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Effect of Gamma Irradiation on Structural and Optical Properties of ZnO/Mesoporous Silica Nanocomposite

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***Abstract*—**The effect of gamma ray irradiation on morphology and optical properties of ZnO/Mesoporous silica (MPS) nanocomposite was studied. The ZnO/MPS nanocomposite was irradiated with gamma rays of doses 30, 60, and 90 kGy and dose-rate of irradiation was 0.15 kGy/hour. Irradiated samples are characterized with FE-SEM, FT-IR, UV-vis, and Photoluminescence (PL) spectrometers. SEM pictures showed that morphology changed from spherical to flake like morphology. UV-vis analysis showed that the band gap increased with increase of gamma ray irradiation dose. This enhancement of the band gap is assigned to the depletion of oxygen vacancies with irradiation. The intensity of PL peak decreased gradually with increase of gamma ray irradiation dose. The decrease in PL intensity is attributed to the decrease of oxygen vacancies at the interface due to poor interface and improper passivation between ZnO/MPS.

***Keywords*—**ZnO nanoparticles, photoluminescence, porous silicon, nanocomposites.

I. Introduction

ZnO is one of the important II-VI semiconductors which is having potential applications in transparent conductive contacts, dye-sensitized photo electrochemical solar cells, ZnO/Cu_2O solar cell hetero-junctions, laser diodes, ultraviolet lasers, thin film transistors, gas sensors, and optoelectronic and piezoelectric applications to surface acoustic wave devices [1]-[4] due to its peculiar properties such as wide and direct band gap of 3.37 eV and large exciton binding energy of 60 meV. The properties of the ZnO nanostructures have been significantly improved by embedding in various types of host materials such as mesoporous silica (SBA-15, MCM-41 and MCM-48), zeolites, activated carbon, etc. [5]. Among these, ZnO/MPS nanocomposites have potential applications as inorganic solid state white light sources (ISSWLS) [5]. SSWLS can be achieved by combining the orange-red emission of MPS [6] with the UV-blue and green emission from the excitons and deep level defects from the ZnO nanocrystallites.

The defects in ZnO can be altered by various treatments like thermal annealing in controlled environment or by ion beam irradiations such as swift heavy ion (SHI) irradiation [7]. Defects can also be introduced by electron and neutron irradiations and they can be studied by electron paramagnetic resonance (EPR) [8]. The PL spectrum of ZnO typically exhibits a green luminescence (GL) band similar to the yellow luminescence in GaN. Both the Zn and O vacancies have been proposed to be the defects responsible for this GL band. It is known that defects in ZnO nanostructures control the PL and hence influence the performance of the optoelectronic devices and sensors. Hence, understanding the origin of defects and their behavior is of great importance for ZnO inclusion in optoelectronic devices.

In this manuscript, we reported the effect of gamma ray irradiation on structural, morphological and optical properties of ZnO/MPS nanocomposite is reported. The ZnO/MPS sample was irradiated with different doses (30, 60, and 90 kGy and dose-rate is 0.15 kGy/hour) of gamma radiation. In particular, the effect of gamma radiation on PL of ZnO/MPS nanocomposite was studied.

II. Experimental Procedure

MPS was prepared by the method reported by Grun et al. The preparation of ZnO/MPS nanocomposite was similar to the method described else-where [9]. To prepare ZnO/MPS nanocomposite, certain amount of zinc nitrate was dissolved in 50 ml of ethanol and stirred at 80 °C for 2 h until it appeared clear and stable. To this solution, 4 ml of Triethanolamine (TEA) is added and stirred for 1 h, and then, 0.9 g of MPS is added and stirred for another 0.5 h. To obtain the fine ZnO nanoparticles, TEA has been used as catalyst and stabilizing agent. Finally, suitable quantity of water and ethanol mixture was added. The solution is stirred for 4h and aged for 24 h. The resultant product was filtered, washed with ethanol several times. After this, sample was calcined in air at 600 °C with a rate of 2 °C/min and stayed at that temperature for 3h to obtain ZnO/MPS nanocomposite.

III. Characterizations

Gamma irradiation was performed using Gamma Chamber 900 (GC-900) made by Board of research & Isotope Technology (BRIT) a unit of BARC, India. The calibrated ^{60}Co based GC-900 with a central dose of 0.15 kGy/hr was used in the present study. Morphology of the nanocomposite was studied by using a JEOL JSM 6390 Scanning Electron Microscope with high resolution of 3 nm and ZEISS FE-SEM having SEM Energy Dispersive Spectroscopy (EDS) attachment. To get the accurate particle size of ZnO

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nanoparticles embedded inside the pores of MPS, JEOL 3010 High Resolution Transmission Electron Microscope (HR-TEM) is used. UV–vis absorption spectrometer was used to find absorption edge of ZnO nanoparticles incorporated in MPS. FT-IR spectra on KBr pellets were measured on a Bruker Optics FT-IR spectrometer Model: Tensor 27. The PL measurements were performed on Jobin Yuon spectro fluorometer, Model: FLUOROLOG-FL3-11 with wavelength resolution of 0.2 nm at room temperature. Xenon arc lamp of 450 W was used as the excitation light source to record excitation and emission spectra of samples. All PL spectra in this study were acquired by exciting the samples at an excitation wavelength of 320 nm.

IV. Results and Discussion

Fig. 1 shows the FE-SEM pictures of pristine ZnO/MPS nanocomposite and irradiated nanocomposite. It is evident from the pictures that pristine ZnO/MPS nanocomposite shows spherical morphology. However, the morphology of irradiated samples is not spherical. The spherical morphology is completely destroyed as the dosage of gamma radiation increased. It can be seen that the irradiated ZnO/MPS silica is having the flake like morphology.

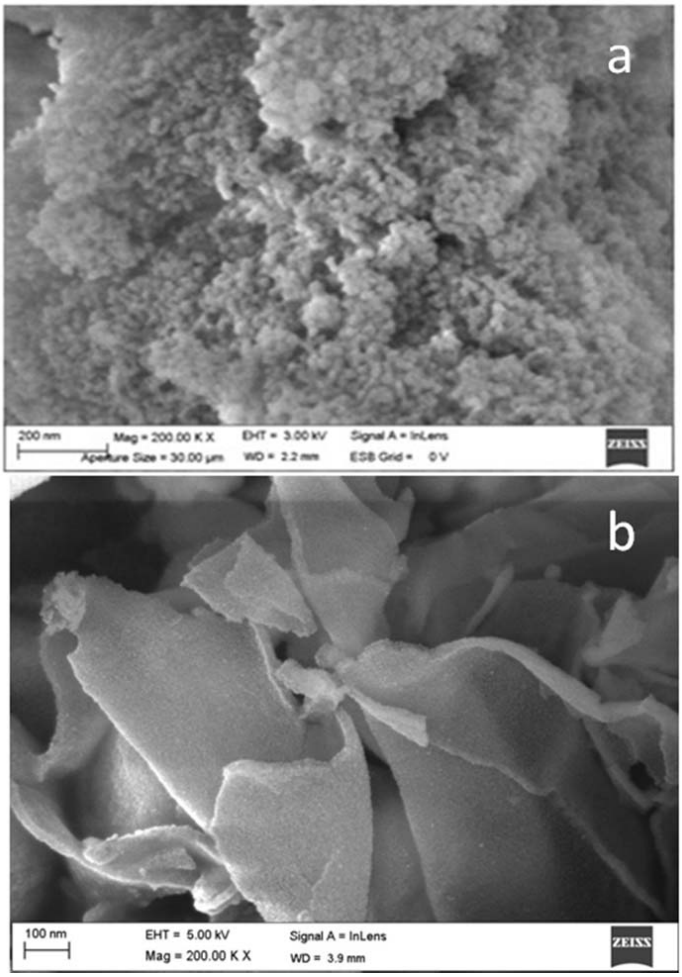

Fig. 1 FE-SEM pictures of (a) pristine ZnO/MPS and (b) ZnO/MPS nanocomposite irradiated with gamma rays

The infrared spectra of pristine ZnO/MPS nanocomposite and ZnO/MPS nanocomposite irradiated with different doses of gamma radiation are shown in Fig. 2. The broad peak positioned at around 3450 cm^{-1} corresponds to stretching vibrations of–OH groups. Another distinct peak at around 1630cm^{-1} observed is assigned to the bending modes of adsorbed water [9]. Two more bands at 1092 and 808 cm^{-1} are corresponding to asymmetric and symmetric modes stretching of Si–O–Si lattice vibrations [9]. It is clear that there are no significant changes in the FT-IR spectra of ZnO/MPS nanocomposite even after gamma irradiation.

The UV-vis absorption spectroscopy measurements on pristine ZnO/MPS and irradiated ZnO/MPS nanocomposites are presented in Fig. 2. For all the samples, the absorption peak is positioned below 200 nm (6.2 eV), and such a huge band gap is not expected for ZnO nanoparticles. Hence, it is quite reasonable to assign this absorption peak to MPS. The absence of absorption peak of ZnO nanoparticles might be due

to their low concentration. Hence, the absorption of MPS is dominating in the absorption spectra. It can also be seen from the figure that the absorption peak is gradually blue shifted as the gamma ray dose increased. This means that the band gap of the MPS is changed with the irradiation with gamma rays. One reason for the enhancement of band gap could be the loss of ordered structure with irradiation. Another important reason is the depletion of oxygen vacancies with irradiation [7].

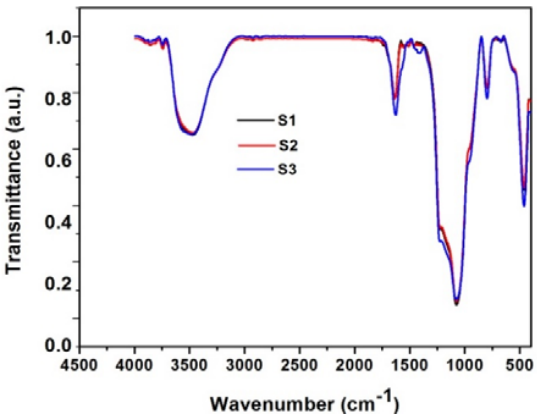

Fig. 2 FT-IR Spectra of ZnO/MPS nanocomposite irradiated with different doses of gamma radiation

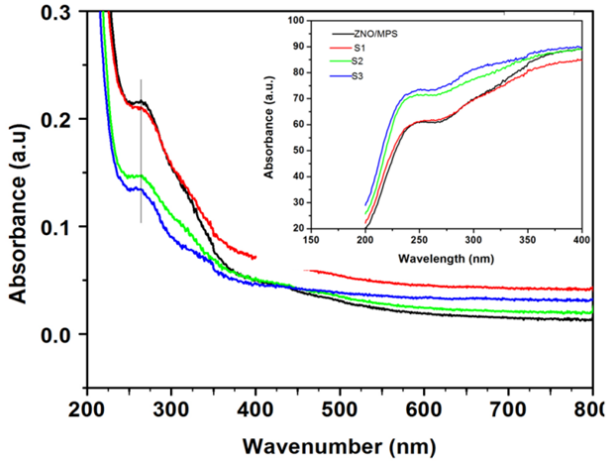

Fig. 3 UV-vis spectra of pristine ZnO/MPS nano-composite and ZnO/MPS nanocomposite irradiated with different doses of gamma radiation

Fig. 4 shows the PL spectra of ZnO/MPS nanocomposite irradiated with different doses of gamma radiation. The detailed analysis of the PL spectra of ZnO/MPS nanocomposite can be found elsewhere [9]. Fu et al. suggested three phenomena responsible for enhancement in emission intensity in ZnO nanoparticles loaded in porous SiO_2 [10]. They are surface passivation of ZnO nanoparticles, formation of interface states between ZnO and SiO_2 and excitation process in the SiO_2. However, the broad emission peak positioned around 400 nm is believed to be due to oxygen vacancies present at the interface of ZnO and MPS [9]. The PL of irradiated nanocomposite shows a peak at 363 nm and another peak at 385 nm. The peak at 363 nm is could be from MPS and 385 nm peak is due to the band gap emission from the ZnO nanoparticles embedded in MPs matrix. From the FE-SEM and UV-vis data, it is clear that morphology and ordered structure of MPS silica is altered. Consequently, the interface between ZnO nanoparticles and MPS could be destroyed due to the irradiation with gamma rays. As a result of the poor interface, the surfaces of the ZnO nanoparticles would not be properly passivated. The poor interface might have given rise to the enhancement of non-radiative transitions and thereby decreasing the UV emission from the ZnO nanoparticles encapsulated in MPS matrix. Hence, it is concluded that oxygen vacancies in ZnO/MPS nanocomposite are decreased with gamma ray irradiation.

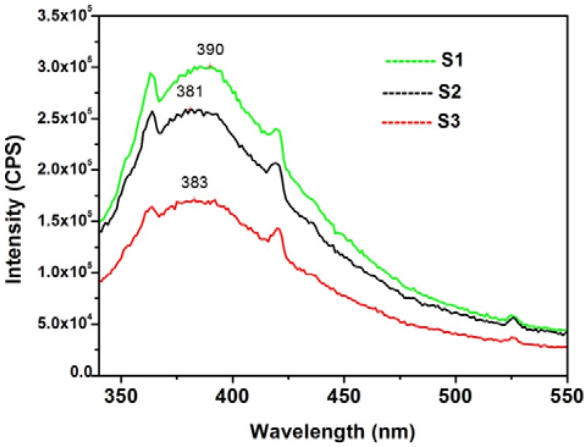

Fig. 4 PL spectra of ZnO/MPS nanocomposite irradiated with different doses of gamma radiation

V. Conclusion

The effect of gamma ray irradiation on morphology and optical properties of ZnO/MPS nanocomposite are studied. FE-SEM pictures showed that the spherical morphology of the ZnO/MPS nanocomposite has been changed with gamma ray irradiation. UV-vis absorption results indicate the band gap of MPS is increased with irradiation. This enhancement of the band gap is assigned to the depletion of oxygen vacancies with irradiation. The intensity of PL peak decreased gradually with increase of gamma ray irradiation dose. The decrease in PL intensity is attributed to the decrease of oxygen vacancies at the interface due to poor interface and improper passivation between ZnO/MPS.

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