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Effect of Manganese Percentage Doping on Optical Properties of Zinc Sulphide (ZnS) Nanofilms prepared by Electrodeposition method

Okafor Patricia C., Ekpunobi Azubike J.

Abstract— Zinc sulphide nanofilms with different Mn percentage doping were prepared from aqueous solution mixture of zinc chloride, manganese chloride, sodium thiosulphate and a complexing agent triethanolamine using electrodeposition method. The experiment was carried out at room temperature, optimum deposition time and deposition voltage using acidic bath maintained at PH 3 while the Mn content in the electrolyte was varied from 3% to 23%. The x-ray diffraction pattern showed that ZnS:Mn nanocrystals have cubic structure with crystallite size of approximatrly 14.19nm. The thickness of the film samples determined by optical method were of range 46.01 – 68.99nm. With the increase of Mn doping% from 3% to 23%, the optical parameters which include absorbance varies from 0,02 to 0,65; transmittance from 0.90 to 0.52; reflectance 0.27 to zero; refractive index 1.14 to 1.02. The band gap energy of ZnS:Mn film with 8% Mn doping was found to be 2.30eV and is lower than 3.65eV reported for undoped ZnS. The results showed that Mn percentage doping has effect on optical properties of ZnS nanofilms. Such nanofilms could be suitable for wide range of applications in thin films solar cells fabrications, luminescence and optoelectronic devices.

Index Terms— Effect of manganese percentage doping, Optical properties, Zinc sulphide nanofilms, Electrodeposition.

1 Introduction

ZINC sulphide (ZnS) is one of the typical II – VI semiconductor compounds with a direct wide band gap of 3.65eV at room temperature [1]. It is an important material with extensive range of applications such as optical coatings, electro-optic modulator, photoconductors, optical sensors, phosphors and other light emitting materials [2, 3, 4, 5, 6, 7, 8]. Zinc sulphide has been used in cathode ray tube and field emission display phosphor for a long time [9]. It can also be used for photoluminescent, electroluminescent and cathodoluminescent devices. [4, 10, 11] In recent years, much effort has been devoted to the research of doped metal chalcogenide nanostructured materials. This kind of nanomaterials exhibit unusual physical and chemical properties in comparison with their materials, such as size- dependent variation of band gap energy [3]. Zinc sulphide as an important II – VI semiconductor material is chemically more stable, low in toxicity and technologically better than other chalcogenides (such as ZnSe) so it is considered to be a promising host material [12]. Impurity ions doped into zinc sulphide material can influence its electronic structure and transition probabilities [12]. Transition metal doped zinc sulphide materials have extensively studied because of their excellent luminescent properties [7].

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Furthermore, transition metal (such as Mn, Fe, Co, Ni) – doped semiconducting materials, generally called dilute magnetic semiconductors DMSs, has drawn a great attention as it offers a great opportunity to integrate electrical, optical and magnetic properties into a single material, which makes them ideal candidates for non – volatile memory, magneto – optical, optoelectronic and spintronic devices [7].

2 Materials and Method

Zinc sulphide (ZnS) nanofilms doped with different manganese content were prepared using electrodeposition method using a three electrode cell apparatus. To obtain Mn doped ZnS (ZnS:Mn) nanofilms, first, the electrolyte solution was prepared by mixing 10.0 ml of 0.05M zinc chloride ($ZnCl_2$), 0.05M manganese chloride ($MnCl_2.2H_20$) 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 ($Na_2S_2O_3.5H_2O$) 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 the films were deposited were degreased in ethanol for 10 minutes, ultrasonically cleaned for 10 minutes and then dried in a desicator. The deposited ZnS:Mn film samples were rinsed with de-ionized water, dried and annealed at temperature 250˚C.

The X-ray diffraction patterns of Mn doped ZnS nanofilms were recorded by X-ray Mini Diffractometer MD 10 Model with Cu-Ka radiation source of λ=0.15406nm. Optical transmission data was obtained by JENWAY 6405 UV-Vis spectrophotometer at wavelength range of 280nm to 1100nm..

3 Results and Discussions

The XRD pattern of ZnS:Mn nanofilm with 8 at.% of Mn content is shown in Fig. 1.

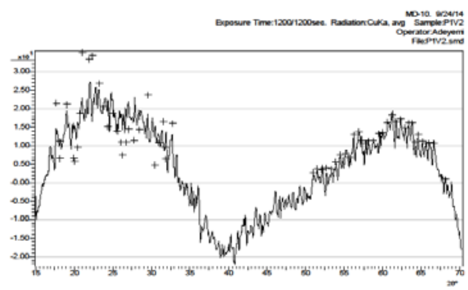

Fig. 1. XRD pattern ZnS:Mn nanofilm with 8% Mn doping

The crystals of the doped film have cubic structure of ZnS with preferential orientation along(220) direction and lattice constant a=b=c=10.045Å. Similar ZnS cubic structure had been-reported for nickel (Ni) doped ZnS [2] and for Mn, Cu co-doped ZnS [13]. Using the DebyeScherrer's formula [14], the mean crystallite size calculated from full width of half maximum(FWHM) of the strongest diffraction peak along (220) direction was estimated to be 14.19nm.The nanocrystalline nature of the film samples confirmed the nanometer size of the film samples.

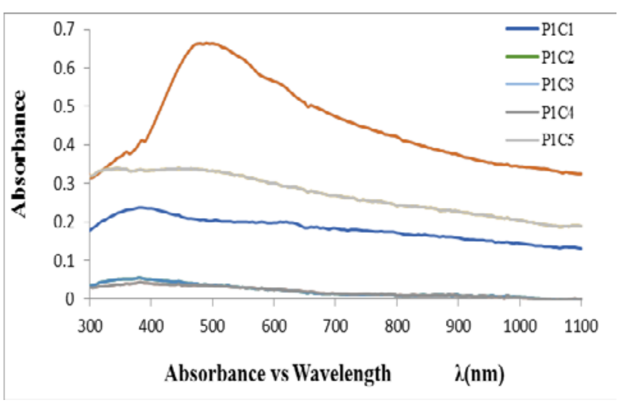

Fig. 2. Absorbance spectra of ZnS:Mn nanofilms with different Mn doping %

The thickness of the films calculated using optical method [11] varied from 46.01nm to 68.99nm. The absorbance, transmittance, reflectance and refractive index spectra of ZnS:Mn film samples are represented in Fig. 2, 3, 4, and 5 respectively.

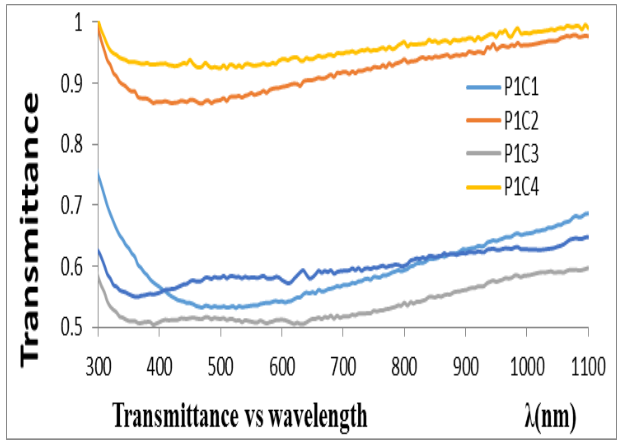

Fig. 3. Transmittance spectra of ZnS:Mn nanofilms with different Mn doping %

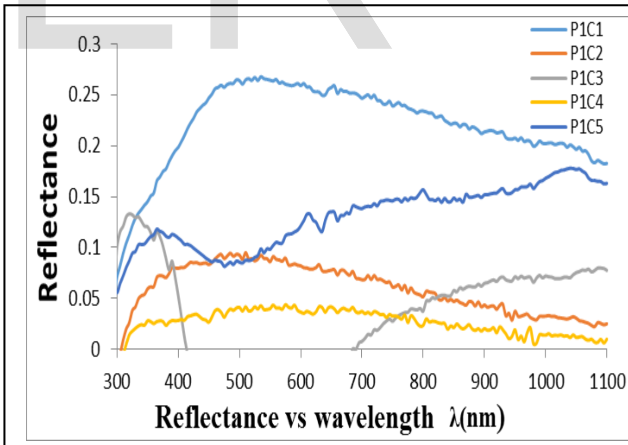

Fig. 4. Reflectance spectra of ZnS:Mn nanofilms with different Mn doping %

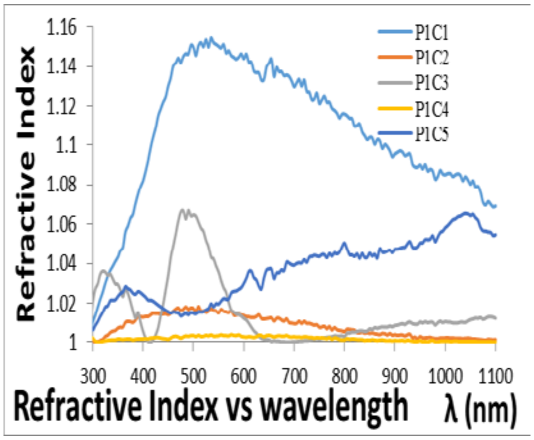

Fig. 5. Refractive index spectra of ZnS:Mn nanofilms with different Mn doping %

The absorbance spectra of ZnS:Mn films with different Mn percentage doping represented in Fig. 2 revealed that the absorbance of ZnS:Mn film sample is high in the wavelength range of 300nm to 500nm and low in NIR region with its value varying from 0.65 to 0.01 as wavelength increased from 300nm to 1100nm. This shows that absorbance decreases with the increase of the wavelength of incident radiation. The difference in the average absorbance values of the ZnS:Mn films may be ascribed to the effect of Mn content in such films. At wavelength of 550nm in the visible region, the average absorbance of the ZnS:Mn films increased from 0.02 to 0.65 as Mn doping % increased from 3% to 8% and then decreased to 0.02 with further increase in Mn doping %. The highest average absorbance value (0.65) was obtained from the sample (P_1C_2) doped with 8% Mn. The results show that all the ZnS:Mn film samples have low absorbance in the visible region with the exception of the sample (P_1C_2) doped with 8% which exhibits a characteristic high absorbance (0.65) in this region. The difference in the average absorbance values of the ZnS:Mn films may be ascribed to the effect of the variation of Mn % doping. Such film with high absorbance in the visible region could be used as absorbers in photothermal devices and in photochemical cells [15]. Other ZnS:Mn film samples with low absorbance could be employed for optical and photosynthetic coatings; and also as window layers in photovoltaic or thin films solar cells [16].

The transmittance spectra of ZnS:Mn nanofilms with different Mn percentage doping represented in Fig.3 revealed that the transmittance of such nanofilms was relatively low in the UV region and high in the NIR region. This shows that transmittance of the film samples increases with the increase of wavelength of incident radiation.. At wavelength of 550nm in the visible region, the average transmittance of the ZnS:Mn films increased from 0.55 to 0.90 as Mn doping % increased from 3% to 8% and then decreased to 0.52 with further increase in Mn doping % with the exception of the film sample (P_1C_4) with 18% Mn doping which exhibited the highest transmittance (0.95) in the visible region. The high transmittance of the ZnS:Mn film samples may be attributed to thinness and low defect density of the films (Choi *et al.*, 2008). The obtained transmittance values compare well with average transmittance range 71% - 83% reported for Mn doped ZnS prepared by CBD method [11]. The observed difference in the average transmittance values of the ZnS:Mn films may be attributed to the effect of the variation of Mn percentage doping. Such films with high transmittance characteristic in the visible region could be employed as window layer for various photo thermal and optoelectronic devices [15].

The reflectance (R) spectra of ZnS:Mn nanofilms (with different Mn content) represented in Fig. 4 revealed that the reflectance of ZnS:Mn nanofilm samples is relatively high in the wavelength range of 300nm to 500nm and low in the NIR region. This shows that the reflectance of the film samples decrease with the increase of wavelength of radiation. The difference in the reflectance peak values of ZnS:Mn films suggests that Mn doping % significantly influenced the reflectance of such films. At wavelength of 550nm, the average reflectance of the ZnS:Mn film samples decreased from 0.27 to zero as Mn doping % increasedfrom 3% to 13% and then increased to 0.10 as Mn doping % increased to 23%.The highest average reflectance value (0.27) was obtained from the film sample (P_1C_1) doped with 3% Mn.

The results revealed that all the ZnS:Mn film samples exhibit low reflectance and the obtained average reflectance values, 0.27 to 0.10 compare well with average reflectance of range 0.20 to 0.07 reported for ZnS:Mn films doped with 0.5% - 4% Mn and prepared by CBD method [11]. Decrease in reflectance observed with the increasing of Mn doping % may be due to reduction in grain boundaries scattering of light as well as decrease in the reflection of incident light by Mn clusters [16]. The zero reflectance of the film sample (P_1C_3) doped with 13% Mn may be attributed to non-uniformity of the film surface. The difference in the average reflectance values of ZnS:Mn films suggests that Mn percentage doping significantly influenced the reflectance of such films. Such ZnS:Mn films with low reflectance and high transmittance characteristics could be employed in antireflection coatings for solar thermal devices and eye glass coatings to reduce solar reflectance and increase transmittance through the glass [15].

The refractive index (n) spectra of ZnS:Mn nanofilms with different Mn percentage doping represented in Fig.5 revealed that the refractive index of the nanofilm samples is relatively high in the wavelength range of 400nm to 550nm and low in NIR region. This shows that refractive index decrease with the increase of the wavelength of incident radiation.The observed difference in the refractive index peak values of the ZnS:Mn films may be ascribed to the effect of Mn content in the film samples. At wavelength of 550nm in the visible region, the average refractive index of the ZnS:Mn films decreased from 1.14 to 1.02 as Mn doping % increased from 3% to 8% and then increased to 1.05 with further increase in Mn doping %. We also observed a window at wavelength of 420nm when the value of refractive index falls to about 1.0. This indicates that the radiation of wavelength 420nm will pass through a relatively shorter path in the film.

All the ZnS:Mn film samples exhibit low refractive index values of range 1.14 to 1.02, thus confirming that the films were of less density and of nanocrystallite structure. The Low refractive index in the visible region implies that the visible radia-

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tions pass through a shorter path in the film, hence interact with few electrons of the material on its path. The observed difference in the average refractive index values of the ZnS:Mn films may be ascribed to the effect of the variation of Mn percentage doping. Such films with low refractive index could find useful applications in antireflection coatings, photosynthetic coatings and in PV cells or thin solar cells [1,11,17].

The band gap energy of ZnS:Mn nanofilm sample with 8% Mn doping was obtained by extrapolating the linear part of the curve of the plot of α^2 versus hυ to hυ axis where $\alpha = 0$ as represented in fig. 6.

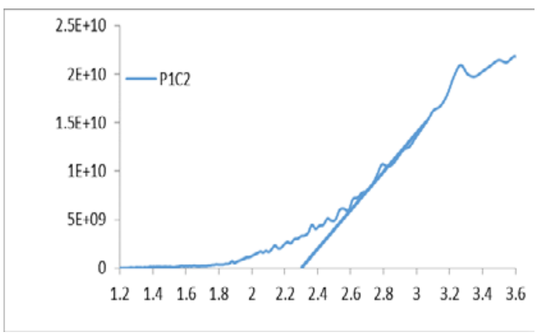

Fig. 6. Plot of α^2 versus hυ for ZnS:Mn nanofilm with 8% Mn doping

The band gap energy of the film was found to be 2.30eV which is lower than 3.65eV reported for the undoped ZnS. The decrease in band gap energy of ZnS film upon doping with the Mn dopant ions may be due to sp–d exchange interaction between the band electrons and localized d- electrons of Mn ions substituting Zn^{+2} ions [16].

4 Conclusion

In conclusion, we have successfully prepared the ZnS:Mn nanofilms with different Mn percentage doping by electrodeposition method using aqueous solution of zinc chloride, manganese chloride, sodium thiosulphate and a complexing agent, triethanolamine. The structural characterization of the film samples was done by X-ray Diffractometer Model MD 10. The optical studies of the ZnS:Mn film samples were carried out by JENWAY 6405 UV – Vis Spectrophotometer. The results obtained showed that Mn percentage doping has significant effect on optical properties of the ZnS. nanofilms.

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