

Swift heavy ion irradiation effect on Cu-doped CdS nanocrystals embedded in PMMA

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Abstract. Semiconductor nanocrystals (NCs) have received much interest for their optical and electronic properties. When these NCs dispersed in polymer matrix, brightness of the light emission is enhanced due to their quantum dot size. The CdCuS NCs have been synthesized by chemical route method and then dispersed in PMMA matrix. These nanocomposite polymer films were irradiated by swift heavy ion (SHI) (100 MeV, Si⁺⁷ ions beam) at different fluences of 1×10^{10} and 1×10^{12} ions/cm² and then compared their structural and optical properties by XRD, atomic force microscopy, photoluminescence, and UV-Vis spectroscopy before and after irradiation. The XRD spectra showed a broad hump around $2\theta \approx 11.83^\circ$ due to amorphous PMMA and other peaks corresponding to hexagonal structure of CdS nanocrystals in PMMA matrix. The photoluminescence spectra shows a broad peak at 530 nm corresponding to green emission due to Cu impurities in CdS. The UV-Vis measurement showed red shift in optical absorption and bandgap changed from 4.38–3.60 eV as the irradiation fluency increased with respect to pristine CdCuS nanocomposite polymer film.

Keywords. Nanocrystals (NCs); ultra violet-visible (UV-Vis); polymethylmethacrylate (PMMA); X-ray diffraction (XRD); photoluminescence (PL).

1. Introduction

Semiconductor CdS nanocrystals (NCs) have been widely synthesized and studied because they have unique properties and are suitable for photo reactivity and photo catalyst applications. The properties of CdS NCs are driven mainly by two factors, viz. large surface to volume ratio and a drastic change in electronic structure of material due to quantum mechanical effects with decreasing particle size (Prabhu and Khadar 2005). The ability to tune the bandgap of CdS by doping the impurity such as Cu, Ag is another important factor which suits any specific application. Copper as an activator may occupy various sites in crystalline lattice of CdS NCs as a result some additional emission centres create and depending on their concentration, either blue or green emission may occur (Bhargava *et al* 1994; Huang *et al* 1997; Xu *et al* 1998; Lee *et al* 2003; Mohanta *et al* 2003, 2006a; Kumar and Choudhary 2007). Que *et al* (1998) reported that Cu as an acceptor defect could give rise to localized level near to the valence band and luminescence arises from radiative recombination of electrons in conduction band with holes trapped at localized acceptor level above the valence

band of CdS. Lui *et al* (2006) suggested that even small quantities of Cu incorporation result in variations in the PL and photoconductive properties. Doping of these impurity ions has been done by different techniques such as wet chemical process, co-evaporation, sol-gel method, thermal evaporation etc. These doped NCs have a wide range of applications in electroluminescence devices, light emitting displays and optical sensors (Mohanta *et al* 2004). Now a days the combination of semiconductor NCs with polymer matrix has received much attention due to their nonlinear optical properties. The advantage of such materials in polymers can be two-fold, first the tiny dots would enhance life of the polymer host and second the enhancement in light emission due to presence of quantum dots (Khanna and Singh 2007). The polymers prevent particles from agglomeration and provided a stable medium. A wide variety of materials modification in polymers has been studied by using ion irradiation technique. While traversing through matter, SHI loses its energy in two ways, nuclear energy losses (S_n) due to elastic collisions of projectile ions with atoms of the solids and electronic energy losses (S_e) due to inelastic collisions with the electrons of the solid medium. The electronic process, S_e , involves MeV energies and use for introducing nanoscale defects (Columnar defects) as well as surface modifications. The interaction of high energy heavy

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ions with polymer, is associated with a considerable amount of linear electronic energy transfer (LET) by interactions (glancing as well as knock-on) with the orbital electrons of the target material, resulting in transient high local energy density deposition along the ion path. The knocked-out target electrons may transfer their energy into polymer matrix either by collision with other electrons or by electron phonon coupling. Consequently, huge electronic excitation and subsequent ionizations along the ion path/track triggers remarkable reorientation in the pristine structure leading to the ion beam modified zone. Therefore, the passage of SHI may give the information related to damage such as size, shape and structure of defects which changes the fluorescence property of semiconductor and this strongly depends on the mass of the incident ion, the irradiation energy and the fluence (Lesueur *et al* 1993; Avasthi 2000; Kanjilal 2001).

In this paper, we report the synthesis process of Cu doped CdS NCs and preparation of CdCuS doped nanocomposite polymer films by solution cast method. These nanocomposite polymer films were characterized by PL, UV-Vis spectroscopy, XRD and AFM techniques before and after SHI irradiation.

2. Experimental

2.1 Materials

Cadmium chloride (CdCl_2) and copper chloride (CuCl_2) were obtained from Sigma-Aldrich (99.9%), dichloromethane was purchased from Merch Specialties Private Limited, Mumbai and polymethylmethacrylate (PMMA) granules were purchased from M/s Gadra Chemicals, Bharuch. All chemicals were used as received.

2.2 Synthesis of nanoparticles

The NCs of CdCuS were synthesized by colloidal route method using Kibb's apparatus as shown in figure 1. Aqueous solution of cadmium chloride (CdCl_2) and copper chloride (CuCl_2) were prepared in deionized water. On reacting this mixture with H_2S gas for 1 h, brownish solution was obtained. The precipitate was then washed with distilled water, filtered and dried in vacuum (Tripathi *et al* 2007).

2.3 Preparation of polymer nanocomposite film

The nanocomposite polymer films of $40\ \mu\text{m}$ ($\pm 2\ \mu\text{m}$) thickness were prepared by dispersion of (0.02 wt.%) CdCuS NCs in 20 ml of PMMA solution where dichloromethane was used as solvent (Awasthi *et al* 2006). This solution was stirred for 3 h on magnetic stirrer at room temperature and then purged in flat bottom petri dish

floated over mercury for 24 h as shown in figure 2. The nanocomposite film was peeled off from Petri dish and dried in vacuum for 2 h to completely remove the solvent.

2.4 Swift heavy ion irradiation (SHI)

As prepared nanocomposite polymer film was cut into the size of $1 \times 1\ \text{cm}^2$ for SHI irradiation. These samples were irradiated by Si^{+7} ion beam (100 MeV energy) in the material science chamber under high vacuum ($\sim 10^{-6}$ mbar), at 1×10^{10} ions/ cm^2 and 1×10^{12} ions/ cm^2 , available from the 15 UD tandem pelletron accelerator at IUAC, New Delhi, India (Mohanta *et al* 2006b).

2.5 Characterization

The XRD measurements of nanocomposite polymer films were performed with powder X-ray diffractometer. The optical absorption measurements were performed using a Hitachi-330 spectrophotometer. Photoluminescence were carried out using He-Cd laser at a excitation wavelength, 325 nm and the surface topography of CdS films before and after irradiation was analysed with an atomic force microscopy (AFM), Digital Instruments Nanoscope III a. Measurements were taken in contact mode.

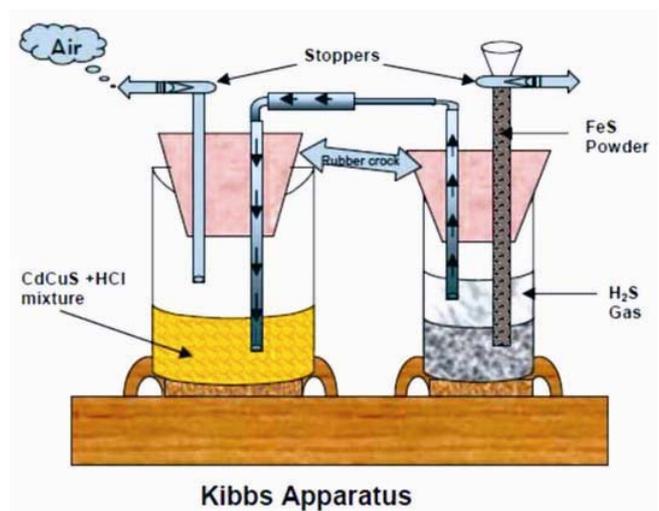


Figure 1. The schematic diagram of Kibb's apparatus.

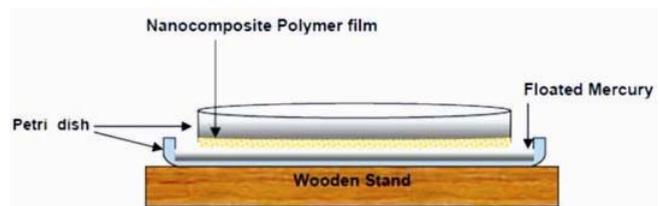


Figure 2. Schematic diagram of solution cast method for preparing the nanocomposite polymer film.

3. Results and discussion

3.1 X-ray diffraction

The structural characteristics of nanocomposite polymer films before and after irradiation are shown in figure 3. The XRD spectra shows a broad hump at $2\theta \approx 11^\circ$ corresponding to amorphous nature of PMMA and other peaks appear at $2\theta \approx 24.917^\circ$, 26.627° , 28.326° , 43.898° , 48.117° , these correspond to hexagonal structure of CdS NCs as compared with standard JCPDS software. After irradiation reduction in peak intensity has been observed for all these samples (Liu *et al* 2003; Wang *et al* 2007).

3.2 Optical absorption

Figure 4 shows the absorbance vs wavelength spectra of CdCuS doped polymer film before and after irradiation. It is observed that the optical bandgap decreased after irradiation, possibly due to the combined effect of change in the grain size or agglomeration of quantum dots due to the interaction of heavy ion with nanocomposite polymer film. It has also been observed that the bandgap shifts from 4.38 eV (figure 4a) to 3.60 eV (figure 4c) as the fluence increases. The increase in grain size can be attributed to the fact that during irradiation the kinetic energy of the electrons ejected from the target atom is transferred to the compound lattice by electron-phonon interaction, which increases the local lattice temperature over the melting point of the material. We may suppose that the heat gets confined within the grain volume. This gives rise to non equilibrium state which, as a conse-

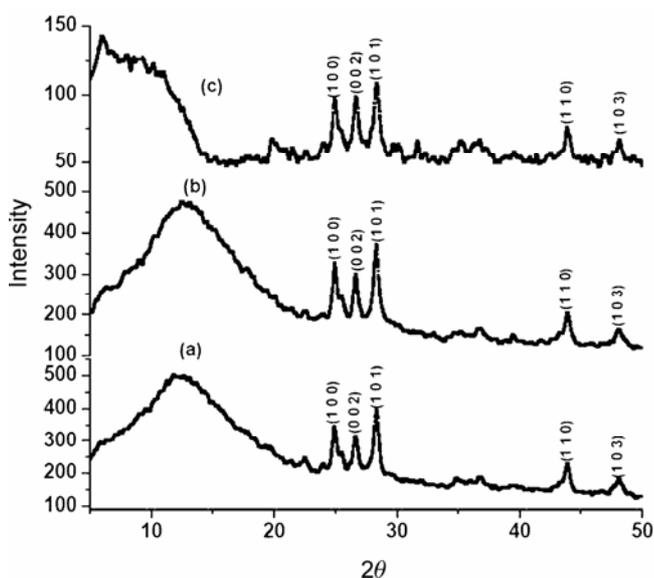


Figure 3. XRD pattern for (a) virgin CdCuS in PMMA, (b) CdCuS in PMMA irradiated at 1×10^{10} ions/cm² and (c) CdCuS in PMMA irradiated at 1×10^{12} ions/cm².

quence, raises the volume of the grains resulting in grain agglomeration on irradiation.

3.3 Photoluminescence

Figure 5 shows PL spectra of pristine and irradiated nanocomposite polymer film. Figure 5(a) shows a luminescence peak, ≈ 530 nm, corresponding to the energy of 2.33 eV, which is less than the bandgap energy. It is important to quote here that instead of well-defined peaks,

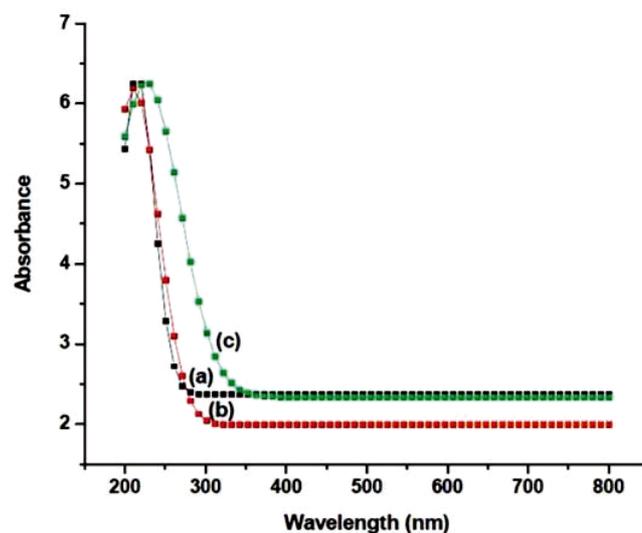


Figure 4. Optical absorption spectra of (a) virgin CdCuS in PMMA, (b) CdCuS in PMMA irradiated at 1×10^{10} ions/cm² and (c) CdCuS in PMMA irradiated at 1×10^{12} ions/cm².

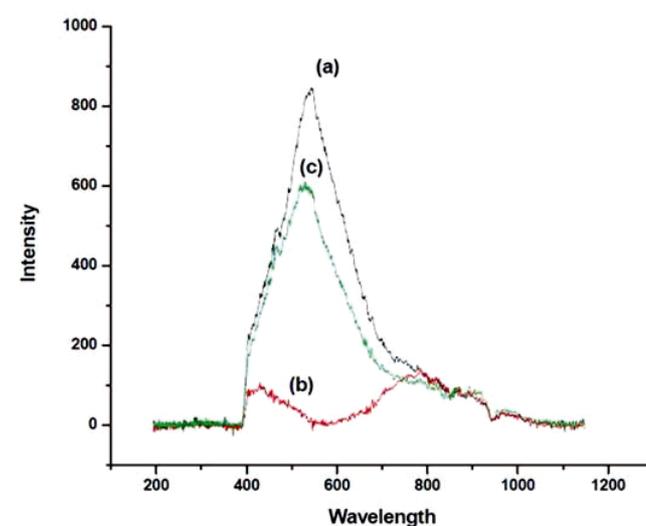


Figure 5. PL spectra of (a) virgin CdCuS in PMMA, (b) CdCuS in PMMA irradiated at 1×10^{10} ions/cm² and (c) CdCuS in PMMA irradiated at 1×10^{12} ions/cm².

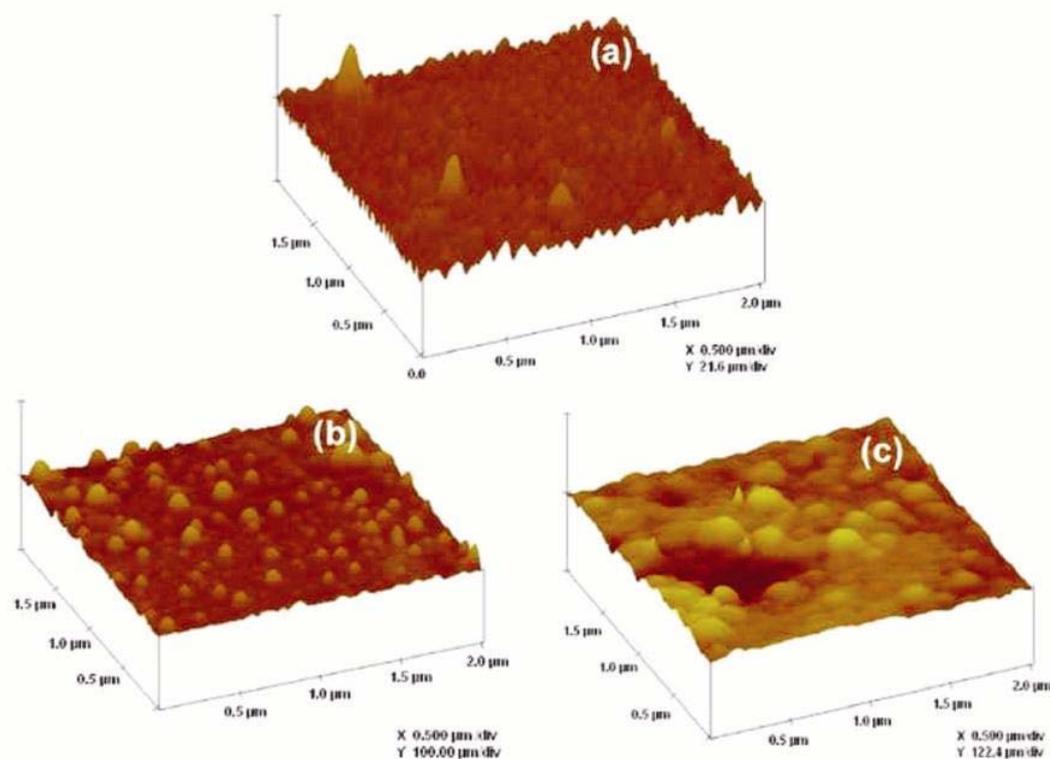


Figure 6. The atomic force micrographs of (a) virgin CdCuS in PMMA, (b) CdCuS in PMMA irradiated at 1×10^{10} ions/cm² and (c) CdCuS in PMMA irradiated at 1×10^{12} ions/cm².

the PL reveals broad band. Therefore, it may conclude that the band edge emission and deep trap emission are very much competitive due to heavy ion impact and finally merge into a single well-defined peak. As shown by our results, there is initial blue shift in the lower excitation wavelength which may attribute to enhanced non-radiative recombination due to additional deep levels at ion fluence of 1×10^{10} ions/cm². At higher ion fluence of 1×10^{12} ions/cm², the additional luminescence centres may form, which may trap electrons and holes and the fluorescence efficiency is increased, therefore, the emission peak shifts to longer wavelengths.

3.4 Atomic force microscopy

The AFM micrographs shown in figure 6 indicate a clear picture of the surface in nanoscale dimensions ($2 \times 2 \mu\text{m}$ scan area), where the morphology predicts compact grain structure. From the micrograph shown in figure 6(a), it is evident that the surface of pristine nanocomposite polymer film is composed of dense grains. It has been observed that most of nanocrystals agglomerate and form an uneven cluster structure after irradiation as shown in figures 6(b) and (c). The effect of SHI irradiation on the surface roughness has also been investigated. The root-mean-square (RMS) surface roughness has been used to better understand the effect of irradiation. The measured

RMS values for $2 \times 2 \mu\text{m}$ scan area is 1.313 nm for pristine films. While for irradiated films at 1×10^{10} and 1×10^{12} ions/cm² fluence RMS values are 3.906 nm and 6.27 nm, respectively. This clearly shows that the surface roughness increases after irradiation.

4. Conclusions

The present study reveals that on SHI irradiation there are significant modifications in the structural and optical properties of nanocomposite polymer films. The stability of embedded CdCuS nanocrystals is more than that of its powder form. XRD confirms the hexagonal structure of CdS without any additional peak corresponding to copper. In photoluminescence the emission peak is observed in green region due to presence of Cu in CdS. In optical absorption bandgap decreases with the fluence, this may be attributed to the formation of conjugated system of bonds due to bond cleavage and reconstruction. The effect of SHI irradiation on the surface roughness has also been investigated and it is observed that the surface roughness increases after irradiation.

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