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Nanocrystalline $Zn_{0.9}Mn_{0.1}S$ Thin Film: Case Studies

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Abstract: Problem statement: The high quality of ZnS:Mn nanocrystals is important in nanotechnology industries. The perfect chemical procedure is significant to produce the best of nanocrystals. Hence, this research is concern on the good chemical method in processing manganese doped zinc sulphide nanocrystals. **Approach:** For the first step, Mn doped ZnS nanocrystals were synthesized by using sol gel spin coating method. After the crystals were obtained, the properties of $ZnS:Mn^{2+}$ on morphology, optical and electrical were determined by using Field Emission Scanning Electron Microscopy (FE-SEM), Ultra Violet Visible Spectroscopy (UV-Vis), Photoluminescence Spectrophotometer (PL) and current-voltage measurement (I-V). **Results:** The particle has diameter size around 22 nm. In this experiment it was found that the current increases with the increasing of applied voltage (-10 V to 10 V). UV-Vis spectra shows appearance of an absorption peak at 250 nm meanwhile in PL analysis spectra, the sample has been recorded at room temperature and two emissions peaks at blue and orange emissions were observed. **Conclusion:** Manganese doped zinc sulphide was successfully synthesized using sol gel spin coating method and it performs in good quality.

Key words: Sol gel, spin coating, zinc sulphide, manganese, optical, electrical

INTRODUCTION

Efficiently luminescing nanocrystalline semiconductors of Mn doped ZnS has attracted much attention due to their unique properties especially in optical and electrical part. Because of these characteristics, this semiconductor which has wider band gap (3.68 eV) is possible to be applied in optoelectronic applications such as optical switches, sensors, electroluminescence devices, biomedical tags, nanophosphors (Monica and Lokendra, 2010; Murugadoss *et al*., 2011; Xiying *et al*., 2011). Actually, Mn^{2+} -doped ZnS nanoparticles have been first reported in 1983 but this ZnS:Mn nanoparticles still have been studied because of their potential applications in future generation due to their extraordinary properties. In producing ZnS:Mn thin film, various technique especially chemical procedures have been mostly used, for example chemical bath deposition, electrochemical fabrication, solvotherma, microemulsion, sol gel method, organometallic methods, passivation procedure, liquid solid solution (Murugadoss *et al*., 2011; Xiying *et al*., 2011). Numerous compound semiconductor nanocrystals have been synthesized using sol gel method has often been reports previously (Yahya *et al*., 2009). Sol gel method is one of the inexpensive and easy method to produce thin film materials. In this paper, we mainly focused on the optical and electrical properties of Mn doped ZnS nanocrystals synthesized via sol gel spin coating method. The optical absorption properties found that the blue shift of the absorption edge is occurred due to quantum confinement effect. In this work, the Mn^{2+} ion is used as a dopant. This ion which has a d configuration can exhibits a broad emission peak (yellow-red emission) corresponding to the $^4T_1$-$^6A_1$ transition (Monica and Lokendra, 2010). While in electrical section, Mn doped ZnS was characterized during external illumination exhibited more current.

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MATERIALS AND METHODS

ZnS:Mn Nanocrystals preparation: Mn doped ZnS nanocrystals were synthesized by using sol gel spin coating method. To obtain thin film nanocrystals, zinc nitrate, thiourea, manganese acetate were diluted with propanol and distilled water. The mixed solution was stirred until a homogenous colorless solution was obtained. The ZnS:Mn thin film was prepared by spin coating on quartz slide and then transferred to programmable furnace and annealed at 400°C.

Optical and electrical measurement: Crystals are almost spherical in shape and their average sizes are in the range of 22 nm. These particles were observed by Field Emission Scanning Microscopy (FE-SEM) as shown in Fig. 1. FE-SEM micrograph of as-synthesized Mn doped ZnS nanocrystals annealed at 400°C is well-orderly aligned. The dried thin film nanocrystals were characterized by using Ultraviolet-Visible Spectroscopy (UV-Vis) and Photoluminescence Spectrophotometer (PL). Meanwhile in electrical measurement, thin film nanocrystals were measured in two conditions (with and without UV exposure). For determining current-voltage (I-V) measurement, electrical tape was used to make electric contacts at two ends side of glass (Fig. 2). Then the current of ZnS:Mn nanocrystals was measured at certain voltages (-10 V to 10 V).

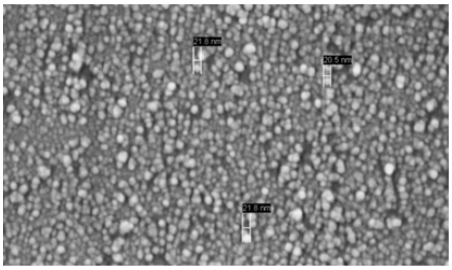

Fig. 1: FE-SEM image of nanocrystalline ZnS:Mn deposited on quartz glass

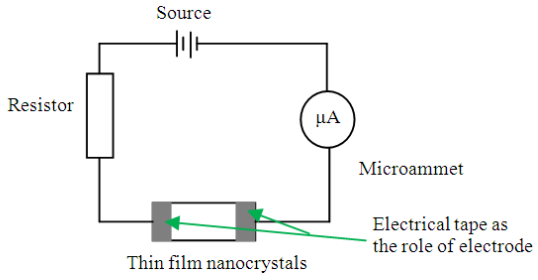

Fig. 2: Test bench circuit to measure I-V characteristics of ZnS:Mn nanocrystals in two conditions

RESULTS AND DISCUSSION

Optical properties: We show the basic characterization of this nanocrystals sample with a dopant concentration of x = 0.1% in term of UV-Vis absorption/transmission spectra and photoluminescence spectra in Fig. 3 as well as Fig. 5. The transmission spectra show above 90% transmittance in the wavelength range of 200-1000 nm. The UV-Vis absorption spectrum shows sharp absorption edge at 250 nm, which can be assigned to an excitonic transition and proves the existence of ZnS nanoparticles (Murugadoss *et al*., 2011). From the absorption edge of ZnS:Mn nanocrystals, we obtained a band gap of 4.78 eV which is different from the bulk band gap value of ZnS (3.68 eV). This implies that the band gap on 0.1% doping of Mn in the ZnS nanocrystals increases by 1.1 eV.

In obtaining the absorption characteristics of the sample, firstly the transmittance (T) at different wavelengths (λ) is measured and then absorption coefficients (α) at the corresponding wavelengths (λ) are calculated using the Beer-Lambert's relation as Eq. 1 (Maurya and Chauhan, 2011):

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (1)$$

where, d is the film thickness. The relation between the incident photon energy ($h\nu$) and the absorption coefficients (α) is given by the following relation (Maurya and Chauhan, 2011):

$$(\alpha h\nu)^{1/m} = c\left(h\nu - E_g\right) \quad (2)$$

Where:

c = A constant

E_g = The bandgap of the material and the exponent m depends on the type of the transition

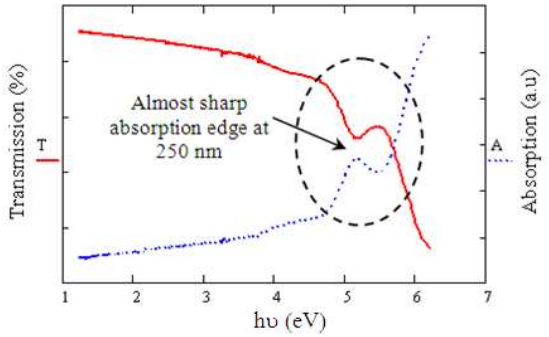

Fig. 3: Optical absorption and transmission spectra for $Zn_{0.9}Mn_{0.1}S$

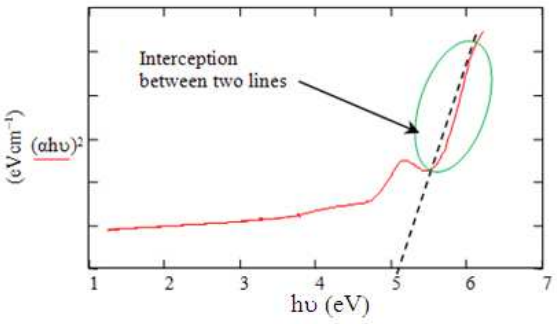

Fig. 4: Calculation of optical band gap from the UV-Vis absorption/transmission spectra by using $(\alpha h\nu)^{1/m} = c(h\nu - E_g)$ where *c* is the constants E_g is the bandgap of the material and the exponent m depends on the type of the transition

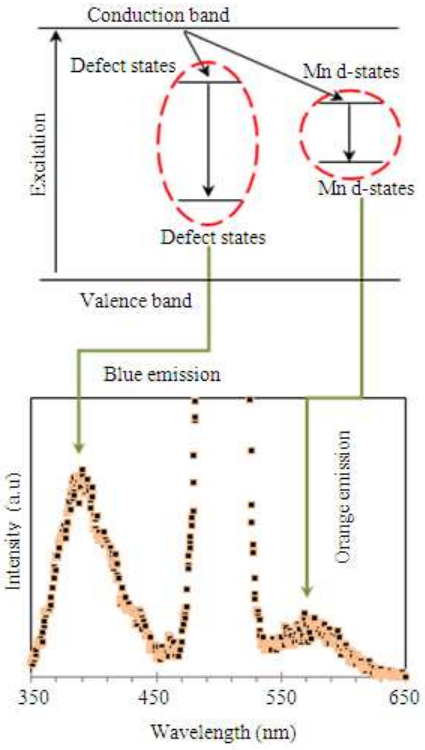

Fig. 5: Photoluminescence spectra for Mn doped ZnS at x = 0.10%

In this calculation, m is considered as ½ corresponding to the direct transition. To measure the direct band gap value, $(\alpha h\nu)^2$ versus hν is plotted and it is shown in Fig. 4. By extrapolating the straight portion of the graph on hν axis, the optical band gap is measured. The obtained values of the bandgap of ZnS:Mn nanoparticles (5.12 eV) are higher than that of the bulk value of ZnS (3.68 eV) (Murugadoss *et al*., 2011).

Figure 4 showed the room temperature emission spectra of $Zn_{0.9}Mn_{0.1}S$ nanocrystals under excitation of 250 nm. It was found that the emission band consists of two broad peaks at the energies of 2.1 eV (590 nm) and 2.9 eV (390 nm). The first peak arises due to transitions forming the orange band of the luminescence in ZnS with the possible contribution of the intracentral transitions $^4T_1$ (excited) -$^6A_1$ (ground) of Mn^{2+} ion. Sokolov et. al found that Mn incorporated into the ZnS lattice leads to the Mn based orange emission. Thus it can be concluded that the Mn ions in our sample is indeed incorporated into ZnS nanocrystals. The appearance of the second peak at the energy of 2.9 eV is caused by the presence of Mn atoms. These can be ascribed to s-p exchange interaction. It can be explained when Mn^{2+} ions were incorporated into ZnS lattice and substituted for host cation sites, the mixing between s-p electrons of the host ZnS and the d electrons of Mn^{2+} occurred and made the forbidden transition of $^4T_1$-$^6A_1$ partially allowed; resulting in the characteristic emission of Mn^{2+} as previously reported by Xiying et. Al (Xiying *et al*., 2011).

Electrical properties: Based on Fig. 6 we can observed that I-V characteristics of nanocrystals thin film exhibited straight line when the current is flowing through the circuit for both condition. This line shows almost constant ratio between voltage and current for both negative and positive values which Ohm's law is obeyed. From the same figure, we can see clearly that for dark condition, current is less than the second condition which nanocrystals thin film was exposed with 10% intensity of UV during I-V measurement. The increment of photocurrent can be related with generation and recombination theory. Sze explained the increasing current when exposed to UV corresponds to the increasing electron-hole pairs uniformly throughout the sample. The initial carriers (minority) recombined with the majority carriers and that is why the carrier concentrations are above from their normal equilibrium values. These majority carriers were known as photogenerated carriers. Based on Fig. 6, we can determine the resistance for dark and photo conditions by using ohm's law. From calculation, dark condition exhibited lower resistance as compared to photo condition with 9.1 MΩ and 12.5 MΩ, respectively. Furthermore, from I-V measurement, film conductivity can be calculated by using equation $\sigma = Il/SU$ where I is the current, l-the sample of length, S-area of cross section, U-voltage. The conductivity of Mn doped ZnS nanocrystal layers is in the range of 10^{-5} $(\Omega)^{-1}$.

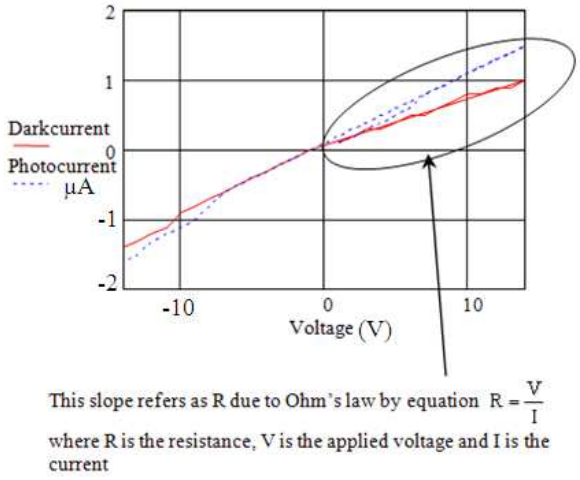

Fig. 6: Current-voltage characteristics for ZnS:Mn nanocrystals exposure with and without UV

CONCLUSION

In the summary, two broad photoluminescence emissions (blue and orange emissions) are obtained from 22 nm sizes Mn doped ZnS nanocrystals synthesized by sol gel method. The blue shift in the band gap of the synthesized nanocrystals is observed from the bulk band gap value of ZnS owing to the quantum confinement effect. This method was found to be an efficient technique for producing current-enhanced ZnS:Mn^{2+} nanocrystals value due to applied voltage for both conditions.

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