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Structural, optical and magnetic properties of ZnS, MZS & CZS thin films prepared by Sol-Gel Spin Coating method

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ABSTRACT

The spin coating method was used for the preparation of ZnS, Mn doped ZnS (MZS) and Cobalt doped ZnS (CZS) thin films and their structural and optical properties were studied. The ZnS thin films were grown on well cleaned glass substrates by spin coating method from aqueous solution of Zinc Sulphide and Thiourea with two different dopants Mn and Co. The properties of ZnS, MZS and CZS thin films and their growth mechanisms were studied using x-ray diffraction, UV-Visible spectroscopy, photoluminescence and VSM studies. Effect of dopants on structural, optical and magnetic properties was reported.

Introduction

ZnS is the most important group II-VI semiconductor, having a typical band gap of 3.68 eV at room temperature and has attracted much research interest due to its potential applications in optoelectronic devices such as photocatalysis, solar cells, and display panels [1-4]. By doping ZnS with different activating metal ions, luminescence properties can be tuned largely. Among many available wide band gap compounds, Manganese is well known as an activator for photoluminescence and Bhargava et al. [5] was the first to report the luminescence properties of Mn-doped ZnS nanocrystals prepared by a chemical process at room temperature [6-8]. Zinc sulphide (ZnS) doped with transition metals and rare-earth ions have been the subject of numerous investigations because of its various practical applications as electroluminescent devices. These devices have a number of attractive advantages such as low power dissipation, capability of large area active light emitting displays, flat cathode ray tubes and flat-panel television [9,10].

In the present work, ZnS thin films have been prepared using chemical bath deposition method and also doped with Mn and Co. The ZnS, MZS and CZS thin films deposited on substrate using hydrothermal process were characterized by using X-ray diffraction (XRD), UV-Visible spectroscopy, Photoluminescence (PL) spectroscopy and Vibrating sample magnetometer (VSM).

Experimental Details

Fig (1) shows the flow diagram of sol-gel deposition process for spin coated ZnS, MZS and CZS thin films. The Zinc Sulphate solution was prepared by adding Zinc Sulphate ($ZnSO_4.7H_2O$) with the de-ionized water and this mixture was stirred with magnet for 20 minutes. Then Ammonia was added as a complexing agent on this $ZnSO_4$ solution drop by drop and solution was stirred continuously. Thiourea solution was prepared by adding it with the de-ionized water and this mixture was stirred with magnet for 80 minutes.

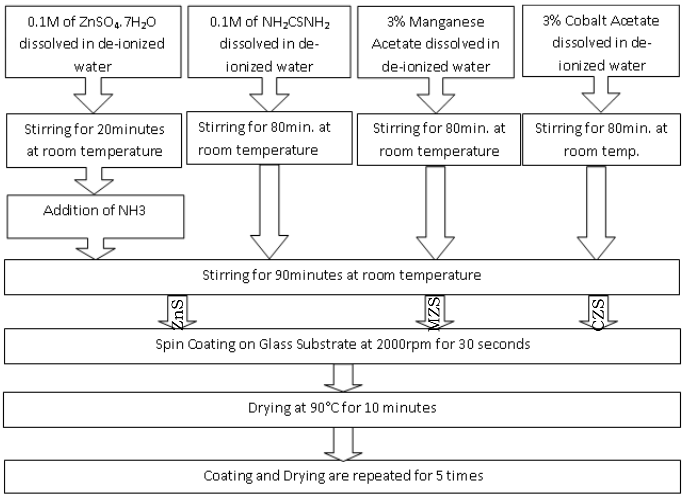

Fig 1. Flow diagram of sol-gel deposition process for spin coated ZnS, MZS and CZS films

In the $ZnSO_4$ prepared solution, Thiourea solution was added drop by drop and continuously stirred this mixture with the magnet for 90 minutes. Spin coating was done with this ZnS solution on well cleaned substrates at 2000 rpm for 30 seconds and dried at 90°C per layer. Totally 6 layers were formed. Dopants Mn and Co were prepared using Manganese Acetate solution and Cobalt Acetate solution by the same way as Thiourea solution prepared. These two solutions were added to ZnS solution separately and stirred for 90 minutes. Same spin coating process of ZnS was repeated to get MZS and CZS thin films.

The structural characterization of the films was carried out using X-ray diffractometer with CuKα radiation (α=1.5404Å) in 2θ range from 10° to 80°. The optical properties like absorption and transmission spectra were taken using a UV spectrophotometer in the range 100 to 1600 nm.

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Photoluminescence (PL) spectra were recorded using luminescence spectrometer. Magnetic properties were studied using VSM.

Results and Discussion

1. Structural properties

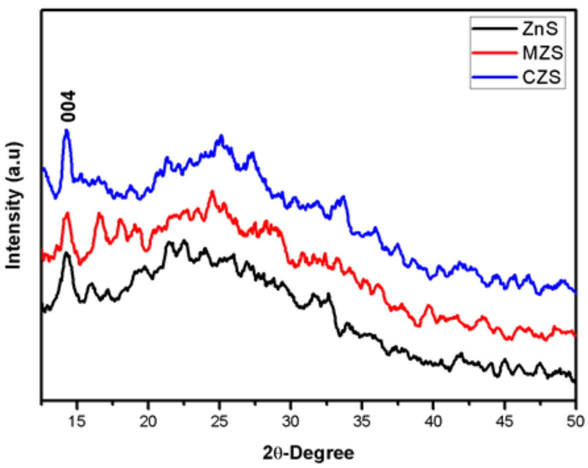

Fig 2. X-ray diffraction pattern of the ZnS, MZS and CZS films

Fig (2) shows the XRD patterns of the obtained ZnS, MZS and CZS thin films. The undoped ZnS, MZS and CZS thin films has the peak were at same 2θ value of 14.26° corresponding to the lattice plane (004) which match with standard JCPDS card no 72-0163 for ZnS.

The XRD patterns clearly show the presence of ZnS, where all diffraction peak is well indexed to the standard diffraction pattern of wurtzite-8H hexagonal ZnS phases. The average grain size of ZnS was estimated by using the well-known Scherrer's formula [11], $D = 0.94\lambda / \beta\cos\theta$ Where λ = 1.5404Å for CuKα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle. The estimated average grain size of the ZnS, MZS and CZS films were around 21nm, 38nm and 42nm respectively.

2. Optical properties

To investigate the optical properties of the prepared ZnS thin films, UV-vis absorption spectra were recorded, as shown in fig (3). The optical absorption edge is approximately located at 340nm. An increase of the absorption values is observed with doped ZnS than undoped ZnS thin films. An estimation of the band gap value was obtained by the intersection point of the tangent of the absorption edge with the extended line of the diffuse reflection at lower wavelength

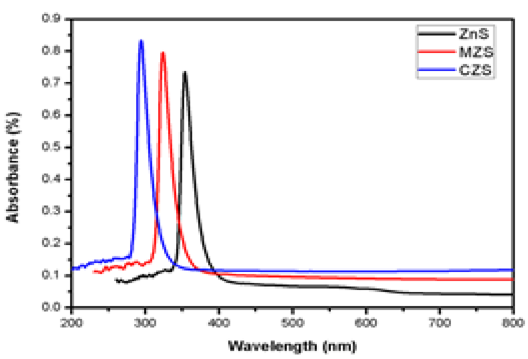

Fig 3. UV-visible absorption spectra of ZnS, MZS and CZS films

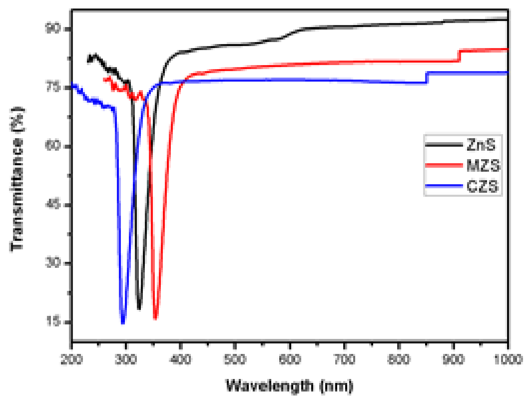

Fig 4. Transmission spectra of ZnS, MZS and CZS films

The obtained band gap value of ZnS films is 3.65eV, MZS is 3.64eV and CZS is 3.63eV which closely agree with the values reported for ZnS thin films obtained by CBD [12,13].

Transmission spectra of ZnS, MZS and CZS were depicted in fig (4). From the transmittance spectra, decrease in the transmission values over the whole spectral range is observed with doped ZnS films compared to undoped ZnS film. Undoped ZnS thin film has good transmittance compared to MZS and CZS films.

Fig (5) shows the PL spectra of the ZnS, MZS and CZS films. The excitation wavelength is 366 nm in each case. PL peaks are found to be broad around 438 nm for MZS film. PL study shows that doped ZnS thin films have very good intensity than undoped ZnS thin film. All the films have broad visible emission. MZS film has the highest intensity compare to CZS and ZnS thin films. All the film shows violet emission (wavelength is around 415nm).

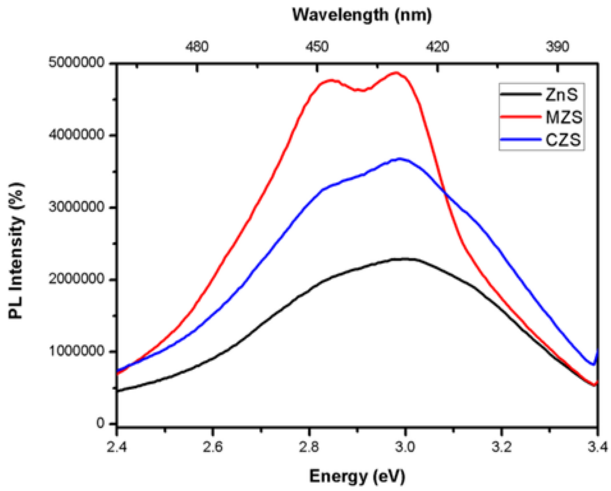

Fig 5. Photoluminescence spectra of ZnS, MZS and CZS films

3. Magnetic properties

Magnetic properties of ZnS, MZS and CZS films were studied using vibrating sample magnetometer (VSM) at room temperature. From the Fig.6, diamagnetic behavior has been observed for all the samples at room temperature. D.A.Reddy and co-authors [14] have observed the diamagnetism in ZnS nanoparticles. Magnetization increases with Mn doped ZnS film compare to ZnS and CZS films.

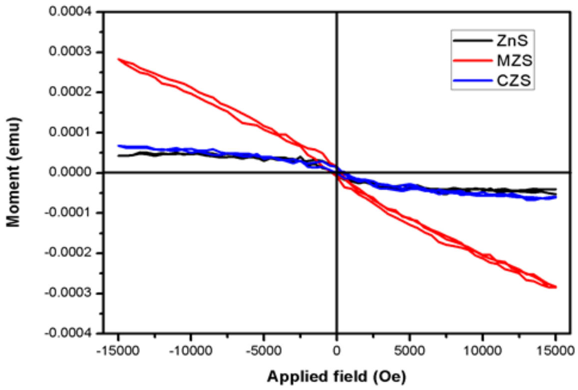

Fig 6. Plot of magnetization versus applied magnetic field of ZnS, MZS and CZS films

Conclusion

ZnS thin films were prepared with two different dopants i.e. Mn and Co using spin coating method. The structural, optical and magnetic properties were determined by XRD, UV-VIS PL and VSM analysis. From the XRD results, it was clearly observed that both undoped and doped ZnS thin films have the same peak. All the films have good structural and optical properties. It is reported that MZS film has good absorbance intensity than CZS and ZnS films. All the films have broad visible emission. VSM results show that all the samples have diamagnetic behavior and magnetization increases with Mn doped ZnS film. It is suggested that prepared ZnS film can be investigated more in order to check the magneto optic applications.

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