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Study of Photoluminescence and Photoconductivity Properties of Chemically Deposited Nanocrystalline ZnS Thin Films

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ABSTRACT

Thin films of ZnS – PVA matrix nanocomposites have been fabricated by chemical bath deposition (CBD) method by preparing equimolar solutions of lead acetate as zinc ion source and thiourea as sulphur ion source with ammonia as complexing agent. The as-deposited thin films are characterized by XRD, SEM, Photoluminescence (PL) spectra and current-voltage (I-V) characteristics. The particle size varies in the range from 6 nm to 27 nm. The PL study shows the formation of low energy band gap in ZnS thin films which exhibits positive photoconductivity. The electrical resistivity of the films increases with increase in concentration (molarities).

Keywords: Zinc Sulphide, Chemical Bath Deposition, Photoconductivity, Photoluminescence, X-Ray diffraction

Introduction

During last decades, materials containing zinc are interesting because of their applications in many areas of modern technology. Zinc Sulphide (ZnS) being a typical n- type semiconductor belonging to the family of II- VI semiconductors [1, 2] exhibits two different crystal structures i.e. zinc blende and wurtzite structures and both structures have the same direct energy band gap of 3.6 eV in bulk state at room temperature. It possesses a number of properties like 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 covers wide application for using as solar control coatings, antireflection coatings for heterojunction solar cells for light emitting diode, photovoltaic cells and blue shift light emitting diode. However, different techniques such as electrodeposition [3], pulsed laser deposition [4], spray pyrolysis [5], chemical vapour deposition [6], molecular beam epitaxy [7] have been used to synthesize ZnS thin films. In this paper we present the analysis of the particle structure, surface morphology, electrical resistivity and photocurrent of ZnS thin films formed by Chemical Bath Deposition (CBD) technique.

Experimental Details

For smooth and uniform deposition of polyvinyl alcohol (PVA) capped nanocrystalline ZnS on glass substrates by CBD technique, 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 was used as the zinc ion source and thiourea was used as the sulphur ion source. The polyvinyl alcohol (PVA) was also used as the capping agent and ammonia solution as the complexing agent. The matrix solutions were prepared by adding 2wt% of polyvinyl alcohol (PVA) to Zinc acetate solutions. The pH value of the same was maintained at 9.6 by adding ammonia solution drop by drop. Then the equimolar solutions of thiourea were added to the precursor matrix solutions. The color of the resulting solutions was slowly turning 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 ZnS thin films.

The chemical process for forming ZnS thin film is considered as follows [8]:

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

During the chemical process, the complex ion ($Zn(NH_3)_4^{2+}$) and sulphide ion (S^-) produced through hydrolysis of thiourea in alkaline medium migrate to the substrate surface where they react to form ZnS. 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 desiccators.

Results and Discussion

Structural Properties

The structural characterization was done by XRD. The X-ray diffraction pattern of ZnS thin films of 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 M are recorded with an X-ray diffractometer using CuKa radiation of wavelength, λ = 1.5406 Å and the typical XRD pattern of 0.10 and 0.20 M are presented in figures 1 and 2. It was found that both 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

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

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 crystalline sizes of ZnS thin films were found to vary in the range 6 -27 nm respectively which is comparatively much small as reported by earlier workers [9, 10].

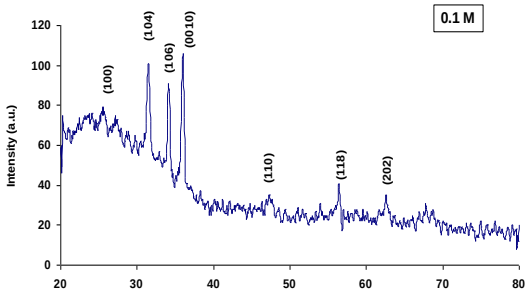

Fig. 1. XRD pattern of ZnS for 0.10 M.

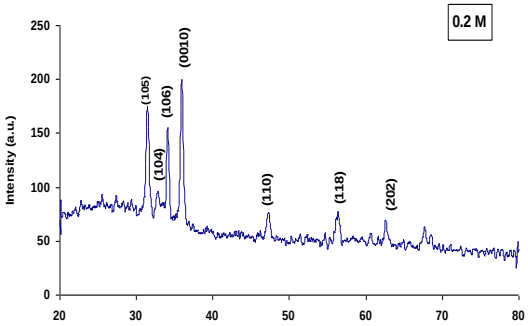

Fig. 2. XRD pattern of ZnS 0.20 M.

Surface morphology

The surface morphology of ZnS thin films on glass substrate was examined by Scanning Electron Microscopy (SEM). The SEM image of ZnS nanocrystallites for molarities 0.10 and 0.15 M are presented in figures 3 and4 respectively. The as-deposited film shows flower like structure of nano size ZnS particles in the range about 25 – 50 nm. Bigger structures are also observed due to the formation of agglomeration of small size nanorods.

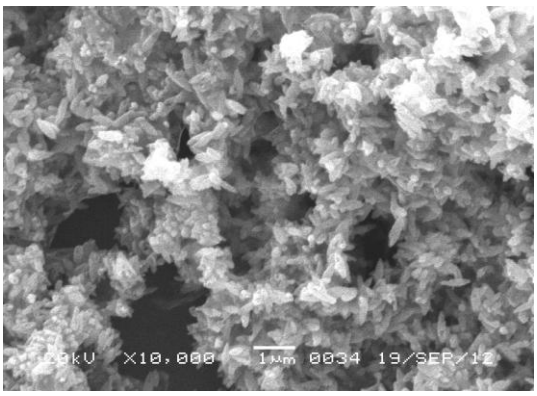

Fig. 3. SEM picture of ZnS thin film at 0.10 M

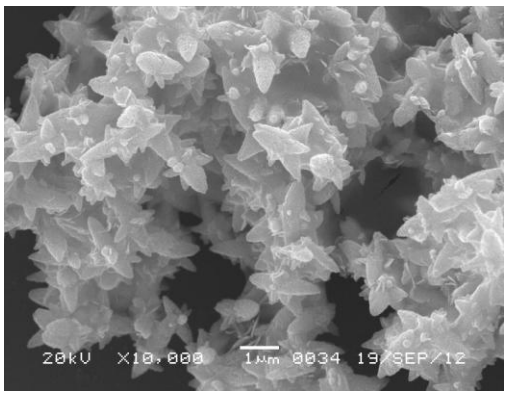

Fig. 4. SEM picture of ZnS thin film at 0.15M

Photoluminescence Study.

The Photoluminescence excitation and emission spectra of Polyvinyl alcohol (PVA) capped ZnS thin film at 0.15 M at room temperature are presented in figure 5 and 6 respectively. The excitation spectra monitoring emission at 448 nm were obtained in

the range from 200 nm to 400 nm while the emission spectra were obtained in the range from 400 nm to 700 nm. The excitation peaks were observed at 235 nm and 375 nm while the strong emission peak was observed at 433 nm after excitation at 328 nm. The energy band gap of ZnS crystal was calculated using the formula $E = hc/\lambda$, where λ is the wavelength of the band gap luminescence [11, 12]. The energy band gap was found to be 2.85 eV which is slightly less than bulk value (3.6 eV) at room temperature. The low energy band is related to deep level transitions, which accounts reasonably a good crystalline quality of the samples. Usually, the energy band gap of a binary semiconductor lies in between 0 and 4 eV. The PL study obviously confirms that the as-prepared ZnS thin films exhibits the nature of semiconductor.

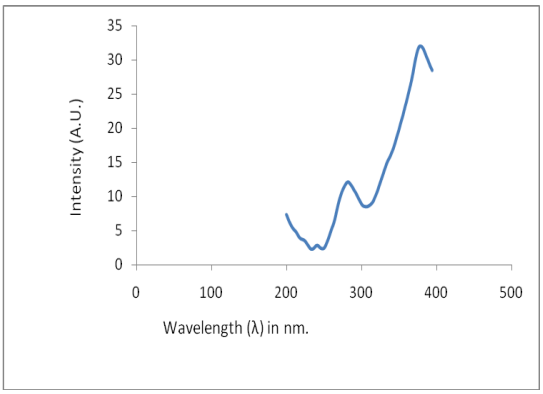

Fig.5. PL Excitation Spectra of ZnS (0.15 M)

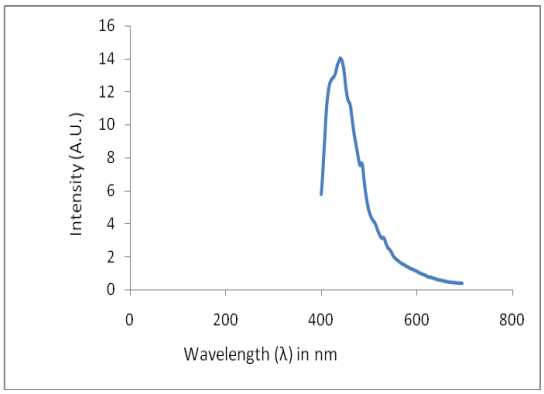

Fig.6. PL Emission Spectra of ZnS (0.15M)

Photoconductivity Measurement

A suitable optical arrangement was made to illuminate the sample uniformly with white light of different intensities. A tungsten halogen lamp (250 W-24V) attached a parabolic focusing mirror was used as the white light source. The block diagram of the experimental set-up is presened in figure 7. The intensity of light was measured with the help of a sensitive digital Light Meter. High ambient temperature was achieved by means of a resistive heater connected to a stabilized power supply. The temperatures of thin films were measured with the help of a copper-constantant thermocouple coupled with Digital Multimeter. The dark currents (I_D) and the currents under illumination (I_L) were measured with the help of a Digital Picoammeter under different dc bias voltages. The pure silver probes were used for the measurements. The whole experimental set-up including the observer was housed inside a suitable sound proof dark room. The observations were taken preferably at night to avoid the high day time noise.

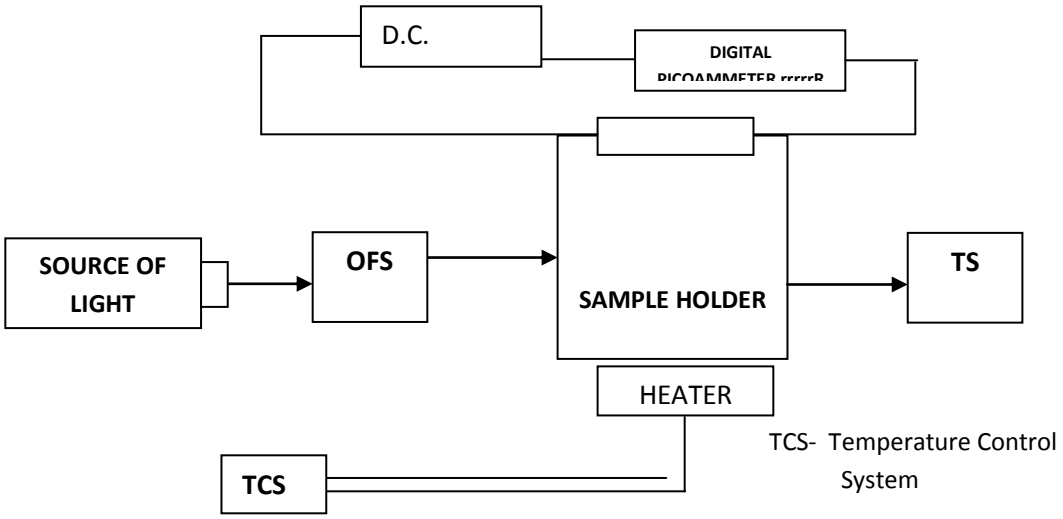

Fig. 7. Block Diagram of experimental set-up for photoconductivity measurement.

Characteristics for Current under illumination and Dark Current

The variation of field dependence dark current (I_D)and current under illumination(I_L) with applied voltage (V) for polyvinyl alcohol(PVA) capped nanocrystalline ZnS films for different molarities are presented in figure 8 to 11 for different molarities. It is observed that both dark currents and currents under illumination of nanocrystalline ZnS films increase with the applied voltage at room temperature. This shows non linear behavior similar somewhat to that of a diode. This may indicate possibility of application in optical devices. The current under illumination of nanocrystalline ZnS film is more than the dark current for the same applied voltage in all the samples, which is termed as positive photoconductivity. All the synthesized ZnS nanocrystalline films considered in the present study are found to exhibit positive photoconductivity. This may be attributed to the generation of mobile charge carriers caused by absorption of photons [13].

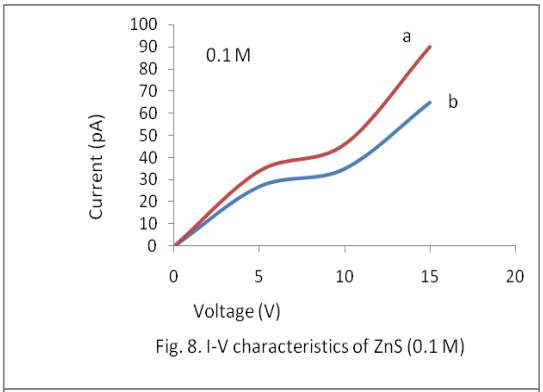

Fig. 8. I-V characteristics of ZnS (0.1 M)

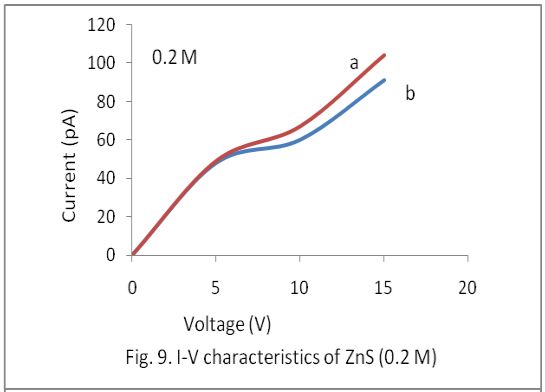

Fig. 9. I-V characteristics of ZnS (0.2 M)

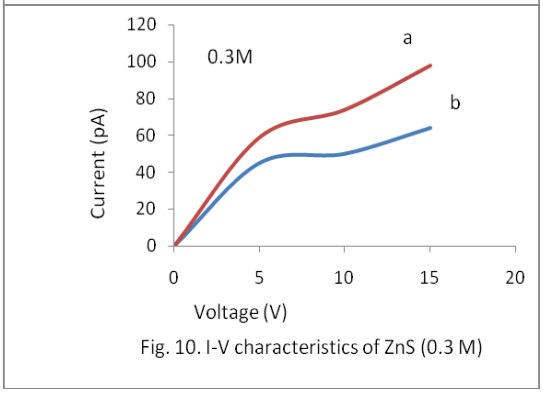

Fig. 10. I-V characteristics of ZnS (0.3 M)

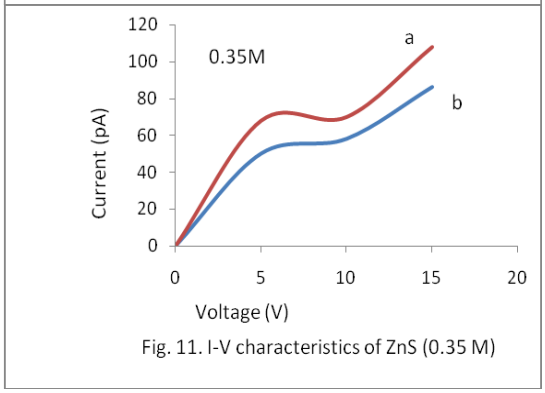

Fig. 11. I-V characteristics of ZnS (0.35 M)

a-correspond to the current under illumination **b-correspond to the dark current**

Electrical Resistivity

The electrical resistivity of the films were determined by I-V characteristics curves using silver electrodes and their values were calculated using the relation, $\rho=RA/L$ where R is the resistance of the films and is measured by the slope of the I-V characteristic curves, A is the area of the film under investigation and L is the spacing between electrodes. The dark resistivity as well as the resistivity under illumination of the films were found to increase with increase in molarities in the range, 3.2 Ω cm to 11.2 Ω cm (in dark) and 4.8 Ω cm to 15.2 Ω cm(under illumination). Thus, the as-deposited ZnS thin films possess high resistivity which is similar as reported by earlier workers [14].

Effect of Incident light and Temperature on Photocurrent

The photocurrent is defined as $I_{ph} = I_L - I_D$, where I_L is the current under illumination and I_D is the current under dark. The variation of photocurrent with intensity of illumination under same biasing voltage at room temperature in all cases is presented in figure 12. The figures shows that the photocurrent increases almost linearly with increase in intensity of illumination in all cases. The variation of photocurrent with temperature in kelvin (K) under same biasing voltage and intensity of illumination in

all cases are presented in figure 13. The figures shows that the photocurrent increases almost linearly with increase in temperature. This indicates the semiconductor nature of PVA capped ZnS thin films synthesized by CBD technique which is consistent with result from PL study.

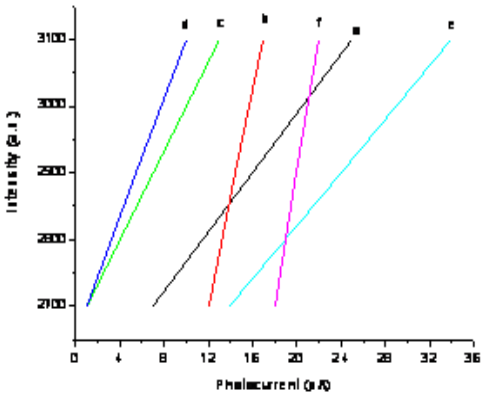

Fig. 12. Photocurrent vs Illumination

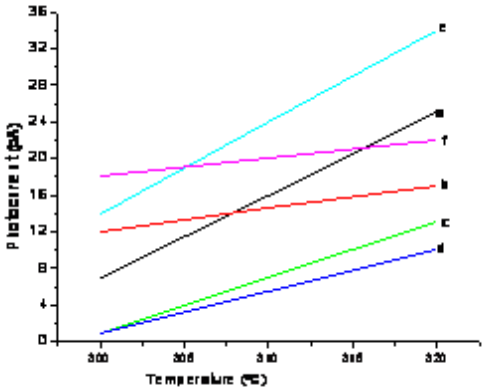

Fig.13. Temperature (K) vs Photocurrent

where a,b,c,d,e,f correspond to 0.10,0.15,0.02,0.025,0.03, 0.35 M.

Conclusion.

PVA capped nano crystalline ZnS thin films were fabricated by Chemical Bath Deposition (CBD) method on glass substrates. The nanostructure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and PL spectroscopy. From XRD result the particle size are found to vary from 6 nm – 27 nm. SEM result shows the presence of flower like structure of nano sized ZnS particles in the range about 25 – 50 nm. The photoluminescence spectra of the films showed strong peaks centered around 433 nm after excitation at 328 nm and the energy band gap obtained from PL study is 2.85 eV. Photo conducting studies show photocurrent to be larger than the dark current for the same voltage. The electrical resistivity of the films increases as molarity increases indicating semiconductor nature.

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