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Synthesis and Characterization of ZnS, MZS and CZS 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 and photoluminescence measurements. Effect of dopants on structural and optical properties was reported.
Keywords: ZnS, Spin Coating, Dopants, Structural and Optical properties.

Introduction

ZnS is an important II-VI group semiconductor with a large direct band gap of 3.5 –3.7eV in the UV range[1] and ZnS thin films have been found useful in various devices. The application of ZnS thin films which cover a wide area of interest are Antireflection coating for the solar cell[2], Environmental friendly buffer layer as compared to CdS layer in CIS based thin film solar cell[3], Wide band gap material for electroluminescent and optoelectronic devices[4], Photosynthetic coating[5], Blue light emitting laser diodes[6] and As α- particle detector[7]. 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.[8] was the first to report the luminescence properties of Mn-doped ZnS nanocrystals prepared by a chemical process at room temperature[9,10,11]. Hamid Reza pouretedal and his co-workers[12] synthesized nanoparticles of zinc sulfide as undoped and with manganese, nickel and copper. They were used as photocatalyst in the photodegradation of methylene blue and safranin as color pollutants. 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.

The sol-gel coating technique is simple and economical which needs no sophisticated instrumentation[13]. In the present work, ZnS thin films have been prepared using chemical bath deposition method and also doped with Mn and Co. CBD method also offers the opportunity of doping the host ions with impurities on different kinds, shapes and size on substrate[14]. The ZnS, MZS and CZS thin films deposited on substrate using spin coating method were characterized by using X-ray diffraction (XRD), UV-Visible spectroscopy and Photoluminescence (PL) spectroscopy.

Experimental

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. The surplus amount of thiourea was required in the solution since it avoids the precipitation of metallic hydroxides and sulfides[15].

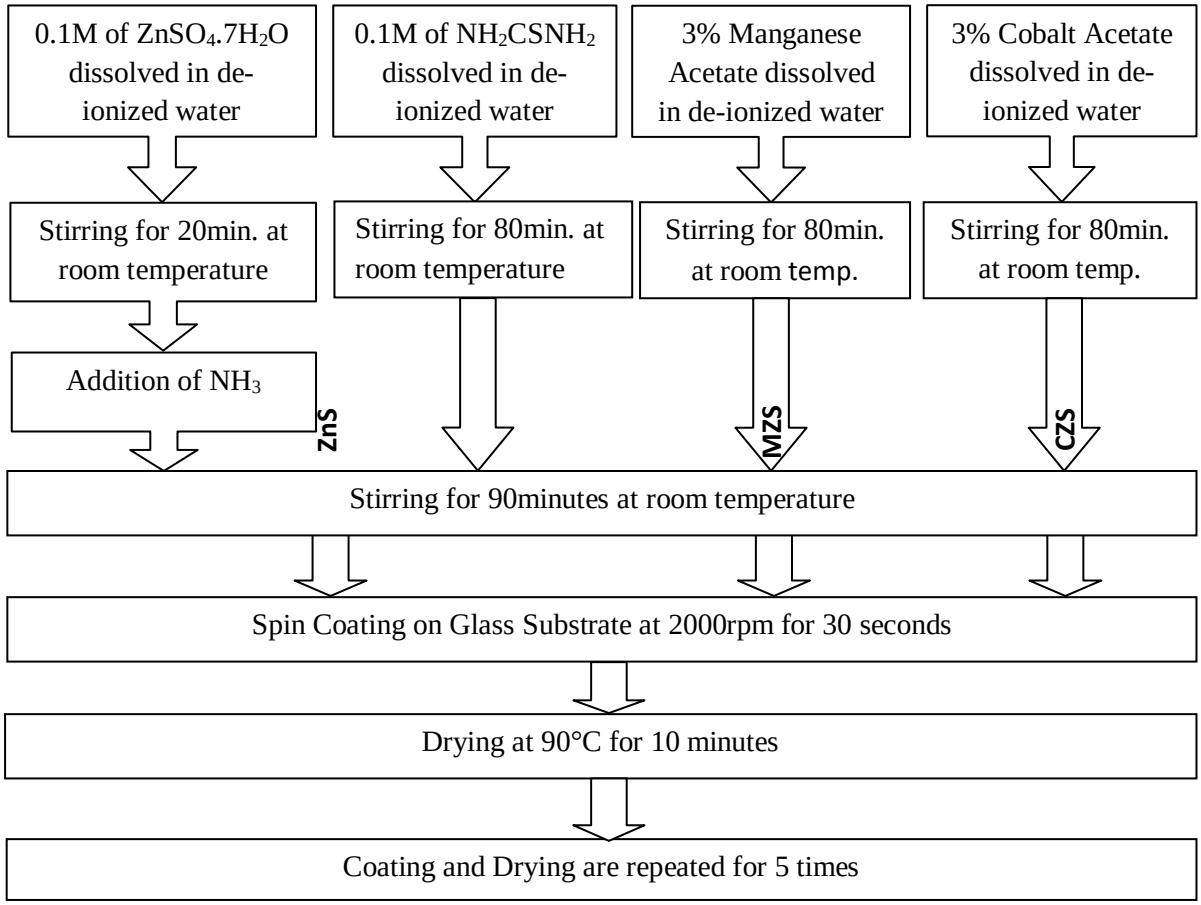

Figure 1.Flow diagram of sol-gel deposition process for spin coated ZnS, MZS and CZS films

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°. UV-Vis spectroscopy and Photoluminescence have been applied to study the optical properties.

Result and Discussion

Structural properties

Fig.(2) shows the XRD patterns of the obtained ZnS, MZS and CZS thin films. The undoped ZnS, MZS and CZS thin films have the peak at same 2θ value of around 14.26° corresponding to the lattice plane

(004) which match with standard JCPDS card no 72-0163 for ZnS. M.Balachander[16] has also observed the major peak in the same plane (004).

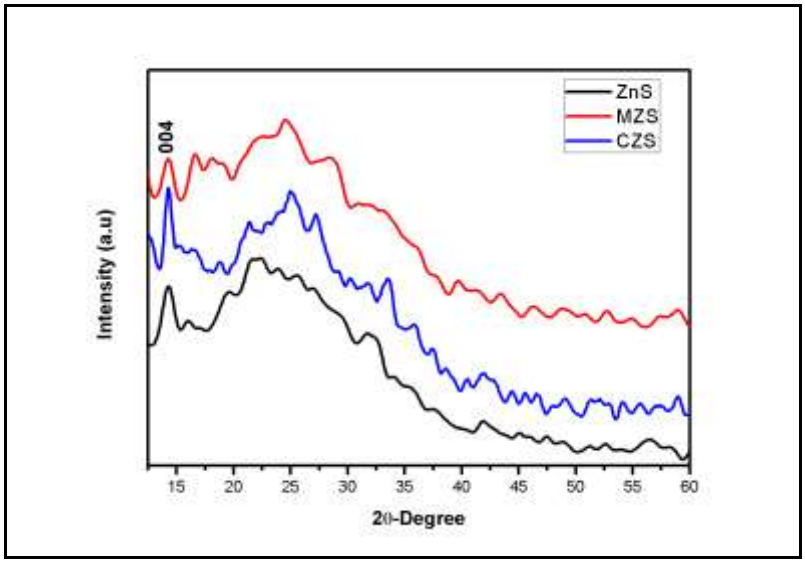

Figure 2.X-ray diffraction pattern of the ZnS, MZS and CZS films

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[17], $D = 0.94\lambda / \beta\cos\theta$ Where $\lambda = 1.5404$Å 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. XRD analysis of all the prepared films show that no other phases were formed which indicates the improvement in the crystallinity of the formed phase.

Optical properties

To investigate the optical properties of the prepared ZnS thin films, UV-vis absorption spectra were recorded, as shown in fig.(3). 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.

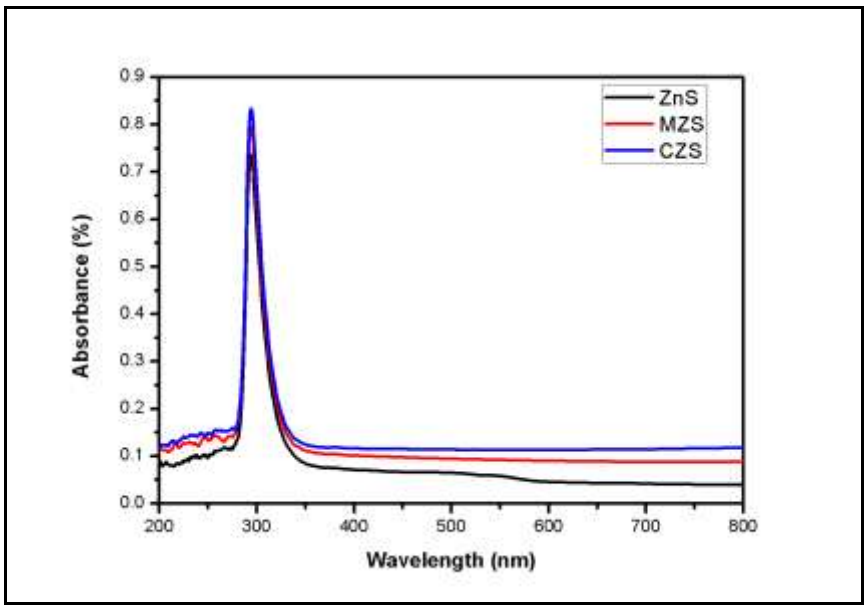

Figure 3.UV-visible absorption spectra of ZnS, MZS and CZS films

The obtained band gap value of ZnS films is 3.73eV, MZS is 3.71eV and CZS is 3.67eV and these values can be compared with the bandgap values of 3.5-3.7eV at room temperature of the bulk ZnS films[18]. Large change (increase) in band gap energy is the evidence of nanocrystalline nature the as prepared films. Another reason could be the improving crystallinity with increasing grain size[19]. It has been found that maximum absorbance observed with Co doped films with decrease in band gap and increase in the grain size.

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. It has been observed that overall %T increases which may be due to the decrease of surface roughness.

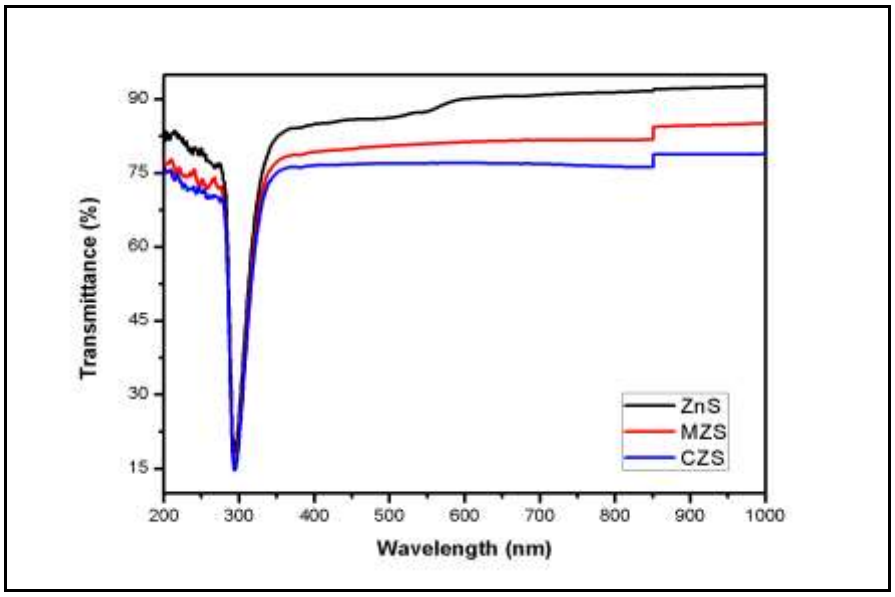

Figure 4.Transmission spectra of ZnS, MZS and CZS films

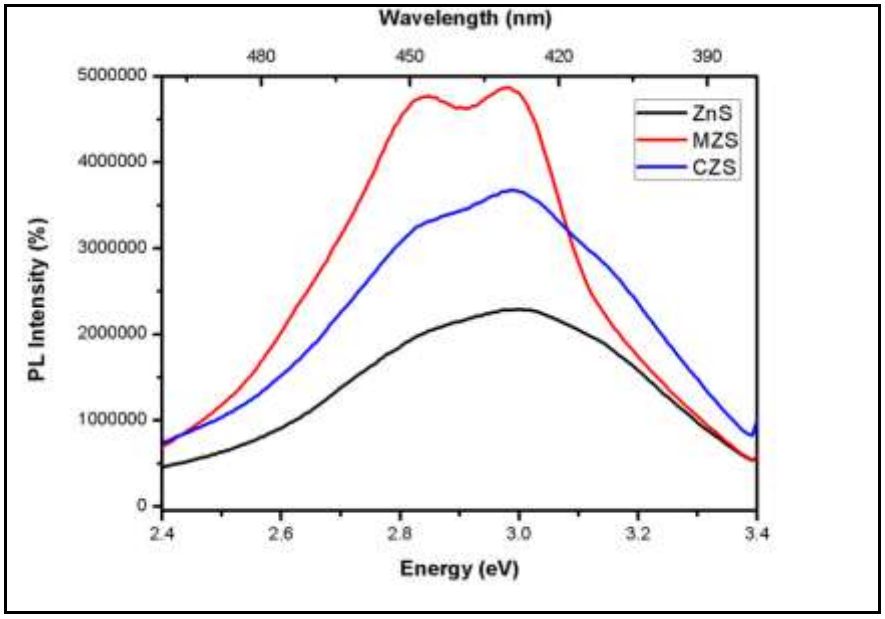

Figure 5.Photoluminescence spectra of ZnS, MZS and CZS films

Fig.(5) shows the PL spectra of the ZnS, MZS and CZS films. The excitation wavelength is 350 nm in each case. The PL peak of all the prepared films is at 420nm as shown in fig.(5) and peak position of this blue emission does not change with the the dopants which indicate that the energy level of sulfur vacancy relative to the valence band nearly keeps constant. The blue emission at 420nm may be ascribed to the transitions

involving vacancy states, which was suggested by Denzler et al. in ZnS nanocrystals[20] and Lee and co-workers in ZnS nanoribbons[21]. The emission peak position is insensitive to the dopant replicates that the peak at 420 nm should result from native defect states, but not from impurity states related with Mn and Co dopants.

Conclusion

ZnS thin films were prepared with two different dopants i.e. Mn and Co using spin coating method. The structural and optical properties were determined by XRD, UV visible spectroscopy and photoluminescence study. From the XRD results, it was clearly observed that both undoped and doped ZnS thin films have the same peak and grain size was found to increase with the dopants. 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. The dopants Mn and Co enhance the visible emission which may be due to enhancement of the defect-related peak intensities for the doped samples compared with the undoped samples. It is suggested that prepared ZnS film can be investigated more in order to check the magneto optic applications.

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