800 nm. Figure 4 shows the absorption spectra of ZnS thin films for different molarities. Figure does not show linearity with film thickness a variation of the absorbance with different molarities which is due to the different film thickness. 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 [13]-[14].

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$$\alpha = 2.3026\ A / t \qquad (3)$$

The absorption coefficient of direct band gap semiconductor is given by [15]:

$$\alpha = c\ (h\nu - E_g)^{1/2} / h\nu \qquad (4)$$

where α is absorption coefficient, c a constant, $h\nu$ incident photon energy and E_g the band gap. Graphs between $h\nu \sim (\alpha h\nu)^2$ is plotted (Figure 5) and 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 so obtained vary from 3.8 to 3.95 eV.

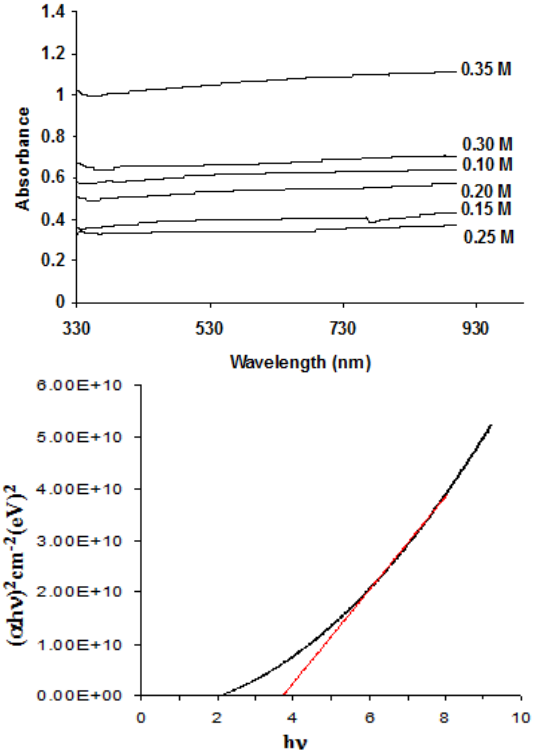

Figure 5 Plot of $h\nu \sim (\alpha h\nu)^2$ of ZnS thin film on glass substrate at room temperature.

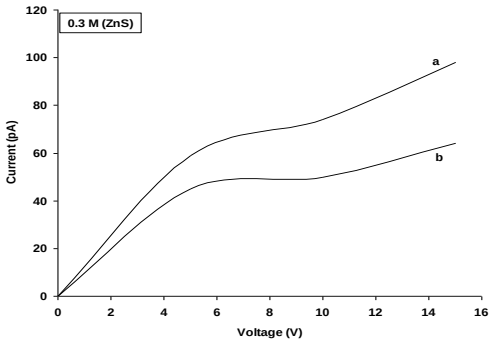

Figure 6 I-V characteristic curve of ZnS thin film (0.30M) (a) Current under illumination (b) Dark current.

PHOTOCONDUCTIVITY

The values of dark current (I_D), current under illumination (I_L), photocurrent (I_{ph}), intensity of incident light (ϕ) and temperature of thin films (T) for different molarities under different d. c. bias voltage are recorded. Plots of I-V characteristics for illumination and dark conditions are shown in figure 6 for 0.30M. Also the characteristic curves of PVA capped ZnS thin films are shown figure 7 (Temperature ~ Photocurrent) and Figure 8 (Photocurrent ~ Intensity of illumination).

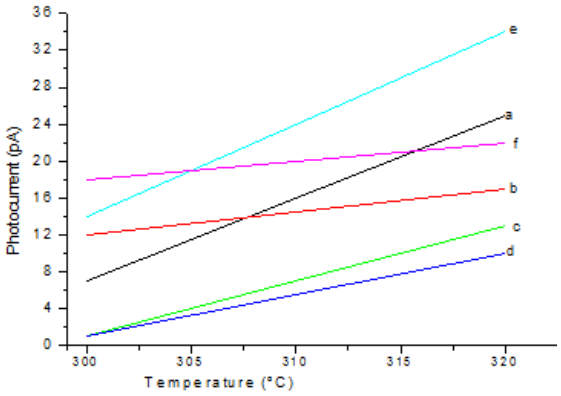

Figure 6 Characteristic curve of Temperature vs Photocurrent of ZnS thin films (a – e correspond to 0.10 – 0.35 M).

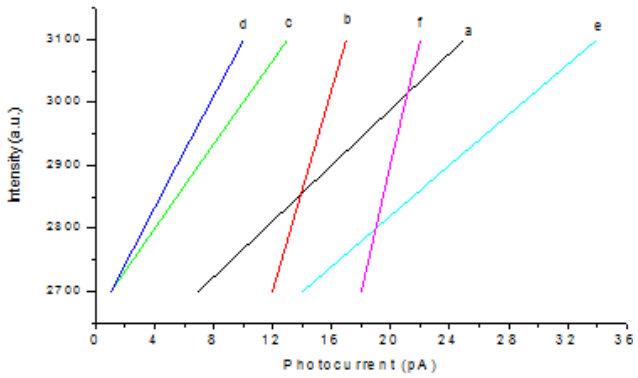

Figure 7 Characteristic curve of Photocurrent vs Illumination of ZnS thin films (a – e correspond to 0.10 – 0.35 M).

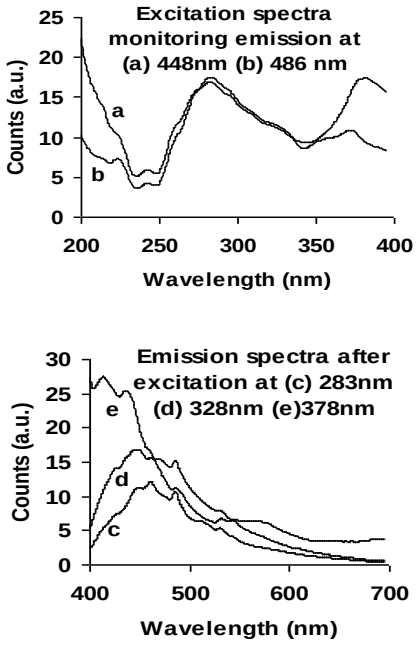

Figure 9 Excitation and emission spectra of nanocrystalline ZnS thin films a - emission at 448 nm, b - emission at 486 nm, c – excited at 283nm d - excited at 328 nm, e - excited at 378 nm

PHOTOLUMINESCENCE

Photoluminescence excitation and emission spectra of ZnS nanocrystallites thin films are shown in figures 9. In all the cases of different molarities (0.1, 0.15, 0.2, 0.25, 0.3 & 0.35 M) the excitation is monitored under 488 and 486 nm wavelength. It is found that a broad excitation from 200 – 400 nm with two peaks one broad at around 288 nm and another narrower at 385 nm are observed. And also the emission spectra from 400 – 700 nm after excitation at 283, 328 and 378 nm observed that:

(a) for 378 nm excitation strong peak is obtained at around 416. Shoulder peaks are also observed at around 440, 463 and 487 nm.
(b) for 328 nm excitation strong peaks are obtained at 440 to 444 nm and shoulder peaks at around 417, 463 and 488 nm.
(c) for 283 nm excitation strong peaks are obtained at 463 nm and shoulder peaks at around 417, 444 and 488 nm.

CONCLUSION

PVA capped nanocrystalline ZnS thin films of six different molarities (0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M) were prepared by CBD method. Their structural characteristics are analyzed by XRD. It was found that the size of the nonstructural particles is in the range 6 – 29 nm. Their surface morphology were studied by SEM and found the shape of the particles is hexagonal and their size is ~ 25 – 50 nm. Their optical properties are studied by UV spectroscopy and their result gives the band gap is in the range 3.8 – 3.95 eV.

REFERENCES

[1]. Dinsmore A.D., Hsu D.S., Gray H.F., Quadri S.B., Tian Y., Ratna B.R., "Mn-Doped ZnS Nanoparticles as Efficient Low-Voltge Cathodoluminescent Phosphor", Appl. Phys., 75, 802,(1999)
[2]. Maity R., Chattopadhyay K.K., "Synthesis and optical characterization of ZnS and ZnS: Mn nanocrystalline thin films by chemical route", Nanotechnology, 15, 812 (2004).
[3]. Gal D., Hodes G., Lincot D. and Schock H.W., "Electrochemical deposition of zinc oxide films from non-aqueous solution: a new buffer/window process for thin film solar cells", Thin Solid Films, 361–362, 79-83 (2000).
[4]. Yano S, Schroeder R, Ullrich B, Sakai H., "Absorption and photocurrent properties of thin ZnS films formed by pulsed-laser deposition on quartz", Thin Solid Films, 423, 276-273(2003).
[5]. Harnadez-Fenollose M.A., Lopez M.C., Donderis V., Gonzalez M., Mani B. and Ramos – Barrado J.R., "Role of precursors on morphology and optical properties of ZnS thin films prepared by chemical spray pyrolysis", Thin Solid Films, 516,1622-1625(2008).
[6]. Barreca D., Gasparotto A., Marago C., Tondello E. and Sada C.,"CVD of Nanophasic (Zn, Cd)S Thin Films: From Multi-Layers to Solid Solutions", Chem. Vapor Depos. 10(4), 229–236 (2004).
[7]. Kavanagh Y. and Cameron D.C., "Zinc sulfide thin films produced by sulfidation of sol–gel deposited zinc oxide", Thin Solid Films, 398-399, 24-28,(2001).
[8]. O'Brien, P. and McAleese, J., "Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS", J. Mater. Chem., 8, 2309-2314, (1998).
[9]. D.K. Dwivedi, Nitesh Shukla, H.P. Pathak and Kedar Singh, "Structural and Optical Properties of Different Composition of $Se_{90}Cd_{10-x}In_x$ thin Films by Vacuum Evaporation Technique" American Journal of Materials Science and Engineering, 2(2),13-17(2014).
[10]. Ubale A.U. and Kulkarani D.K., "Preparation and study of thickness dependent electrical characteristics of zinc sulfide thin films", Bull. Mater. Sci., 28(1), 43–47, (2005).
[11]. Shinde M.S., Ahirrao P.B., Patil I.J. & Patil R.S., "Studies on Nanocrystalline ZnS thin films prepared by modified Chemical bath deposition method", Indian Journal of Pure & Applied Physics, 49,765-768. (2011) .
[12]. Shinde M.S., Ahirrao P.B. and Patil R.S., "Structural, Optical and Electrical Properties of Nanocrystalline ZnS thin films Deposited by Novel Chemical Route", Scholars Research Library, Archives of Applied Science Research, 3(2),311-317(2011).
[13]. Cottrell A., "An Introduction to Mettallurgy", Edward Arnold (Publishers) Ltd., London, 173,(1975).
[14]. Longhurst R.S., "Geometrical and Physical Optics", Longmans Green, (1957).
[15]. Ray, S.C., "Preparation of copper oxide thin film by the sol–gel-like dip technique and study of their structural and optical properties", Solar Energy Mater and Solar Cells, 68 (3-4),307-312(2001).