

Effect of Manganese Percentage Doping on Thickness and Conductivity of Zinc Sulphide Nanofilms Prepared by Electrodeposition Method

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Abstract: Manganese doped zinc sulphide nanofilms were deposited on ITO glass substrates by electrodeposition method using aqueous solution of zinc chloride, manganese chloride, sodium thiosulphate and triethanolamine as a complexing agent triethanolamine. In the present work the effect of manganese percentage doping on thickness and conductivity of zinc sulphide were investigated. Structural characterization by X-ray diffraction revealed that Mn doped ZnS:Mn nanofilms have cubic structure with mean crystallite size of approximately 14.19nm. Optical analysis showed that all films exhibited good transmittance and low absorbance in the visible region. With the increasing of Mn percentage doping, the thickness of the ZnS:Mn films ranged from 46.01 – 68.99nm, optical conductivity from 1.20×10^{13} to 2.75×10^{13} and electrical conductivity from 1.73×10^2 to 1.51×10^2 . Such ZnS:Mn films in nanometer size range with high conductivity could be suitable for applications in the fabrications of thin films solar cells and various optoelectronic devices.

Keywords: Effect of manganese percentage doping, Thickness, conductivity, Zinc sulphide nanofilms, Electrodeposition

1. Introduction

In recent years considerable interest has been drawn to nanometer sized materials particularly II – VI metal chalcogenide compounds because of the very important role they play in materials research. This kind of nanomaterials exhibits unusual physical and chemical properties in comparison with their bulk materials, such as size dependent variation of the band gap energy and have many potential applications in photochemistry, catalysis and electronic/optical materials [1; 2]. Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities [3].

Semiconductors with small fractions of cations replaced by magnetic ions are called dilute magnetic semiconductors (DMSs).[4]. Such DMS materials provide unique link between impurity and alloy physics; and a link between magnetism and semiconductivity [4]. As an important II – VI semiconductor material, Zinc sulphide (ZnS) with a wide direct band gap of 3.68eV [5] is chemically more stable and technologically better than other chalcogenides (such as ZnSe), so it is considered to be a promising host material [6]. Doped ZnS is an important material with an extensive range of applications such as optical coatings, electro-optic modulator, photoconductors, phosphors, light emitting displays and optical sensors [1,6,7,8]. Such doped material has been used widely as an important phosphor for photoluminescence, electroluminescence and cathodoluminescence devices due to its better chemical stability [7].

2. Literature Review

The properties of thin film materials depend on the method of preparation among other factors which include deposition parameters [9], level of impurity [6,7,10] and annealing process [6,9], level of impurity. Zinc sulphide may exist in form of stable cubic phase at room temperature or in form of hexagonal phase above room temperature or a mixed phase depending on the deposition method, deposition parameters and level of impurity [9]. Many authors had reported the cubic structure for solution growth ZnS thin films [1,2,6,9,10,11]. A phase transformation from stable ZnS cubic to a hexagonal phase at higher annealing temperatures ($\geq 300^\circ\text{C}$) had been reported by various authors [1,8].

The thickness of the films increase with the electrolyte concentration and pH [12,13,14], deposition time [9,15], deposition voltage [9], annealing temperature [16] and dopant ions percentage [6,7,10]. The ionic radius (0.083Å) of Mn^{2+} ion is larger than (0.074Å) for Zn^{2+} ion, suggesting that upon doping with slightly large Mn doping ratio (10%), the dopant ion enters to the host lattice substitutionary interstitially leading to increasing of the inter-planer spacing (d) values [17]. The interstitial entrance of the dopant ions lead to expansion of host lattice and particle size increasing [17], an indication of increase in film thickness [9].

The resistivity and conductivity of doped ZnS thin films are influenced by dopant concentration annealing process and physical factors such as crystal structure, carrier concentration and mobility [6,18]. Doping of film samples increases the carrier concentration and enhances the conductivity [6,10,18]. Electrical conductivity increase with dopant ions concentration at low doping region but decrease with dopant ions concentration at higher doping region [6,10,18]. Decrease in electrical conductivity for heavily doped films may be ascribed

to the increasing lattice defects and dislocations of the films [6,10]. Decrease in mobility reported for heavily doped film samples may be due to the contribution of scattering mechanism such as ionized impurity scattering [18]. Annealing process improves the crystallinity and increases conductivity of the thin films [6,16]. The increase in electrical conductivity for annealed ZnS:Mn was attributed to improved O₂ vacancies in ZnS:Mn lattice. Different O₂ partial pressure controls the metal interstitial and O₂ vacancies which leads to crystal defects, an important role for increase in electrical conductivity of ZnS. Zinc sulphide has been reported to have n-type of conductivity [6,10].

Thin films have been grown by different techniques such as RF magnetron sputtering [19], chemical bath deposition [15], sol gel [20] pulsed laser deposition [21], spray pyrolysis [10], hydrothermal [8], electrodeposition [9]. Among these techniques, electrodeposition was adopted because of its low cost and does not require high temperature and pressure selectivity [9]. Furthermore, this method is scalable with high degree of controllability and reproducibility, hence it is widely applied commercially, [22].

The main purpose of this study is to investigate the effect of manganese percentage doping on the film thickness and conductivity of zinc sulphide nanofilms prepared by electrodeposition method and also to ascertain the possible applications of such DMS nanofilms.

3. Methodology/ Approach

Zinc sulphide (ZnS) nanofilms doped with different manganese content were prepared using electrodeposition method using a three electrode cell apparatus. Mn doped ZnS (ZnS:Mn) nanofilms were prepared by first mixing 10.0 ml of 0.05M zinc chloride (ZnCl₂), 0.05M manganese chloride (MnCl₂·2H₂O) and 10.0ml of 0.05M triethanolamine (TEA). The concentration of manganese ions were adjusted by controlling the quantity of manganese chloride in the above mixture, varying from 3% to 23% (in molar ratio of manganese ions to zinc ions). Then, 10.0ml of 0.05M and sodium thiosulphate (Na₂S₂O₃·5H₂O) were added to the reaction medium and deionized water was added to make the total volume of the solution 50.0ml. The mixture was thoroughly stirred using magnetic stirrer and PH of the reaction bath was adjusted to constant PH 3 by addition of few drops of hydrochloric acid. The experiment was carried out at room temperature, optimum deposition time (60 seconds) and deposition voltage (1.0V) with manganese ions concentration varied from 3% to 23%. All the reagents used for the electrodeposition were of high analytical grade. Prior to electrodeposition, the ITO glass substrates on which surface the films were deposited were degreased in ethanol for 10 minutes, ultrasonically cleaned for 10 minutes and then dried in a desiccator. The deposited ZnS:Mn film samples were rinsed with de-ionized water, dried, annealed at temperature 250°C and kept for analysis.

The X-ray diffraction patterns of Mn doped ZnS nanofilms were recorded by X-ray Mini Diffractometer MD 10 Model with a rotating anode and Cu-Kα radiation source (λ=0.15406nm) at 40KV and 30mA. Optical transmission data was obtained by JENWAY 6405 UV-Vis spectrophotometer. The thickness and conductivity of the films were determined by optical method.

4. Results and Discussion

The XRD pattern of ZnS:Mn nanofilm sample doped with 8% Mn is shown in Fig. 1. The XRD pattern shows that the crystals of ZnS:Mn films have cubic structure with preferential orientation along (220) direction and lattice constant a=b=c=10.045Å. The mean crystallite size calculated using Debye-Scherrer's formula [23], was estimated to be 14.19nm. Similar ZnS cubic structure had been reported for nickel (Ni) doped ZnS [7] and Mn, Cu co-doped ZnS [24]. The nanocrystalline nature of the film samples confirmed the nanometer size of their thickness.

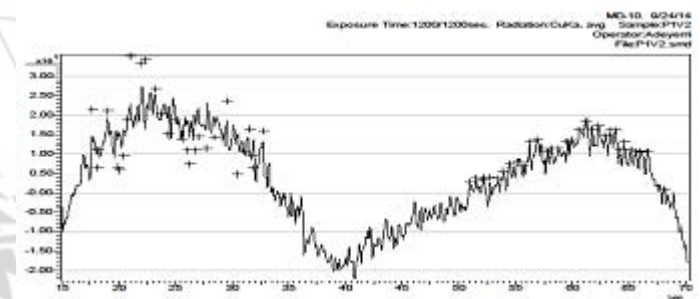


Figure 1: XRD pattern ZnS: Mn film with 8% Mn doping

The variation of film thickness with manganese percentage doping is shown in Fig.2. The thickness of ZnS:Mn films increased from 14.67nm to 92.48nm as Mn doping % increased from 3% to 8% and then decreased to 31.80nm as Mn doping % increased to 23%. The highest (92.48nm) was obtained from the film sample (P₁C₂) doped with 8% Mn. The results showed that at low Mn doping level, the film thickness increased with the increasing of Mn doping % but decreased with the increasing of Mn doping % at higher Mn doping level. Similar results had been reported for Mn doped ZnS prepared by CBD [6] and spray pyrolysis [7] respectively.

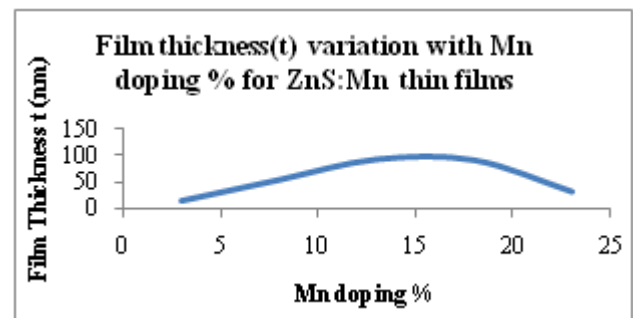


Figure 2: Film thickness variation with Mn doping % for ZnS:Mn films

Also, decrease in film thickness with the increasing of Ni-doped ZnS thin films with the increasing of Ni²⁺ dopant ions concentration had been reported [10]. The film thickness variation with Mn²⁺ ions concentrations can be explained on the basis of ions concentration in the electrolyte and film formation. When a few percentages of Mn dopant atoms are added into the reaction bath, the electrolyte ions concentration slightly increased thereby resulting to increase in the film growth rate. Because the dopant Mn²⁺ ions are small, they can easily occupy both the substitutional and interstitial sites of the host lattice. The interstitially entrance of Mn dopant ions with larger ionic radii (~ 0.083) than that of Zn (~ 0.074) leads to expansion of the host lattice and hence particle size increasing as well as increase in the film thickness. At higher Mn²⁺ ions concentrations, more ions are presence in the electrolyte and this results to decrease in the mobility and reduction in the growth rate thereby leading to decrease in the grain size, an antecedent to decrease in the film thickness. Based on the results obtained, we, therefore, conclude that Mn doping % has strong effect on the thickness of ZnS:Mn films and electrodeposition using 13% Mn doping at room temperature was the best condition for the preparation of good quality of such nanofilms at the current condition. Such ZnS:Mn nanofilms are good candidate materials for

applications in various fields of nanofilms technology such as nanofilms solar cells and various optoelectronic devices [6,9,10].

The absorption, optical and electrical conductivity spectra of Mn doped ZnS are respectively shown in Fig.3,4 and 5

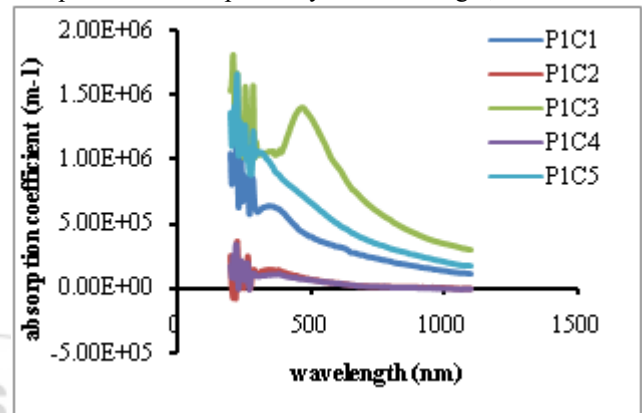


Figure 3: Absorption Spectra of ZnS:Mn films with different Mn doping %

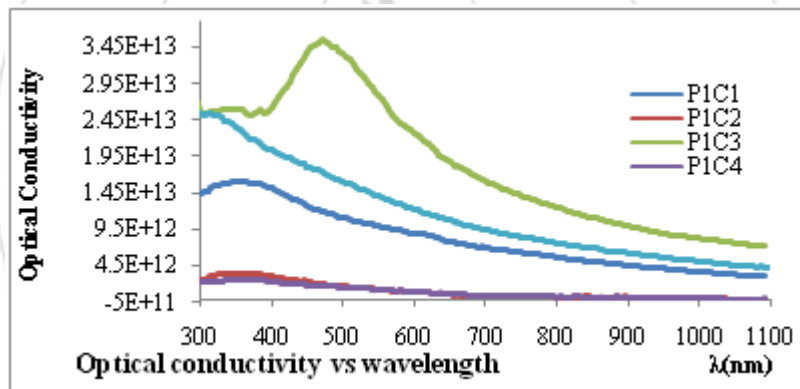


Figure 4: Optical conductivity spectra of ZnS:Mn films with different Mn doping%

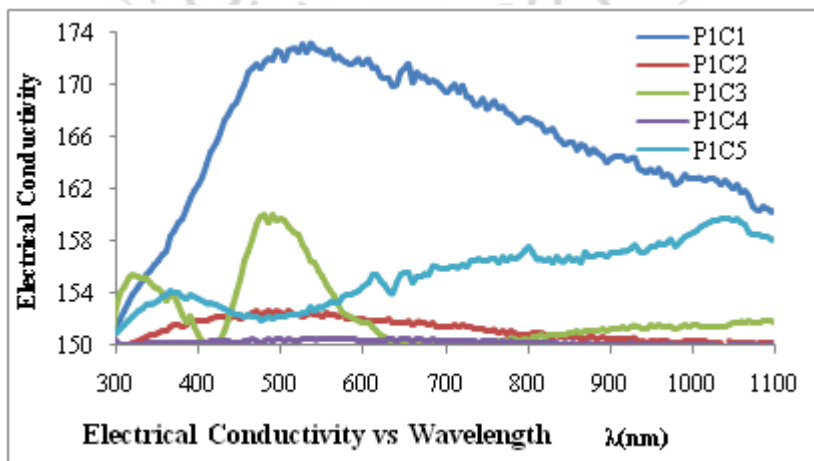


Figure 5: Electrical conductivity spectra of ZnS:Mn films with different Mn doping%

Fig 3 revealed that the absorption coefficient (α) of ZnS:Mn nanofilm samples were relatively high in the UV-

Vis and low in the NIR region. At wavelength of 550nm in the visible region, the average absorption coefficient of the

ZnS:Mn films decreased from 0.40×10^6 to 0.10×10^6 as Mn doping % increased from 3% to 8% and then increased to 1.20×10^6 with further increase in Mn doping %. The highest absorption coefficient was obtained from the film sample (P₁C₃) doped with 13% Mn. The observed difference in the absorption coefficient peak values of the ZnS: Mn films indicates that Mn doping % has strong effect on the absorption coefficient of the film samples. The obtained absorption coefficient values of magnitude 10^6 compare well with 10^6 reported for undoped ZnS deposited in alkaline medium at PH 9-11 [14]. The obtained absorption coefficient of magnitude 10^6 are within the range of 10^6 to 10^7 required for semiconductor thin film solar cells. Such films with high absorption coefficient in the visible region are good candidate materials for optical coatings, thin films solar cells fabrications, optoelectronic and electroluminescent devices applications.

The optical conductivity σ_o spectra of ZnS:Mn nano films with different Mn percentage doping shown in Fig 4 revealed that the optical conductivity of the ZnS:Mn nano films samples are relatively high in UV-Vis regions and low in NIR region with its value varying from 3.55×10^{13} to 1.0×10^{13} with the increasing of wavelength from 300nm to 1100nm. At wavelength of 550nm in the visible region, the average optical conductivity of ZnS:Mn films increased from 1.25×10^{13} to 2.75×10^{13} as Mn doping % increased from 3% to 13% and then decreased to 0.12×10^{13} with further increase in Mn doping %. The difference in the peak values of optical conductivity of ZnS:Mn film samples indicates that Mn doping % has significant effect on the optical conductivity of the film samples. The obtained results compare well with the average optical conductivity of magnitude 10^{13} to 10^{12} reported by for undoped ZnS [14]. The high optical conductivity of magnitude 10^{13} of the deposited ZnS:Mn films indicates that they have good photo response and could be employed as photoconductors [1]. Such films are good candidate materials for thin film solar cells fabrication and various optoelectronic devices applications. [1,6,7,10].

The electrical conductivity (σ_e) spectra of ZnS:Mn nano films doped with different Mn doping % shown in Fig.5 revealed that electrical conductivity (σ_e) of all the ZnS:Mn nano films were high in the wavelength range of 350nm and 800nm with its value varying from 1.72×10^2 to 1.50×10^2 as wavelength increased from 300nm to 1100nm. At wavelength of 550nm in the visible region, the average electrical conductivity of ZnS:Mn nano films decreased from 1.73×10^2 to 1.53×10^2 as Mn doping % increased from 3% to 8% and then increased to 1.56×10^2 with further increase in Mn doping % with the exception of the film sample doped with 18% Mn which exhibited the lowest average electrical conductivity of 1.51×10^2 . The average electrical conductivity of magnitude 10^2 obtained for the film samples falls within the electrical conductivity range of 10^{13} to 10^2 for reported semiconductor. The decrease in electrical conductivity may be attributed to the surface tension due to substitution of Zn^{2+} with Mn^{2+} causing electro neutral effects [10] and could also be ascribed to

increasing of lattice defects and dislocations of the films [6,10].

5. Conclusion

Manganese doped ZnS nano films with different Mn percentage doping have been successfully deposited on ITO glass substrates by electrodeposition method. The XRD studies revealed that ZnS:Mn nano films have cubic structure with crystallite size of approximately 14.19nm. The optical analysis showed that all the films had high transmittance in the visible region. With the increase of Mn percentage doping, the thickness of the ZnS:Mn nano films ranged from 46.01nm to 68.99nm, optical conductivity from 0.20×10^{13} to 1.63×10^{13} and electrical conductivity from 1.520×10^2 to 1.63×10^2 . The results revealed that the thickness and conductivity of ZnS:Mn nano film were dependent on Mn percentage doping. Such ZnS:Mn thin films with thickness in nanometer size range and high conductivity are promising candidate materials for thin films solar cells fabrications and various optoelectronic devices applications. We recommend that other research work should be carried out on CdS nano films co-doped with Mn and any other transition metal using the same deposition conditions.

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