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Synthesis and Characterization of ZnS Nanostructured Thin Films

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Abstract
Polyvinyl alchohol (PVA) capped nanocrystalline zinc sulphide (ZnS) thin films were fabricated by deposition on glass substrates by chemical bath deposition (CBD) method. The nanostructure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV spectroscopy. XRD results show the particle size varies from 6.0 – 27 nm. SEM result shows the surface of the particles to be hexagonal in structure. UV spectroscopy result gives the band gap is in the range 3.8 – 3.9 eV.
Keywords: Nanostructure, ZnS, CBD, XRD, SEM, UV- Visible spectroscopy.

1. 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. ZnS is one of the first semiconductors discovered [3] and it has traditionally shown remarkable fundamental properties versatility and a promise for novel diverse applications, including light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers, and biodevices, etc. Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. For example, ZnS has a larger bandgap of ~ 3.72 eV and ~ 3.77 eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively) than ZnO (~ 3.4 eV) and therefore it is more suitable for visible-blind ultraviolet (UV) - light based devices such as sensors / photo detectors. On the other hand, ZnS is traditionally the most suitable candidate for electroluminescence devices. However, the nanostructures of ZnS have not been investigated in much detail relative to ZnO nanostructures. It has high refractive index (2.25 at 632nm), high effective dielectric constant (9 at 1 MHz) and wide wavelength passband (0.4 - 13μm).

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 by X-ray diffraction (XRD), surface morphology scanning electron microscopy (SEM) and optical properties by UV-Visible spectroscopy, photoconductivity and photoluminescence of ZnS nano thin films.

2. EXPERIMENTAL DETAILS

Fabrication of polyvinyl alcohol (PVA) capped nanocrystalline ZnS thin film on glass substrate by CBD technique was performed by the following processes. The glass substrates were first 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.

Zinc acetate solution of six different molarities (0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 M) were added to an aqueous solution (2 wt%) of polyvinyl alcohol (PVA) separately with constant stirring at 70°C for 2 hour for preparing six 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 [4]:

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

After deposition of ZnS thin films, the glass substrates were taken out and washed thoroughly in

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distilled water several time and dried in air and then placed in a dessicator.

3. 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 is calculated by using Scherrer's formula

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

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 varies in the range 6 - 27 nm which is comparatively much small as reported by earlier workers [5,6]. Structural parameters of as-deposited ZnS thin films is given in table 1.

Surface morphology

The surface morphology of ZnS thin films on glass substrate was examined by scanning electron microscopy (SEM). Figure 2 shows the SEM image of ZnS nanocrystallites. The as-deposited film shows flower like structure (hexagonal wurtzite) of nano size ZnS particles in the range ~ 25–50 nm. Clusters are also observed due to the formation of strong agglomeration of small size nanorods.

Film thickness

The film thickness of ZnS is measured by Gravimetric method using a sensitive microbalance (Magnetic Analytical Balance, Wesnar Weighing Scales Ltd., Model MAB 182) using the relation,

thickness $t = M/\rho A \quad \ldots\ldots\ldots (2)$

where M is the mass of the deposited film, ρ is the density of ZnS (= 4.1gcm^{-3}) and A is the area of the film.

Optical properties

The optical properties of the ZnS thin film is determined from the absorbance measurement in the range 300 – 800 nm. Figure 3 shows the absorption spectra of ZnS thin films for different molarities. Figure 3 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 [7, 8]

$$\alpha = 2.3026\ A / t \quad \ldots\ldots\ldots\ldots (3)$$

The absorption coefficient of direct band gap semiconductor is given by [9]:

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

where α is absorption coefficient, c a constant, hν incident photon energy and E_g the band gap. Graphs between $h\nu \sim (\alpha h\nu)^2$ is plotted 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 3.9 eV.

Excitation and emission spectra are shown in Figure 4. Excitation monitored under 488 and 486 nm wavelength show two peaks at 288 & 385 nm and the emission spectra after excitation at 283nm gives strong peak at 466 nm, 328nm gives at 452nm and 378nm gives at 417 nm.

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

olarity	Thickness	(hkl)	d spacing	Size (nm)
0.1	45.46	104	2.84	18.39
		106	2.62	26.77
		1010	2.49	25.74
0.15	45.75	104	2.831	24.36
		105	2.702	3.834
		106	2.618	28.15
0.2	49.82	104	2.84	20.16
		105	2.71	6.03
		106	2.63	27.56
0.25	54.17	104	3.84	20.50
		105	2.72	20.92
		106	2.62	20.65
0.3	85.49	104	2.85	26.97
		105	2.72	7.46
		106	2.63	27.24
0.35	40.19	104	2.84	25.40
		105	2.71	6.47
		106	2.62	28.46

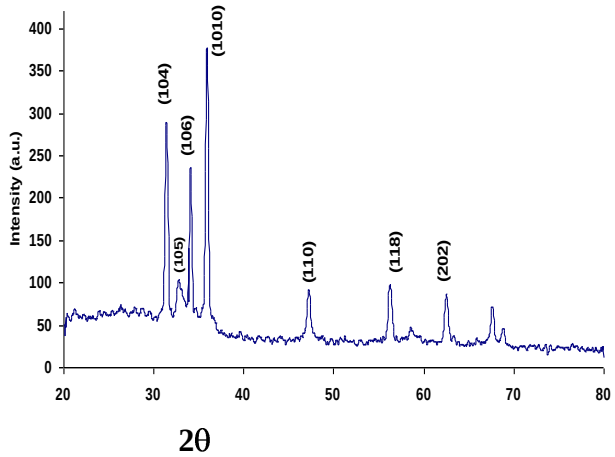


Fig. 1 The XRD pattern of as-deposited ZnS on glass substrate at 50ºC temperature.

Fig.2 SEM surface morphology of ZnS as-deposited on glass substrate

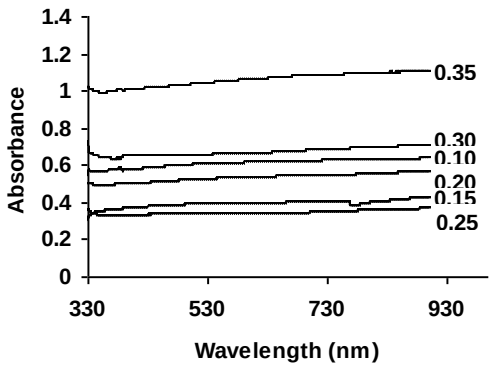
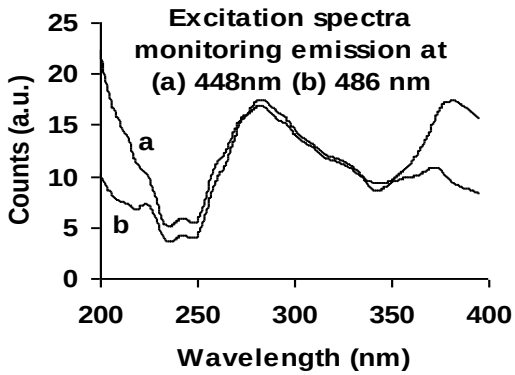


Fig.3 UV absorption spectra of ZnS thin films for different molarities



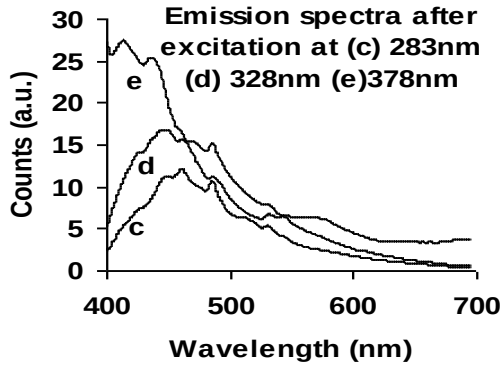


Fig 4. Excitaion and Emission spectra of ZnS thin films

4. CONCLUSION:

PVA capped nanocrystalline ZnS thin films of six different molarities were prepared by CBD method. XRD analysis found that the size of the nonstructural particles is in the range 6 – 27 nm. Their surface morphology were studied by SEM and found the shape of the particles is hexagonal. Their optical properties are studied by UV spectroscopy and fund the band gap is in the range 3.8 – 3.95 eV.

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