Digest Journal of Nanomaterials and Biostructures Vol. 5, No 1, March 2010, p. 161 – 167

PHOTOCONDUCTIVITY AND DARKCONDUCTIVITY STUDIES OF Mn-DOPED ZnS NANOPARTICLES

S. SRIVASTAVA*, S. K. MISHRA, R. S. YADAV[a], R. K. SRIVASTAVA, A. C. PANDAY[a], S. G. PRAKASH
Department of Electronics & Communication, University of Allahabad, Allahabad-211002 India
[2]Nanophosphor Application Centre, Department of Physics, University of Allahabad, Allahabad-211002 India

In the present work an attempt has been made to study the photoconductivity and dark-conductivity characteristics of doped ZnS nanoparticles. Photoconductivity and dark-conductivity are measured at room temperature under visible illumination. The Mn-doped ZnS nanoparticles synthesized by co-precipitation technique are found to exhibit anomalous behavior of photocurrent which decreases with increased intensity of illumination. At 5000 lux of illumination photocurrent is found to be even lower than the dark-current. The variation of photocurrent with applied voltage is super-linear. Structural studies using XRD and TEM have been performed. The calculated particle size of ZnS: Mn nanoparticles is 2.8 nm.

(Received January 25, 2010; accepted February 26, 2010)

Keywords: Photoconductivity, ZnS, photocurrent, dark-current, anomalous behavior.

1. Introduction

Since last two decades, II-VI compound-semiconductors with dimension in the nano-meter range have generated considerable interest for researchers and scientific community. This gives us the opportunity to study physics in small dimensions which in turn provides optical and transport properties exhibited by these materials. Among II-VI semiconductor materials such as ZnO, CdS, CdO, and ZnS researchers have shown great interest in the investigation of transport properties including photoconductivity properties under UV and visible excitation. Zinc sulphide (ZnS) is an important optoelectronic device material for its use in the violet and blue regions owing to its wide band gap (~3.7eV) and having exciton binding energy of 40 meV [1]. Since last two decades scientists and researchers have started working on doped ZnS nanopaticles with ions such as Cu and Mn (ZnS:Cu, ZnS:Mn). In doped compound semiconductors in contrast with the undoped ones, the impurity states play an important role in affecting the electronic energy structures and transition probabilities [2]. For doped nanocrystalline semiconductor compounds, confinement effect in the energy states also produces unusual physical and optical behavior. This paper deals with the photoconductivity properties of Mn doped ZnS nanocrystals.

Photoconductivity is considered to be an important tool for providing information regarding the nature of the photo-excitations. Since last decade the photoconductive properties of the inorganic nanoparticles have become subject of intensive study [3]. Not only because of fundamental interests in the nature of the electronic excitations but also due to their applications in wide range of optical and electronic devices. A good photoconductive device requires not only efficient charge separation but also efficient transport of charge carriers to electrode [4]. It is well known that the rise and decay curves of photocurrent are governed by the trapping states or

*Corresponding author: smritim29@rediffmail.com

recombination centers lying in the forbidden energy zone of a photoconductor. Therefore these curves can be used to understand the nature and distribution of traps and recombination centre [5-6].

There are a number of chemical methods for the synthesis of nanomaterials e.g. co-precipitation, sol gel, hydrothermal, solvo-thermal and auto-combustion etc [7] . Among these chemical techniques, co-precipitation is a popularly used method which provides simple and rapid preparation and easy control of particle size composition [8]. In this paper we report the dark-conductivity and anomalous photoconductivity properties of Mn doped ZnS nanoparticles synthesized by co-precipitation method. Dark-conductivity and negative photoconductivity measurements are taken as a function of illumination intensities and applied voltages. The time resolved rise and decay curves have also been studied under visible illumination.

Study on the effect of UV irradiation on Mn doped ZnS nanoparticles has been reported by Cruz et. al.[9]. There is perhaps no report on negative photoconductivity of Mn doped ZnS nanoparticles under visible illumination.

2. Experimental section

2.1. Chemicals

The zinc acetate dehydrate (Zn (CH3COOH)2.2H2O), manganese acetate (Mn (CH3COOH)2 .4H2O)and sodium sulphide (Na2S) were purchased from E. Merk Ltd. Mumbai, 400018, India. These chemicals were directly used without special treatment.

2.2. Sample preparation

The chemicals used for Mn doped ZnS were zinc acetate, manganese acetate and sodium sulphide. In a typical experiment 1M zinc acetate and 0.1M manganese acetate were mixed in 50ml of ethanol. In the above solution 50ml of 0.01M sodium sulphide aqueous solution was added drop wise under vigorous stirring to form ZnS: Mn nanoparticles. The precipitate was finally washed with ethanol and dried in vacuum oven at 40 0C

2.3. Instrumentation

The crystal structure of ZnS: Mn nanoparticles were characterized by X-ray diffraction (XRD) using a Rigaku D/MAX- 2200H/PC with Cu Kα radiation (λ = 1.54178A˚). Transmission electron microscopy (TEM) was performed using a Tecnai 30 G2 S-Twin electron microscope operating at 300 kV accelerating voltage. For photoconductivity and dark conductivity measurements, a cell was formed by spreading a thick layer of powdered samples in between two Cu electrodes etched on a Cu plate (PCB), having a spacing of 1 mm (Fig 1(a)). The powdered layer was pressed with transparent glass plate. This glass plate has a slit for providing illumination area of 0.25 cm 2. In this cell type device, the direction of illumination is normal to field across the electrodes. The cell was mounted in a dark chamber with a slit where from the light is allowed to fall over the cell. The visible photo-response was measured using a commercial bulb of 200 W as a photo-excitation source. A stabilized dc field (50 V/cm to 500 V/cm) was applied across the cell to which a digital dc nano-ammeter, NM-121 (Scientific Equipment, Roorkee) for the measurement of current and RISH Multi 15S with adapter RISH Multi SI 232 were connected in series (Fig 1(b)). The light intensity over the cell surface was changed by varying the distance between slit and light source. Before measuring photoconductivity of the sample, the cell is first kept in dark till it attains equilibrium.

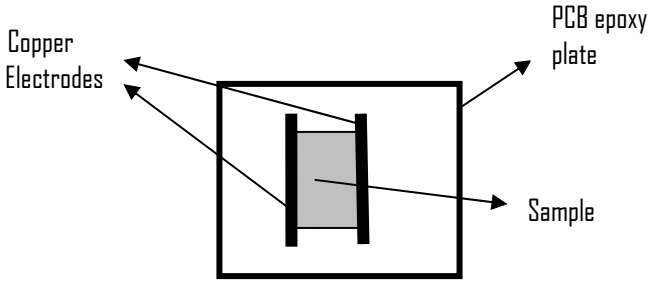

Fig. 1(a) Photoconductive cell.

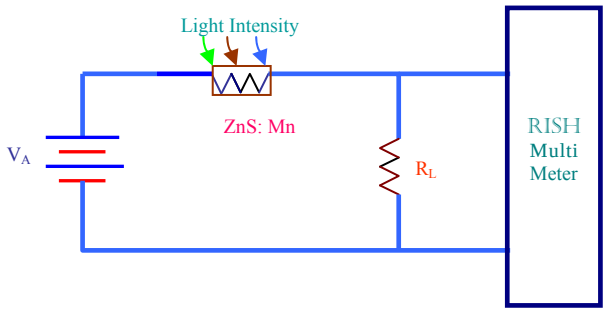

Fig. 1(b) Measurement setup used for observation of photoconductivity.

3. Results and discussion

3.1 Structural study

The Figure 2 shows the XRD patterns for Mn-doped ZnS nanoparticles synthesized by co-precipitation method. The obtained results are very well matched with that of standard cubic ZnS. The peak broadening in the XRD pattern indicates that small nanoparticles are present in the Mn-doped ZnS [10]. The XRD pattern shows peaks at 2θ values of 29.16, 48.67 and 56.92 referring to diffraction from (111), (220) and (311) planes respectively. The peak (111) at 2θ = 29.16o indicates a cubic (zinc blend) crystalline structure. The crystallite (or grain) size of Mn-doped ZnS nanoparticles was estimated using the Scherer's formula

$$D = \frac{0.94\lambda}{\beta Cos\vartheta}$$

where β is full width at half maximum [FWHM] in radians, λ is the X-ray wavelength and θ is the Bragg's angle. The average particle size of Mn-doped ZnS nanoparticles is estimated as 2.8 nm.

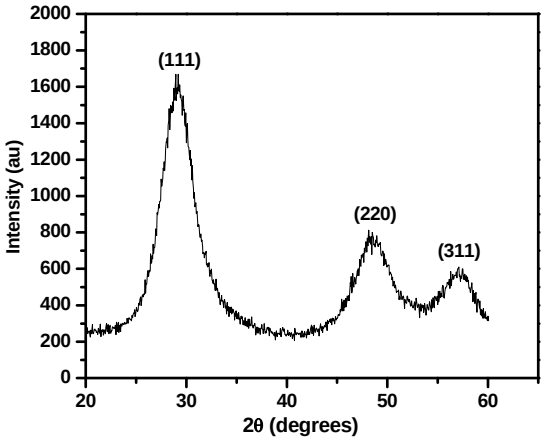

Fig. 2. XRD pattern of Mn-doped ZnS nanoparticles synthesized by co-precipitation method.

3.2 Morphology study

Fig. 3 shows the TEM image of Mn-doped ZnS nanoparticles synthesized by co-precipitation method. The nanoparticles are spherical with little agglomeration. The size of these spherical nanoparticles are found to be 2-4 nm.

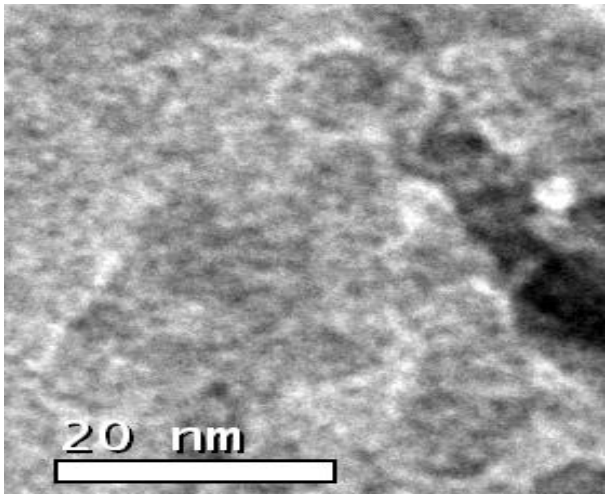

Fig. 3. Transmission electron microscope (TEM) image of the ZnS: Mn nanoparticles.

3.3 Photoconductivity study

3.3.1 Effect of field

Fig. 4(a) shows variation of dark current and photo current with applied voltage. The Figure 4(b) shows the variation in photo and dark current on an *ln-ln* scale. The *ln* (*I*) versus *ln* (*V*) for the photo and dark current curves are straight lines. Thus the variation of photo and dark current may be represented by power law *i.e. I α Vr* where *r* is the slope of a straight line. From the figure 4(b), it is observed that the behavior of dark current with the applied voltage is super-linear ($r > 1$). Variation of photocurrent with the applied voltage is also found to be super-linear. Super-linear behavior with $r > 1$ suggests that some charge carriers are being injected into the sample from one of the electrodes [11]. As the intensity of illumination increases, the variation of photocurrent with voltage remains super-linear but photosensitivity gets reduced which may be attributed to anomalous behavior of the photocurrent as explained in the section 3.3.3.

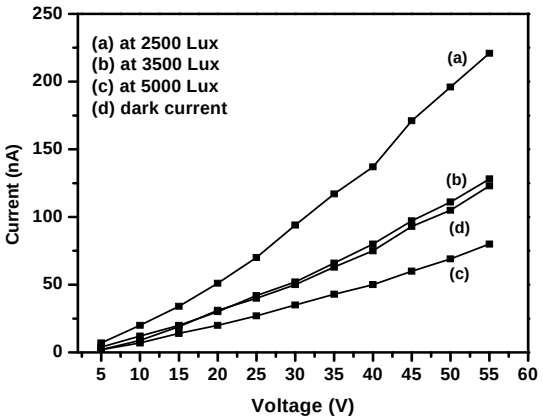

Fig. 4(a): Variation of photocurrent and dark current with voltage at different light intensities

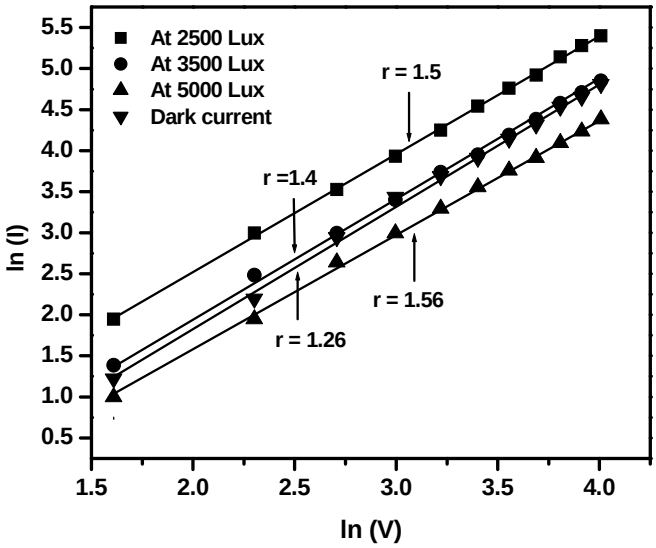

Fig. 4(b): Variation of photocurrent and dark current with voltage at different light intensities on ln-ln scale for ZnS: Mn2+ nanoparticles.

3.3.2 Effect of intensity

The Figure 5 illustrates the variation of photocurrent (*Ipc*) with light intensity (*IL*) for ZnS: Mn NPs on an *ln-ln* scale. With increased intensity of illumination, photocurrent is found to decrease. This anomalous behavior of photocurrent is evident by time-resolved rise and decay photocurrent spectra (Figure 6).

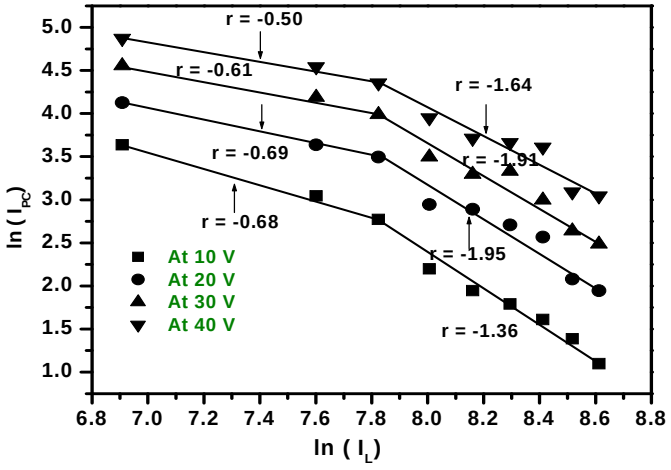

Fig. 5. Variation of photocurrent versus light intensity at different voltages.

3.3.3 Time-resolved rise and decay photocurrent spectra under visible illumination

Fig. 6 shows time-resolved rise and decay photocurrent spectra of ZnS: Mn nanoparticles under visible illumination with fixed illumination intensity and bias voltage. Mn doped ZnS nanoparticles are found to exhibit anomalous behavior of photo-current where photocurrent decrease even during steady visible illumination which may be explained on the basis of adsorption and desorption of O2 molecules. In the dark O2 molecules adsorbed on the surface of nanoparticles are converted to O2- by capturing electron. On visible illumination, the electrons

captured by negatively charged oxygen ions are released into conduction band which enhances the photoconductivity. During steady illumination, the reduction in photoconductivity may be attributed to re-adsorption of oxygen molecules [12-13]. Anomalous behavior has also been reported by Ahn et al., Nelson et al., Bera et al. in ZnO nanorods, TiO2 nanocrystalline films and ZnO nanowires respectively [14-16]. During steady illumination, the initial fast decay, which may be attributed to high rate of re-adsorption of oxygen molecules, is fitted separately following the equation $I = I0 \exp(-t/\tau d)$ which gives a time constant of 19 second (inset in figure 6). The rest of the curve is fitted entirely with another exponential equation of the above type and time constant in this case is found to be 767 second.

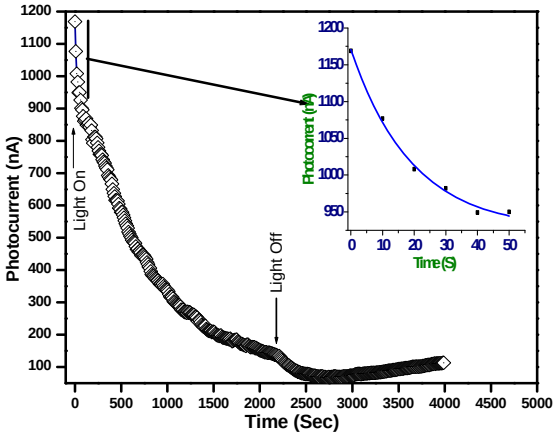

Fig. 6. Time-resolved rise and decay photocurrent spectra for ZnS: Mn under visible illumination. The inset shows the magnified graph of initial quick fall of the photocurrent with time and corresponding decay exponential fit.

3.3.4 Spectral analysis

Fig. 7 shows wavelength dependence of *Ipc* for ZnS: Mn nanoparticles. Different wavelengths of fixed intensity were obtained with the help of an Hg-lamp and filters. Measurements were made for a fixed incident photo flux and a fixed bias voltage. Photocurrent spectra of ZnS: Mn nanoparticles show apparently two peaks. The highest photocurrent is observed in UV region at approximately 366 nm and a broad peak centered around 577 nm. UV peak may be attributed to band to band transition [17]. The broad photocurrent peak may be attributed to electronic transitions between deep levels and conduction band. In this higher wavelength region, both excitation and quenching may take place and magnitude of the photocurrent would be the resultant value of the two mechanisms.

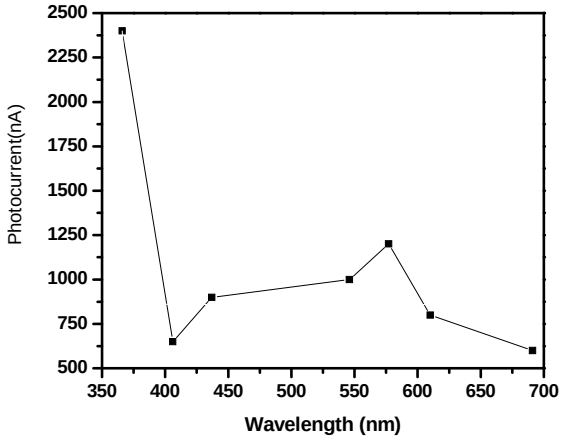

Fig. 7. Variation of photocurrent as a function of wavelength for 30V at room temp.

4. Conclusions

Mn doped ZnS nanoparticles were synthesized by co-precipitation method. The XRD pattern exhibits cubic (zinc blend) structure of ZnS. The size of nanoparticles is estimated to be 2.8 nm. ZnS:Mn nanoparticles are found to exhibit anomalous behavior of photocurrent where the photocurrent reduces even during steady illumination. Super-linear variation of photocurrent with voltage suggests injection of additional charge carriers into the sample from one of the electrodes.

References

[1] N Karar, F Singh, B. R Mehta, J. Appl. phy. **95** 48-52 (2004).

[2] Y. L Soo, Z. H. Ming, S. W Huang, Y. H. Kao, Phys. Chem. **87,** 4888-4892. (1983).

[3] Ai-wei Tang, Hui Jin Teng, Gao Yin-hao, Chun-jun Yan-bing Liang,Yong-sheng Wang, Materials Letters **61,** 2178-2181 (2007).

[4] Tadahiro Murakata, Kouske Aita, LiuHu.i Iha, Higuchi Takeshi Sato Shimio, Mater Sci. **42**, 6279 (2007).

[5] S. Devi, S.G. Prakash, PRAMANA-journal of physics **43**, 121-127 (1994).

[6] S. Devi, S. G Prakash, Indian J. Appl. Phys. **51,** 161-165 (1992).

[7] G. Murugadoss, B. Rajamannan, U. Madhusudhanan, Chalcogenide Letters **6,** 197-201 (2009).

[8] V.V. Deshpande, M. M Patil, S.C. Navale and Ravi, Bull. Matr. **28,** 205-207 (2005)**.**

[9] A.B. Cruz, Qing Shen, Taro Toyoda, Material Science and Engineering **C 25,** 761-765 (2005).

[10] Song Wei Lu, Burtrand Lee, Zhong LinWang, Wusheng Tong, Brent K.Wanger,Wounjhang Park, Christopher, J. Lum. **92,** 73 (2001).

[11] R. K. Srivastava and S. G. Prakash, Nat. Acad. Sci. Lett. **30,** 11-14 (2007).

[12] A. Bera, D Basak, Appl. Phys. Lett. **93**, 053102 (2008).

[13] Q.H. Li, T. Gao, Y. G. Wang, and T.H. Wang, Appl. Phys. Lett. **86,** 123117 (2005).

[14] S. E. Ahn, H. J. Ji, K. Kim, G. T. Kim, C. H. Bae, S. M. Park, Y.K. Kim, and J. S. Ha, Appl. Phys. Lett. **90,** 153106 (2007).

[15] S. J. Nelson, A. M. Eppler, and I. M. Ballard, J. Photochem. Photobiol, A1 **48,** 23-28 (2002).

[16] J. Carry, H. Carrere, M.L Kahn, B. Chaudret, X. Marie and M. Respaud, Semicond. Sci. Technol. **23,** 025003 (2008).