IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 15, Issue 5 Ser. I (Sept. – October. 2023), PP 67-72
www.Iosrjournals.Org

Synthesis And Characterization Of Photoelectrical Transport Properties Of Nanocrystalline Zns Films

M. Dinendra Singh . K. Kunjabali Singh*
Department of Physics, Himalayan University, Itanagar, Arunachal Pradesh, India
**Thin Films and Nanomaterials Research Laboratory*
Department of Physics, Thambal Marik (Govt.) College, Oinam-795134, Manipur, India.

Abstract:
Molar concentrations have significant effect in the growth, structural, optical and phototransport properties of nanocrystalline ZnS thin films. Bimolecular recombination mechanisms of carriers exhibit is observed in the study of photocurrent vs. intensity of activation of white light (WL) illumination on the ZnS films. The effect of light intensity on the biased films showed that photosensitivity increases linearly with intensity of WL illumination due to effective carrier transport mechanism with increasing concentrations of Zn^{2+} and S^{2-} ions. Two types of distinct dark and photoconductivity activation processes are found in low and high temperature regions in the films. The spectral response characteristics at different concentrations of Zn^{2+} and S^{2-} ions in the films showed blue shift at 305nm and peak heights increase with increase of molar concentrations.

Keywords : *molar concentration, ZnS, photoconductivity, activation energy*

Date of Submission: 21-10-2023 Date of Acceptance: 01-11-2023

I. Introduction

In the past two decades, synthesis of “small particles” by different methods become fascinating field of research in various fields of physics and chemistry. The “small particles” materials now we call nano-materials (1-100nm in diameter) are very interesting materials for scientific reason and technological applications[1] due to their unique characteristics that cannot be obtained from conventional macroscopic materials[2]. More precisely, semiconductors in nanoscale have attracted much attention because of their novel properties originating from quantum confinement effect – the effect produced by trapping the excitons (electrons & holes) in quantum wells incompatible in macroscopic materials and quantum size effects [3,4,5]. These trapped excitons can be confined into preferred direction- in the form of wires that we call quantum wires, or nanosheets, nanotubes etc. Most studied nanocrystalline semiconductors belong to II-VI and IV-VI groups as they are relatively easy to synthesize and are generally prepared as particles or in thin film form. In this paper, Chemical Bath Deposition (CBD) method is used for synthesis of ZnS nanocrystalline thin films as the method can vary the dimension of the crystallites by controlling various parameters : the reaction time, bath temperature, pH value, concentration of reaction materials [6], number of immersion cycles and immersion time[7].

ZnS belongs to II-VI group of compound semiconductors with a large direct band gap ($E_g = 3.7eV$) in near UV region which makes it suitable for fabrication of blue light emitting diodes (BLEDs)[8] and other opto-electronic devices, electroluminescence[9], cathodoluminescent displays, multilayer dielectric filters[10,11]. A large number of people have given considerable efforts towards the synthesis of ZnS nanocrystals using different techniques such as thermal evaporation, spray pyrolysis molecular beam epitaxy, etc. Most of the researchers have used equal concentration of Zn^{2+} and S^- ion precursors in the synthesis works[12]. However, reports on variation of Zn^{2+} and S^- ion concentrations in synthesis of ZnS nanocrystals by different chemical methods show unsubstantial works.

II. Experimental details

The synthesis of ZnS thin films was carried out in our laboratory by simple chemical bath deposition (CBD) technique. In the synthesis process, we use Zinc acetate[$Zn(CH_3COO)_2$] (AR grad) for Zn^{2+} ions source, thiourea [$SC(NH)_2$] for S^{-2} ions source in presence of hydrazine hydrate as reducing agent, ammonium hydroxide[$NH_4(OH)$] as catalyst and polyvinyl alcohol (PVA) as matrix to control agglomeration of particles in the ionic solution. In the process, 10ml of zinc acetate [$Zn(CH_3COO)_2$] was mixed with 10 ml of hydrazine hydrate in 100 ml glass beaker and stirred for 30 minutes till it turns into clear solution. Then 10 ml of thiourea $CS(NH_2)_2$ solution was added to the precursor. Next, de-ionized water was added to the solution to obtain 50ml of the solution. A few drops of NH_4OH solution was added. The p^H of the solution was measured and maintained at 10. Then 20ml of pre dissolved 2wt % PVA matrix solution was added to the above solution and stirred continuously at 70^{0}C for 2 hours till PVA dissolves in the solution. The chemically and ultrasonically cleaned glass ITO (40x25x2mm^3)substrates were then immersed in the matrix solution for 120 hours. The ZnS films deposited on the substrates were then washed with double distilled water several times for removal of any grains to obtain fine ZnS nanocomposite matrix films. The thickness of the films were measured by microbalance technique. Prior to the photoconductivity measurement, gap-type electrodes were deposited on the host ZnS molared films using HINDHIVAC Coating Unit under vacuum pressure 1.33 x 10^{-5} Torr.

III. Results and discussion

Molar dependent photocurrent and photosensitivity in ZnS film

The I-V characteristics for dark current (I_D) and current under illumination (I_L) over entire range of applied bias of the as chemically deposited ZnS films grown at different molars at room temperature were found to be almost ohmic Fig. 1.-

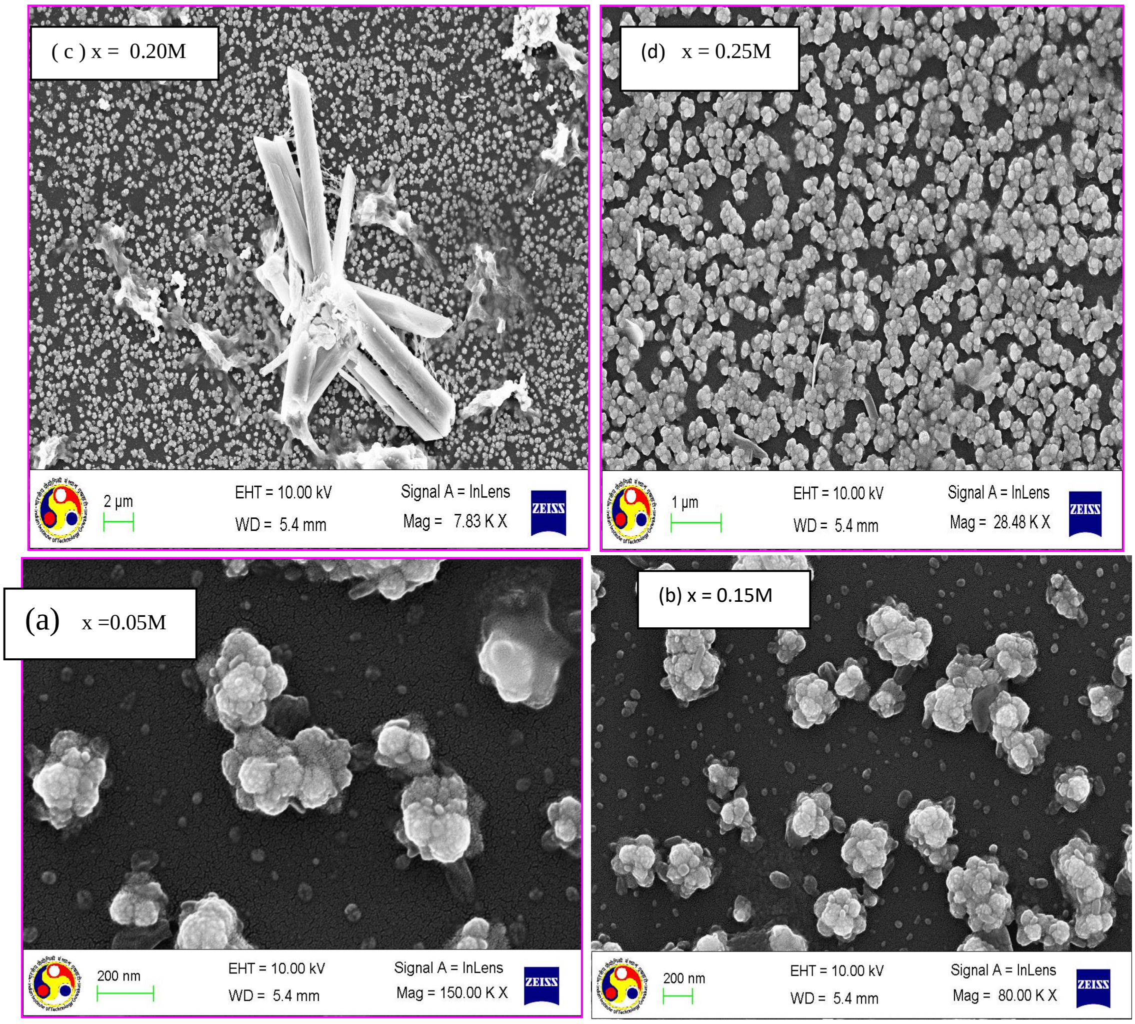


Figure 2. FESEM Images of ZnS nano crystals at different molars

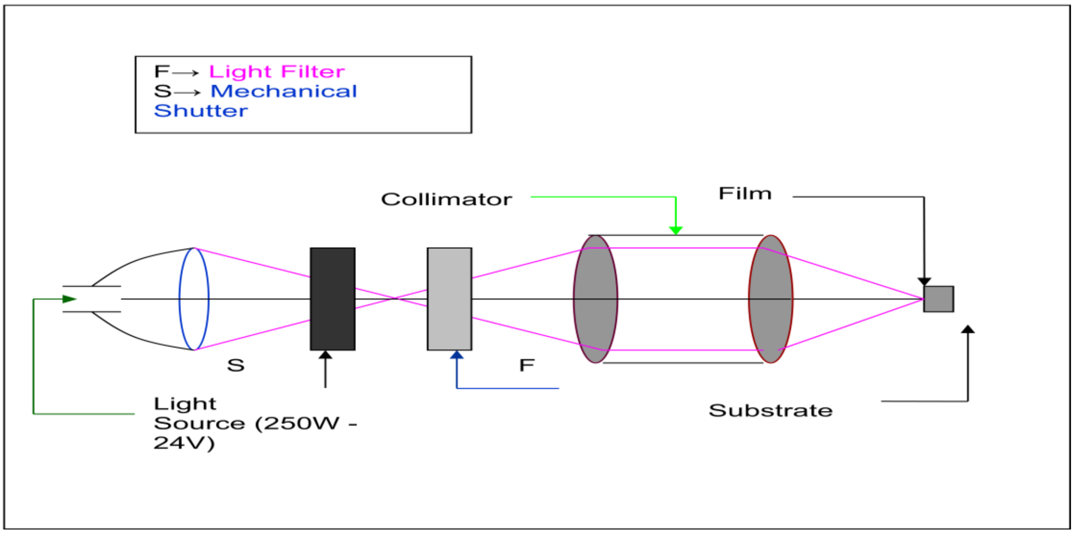


Figure 3. Optical focusing system on ZnS films inside ambient temperatures.

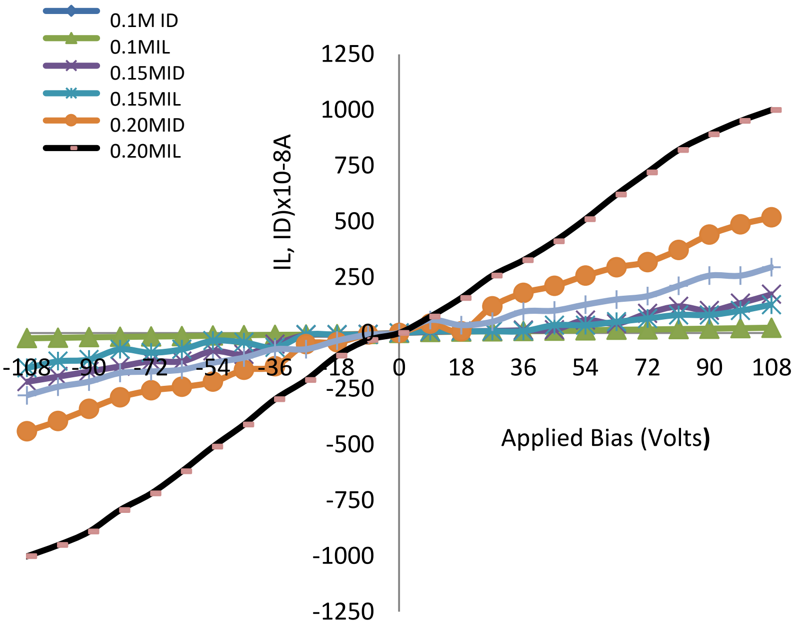


Figure 4. I-V characteristics of ZnS n crystals at molars

We have studied the effects of molars on the photocurrent of the films after excitation of white light of different intensity under a fixed applied bias in vacuum. It is found that over the entire range of light intensities, the photocurrent (I_{ph}) is related to the excitation light intensity (Φ) through the power law relation,

$I_{ph} \alpha \Phi^{\gamma}$,   -(1)

The values of exponent γ determined from the slops of InI_{ph} vs. $In\Phi$ of the linear plots of ZnS nano-films (Fig.5) as shown in Table-1 reveal that the bimolecular recombination mechanism of the carriers takes place in the photo-transport mechanism in the films.

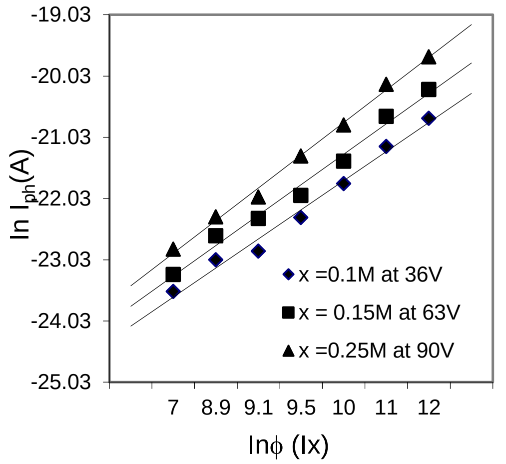


Figure5. lnI$_{ph}$ vs lnϕ of nZnS thin films, 150nm (t),under WL excitation.

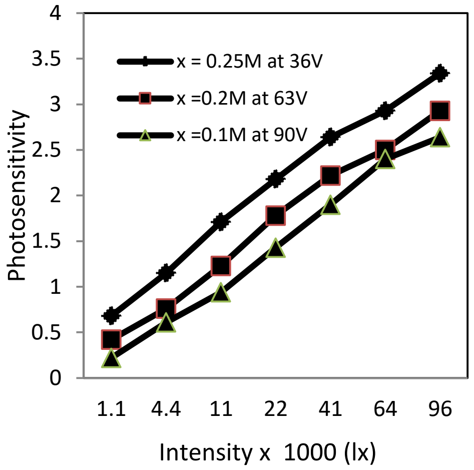


Figure6.. Photosensitivity vs. WL. intensity of nZnS films

Table:1. Exponent γ-values at different molars of nZnS nano-films

Sl. No.	Molar (M)	Film thickness (μm)	ν -value
a	0.10	0.20	0.61
b	0.15	0.45	0.65
c	0.25	0.55	0.60

The photosensitivity of a material is expressed as

$$S=(I_L-I_D)/I_D \qquad -(2)$$

where I_L is the current under illumination, I_D the dark current**.** The variations of photosensitivity with light intensity of nZnS films of molar, x = 0.10M and t = 0.20μm, x = 0.20M and t = 0.45μm and x = 0.25M and t = 0.45μm grown at room temperature substrate at varied biased voltages illuminated with different white light(WL) intensity have been shown in Fig.6. It is observed from these linearity plots that photosensitivity in these thin films increase with increase in the intensity of illumination of white light, molars and film thickness (t). It may be interpreted as enhancement of mobility activation energy with increase in concentration of charge carriers with molars and film thickness.

Molar dependent photoconductivity

The variation of dark and photoconductivity, In σ vs. 1000/ T (where T being the ambient temperature of the film system) of four representative nZnS films grown at x = 0.10M to x = 0.20M grown at room temperature and illuminated with a suitable white light intensity (11,000 Lx) biased 36V have been shown in the adjoining Figs.7,8 and 9 respectively. The characteristics show distinct regions of activation processes from ambient temperature (30-180)^{0}C (in low and high Temperature Regions) in nZnS films. The values of the observed activation energies (ΔE) and the mobility activation energies (ΔE_μ) in dark and illuminated regions in the curves shift to lower values with increasing molars as shown in Table-2.

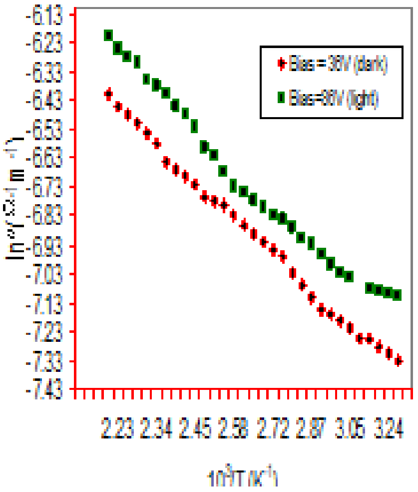
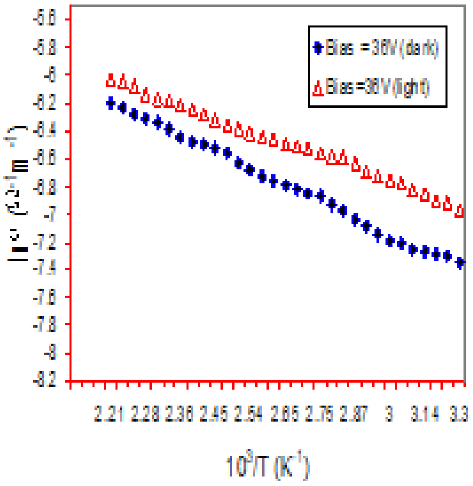


Figure7. lnσ vs. 10^3/T plots of n ZnS film (x=0.1M)



Fi **Figure.8. lnσ vs. 10^3/T plots of n ZnS films (x-0.15M)**

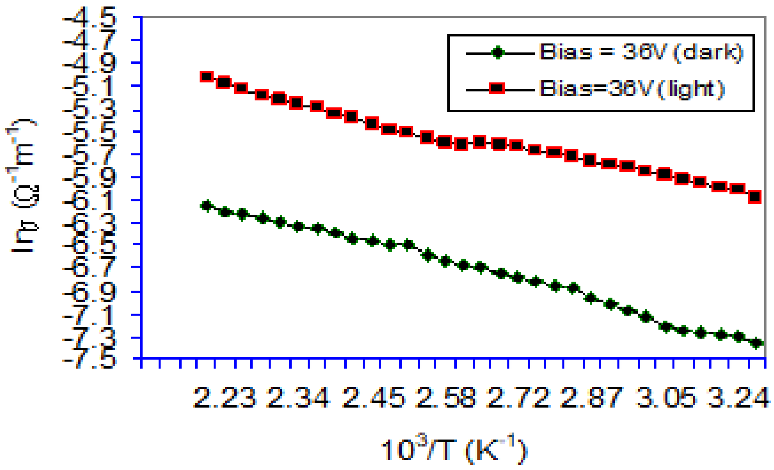


Fig **Figure.9. lnσ vs. 10^3/T plots of nZnS film (x=0.25M)**

The reduction is mainly due to the reduction in the grain boundary potential barrier by some excess photo-generated carriers in the films as suggested by Petritz [13]. It is also observed from the experimental data that the values of photoactivation energy (ΔE_L) in high and low temperature regions in the curves are comparatively lower than their corresponding dark values (ΔE_D).

Spectral response characteristics

The spectral response characteristics of the host ZnS nanocomposite films have been studied using monochromatic radiations with wavelengths 250nm – 500nm. The monochromatic radiations were obtained from a white light source of a 250W-24V tungsten halogen projector bulb provided with a parabolic focusing mirror using a set of Carl Zeiss [GDR] metal interference filters. The spectral response characteristics of chemically bath deposited ZnS thin films grown at

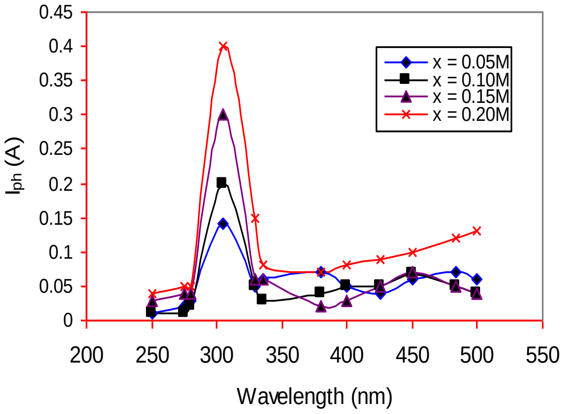


Figure.10.. Spectral response characteristics of ZnS nanocomposite films.

different molars is shown in Fig.10. It is observed that ZnS nano-films at different molars show maximum peak at λ ≈ 305nm wavelength and the peak heights increase with increasing molars of the host samples. The spectral analysis reveals that the synthesized ZnS nano-films at different molars show remarkable increase in photocurrent with increase in molars in the synthesis process. It is observed from the characteristics of the figure that photocurrent increases with wavelengths up-to 500nm. This can be given with the precisions that maximum photoconductivity is normally produced at a wavelength slightly above the absorption edge. For wavelengths longer than the maximum photocurrent to produce, the excitation energy (E = hc/λ) decreases simply because the absorption producing free carriers to the conduction band are decreasing, which results a decrease in photoconductivity. Similarly, at shorter wavelengths than the maximum, the radiation is strongly absorbed and produces excitation only near the film surface. The surfaces of the films at shorter wavelength regions are, therefore, non-radiative due to recombination of carriers (electrons and holes), and hence the excitation to cause photoconductivity is reduced. In other words, the concentration of free carriers in the small restricted volume of the surface at shorter wavelength regions become very high which causes sharp increase in recombination rate. In addition to this, the presence of various impurities and defects in the surface layer also enhances the recombination rate of the carriers (*electrons and holes*) which decreases the surface life time, and hence reduction in photoconductivity . Further, the increase of photocurrent with increasing of molars is mainly due to the increase of particle size which resultants decrease in the grain boundary barrier heights of the ZnS films. The observed optical band edge corresponding to the maximum spectral sensitivity in ZnS at wavelength 305nm (*threshold wavelength*) is estimated using the relation, E_g (eV) = 1.24/λ_g where λ_g is in μm and is found to be 4.1eV. This mean experimental value of E_g of ZnS (x = 0.20M) at 4.1eV is above the actual bulk band gap value3.7eV at 300K .

Acknowledgements

We are thankful to the UGC, New Delhi for granting Financial Assistance to carry out the Research Project Ref. F.No. 34-19/2008(SR) dated 29th Dec., 2008 , SAIF, Gauhati University for XRD and CIF, IIT, Gauhati for FESEM data analysis.

References

[1]. A Rahdar, V Arbabi And H Ghanbari, World Academy Of Science, Engineering And Technology 61 2012 P657
[2]. V L Gayou, B Salazar-Hernandez, R Delgado Macuil, G Zavala, P Santiago And Aloliva, Journal Of Nano Research Vol. 9(2010)125
[3]. Schmid Et Al, Nanotechnology Assessment And Perspectives Mackmillan India Ltd (2006)79
[4]. R H Roussingnol, D Richard, C H R Flytzanis, Appl. Phys. B51(1990)437
[5]. K Fgukumi, A Chayahara, K Kodono, T Saguchi, Y Horino, M Miya, J Hayakawa, M Satou, J. Appl. Phys. 30(1991) L742
[6]. Hu J Odom JW & Lieber CM. Acc Chen Res. 32(1999)435
[7]. M S Shinde, P B Ahirrao, I J Patil And R S Patil, Indian Jr. Of Pure & Appl. Phys. Vol. 49, Nov. 2011, 765
[8]. Pawan Kumar, Arvind Kumar, P N Dixit And T P Sharma, Indian Jr. Of Pure & Appl. Phys. Vol. 44, Sep. 2006, 690
[9]. Jyoti P Borah, J Barman, K C Sarma, Chalcogenide Letters Vol. 5, 9, Sep. 2008 201
[10]. Li Dyuer A M, Appl. Optics, 18 (1979)2979
[11]. Jones P L, Moore D M And Smith D C, Journal Physics E(1976) 312
[12]. Suyver J F, Weister S F, Kelly J J And Meejerenk A, Nano Lett. 1(2001)429
[13]. R L Petriz,Phys. Rev. 104 (6) (1956)1508