

*J. Nano- Electron. Phys.*  
3 (2011) No2, P.5-10

© 2011 SumDU  
(Sumy State University)

PACS number: 62.23.Hj

## SYNTHESIS AND PHOTOLUMINESCENCE STUDIES ON CATALYTICALLY GROWN $Zn_{1-x}Mn_xS$ NANOWIRES

**R.P. Vijayalakshmi<sup>1\*</sup>, G. Murali<sup>1</sup>, D. Amaranatha Reddy<sup>1</sup>, R. Venugopal<sup>2</sup>,  
B.K. Reddy<sup>1</sup>**

<sup>1</sup> S.V. University, Dept. of Physics,  
517 502, Tirupati, A.P., India

\* E-mail: [vijayaraguru@gmail.com](mailto:vijayaraguru@gmail.com)

<sup>2</sup> Govt. Degree College, Puttur.  
Dept. of Physics, Chittoor, A.P., India

*$Zn_{1-x}Mn_xS$  alloy nanowires with composition ( $x = 0.0, 0.1$  and  $0.3$ ) have been successfully synthesized by a simple thermal evaporation on the silicon substrate coated with a gold film of 2 nm thickness. X-ray powder diffraction measurements reveal that as synthesized products were hexagonal wurtzite structure. The as grown nanowires have been investigated by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive Analysis of X-rays (EDAX) and photoluminescence studies. The results reveal that the as grown nanowires consist of Zn, Mn, and S material and diameter ranging from 70 - 150 nm with lengths up to several tens of micrometers. Photoluminescence studies on  $Zn_{1-x}Mn_xS$  exhibited peaks at 600 and 613 nm for  $x = 0.1$  and  $0.3$  respectively.*

**Keywords:**  $Zn_{1-x}Mn_xS$  NANOWIRES, CVD PROCESS, EDAX, TEM, XRD, PHOTOLUMINESCENCE.

(Received 12 January 2011, in final form 16 February 2011,  
published online 02 April 2011)

### 1. INTRODUCTION

One dimensional nanostructures have been a subject of intense research interest and have attracted considerable attention due to their novel properties and potential applications in nanoscale devices. In recent years exploring results have been achieved in nanoresearch [1-4]. Because of the ability to synthesize II-VI compounds in numerous configurations these materials attracted great research interest [5-7]. Among II-VI compounds ZnS is a direct band gap semiconductor with band gap of 3.7 eV (bulk). Under ambient conditions it has two phases, cubic Zinc blended and hexagonal wurtzite. Cubic ZnS is stable at room temperatures, where as the hexagonal ZnS is stable at high temperature ( $> 1000$  °C). ZnS is widely studied material for its wide applications as base material for cathode ray tube luminescent materials, phosphors and catalysts [8, 9]. When doped with some transition metal ions it exhibit a variety of luminescent properties such as photoluminescence, thermoluminescence and triboluminescence [10-11]. In addition to that it is a dilute magnetic semiconductor and is used in spintronic devices [12, 13]. Mn doping in ZnS attracts a great deal of interest since Mn doping can not only enhance its optical transition

efficiency, increase number of luminescent centers and induces the semi magnetic behavior [12-16]. The reports on  $Zn_{1-x}Mn_xS$  nanostructures are few. Yu et al. [17] reported composition dependent characterization  $Zn_{1-x}Mn_xS$  epilayers prepared by HWE. Biswas and co-worker [18] have synthesized  $ZnS:Mn^{2+}$  nanorods at 200 °C with a solvothermal method, and Mandel et al. [19] have obtained  $ZnS:Mn^{2+}$  nanorods within the pores of a polycarbonate membrane. Ge et al. [20] have reported a halide transport chemical vapor deposition method to fabricate  $ZnS:Mn^{2+}$  nanobelts and nanowires at 750 °C. Synthesis of  $ZnS:Mn^{2+}$  nanowires by a chemical vapor deposition technique at 700 °C using Zn and S powders as precursors have been reported by Yan et al. [21]. The synthesis of nanowires with required dimension is technological importance.  $Zn_{1-x}Mn_xS$  nanowires with required diameter can be prepared by catalytic growth of CVD process. The choosing of catalyst is the prime concern; one can get particles of required size by chemical route method with the capping agent. In the present work we synthesized the nanowires by physically mixing the appropriate quantities of ZnS and MnS. By this method one can grow a nanowires of different diameters.

## 2. EXPERIMENTAL STUDIES

### 2.1 Catalytic growth of $Zn_{1-x}Mn_xS$

The experimental design to synthesize  $ZnMnS$  nanowires is described elsewhere [22]. In the fabrication of  $Zn_{1-x}Mn_xS$  nanowires, high purity ZnS and MnS powders (99.999 %) were used. The source materials were prepared first by physically mixing the desired quantities ( $x = 0.0, 0.1$  and  $0.3$ ) of ZnS and MnS and then sintering the mixture at 1000 °C in a vacuum sealed quartz tube for 18 hours. The sintered mixture was cooled slowly to room temperature in 5 hours and was then used as source material for the fabrication of  $ZnMnS$  alloy nanowires. The sintered mixture was put in the alumina boat and placed inside a quartz tube in the middle of the furnace. Prior to the synthetic reaction, the quartz tube was evacuated and heated up to 900 °C. The Au film (2 nm thickness) coated on a Si Substrate ( $20 \times 10$  mm) used as a product collection substrate and located down stream to the carrier-gas mixture outlet was vacuum annealed at 550 °C to recrystallize into Au nanoparticles. A carrier-gas mixture of Ar (90 %) and  $H_2$  (10 %) with flow rate of 220 sccm was frequently introduced into the quartz tube till the pressure reach 250 torr. X-ray diffraction (XRD) spectra of the as synthesized nanowires were recorded using Scintag XI diffractometer with  $CuK_{\alpha}$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at scanning speed of 2 °C/min in  $2\theta$  ranging from 20 °C to 80 °C. Further the nanowires were also characterized by scanning electron microscopy (SEM) (LEO 1530, Field Emission SEM), transmission electron microscopy (Philips TECHNAI FE 12) and the composition of the  $Zn_{1-x}Mn_xS$  nanowires were determined by energy dispersive analysis of X-rays (EDAX). The PL excitation spectrum was recorded at room temperature using xenon arc lamp.

### 2.2 Growth Mechanism

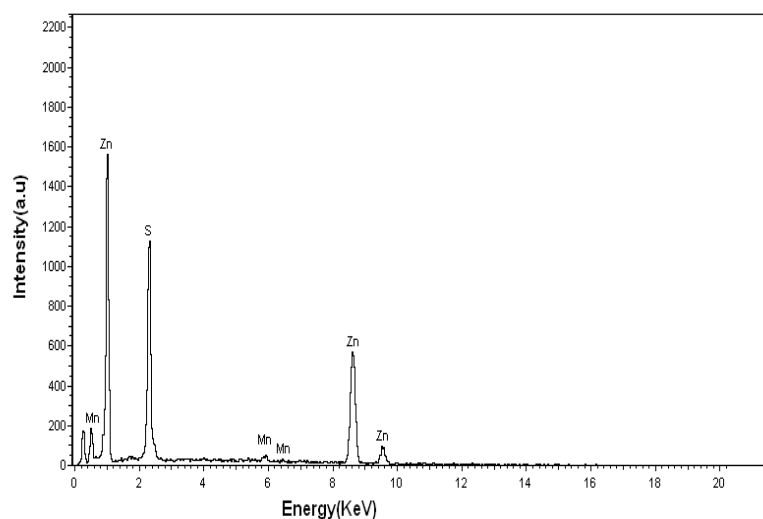
In this study, the formation of  $Zn_{1-x}Mn_xS$  nanowires follow a vapor-liquid solid (VLS) growth mechanism as evidenced by the eutectic tips containing

Au, Zn, Mn and S. At an early reaction stage in the formation of  $Zn_{1-x}Mn_xS$  nanowires, a vapour mixture of Zn, Mn and S was carried by the Ar and  $H_2$  gases and deposited onto catalytic Au nanodroplets. When the dissolution of Zn, Mn and S in the Au nanodroplets became supersaturated  $Zn_{1-x}Mn_xS$  nanowires extruded from the liquid eutectic Au nanodroplets and precipitated at the liquid-solid interface. This process basically complies with an ordinary VLS growth model proposed originally by [22] in which a liquid cluster of metal catalyst provides energetically favored sites for the absorption /adsorption of gas phase reactants [23]. The sizes of the catalysts are considered to be responsible for the diameters of resultant nanowires.

### 3. RESULTS AND DISCUSSION

#### 3.1 EDAX analysis

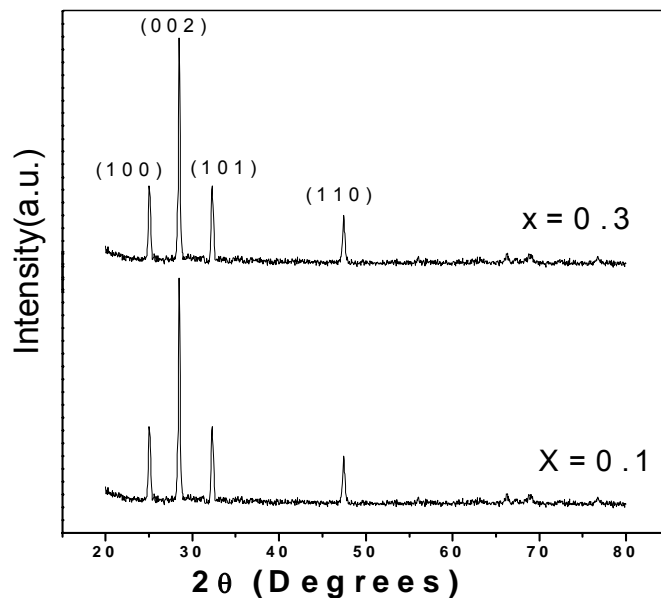
The EDAX analysis showed that the nanowires were well stoichiometric with the components of zinc, sulphur and manganese. EDAX pattern of  $Zn_{0.9}Mn_{0.1}S$  is shown in Fig. 1.



*Fig. 1 – EDAX Pattern of  $Zn_{0.9}Mn_{0.1}S$*

#### 3.2 Structural Analysis:

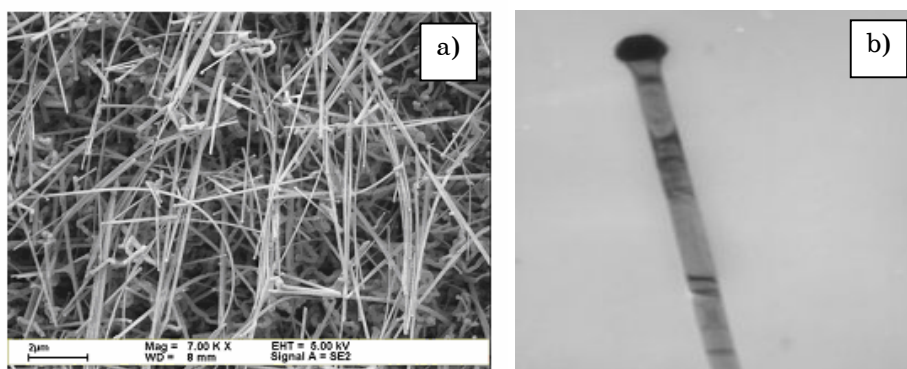
The XRD patterns of  $Zn_{1-x}Mn_xS$  ( $x = 0.1$  and  $0.3$ ) nanowires were shown in Fig. 2. All the diffraction peaks can be well indexed as hexagonal wurtzite structure and are consistent with the standard data. Similar structure was reported by Geng et al. in ZnMnS nanobelts [24] and in ZnMnS nanowires [25]. From the XRD spectra we can observe that (002) diffraction peaks is stronger and narrower than the other peaks, suggesting a preferential growth direction along the c-axis.



**Fig. 2** – XRD Pattern of  $Zn_{1-x}Mn_xS$

### 3.3 Morphological studies

General SEM morphologies of the synthesized  $Zn_{1-x}Mn_xS$  ( $x = 0.1$ ) nanowires orienting randomly on the Si substrate are shown in Fig. 3a, the diameters of the nanowires are distributed in the range of 70 - 150 nm. Lengths of the nanowires can be up to several tens of micrometers and respond sensitively to the synthetic reaction time. The TEM images of the  $Zn_{0.9}Mn_{0.1}S$  nanowire is shown in Fig. 3b.



**Fig. 3** – SEM images of  $Zn_{0.9}Mn_{0.1}S$  nanowires (a); TEM images of  $Zn_{0.9}Mn_{0.1}S$  nanowires (b)

### 3.4 Photoluminescence studies

From the luminescence spectra (See Fig. 4), no band edge emission was observed in ZnS:Mn nanowires. The peaks at around 600 and 613 nm were observed in  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{S}$  and  $\text{Zn}_{0.7}\text{Mn}_{0.3}\text{S}$  nanowires respectively. This so called yellow PL band originates from the  ${}^4\text{T}_1$  to  ${}^6\text{A}_1$  transition within the  $3\text{d}^5$  shell of  $\text{Mn}^{2+}$  on a cation site with tetrahedral symmetry. It is known that the  $\text{Mn}^{2+}$  ion electron states act as luminescence centers, because of strong interaction with the s-p electron states of the ZnS host crystals. Sooklal et al. [26] have studied the effect of the location of the  $\text{Mn}^{2+}$  ions on the photo physics of ZnS nanomaterials. They found that the  $\text{Mn}^{2+}$  ions incorporated into the ZnS lattice would lead to the yellow-orange emission, while the  $\text{Mn}^{2+}$  ions distributed on the surface of ZnS would yield the ultraviolet emission. By comparison of our results we can conclude that the  $\text{Mn}^{2+}$  ions are incorporated into the ZnS lattice occupying the tetrahedral cationic site. As the  $\text{Mn}^{2+}$  concentration increased the intensity of yellow emission increased. Because the  $\text{Mn}^{2+}$  ions would capture more electron-hole pairs and emit more photons [24], leading to the enhancement of the yellow emission. Red shift was observed with the increasing Mn concentration. The origin for the peak position change as a function of Mn composition is not well understood. However it has been reported that the emission of the  $\text{Mn}^{2+}$  related peaks are virtually independent of  $x$  in  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ . Presumably because the Mn-S bond lengths are independent of composition [27].

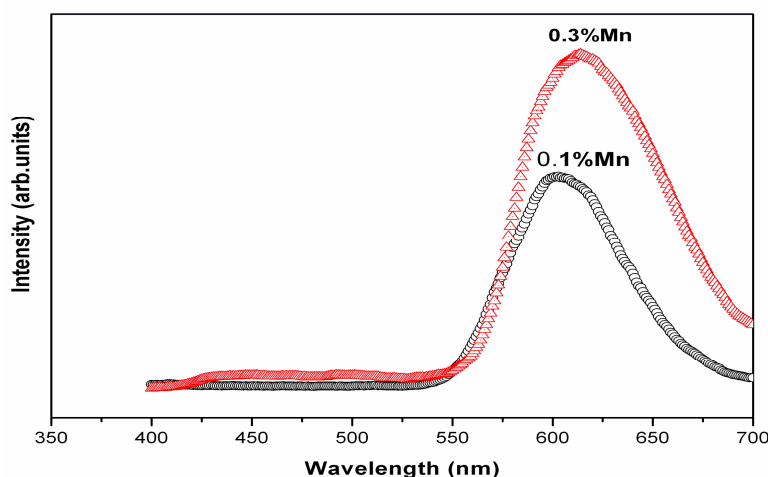


Fig. 5 – Photoluminescence Spectra of  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$  ( $x = 0.1$  and  $0.3$ ) nanowires

## 4. CONCLUSIONS

$\text{Zn}_{1-x}\text{Mn}_x\text{S}$  nanowires were synthesized by CVD with Au as catalyst. Crystalline structure and lattice parameters were determined by XRD studies and the structure was hexagonal wurtzite in all the wires. TEM studies revealed that the growth direction of the nanowires is near to the c-axis. The luminescence intensity increased with Mn concentration.

## ACKNOWLEDGEMENTS

The author wishes to thank the University Grant Commission, New Delhi for the financial Assistance through Major Research Project.

## REFERENCES

1. C. Lu, L. Qi, J. Yang, L. Tang, D. Zhang, J. Ma, *Chem. Commun.* **33**, 3551 (2006).
2. L.W. Yin, Y. Bando, *Nature Mater.* **4**, 883 (2005).
3. R. Venugopal, P.I. Lin, C.C. Liu, Y.T. Chen, *J. Am. Chem. Soc.* **127**, 11262 (2005).
4. Y. Jiang, X.M. Meng, W.C. Yiu, J. Liu, J.X. Ding, C.S. Lee, S.T. Lee *J. Phys. Chem. B* **108**, 2784 (2004).
5. S.Q. Wang, *Appl. Phys. Lett.* **88**, 061902 (2006).
6. Y.P. Leung, W.C.H. Choy, I. Markov, G.K.H. Pang, H.C. Ong, T.I. Yuk, *Appl. Phys. Lett.* **88**, 183110 (2006).
7. Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* **291**, 1947 (2001).
8. M. Bredol and J. Merikhi, *J. Mater. Sci.* **33**, 471 (1998).
9. S. Gupta, J.S. Meclure, and V.P. Singh, *Thin Solid Films* **33**, 299 (1997).
10. J. Planelles-Arago, B. Julian-Lopez, E. Cordocillo, P. Escribano, F. Pelle, B. Viana, C. Sanchez, *J. Mater. Chem.* **18**, 5193 (2008).
11. S. Hou, Y. Yuen, H. Mao, J. Wang, Z. Zhu, *J. Phys. D: Appl. Phys* **42**, 215105 (2009).
12. H. Ohno, *Science* **281**, 951 (1998).
13. S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. Von molnar, M.L. Roukes, A.Y. Chtchelkanova, and D.M. Treger, *Science* **294**, 1488 (2001).
14. V. Wood, J.E. Halpert, M.J. Panzer, M.G. Bawendi, and V. Bulovic, *Nano Lett.* **9**, 2367 (2009).
15. S. Kar, S. Biswas, *ACS Appl. Mater. Interfaces* **1**, 1420 (2009).
16. T.P. Surkova, V.R. Galakhov, and E.Z. Kurmaev, *Low Temp. Phys.* **35**, 79 (2009).
17. Y.-M. Yu, D.J. Kim, S.H. Eom, Y.D. Choi, T.-H. Kim, O. Byung-sung, *J. Vac. Sci. Technol. A* **23**, 777 (2005).
18. S. Biswas, S. Kar, S. Chaudhuri, *J. Phys. Chem. B* **109**, 17526 (2005).
19. S.K. Mandal, A.R. Mandal, S. Das, *J. Appl. Phys.* **101**, 114315 (2007).
20. J. Ge, J. Wang, H. Zhang, X. Wang, Q. Peng, Y. Li, *Adv. Funct. Mater* **15**, 303 (2005).
21. R.F. Zhuo, H.T. Feng, D. Yan, J.T. Chen, J.J. Feng, J.Z. Liu, P.X. Yan, *J. Cryst. Growth* **310**, 3240 (2008).
22. D. Moore, Z.L. Wang, *J. Mat. Chem.* **16**, 3898 (2006).
23. Y.H. Yang, S.J. Wu, H.S. Chui, P.I. Lin, Y.T. Chen, *J. Phys. Chem. B* **108**, 846 (2004).
24. B.Y. Geng, L.D. Zhang, G.Z. Wang, T. Xie, Y.G. Zhang, G.W. Meng, *Appl. Phys. Lett.* **84**, 2157 (2004).
25. J. Cao, J. Yang, Y. Zhang, L. Yang, D. Wang, M. Wei, Y. Wang, Y. Liu, M. Gao, and X. , *J. Phys. D: Appl. Phys* **43**, 075403 (2010).
26. K. Sooklal, B.S. Cullum, S.M. Angel, C.J. Murphy, *J. Phys. Chem.* **100**, 4551 (1996).
27. F.J. Brier, P. Grundmann, M. Froba, L. Chen, P.J. Klar, W. Heimbrod, H.-A.K. von Nidda, T. Kurz and A. Loidl, *J. Am. Chem. Soc.* **126**, 797 (2004).