International Journal of Pure and Applied Physics.
ISSN 0973-1776 Volume 12, Number 1 (2016), pp. 1-8
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Structural, Morphological, Optical and Electrical properties of Nanostructured ZnMnS thin film prepared by Chemical Bath Deposition method

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ABSTRACT
Mn-Doped ZnS were deposited on glass substrates using a chemical bath deposition (CBD) method in an aqueous solution is an important semiconductor with a wide band gap and high transparency in the UV-visible region . The crystallite size of the ZnMnS thin film was estimated from the x-ray diffraction pattern by using Scherrer's formula. X-ray diffraction patterns revealed that the cubic crystal structure. The scanning electron microscope images showed the formation of a fairly uniform surface . The optical properties of the film were studied using measurement from UV-Vis spectrophotometer; the results appear that an optical absorption edge was blue shifted region and estimated band gap value of ZnMnS was 3.93eV. The electrical properties of these films were studied by I –V measurement in dark and illumination (100 mW/cm^2) condition. The films were characterized by energy-dispersive X-ray spectrometer (EDX), X-ray diffractometer (XRD),Scanning electron microscopy (SEM), ultraviolet -visible light (UV-vis) spectroscopy

Keywords: Nanostructured, CBD, cubic, ZnMnS, doped,.. etc.

1. INTRODUCTION

The II-VI compounds semiconductor thin films (e.g. CdS ,ZnS ,CdSe, ZnSe) have received an intensive attention due to their application in thin film solar cells, optical coatings , optoelectronic devices ,and light emitting diodes [1-2].Among these metal chalcogenids , ZnS is an important semiconductor material because of its broad, direct band gap energy(~3.6eV) at room temperature, high refractive index (2.35), and high dielectric constant. Zinc sulfide is a semiconductor suitable for use as a host matrix for a wide variety of dopants on account of its wide energy band gap. The luminescence properties of this material doped with Mn have proven to be suitable for

electroluminescence applications[3-5] .Manganese is generally incorporated as Mn^{2+} ion in the substitutional sites of the ZnS lattice. The techniques used to deposit ZnS films have different natures. Among them, the most common are sputtering,[6] sol-gel,[3,7] spray pyrolysis,[8,9] chemical vapor deposition (CVD),[10,11] molecular beam epitaxy,[12] atomic layer epitaxy (ALE),[13] and chemical bath deposition (CBD)[14-20]. Among these ,the CBD method is much more attractive since the technique possesses a number of advantages over the conventional thin film deposition methods including the simplicity in experimental set up .It does not require an expensive vacuum system. The main advantages of the CBD method are low cost, low deposition temperature, easy coating of large surfaces, and having the capacity to deposit optically smooth, uniform, and homogeneous layers [21-22].

2. MATERIALS AND METHODS

2.1 Materials

All chemical used in the experiment were analytic reagent grade. Zinc sulphate hepta hydrate $ZnSO_4.6H_2O$, manganese sulphate ($MnSO_4.H_2O$) and Thioacetamide were purchased from Merck chemical (India) Pvt. Ltd. Ammonia and triethaloamine also purchased from Merck chemical (India) Pvt. Ltd, Double deionized water was used through out the experiment.

2.2 Synthesis of nanostructured ZnMnS thin film

Preparation of Mn^{2+}-Doped ZnS Thin Films. Nanocrystalline ZnMnS thin films were deposited on commercial microscope slide glass substrates . A very attractive method for producing ZnS thin films due to possibility of large area deposition of sulphides, oxides so called chemical bath deposition method. ZnS thin films are prepared by decomposition of triethaloamine in an alkaline solution containing a zinc salt, manganese sult and a suitable complexing agent .The deposition process is based on the release of Zn^{2+}, Mn^{2-} and S^{2-} ions in solution which then condense on the substrate. Before film deposition, the substrates were first cleaned in chromic acid solution and were subsequently washed in detergent solution, rinsed in deionized water. The substrates were then dried in air(The cleaned glass surface provided nucleation centre for growth, good adhesion and uniform deposition of the films). 20ml (0.2M) zinc sulphate solution, 5ml (0.2M) manganese sulphate solution, 0.5 ml ammonia and 15 ml (0.6M) Thiourea solution were placed in 50 ml beaker. Deionised water was added to make the volume up to 50 ml. The pH of the resulting solution is measured about 10 after the mixture of chemical components . The prepared solution was mixed with a magnetic stirrer, after obtaining a clear homogenized solution the stirrer was turned off and glass slides were placed in the bath vertically for 1 hours at

70^{o}C temperature. The chemical bath solution was not stirred during the film deposition. The coated substrates were removed at the end of deposition, washed in deionized water, dried in air at room temperature, and then characterized. Both sides of the glass substrates were coated with the films.

2.3 Characterization

The XRD pattern was recorded using X-ray diffractrometer Bruker AXS, Germany (Model D8 Advanced). The Energy Dispersive analysis of X-rays (EDAX) and Field Emission Scanning Electron Micrographs (FE-SEM) were taken by using Bruker and S-4800 hitachi respectively. UV-Vis spectrophotometer (Perkin Lembda-25) in the range from 300-900 nm was used to measure its optical properties. I-V characteristic were calculated by Lab-equipped model 24 (2004) computer interfaces measurement unit.

3. RESULTS AND DISCUSSIONS

3.1 Structural Studies

The XRD pattern of Mn doped ZnS was displayed in figure1. It can be identified as the cubic zinc blende structure with a comparison to the standard card (JCPDS, no. 05-0566). The sample shows the characteristic reflections from (111), (220), and (311) planes. No peaks corresponding to manganese compounds were observed, demonstrating that Mn ions are dispersed in ZnS matrix. Also no peaks corresponding to other impurities were identified in the pattern, indicating the high purity of the thin film. The large width of the diffraction peaks is an indication of the nanosize of the particles. The peaks of the XRD pattern of manganese-doped ZnS clearly show no shifting of the center of the diffraction peaks. The XRD corresponds to the light reflected from the planes where the periodic arrangement of the atoms is perfect and continuous [23]. The ionic radius of Mn^{2+} is 0.8 A^{O} whereas that of Zn^{2+} is 0.74 A^{O}. As doping of Mn^{2+}does not appreciably disturb the plane. The lattice parameter values are a=b=c=5.3 A^{O} .

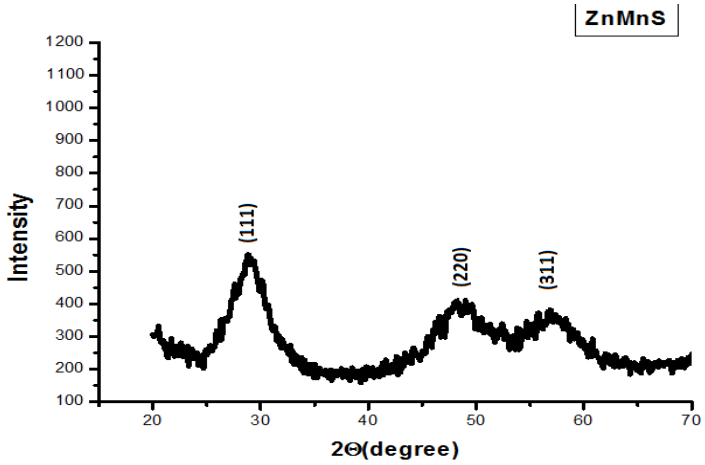

Fig.1. Shows the XRD pattern of Nanostrctured ZnMnS thin film

From the width of the XRD peak broadening, the crystalline size can be calculated using Scherrer's equation:

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

Where D is crystallite size, 'λ' is the X-ray wavelength used, β is the angular line width of half maximum intensity, θ is Bragg's diffraction angle and K is constant. Fig. 1 shows the crystalline size was estimated to be about (2.5 nm). The lattice constant (d) was evaluated as 3.11 A^o .This is in good agreement with lattice constant of cubic ZnS with a d of 3.123 A^o for [1 1 1] plane . The peak broadening in the XRD pattern clearly indicates that very small nanocrystals are present in the sample.

3.2 Morphological and Compositional studies

Scanning electron microscopy is a convenient method for studying thin films. Figure 2 (a, b) show scanning electron micrograph for deposited nanostructured ZnMnS thin film in different resolution images. Surface morphological studies play an important role to observe smoothness and nature of the film. The surface morphology of doped ZnS thin film have spherical shape In some places, various sizes of the particles (small and large size) are observed, i.e. nano-sized particles seem to be randomly distributed in the film [24].

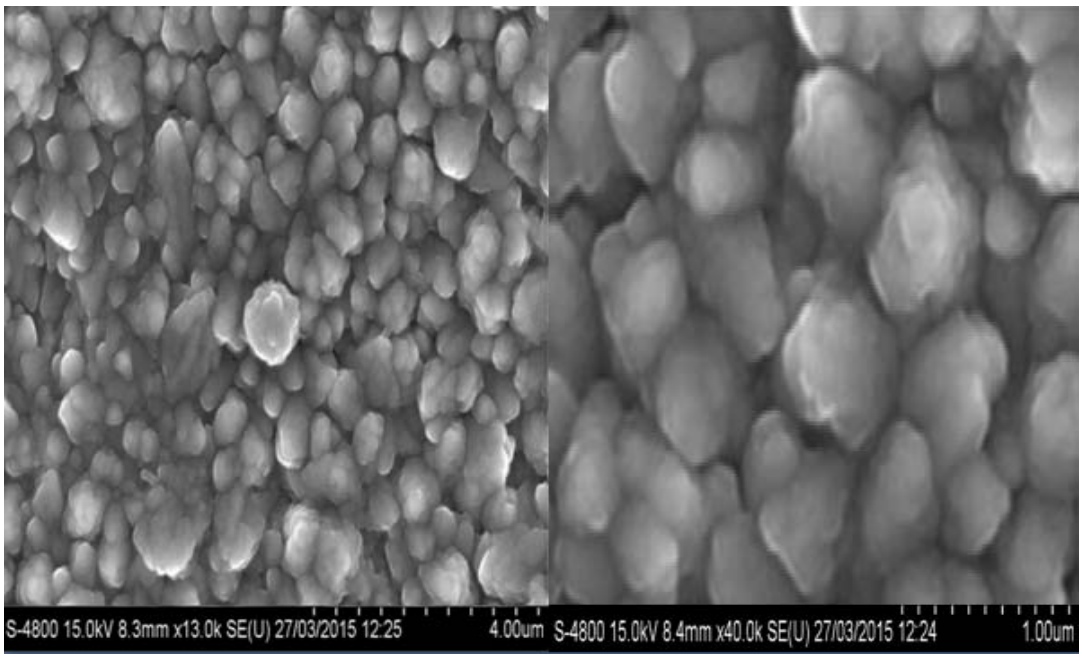

Fig.2. (a, b) Show the different resolution images of Nanostructured ZnMnS thin film

Composition of the nanocrystalline ZnMnS thin film was studied by Energy dispersive X-ray analysis (EDAX). EDAX indicated the presence of zinc, manganese and sulfur for the substrate fig (3).

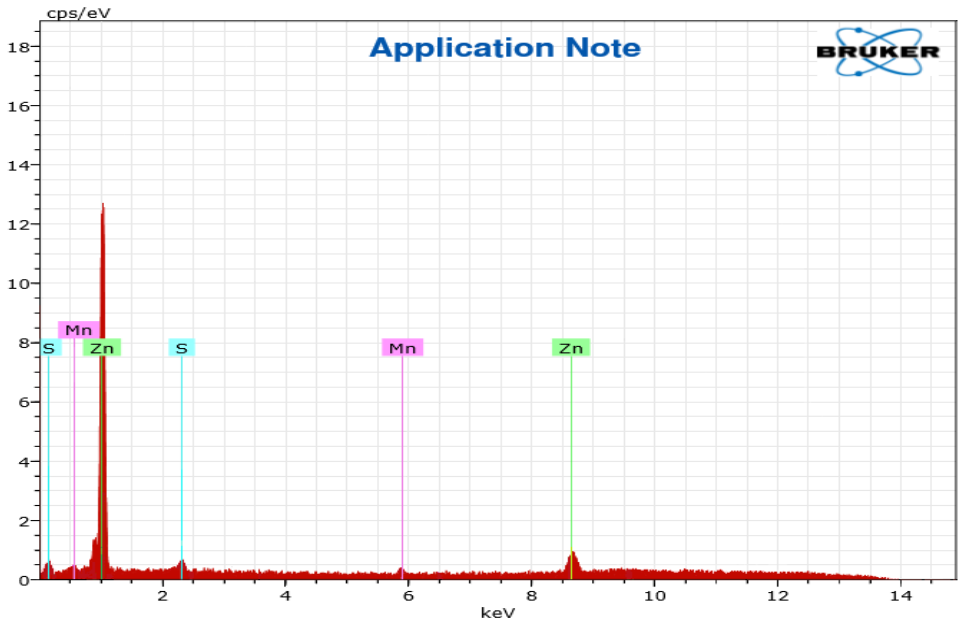

Fig.3. Show the EDAX spectra Nanostructured ZnMnS thin film

3.3 Optical study of ZnMnS thin film

The optical absorbance of ZnMnS thin film is determined from the range 300-900 nm**.** Fig. 4 exhibits the UV-visible absorption spectrum of Mn^{2+}-doped ZnS thin film deposited on a glass substrate. This absorption spectrum exhibits a shoulder at 315 nm (3.93 eV), resulting from the quantum confinement effect of Mn^{2+}-doped ZnS thin film . It suggests a large blue shift of 0.26 eV of the absorption band from that of 338 nm (3.67 eV) for bulk ZnS crystals at room temperature [1,2]. Thus, the band gap of Mn^{2+}-doped ZnS nanoparticles has been enlarged.

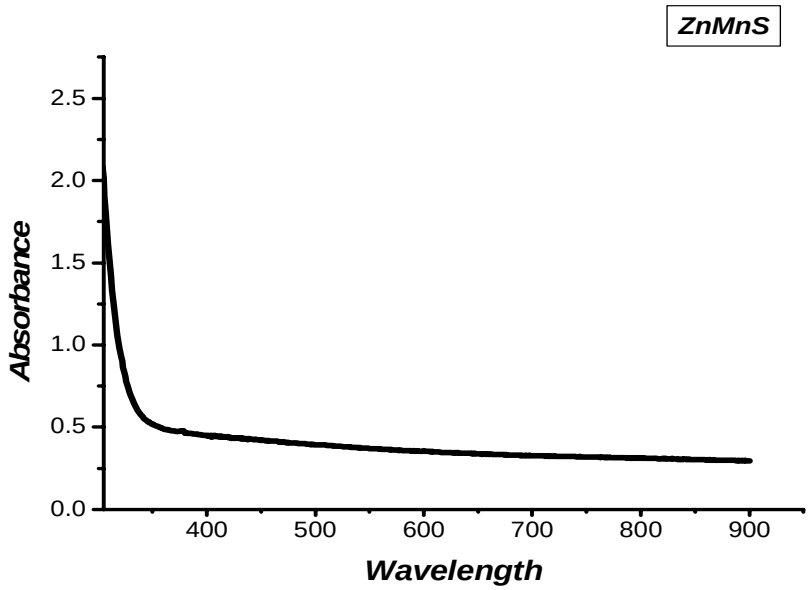

Fig.4. Shows absorption spectra of Nanostructured ZnMnS thin film

Fig 5 shows band gap of nanostructured ZnS thin film obtained from absorption spectra. The relation between the absorption coefficient α and the incident photon energy (hν) is given by relation:

$$\alpha = \frac{A\left(h\nu - E_g\right)^n}{h\nu}. \qquad (2)$$

In this relation n= ½ is taken for direct allowed transition and 'Eg' is optical band material. Absorption coefficient (α) is associated with the strong absorption region of thin films was calculated from absorbance (A). Eg is the separation between the valence and conduction bands and n is a constant that is equal to 1 for direct band gap semiconductors. These band gap values are higher than the bulk value of hexagonal ZnS because of quantum confinement in ZnS nanocrystals. The band gap energy could be obtained from the plot of $(\alpha h\nu)^2$ as a function of $h\nu$ (Figure 5). A sharp cut off is obtained from absorption spectra at ~315 nm which corresponds to band gap energy of 3.93eV .

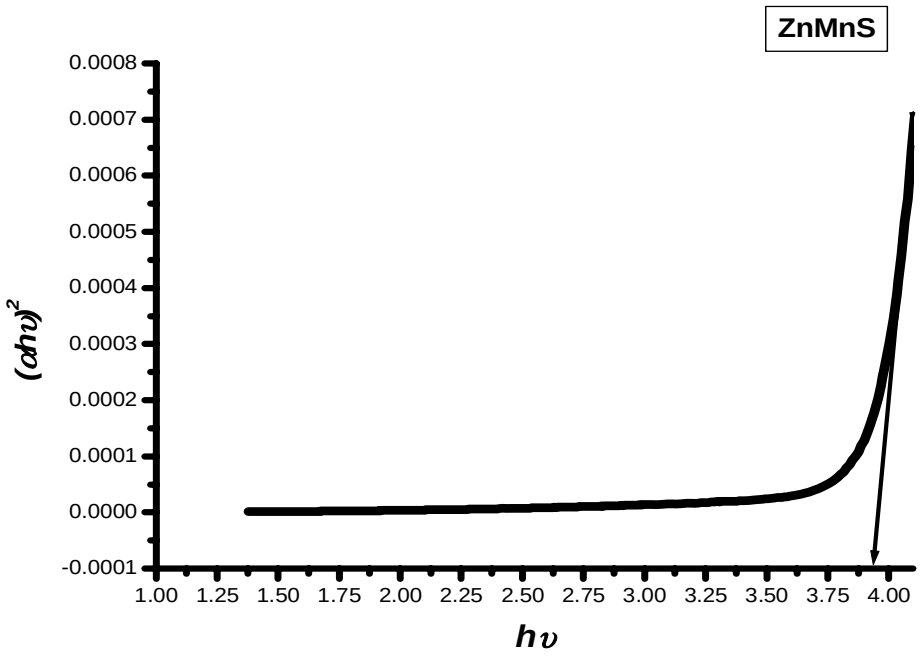

Fig.5. shows the band gap of nanostructured ZnMnS thin film.

3.4 Electrical Studies

Fig.6 show I-V characteristic of as deposited in dark & illumination condition (100mw/cm^2).The photogenrated charge carrier's increases with increase in power. The photogenerated current increases due to an increase in conductivity and resistivity decreases. The excitations of valence electrons into the conduction band significantly improve the electrical conductivity of the semiconductors; this phenomenon is known as photoconductivity. Therefore, observing the variation in the I-V plots with respect to the intensity with which the optimized samples were illuminate suggests that Nanocrystalline ZnMnS thin film exhibits photoconductivity.

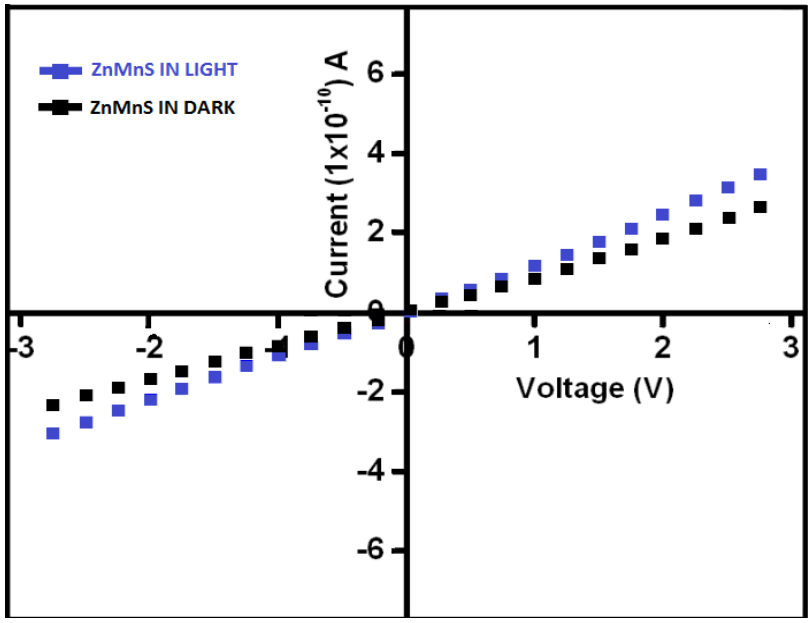

Fig.6. shows I-V Characteristics in dark and light of nanostructured ZnMnS thin film

Fig.6. shows I-V Characteristics of ZnS thin film has increase photocurrent in illumination condition and decrease the resistance, it shows semiconductor behavior.

4. CONCLUSIONS

This work has presented how ZnMnS thin film was grown using Chemical bath deposition techniques. In summary, Mn doped ZnS nanoparticles have been successfully synthesized by using chemical bath deposition as an easy and very fast method through the reaction between zinc sulphate manganese sulphate and thioacetamide as zinc, manganese and sulfur sources respectively. XRD results showed that the obtained Mn doped ZnS thin films were composed of cubic phase with very good crystallinity. The crystallite size was estimated to be about (2.5nm) using Scherrer's equation. The Zn, Mn and S were available on ZnMnS thin film confirmed by EDAX studies. The absorbance of ZnMnS thin film shifted in blue region and band gap was 3.93eV. The I-V Characteristics of ZnS thin film has increase photocurrent in illumination condition and decrease the resistance, it shows semiconductor behavior.

ACKNOWLEDGEMENT

The one of author are thankful to the Head, department of Nanotechnology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing the laboratory facility to carry out the research work.

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