

INFLUENCE OF LOW CONCENTRATION OF Co IONS ON THE OPTICAL AND STRUCTURAL PROPERTIES OF ZnS NANOPARTICLES

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ABSTRACT

Zinc sulfide (ZnS) nanoparticles doped with cobalt ions (Co^{2+}) have been prepared by the chemical bath deposition method (CBD) from homogeneous solutions of zinc acetate, cobalt acetate, thiourea and tri-sodium citrate as a complexing agent. The optical, and structural characteristics of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ ($0.0 \leq x \leq 0.2$) films have been investigated using photoluminescence (PL), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The PL spectrum of the thin films nanoparticles showed two emission peaks, the first at $\lambda = 335$ nm, refer to band to band transition and the second is at around $\lambda = 660$ nm. The intensity of the PL peaks in the red region increases with the increase of Co^{2+} concentration, the maximum intensity recorded was for $x = 0.2$ of Co^{2+} doped. X-ray diffraction showed that the average size of ZnS doped Co is about 1.5 - 2.5 nm, and three diffraction peaks corresponds to the cubic crystalline ZnS. The SEM micrographs showed variation in diffracted morphology with Co^{2+} concentration, and the surface of the films became smoother with the rise of the Co^{2+} doping, the thickness of the films was estimated to be in the range of 223.3 - 461.2 nm.

INTRODUCTION

Semiconductor nanoparticles are described as a state of matter that is intermediate between individual molecule and bulk [1]. The small size and high optical activity of certain semiconductor makes them interesting. Among many semiconductor, Zinc sulphide (ZnS), an II-VI semiconductor with a large bandgap [2], is a good luminescence material used in displays, sensors and lasers apart from applications in photo catalysis [2]. Since both electronics states and electromagnetic field are modified via doping, optical and structural properties may change drastically in nanoparticles. Doping ZnS nanoparticles by transition metal ions like Mn^{2+} [3,4], Cu^{2+} [5] and rare earth ions like Eu^{2+} [6] have been successfully done by several methods such as thermal evaporation, sol-gel processing, co-precipitation and any other method. these doped

ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors. In addition emission in different visible bands to various dopants are been reported. This includes orange luminescence in ZnS:Mn nanoparticles, attributed to the ${}^4T_1-{}^6A_1$ transition in Mn^{2+} ions excited via energy transfer for the host ZnS [7], red emission from the characteristic $4f^7-4f^65d^1$ transition of Eu^{2+} in ZnS:Eu nanoparticles [8]. However for ZnS: Co there is not much work done. Cobalt substitution of zinc in ZnS has d^7 [9] configuration when the impurity is neutral. This configuration has been studied in absorption by Weakliem (1962) [10] who reported transition from the ground state ${}^4A_2(F)$ to excited states ${}^4T_2(F)$ [9]. In this paper we report the optical characteristics (photoluminescence), the structural characteristics using x-ray diffraction and surface modification using SEM of $Zn_{1-x}Co_xS$.

EXPERIMENT DETAILS

Zinc sulfide (ZnS) doped with cobalt (Co^{2+}) films were prepared by chemical bath deposition (CBD) method at room temperature. An aqueous solutions of 0.2M zinc acetate ($Zn(CH_3COO)_2$), 0.6 M, thiourea ($SC(NH_2)_2$) and complexing agent (ammonia, and 0.13 M tri-sodium citrate (CH_4N_2S)) were used to prepare ZnS. First, 10 ml zinc acetate solution and 10 ml tri-sodium citrate were placed in 100 ml beaker. After stirring for several minutes, the solution became clear and homogeneous. Then under continuous stirring, 10 ml thiourea solution was introduced. The pH value of the result solution was adjusted to about 10 using ammonia. For the synthesis of the dope, 0.2 M cobalt (II) acetate ($Co(CH_3COO)_2.H_2O$) were prepared in deionized water, then the solution was stirred for 30 min. Different volume was added to different beakers of ZnS solution with ($x = 0.0, 0.05, 0.1, 0.15, 0.2$ and 0.3) is the molar concentration of Co. quartz and glass substrates were used in this study. The substrates were cleaned using acetone, methanol and 2-propanol in ultrasonically cleaner for 20 min, and then dried in air. The $Zn_{(1-x)}Co_xS$ films were prepared using two methods. In the first method the prepared solution was dropped on a quartz substrates using the spin coating process for the optical characterizations. In the second method the films were prepared using the evaporation method for the optical and structural test. Finally, the samples were annealed at $300\text{ }^{\circ}C$ for 3 hours.

RESULTS AND DISCUSSION

A photoluminescence (PL) spectrum of nanocrystalline $Zn_{(1-x)}Co_xS$ thin films at room temperature is shown in Figure. 1.

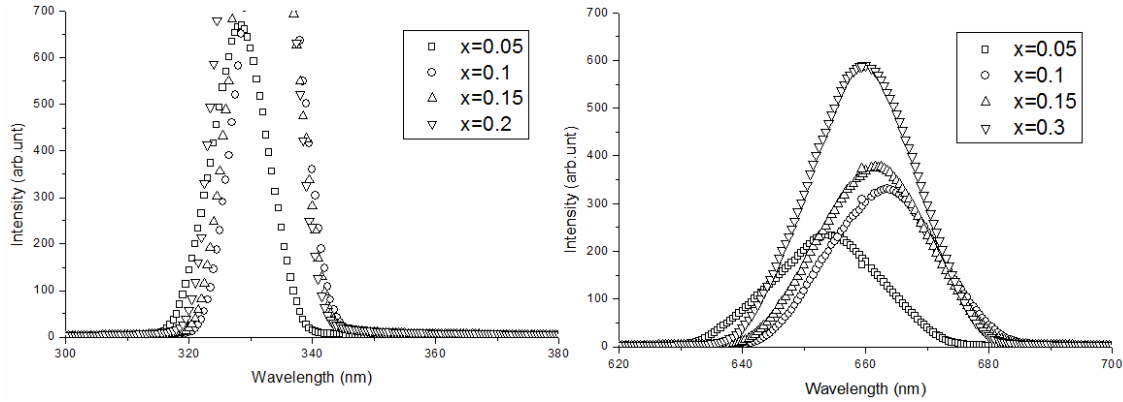


Figure. 1: PL spectra of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ thin films with $(0.05 \leq x \leq 0.2)$

The PL spectra showed two peaks, the first is at $\lambda = 340$ nm, and the second is around $\lambda = 660$ nm. As the position of the first peak is not shifted with the variation of the Co^{2+} concentration in the films, the photoluminescence in this region is due to the sulfur vacancies in the lattice [12, 9]. The second peak of the thin films, which around $\lambda = 660$ nm is attributed due to $^4\text{T}_1\text{-}^4\text{A}_2$ transition of Co^{2+} d [13.9]. Doping with Co atoms leads to some broadening of the core level line as well as of the valance band spectrum. This occurs due to a distortion of the crystal lattice of the material [14]. The PL Intensity of Co impurity in ZnS compound is excited mainly by the intra impurity absorption processes. Which primarily changes the $^4\text{A}_2$ (^4F) ground electronic state of the Co^{2+} ion to $^4\text{T}_1$ (^4F) or $^4\text{T}_1$ (^4P) state [9, 15]. The intensity of the PL peaks increases with the increase of Co concentration in the film. The transfer is most likely from the ZnS band edge. The excited charge carriers can decay non-radiatively to the ZnS surface states or Co^{+2} 3d states. In the first case the recombination occurs via surface states with emission in the violet region of the spectrum and the other, Co^{+2} d-d transition leads to the red emission[16, 15]. The emission intensity of the violet or red depends upon the transition probabilities and it also depends on the concentration of Co^{+2} ions. The maximum PL intensity was observed for $x = 0.2$.

Figure 2, displays the X-ray diffraction of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ ($x = 0.0, 0.05, 0.1, 0.15$ and 0.2) samples. The wide angle XRD pattern for the thin films system exhibits three distinct peaks in the range of $2\theta = 20 - 60^\circ$, which are the characteristics peaks of cubic structure of ZnS: Co. the main peak is fairly broad suggesting the nanostructure of ZnS: Co. The three strong peaks appeared at angles (2θ) of 28.55° , 47.50° and 56.85° correspond to (111), (220) and (311) planes of cubic ZnS respectively. The mean size (D) of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ nanoparticles of the nanocomposite is calculated following the Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where $K=0.89$, D represent coherent length, λ is the x-ray wavelength and β , the corrected value at full width at half maxima (FWHM) of the main diffraction peak. at $2\theta = 28.55^\circ$, corresponding to the characteristics peaks of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$, is chosen to

calculate D . the estimated size of nanocrystalline ZnS doped Co is in the range of 1.2-2.2 nm.

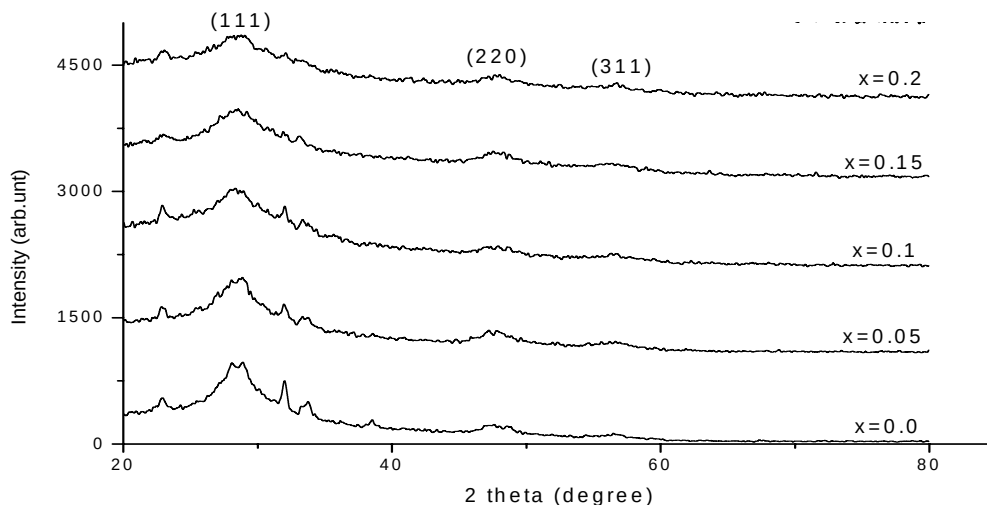


Figure 2: XRD pattern of the $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ nanoparticles with $(0.0 \leq x \leq 0.2)$

The SEM micrographs of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ nanoparticle thin films are shown in Figure 3. The $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ thin films showed compact distribution over the surface and the growth of the grain with the rise of Co concentration. For $x=0.2$ flake type formation with agglomerations distribution. In the case of $x=0.15$, the flake type structure broke into small size, and fluffy mass was spread randomly over the surface. When the Co concentration was reduced to $x=0.05$, the morphology of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ was totally dispersed and not smooth. The agglomerations size was very small. The surface of the films was presented in cluster form and they were not uniform distributed.

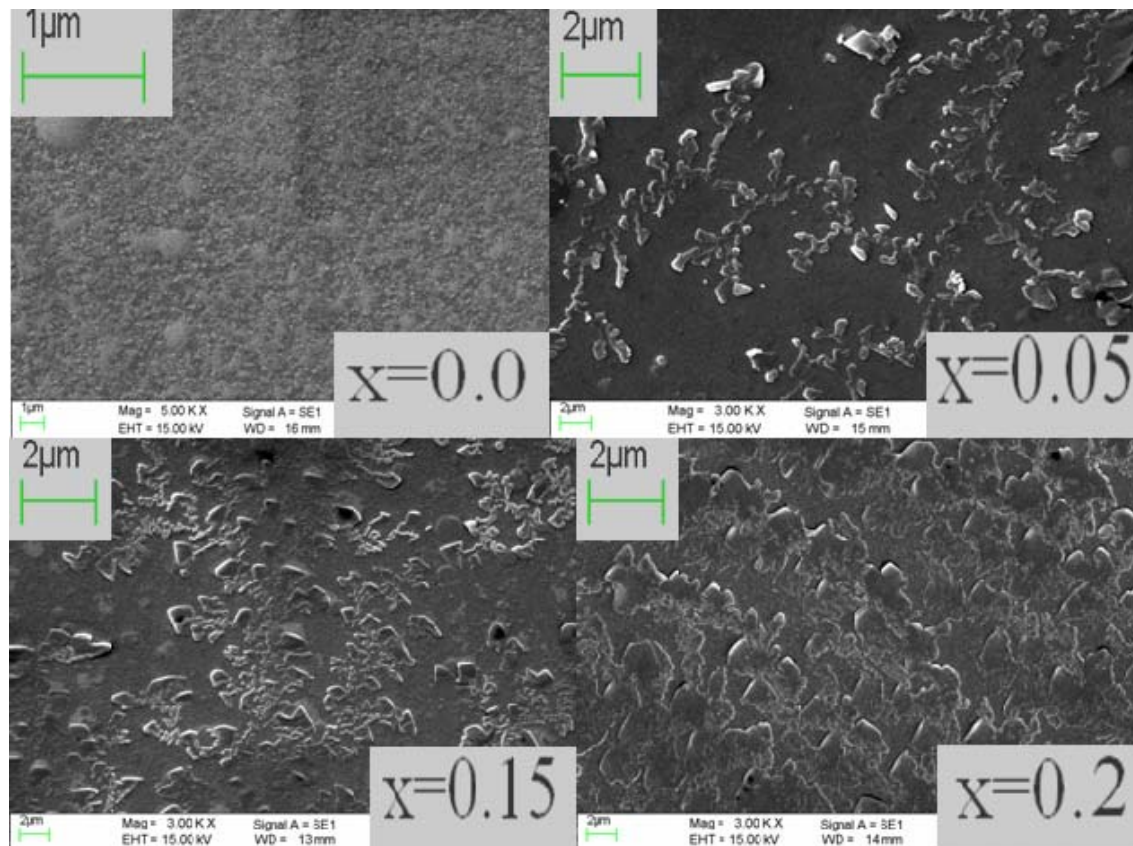


Figure 3: SEM photographs of $\text{Zn}_{(1-x)}\text{Co}_x\text{S}$ samples

Figure 4, depict the film thickness of the thin films using SEM. It lies in the range of 223.3 - 461.2 nm. There is no relation between the thickness of the films and the Co concentration (the aggregation of the ZnS with Co is done during the experiment time).

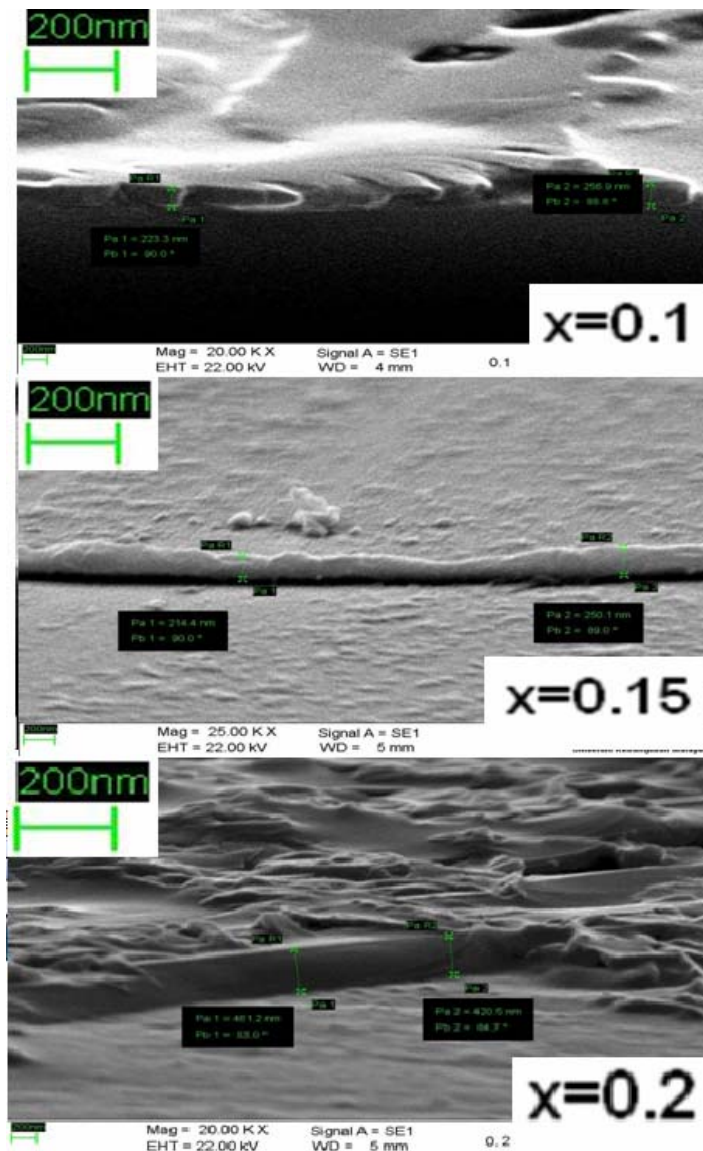


Figure 4: Film thickness of ZnS:Co thin films using SEM photograph

CONCLUSION

Zn_(1-x)Co_xS nanoparticles with x in the range $0.0 \leq x \leq 0.2$ were successfully synthesized by chemical bath deposition method. The PL spectrum of ZnS doped Co nanoparticles showed one peak in the violet region, this is due to the sulfur vacancies in the lattice, the second peak appeared in the red region. The intensity of PL peaks in the red region increases with the increase of Co concentration in the films. X-ray diffraction pattern confirmed the nanocrystalline cubic zinc blend formation. From SEM micrographs, we can see that by varying in Co concentration, the morphology of the films can be modified and the flake type formation on the surface of the film became totally dispersed and not smooth with the increases of Co concentration.

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