OPTICAL STUDIES OF DOPED ZNS WITH TRANSITION METALS AND UNDOPED ZNS NANOMATERIALS

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ABSTRACT

The study of nano crystalline semi-conductor thin films is a great deal of interest among the researchers for its number of application in opto-electronic and semi-conductor devices. Thin films of ZnS nano-crystals were grown into poly-vinyl alcohol matrix by chemical route at different molar concentrations. Optical properties of both un-doped and doped with transitional elements (e.g. Fe, Mn) of ZnS nano-crystalline compounds were studied. The nano structure was characterized with the help of X-ray diffraction (XRD) and Hi-resolution Transmission Electron Microscopy (HRTEM). Surface morphology was studied with the help of Scanning Electron Microscopy (SEM). Average particle size of ZnS-Mn and ZnS-Fe were found to be 5 and 30 nm. Optical absorption studies were carried out with UV-VIS Spectrophotometer and showed a strong absorbance at wavelength 297.2 nm with a tendency towards blue shift . Peak of Photo-luminescence (PL) emission spectra was obtained at 346 nm at room temperature, Mn dependant emission was found at 580 nm whereas Fe dependant emission was found around 490 nm. These data showed successful doping, X_ray Fluorescence (XRF) studies showed larger peaks for Zn and S compared to presence of peaks of dopants Mn and Fe. PL studies also confirmed presence of dopant in the nano crystallites. Selected area electron diffraction (SAED)

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shows a set of four well defined rings corresponding to diffraction from different planes of the nano crystallites. HRTEM image showed a well crystalline ZnS doped with Fe.

Key Words : Nano-crystalline, Thin film, XRD, XRF, SEM, HRTEM

Introduction

Optical properties [1, 2] and characterization of synthesized nano crystals grown with different chemicals have generated lots of interest among the researchers. Low-dimensional semiconductors, especially ZnS composite nano-structured thin films have attracted much interest because of their valuable photoluminescence properties. Chemical growth process is a very simple, efficient, economical and convenient method among the various researchers. In phosphors, optical sensors, electroluminescence devices, digital displays, etc. doped ZnS nano materials are being used extensively. The optical properties of ZnS thin film is very suitable for its use as filter, reflector and planar wave guide. Photo luminescent properties and efficiency of ZnS depends on intrinsic surface states of the particles, and nature of the chemicals treatment employed in their fabrication. Research is also noticed on the application of these types of films in light-emitting materials as well as on their optical properties. The optical light emission in blue – red spectral region is characterized by blue shift at smaller crystallite dimension. We are trying to characterize the properties of ZnS with different doping agents (Cu, Fe, Mn) with the help of instrumental means like X-ray Powder Diffractometer (XRD), Scanning Electron Microscopes (SEM), High Resolution Transmission Electron Microscopes (HRTEM), Photo-luminescence spectrometer (PL), UV visible spectrophotometer (UV-VIS), etc.

Experimental

(A) ZnS nano-particles were synthesized by using Polyvinyl Alcohol (PVA) as a matrix. Different %w solutions of PVA and $ZnCl_2$ of deionized water were taken. They were stirred at 200 rpm in a magnetic stirrer . The temperature was kept constant at 70^{o} C for 3 hours . The solution was kept overnight for complete dissolution and found to be transparent . Different pH of the solution were made by adding concentrated HNO_3. A 2 %w Na_2S solution was added till the whole solution

appears milky. The solution was kept over night inside a dark chamber. As soon as the nano-structure was formed, it embedded into the gap. The chemical reaction took place as follows

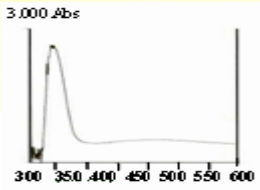
$$ZnCl_2 + Na_2S = ZnS + 2NaCl$$

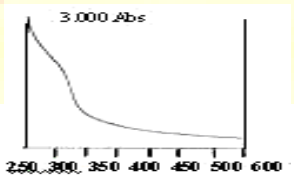
(B) To make different molarities of ZnS : Mn solution, $MnCl_2.4H_2O$ was mixed with deionized water . Solution so obtained was mixed with a another solution of PVA and $ZnCl_2$. Then the solution was stirred at 200 rpm in a magnetic stirrer. The temperature was kept constant at 70^oC for 3 hours . 0.08 M %w Na_2S solution was added to the solution. Precipitation found was washed with deionized water and taken for study. The colour of the solution appears light pink after doping.

(C) Next, 0.05 mole of ZnS:Fe solution was made. Dopant solution was obtained by adding $FeCl_3$ with deionized water. This solution was mixed with another solution of 5% PVA and 0.1 mole ZnCl2. Then the solution was stirred at 200 rpm. The temperature was kept constant at 70^oC for 3 hours . 0.08 %w Na_2S solution was added to the solution. Precipitation found was washed with deionized water and taken for study. PH of the solution was found to be 3.2 without any acidification. The colour of the solution appears deep brown after adding doping agent.

(D) Another solution was made by the procedure stated above for Cu doping. [$CuCl_2.2H_2O$ was taken for the purpose]. Influence of the concentration of Cu^{++} [3] was adjusted by controlling the quantity of $CuCl_2.2H_2O$ in the solution from 0.5% to 1% (in molar ratio of Cu++ to Zn++)

The solutions (A), (B), (C) & (D) were cast separately over glass substrates to produce thin films.





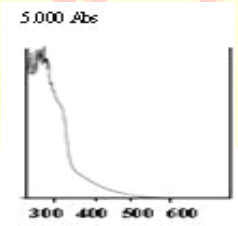
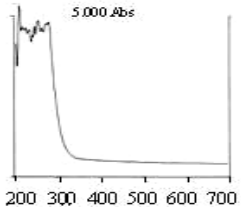


Fig. 1(a) UndopedZnS Fig. 1(b) ZnS-Mn (0.05M) Fig. 1(c) ZnS-Fe (0.05 M)



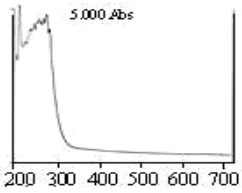


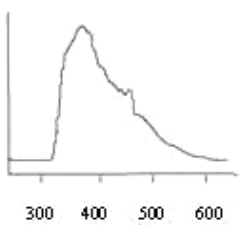
Fig. 1(d) ZnS-Cu (0.05%) Fig. 1(e) ZnS-Cu (1%)

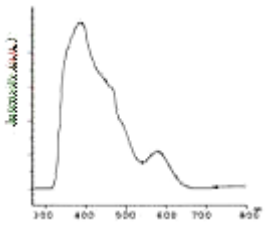
Fig. 1 : UV – visible absorption spectra

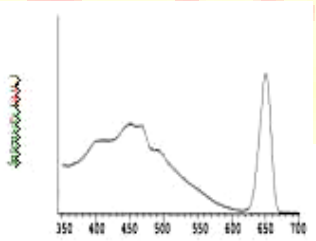
Results and discussion

Optical absorbance study

The optical absorbance of ZnS was recorded at room temperature using a Double Beam Automated Spectrophotometer (Hitachi – U3210). The measurement of optical absorbance of the films of different pH in the range 250 – 600 nm wavelength showed the strong absorption at slightly different wavelength. The peak of the absorption showed blue shift with respect to bulk attributing quantum confinement effect in the nano- particles. Optical absorption studies were carried out with UV-VIS Spectrophotometer and showed a strong absorbance at wavelength 297.2 nm with a tendency towards blue shift . Optical absorbance spectrum of ZnS-Cu (0.5%, 1.0%) features a strong peak around 279.2 nm and 274.9 nm. This indicates a blue shift of the peak of about 20nm due to quantum confinement effect. So, UV-visible spectra of undoped ZnS or Cu doped ZnS shows a peak with a blue shift. This indicates that Cu doping has an effect on the electronic absorption spectra of ZnS [4].







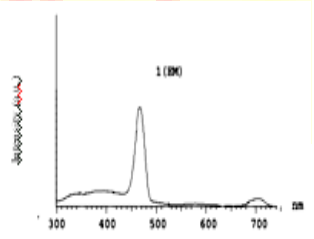


Fig. 2(a) Undoped ZnS Fig 2(b) ZnS-Mn (0.05M) Fig. 2(c) ZnS-Fe (0.05M) Fig. 2 (d) ZnS-Mn (0.05%)

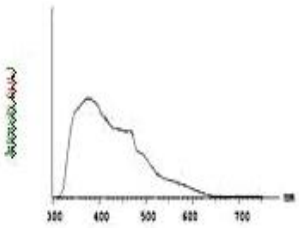


Fig. 2(e) ZnS-Mn (1%)

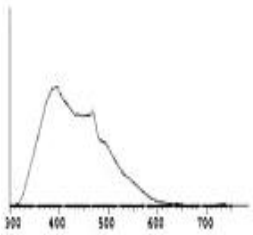


Fig. 2(f) ZnS-Cu (0.05%)

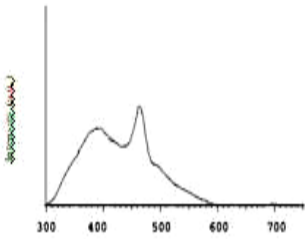


Fig. 2(g) ZnS-Cu (1%)

Fig. 2 : PL Spectra

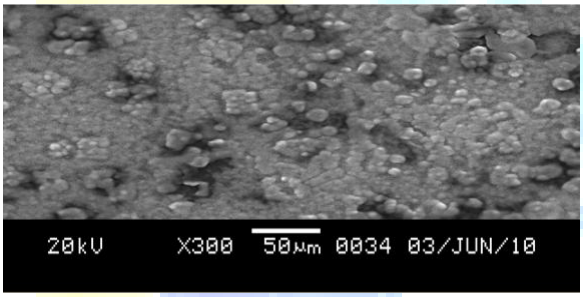


Fig. 3(a) : SEM micrograph of ZnS

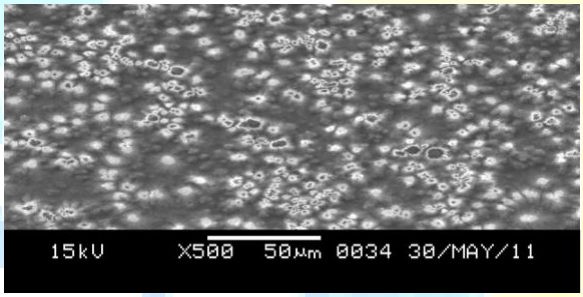


Fig. 3(b) : SEM micrograph of ZnS doped with Mn

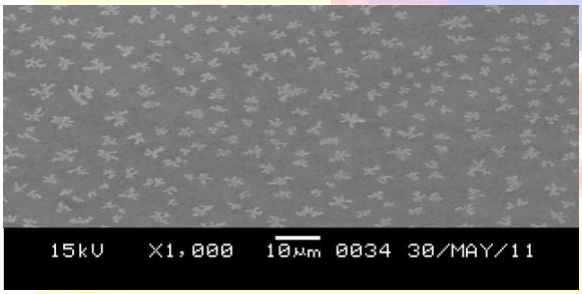


Fig. 3(c) : SEM micrograph of ZnS doped with Fe

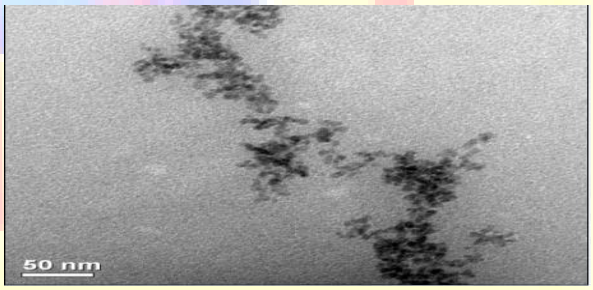


Fig. 4(a) HRTEM image of undoped ZnS

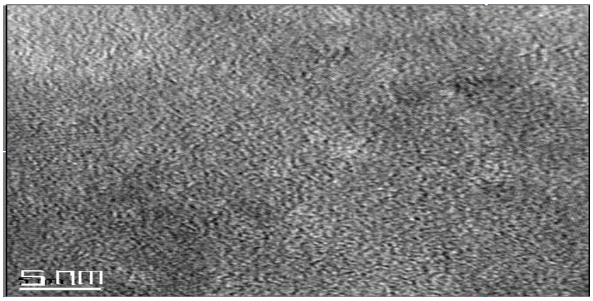


Fig. 4 (b) HRTEM image of ZnS-Mn (0.05M)

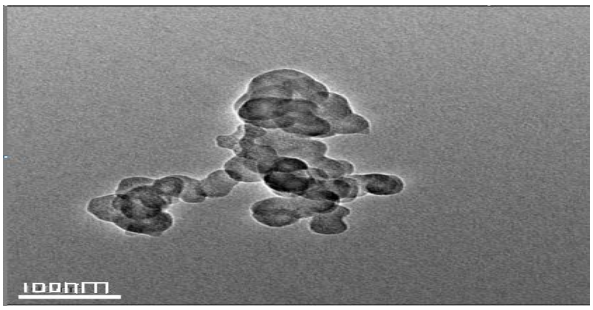


Fig. 4 (c) HRTEM image of ZnS-Fe (0.05)

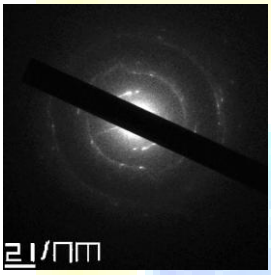


Fig 5(a) Undoped ZnS

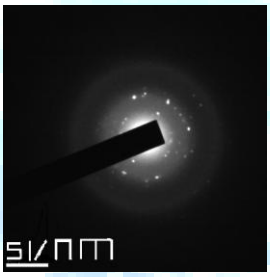


Fig 5(b)) ZnS-Mn (0.05M)

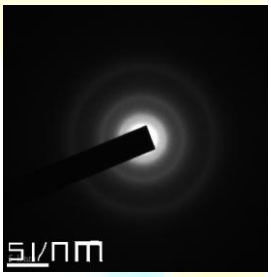


Fig. 5 (c) ZnS-Fe (0.05M)

Fig. 5 : Selected area electron diffraction patterns

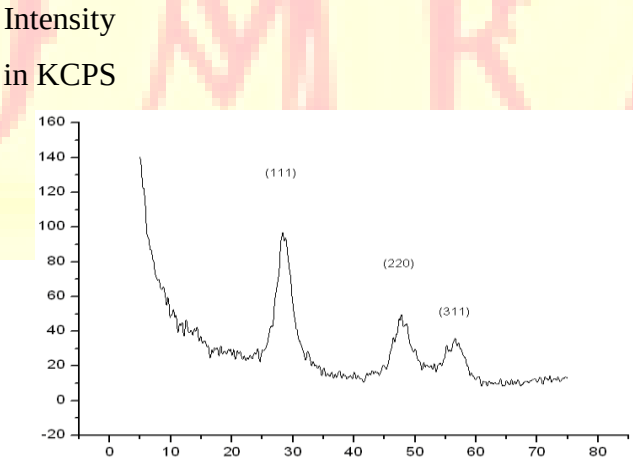


Fig. 6 : X-ray diffractogram of ZnS

Photo luminescence studies

The photo luminescence studies of nano crystalline doped & un-doped ZnS (Fig. 2) were done at room temperature by using F-2500 FL Spectrophotometer. In all the measurement the excitation wavelength was 240 nm. Emission spectra showed a broad peak at 346 nm and another small broad peak at 468 nm. PL in this region is due to the presence of S vacancies in the lattice. This was also supported by XRF studies. PL spectra of ZnS:Mn thin film revealed yellow-orange emissions. Mn dependent yellow emission was found at 580 nm which was also a confirmation successful Mn doping. Starting with the blue emission (at 468 nm), intensity decreases towards the orange emission (at 580 nm) [5]. The PL spectra of Fe doped ZnS showed a broad peak at 330 nm and sharp peak at 450.5 nm. The excitation wavelength is 320 nm. The intensities shifts to higher wavelength with doping and this is due to the band to band transition [6]. The PL studies of ZnS-Cu and ZnS-Mn with doping (0.5 – 1.0) % , are shown in Fig 2 (d), (e), (f), (g).

SEM studies

Photographs of the nano-crystalline thin film were taken with (JEOL, JSM-6360) SEM and shown in Fig. 3. The surface morphology of the film prepared at 70^{o}C with PVA was observed and found that all the particles thus formed not exactly spherical. Study showed surface of the film was smooth, uniform and without any crack. Average particle sizes of ZnS-Mn and ZnS-Fe were found to be 5 and 30 nm.

HRTEM

HRTEM image shows clear lattice fringes of the (001) plane indicating crystal growth along [001] direction.

Electron diffraction studies.

Selected area electron diffraction (SAED) was done with the help of HRTEM. Photo of SAED of undoped ZnS [fig. 5 (a),(b),(c)] also showed a set of three well defined rings corresponding to the planes (111), (220) and (311) in case of undoped ZnS, which is also in good agreement with that of XRD data.

XRD studies.

For XRD studies, film was obtained by casting the solution over a glass slide of 20mm x 15mm size. Diffractogram was obtained from a Philips X'pert Pro Powder diffractometer using Cu K□ radiation with the operating voltage 40 kV and current 20 mA. The pattern observed was found to be within the nano range [7,8]. XRD patterns revealed the films to be polycrystalline [9] . Planes (111), (220) and (311) were found to be present. The average particle size corresponding to the FWHM was calculated with the Scherrer formulae and found to be 2.8 nm[10].

$$Dp = \frac{0.94\,\square}{\square_{1/2}\ \cos\ \square} \qquad (1)$$

Where, Dp is particle size of the crystallite, □ is wavelength of X-ray used, □ is the full width at half maxima (FWHM) and □ is the angle of diffraction.

Conclusion

ZnS nano crystalline films (un-doped and doped with Mn) of different pH have been synthesized by chemical route. The structural and optical characterization of the films done with the help of XRD, TEM, SEM, SAED, UV-VIS spectrophotometer and PL reveals formation of doped as well as un-doped nano particles. XRF study reveals the presence of Zn and S in the film and also indicates an interesting result about oxidation of the film which is found to take place due to ageing. The emission bands with respect to 346 nm & 468 nm may be attributed to impurities or defect states. The third emission band at 580 nm may be attributed due to transition took place in the 3d shell of Mn++. The PL spectra of Fe doped ZnS shows a broad peak at 330 nm and sharp peak at 450.5 nm. From Photo luminescence study it has been observed that in case of ZnS-Cu, with the increase of doping %

(from 0.5 – 1.0) , the intensity of doping related emission spectra is found to decrease. But in case of ZnS-Mn, with the increase of doping % (from 0.5 – 1.0), the intensity found to increase . It is also observed from the PL that with the increase of doping % (from 0.5-1.0) of both ZnS-Cu and ZnS-Mn , there is blue shift of doping related emission spectra. In our future study we will try to explore the relation between grain size and shift of wavelength and intensity of doping related emission spectra.

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