Irradiation induced grain growth and surface emission enhancement of chemically tailored ZnS : Mn/PVOH nanoparticles by Cl^{+9} ion impact

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Abstract. Manganese doped zinc sulfide nanoparticles are fabricated on polyvinyl alcohol dielectric matrix. They are bombarded with energetic chlorine ions (100 MeV). The size of the crystallites is found to increase with ion fluence due to melting led grain growth under ion irradiation. The increased size as a result of grain growth has been observed both in the optical absorption spectra in terms of redshift and in electron microscopic images. The photoluminescence (PL) study was carried out by band to band excitation (I_{ex} = 220 nm) upon ZnS : Mn, which results into two emission peaks corresponding to surface states and Mn^{+2} emission, respectively. The ion fluence for irradiation experiment so chosen were 1×10^{11}, 5×10^{11}, 5×10^{12} and 10^{13} Cl/cm^2.

Keywords. Quantum dot; irradiation; redshift.

1. Introduction

Semiconductors with dimensions in the nanometer realm are important because their electrical, optical and chemical properties can be tuned with particle size. During recent years, fabrication of nanosized crystallites in the form of capping (Mahamuni *et al* 1993), coating and embedding in glass (Borelli *et al* 1987; Yan and Parker 1989; Tanaka *et al* 1992) as well as in polymer matrix (Wang *et al* 1987, 1990; Henglein 1988; Deki *et al* 1999) by various methods have been reported. Interest in properties of sulfide nanocrystals stems from their potential use in nonlinear optical devices (Norris and Bawendi 1996). A large number of reports relating to structural, spectroscopic and luminescence properties (Bhargava and Gallagher 1994; Bhargava *et al* 1994; Wang and Zunger 1998; Schoos *et al* 1999; Nanda *et al* 1999; Balandin *et al* 2000; Dinsmore *et al* 2000; Qadri *et al* 2001) are available for both Mn-doped and undoped metal sulfide nanoparticle systems. Synthesis of ZnS, CdS etc by ion implantation have been reported by various workers (Budai *et al* 1997; Bonafos *et al* 1998; Meldrum *et al* 1999). On the other hand, understanding ion–matter interaction is an important issue in materials science because of nature of electronic and nuclear energy losses. Accordingly, two models viz. ion spike model and thermal spike model are in balance. Grain evaporation and grain fragmentation have been observed in nanometric powder systems (Berthelot *et al* 1998), whereas radiation resistant

behaviour was noticed in case of Sr-ferrite nanoparticle system (Shinde *et al* 1998). In this context, ion impact on embedded nanoparticle system is interesting due to suppression of weak link boundaries which is inherent in case of nanostructured films. Recently, we have investigated optical absorption study of ion irradiated ZnO quantum dots (Mohanta *et al* 2002) and matrix dependent grain growth and grain fragmentation effects in CdS systems (Mohanta *et al*, to be published).

After growing Mn doped zinc sulfide nanoparticles in a aliphatic polymer viz. polyvinyl alcohol, we have irradiated them with 100 MeV chlorine beam at doses 1×10^{11}, 5×10^{11}, 5×10^{12} and 10^{13} Cl/cm^2. The intention of Mn doping was to correlate luminescence response with ion fluence. Optical absorption spectra of pristine and exposed samples were analysed in consistency with high resolution scanning and transmission micrographs. Photoluminescence was carried out to reveal surface emissions and size dependent emission spectra.

2. Experimental

The polymers being useful materials for the protection of nanosized particles against agglomeration and precipitation (Hirari and Toshima 1986), we have selected an aliphatic polymer to embed ZnS nanoparticles. First, an aqueous solution of 0·15 M $ZnCl_2$ and 0·0045 M $MnCl_2$ was made such that the molar ratio of Mn to Zn was 3 : 100. The aqueous solution was mixed into as prepared 2·5 wt.% transparent polyvinyl alcohol (PVOH) matrix under ~ 200 rpm stirring condition. Temperature was

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Table 1. Stopping energies and projectile range of energetic chlorine beam through ZnS : Mn/PVOH.

Energy (MeV)	Electronic energy loss, $S_e = (dE/dx)_e$ (eV/Å)	Nuclear energy loss, $S_n = (dE/dx)_n$ (eV/Å)	Projectile range, R (μm)
10^{-2}	11·19	63·32	$1·02 \times 10^{-2}$
10^{-1}	33·02	58·21	$7·82 \times 10^{-2}$
1	249·0	20·08	$7·63 \times 10^{-1}$
10	502·5	3·92	3·30
100	553·0	0·58	18·07

maintained to 65°C. Into this, dropwise injection of Na_2S solution led to growth of ZnS quantum particles in PVOH matrix. Also, the ZnS nanoparticles are synthesized by grinding as received ZnS powder (99% pure, Lab Chem) mechanically, followed by sintering (~ 900°C) and finally quenching into ice-cold PVOH matrix. Colourless or faint milky coloured Mn doped ZnS samples were developed on the laboratory glass slides. The samples of size 1×1 cm² were made for irradiation experiment.

For each sample type, one sample was reserved as virgin to compare with irradiated sample. The irradiation was carried out on four identical samples. The nanoparticle samples were mounted on a vacuum shielded vertical sliding ladder having four rectangular faces. They were irradiated in the Mat. Sc. chamber under high vacuum ($6·0 \times 10^{-6}$ Torr) by using the 100 MeV Cl^{+9} beam with approximate beam current of 1·0 pnA (particle nanoampere), available from the 15UD tandem Pelletron Accelerator at NSC, New Delhi (Mehta and Patro 1988; Kanjilal *et al* 1993). The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. The fluence was varied in the range 10^{11}–10^{13} ions/cm². In order to expose whole target area the beam was scanned over the *x–y* plane. The energy of the beam was chosen in such a way that the projectile range of the incident ion (as computed by SRIM program, Zeigler *et al* 1997) exceeds thickness of the sample films. Again, the ion beam energy and thickness of the target were selected so that modification due to electronic energy loss (S_e) affects the exposed sample. The nature of the ion beam induced modification has been analysed by using UV-VIS spectrophotometer in the range 200–800 nm and electron microscopy images. The photoluminescence spectra beyond band gap excitation show evolution of intense surface emission with fluence variations.

3. Results and discussion

The characterizations of pristine and ion irradiated embedded zinc sulfide nanoparticle samples include high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), optical absorption spectroscopy (OAS) and photolumi-

Table 2. Energy deposition with ion dose and nanoparticle grain growth.

Irradiation dose (ions/cm²)	Absorbed energy (Joules)	Absorption edge (nm)	Avg. grain size (nm)
0	0	310	11
1×10^{11}	0·539	314	14
5×10^{11}	2·698	320	–
5×10^{12}	26·976	325	32
1×10^{13}	53·952	326	41

nescence (PL). The energy of the beam was so selected so as to travel through the samples without stop. In otherwords, sample thickness (6·5 μm) was kept sufficiently lower than the projectile range i.e. 18·06 μm (table 1). As shown in the table for 100 MeV chlorine beam, electronic energy loss is predominant over nuclear energy loss and so we had to consider energy deposition due to the former cause. The electronic stopping power (S_e) of the beam was 553 eV/Å. The irradiation doses deposited in embedded Mn : ZnS/PVOH samples at four different fluences are calculated to be 0·539, 2·698, 26·98, and 53·95 joules, respectively. The amount of heat deposition as a function of fluence results into melting followed by grain growth (table 2).

3.1 *Optical absorption studies*

Optical absorption spectroscopy has become an important tool to observe size quantization effect in terms of blue shift and excitonic absorption (Brus 1992). As shown in figure 1, there is significant redshift of the onset of absorption of the ion irradiated ZnS : Mn nanoparticle samples. As the amount of energy shift is size dependent for a particular material and the size of the nanoclusters alters with fluence we believe there has been significant grain growth of nanoparticles under ion irradiation. It was known that the compounds with oxygen and nitrogen (containing non-bonding electrons) are capable of displaying characteristic absorption in the UV region (Virk *et al* 2001a,b) due to promotion of electrons in *s*, *p* orbitals (Dyer 1994). It was proposed that due to the presence of imide group (NC=O), absorption spectra possess transition peaks in UV regime. Although in aliphatic alcohols,

the hydrogen atom was reported to be removed by inter-action of radiation yielding **a**-hydroxy alkyl radical which has already been investigated (Abraham and Whiffen 1958; Ogawa 1960; Rao and Murthy 1987), polyvinyl alcohol is aliphatic and it has neither element like 'N' nor double bonds to facilitate carrier transition in the ultra-violet regime.

In addition to redshift of the onset of absorption, we see absorption band at around 300 nm, corresponding to exciton absorption of the particles, which has been studied extensively (Brus 1991; Yoffe 1993) in case of un-doped ZnS systems. It has been reported in representative ZnS nanoparticle systems (Chen *et al* 1997) that surface states are mainly responsible for evolution of second broad band in the long wavelength (~ 500 nm) region. Moreover, they say that the second band disappears for capped in comparison to uncapped ZnS nanoparticles because of relatively less number of surface states in cap-ped nanoparticles. We do not see any second absorption band in the virgin and low dose exposed samples. But interestingly, for the samples irradiated with high fluen-ces a second band emerges at around ~ 400 nm (figure 1). We believe appearance of such a band in the absorption spectra possibly due to the presence of surface states of ZnS : Mn nanoparticles which are now free from matrix encapsulation. Thus, even if ZnS : Mn nanoparticles have grown from an average size of 11 nm to 41 nm (table 2) due to ion impact, we observe recovery of the second band due to the surface states when the nanoparticles are free from matrix encapsulation.

3.2 *Illustration of electron microscopic images*

Although red shift in the absorption threshold in the absorption spectra is the first hand signature of signifi-
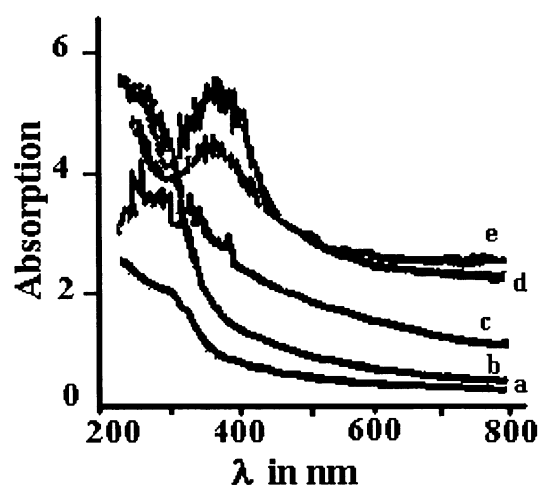

Figure 1. Optical absorption spectra of a. virgin and irra-diated, b. 1×10^{11} ions/cm^2, c. 5×10^{11} ions/cm^2, d. 5×10^{12} ions/cm^2 and e. 1×10^{13} ions/cm^2 Mn : ZnS polymer embedded nanoparticles.

cant grain growth, high resolution electron microscopic images provide the best of informations relating to irra-diation-led modification in nanoparticle systems. As depicted in figure 2, the electron micrographs show modi-fied behaviour of ion irradiated nanograins with respect to virgin. Figure 2a represents high resolution SEM image of Mn : ZnS nanoparticles in the form of assembly embedded in PVOH whereas TEM image of individual nanograins of size about 11 nm is shown in figure 2b. Swift ion irradiation leads to deposition of huge amount of energy which causes rise in electronic temperature ($\times 10^5$ °K) and afterwards (10^3 s) cause lattice tempera-ture rise ($\times 10^3$ °K). The enormous rise in temperature (which exceeds melting point of ZnS i.e. 2100°K) within a time scale of 10^{-12} s melts easily, all nearby particles along with the matrix represented in figure 2c. Rapid quenching gives rise to recrystallization as if grains have grown independently into definite sizes. The process of grain growth is a combined result of heat deposition and pressure effect. For the samples irradiated with highest dose (1×10^{13} ions/cm^2), we obtained well developed regular nanoclusters of average size 41 nm (figure 2d). The cluster of grains is displayed in a cross sectional view in figure 2e. They are supposed to be freestanding as already the polymer matrix has been damaged by com-plete amorphization. The complete amorphization was confirmed by no weight loss observation of the heavily exposed sample.

3.3 *Photoluminescence (PL) studies*

The PL study is important as it provides information relating to different energy states available between valence band and conduction band responsible for radia-tive recombination. It has been studied that the photolu-minescent efficiency of coated ZnS : Mn nanocrystals is higher than the powder samples due to passivation of surfaces (Bhargava *et al* 1994). The ZnS nanoparticles have a weak PL emission relative to Mn doped system. The band to band excitation in ZnS has been used to excite the Mn^{+2} emission. The subsequent transfer of ele-ctron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn^{+2} in ZnS (Brus 1986). In consistency with these reports, we have noticed yellow–orange emission for ZnS : Mn nanoclusters with peak wavelength ~ 582 nm. It is attributed to transitions involving d-electrons of the Mn^{+2} ions (Busse *et al* 1976; Gumlich 1981). The Mn^{+2} ion *d*-electron states act as efficient luminescent centres while interacting strongly with *s–p* electronic states of host ZnS nanocrystal into which external electronic excitation is normally directed. In an undoped quantum dot system, the external band edge as well as impurity related luminescent efficiency at room temperature is too low to be of any practical conse-quence (Benisty *et al* 1991). We also do not expect such emission for undoped ZnS system (figure 3a).

With increase in ion dose, there is no significant shift of the emission peaks arising out of Mn^{+2}. It is well known that when PL emission peak energies are less than the band gap energy of the material, these bands correspond to transitions involving donors, acceptors, free electrons and holes. The appearance of the PL peaks at energies substantially lower than the band gap suggests that transitions from energy states in the band gap are being favoured for the luminescence process in these nanocrystalline ZnS films (Pal 1999). As depicted in figure 3, the first emission peak position shifts towards blue with increase in ion dose. We recognize these peaks as a result of trapped luminescence, which were reported

in the form of broad bands in the PL spectra (Eychmuller 1991). Such peaks were attributed to the presence of surface states in nanocrystals. The surface emissions become more intensive with ion dose because the extent of free standing ZnS : Mn depends on degree of amorphization of the polymer matrix.

The shift of surface emission due to size variation has already been discussed (Chestnoy *et al* 1986). However, in case of second emission peak arising from Mn^{+2} site, particle size does not significantly affect the emission wavelength (Dinsmore *et al* 2000). As shown in table 3, in consistency with our observations, the shifting of surface emission peak towards blue is due to grain size
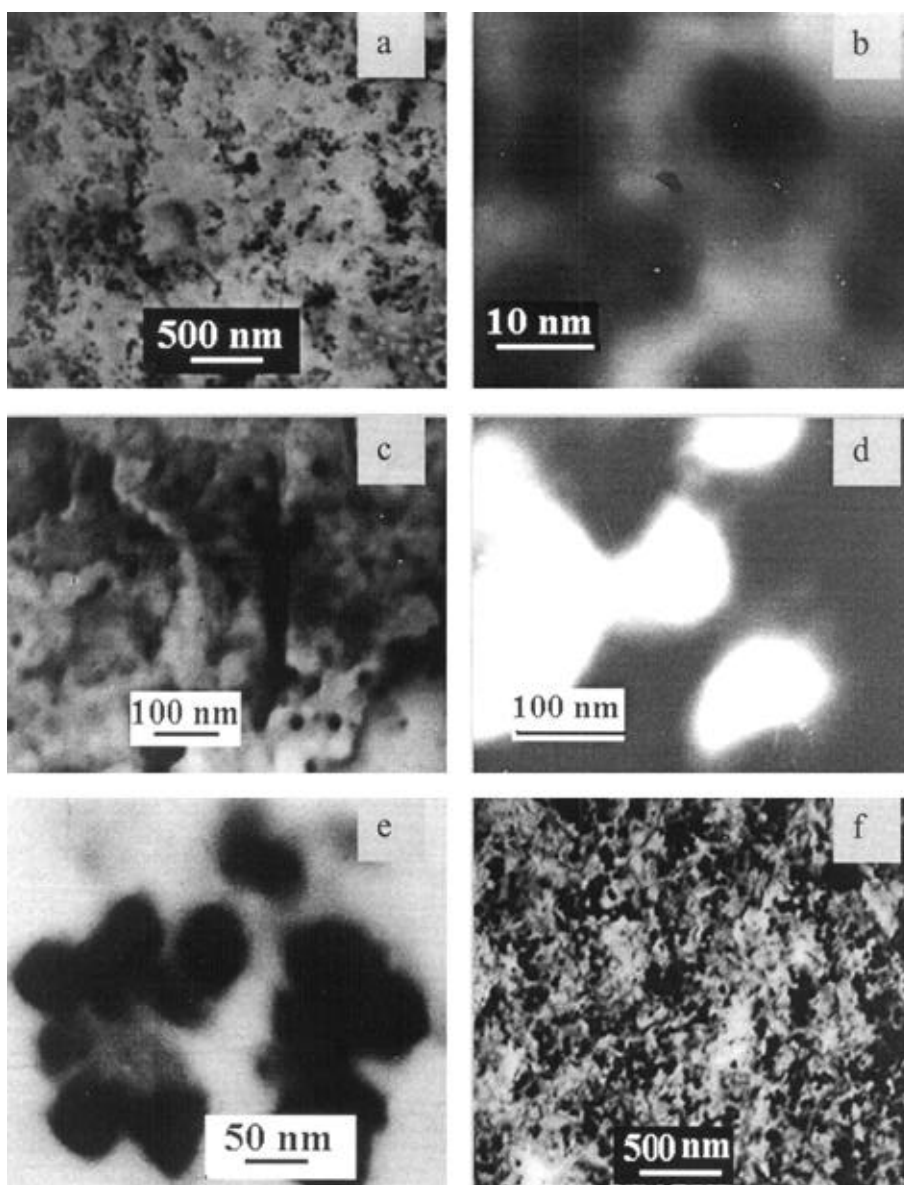

Figure 2. **a.** HRSEM and **b.** bright field TEM image of virgin, **c.** melting of the ion irradiated (5×10^{11} ions/cm^2), **d.** a cluster of individual grains grown as a result of irradiation (1×10^{13} ions/cm^2) and **e.** a cross sectional view of the heavily exposed polymer embedded Mn : ZnS nanoparticle sample.

Table 3. Photoluminescence emission of virgin and irradiated Mn : ZnS nanoparticles.

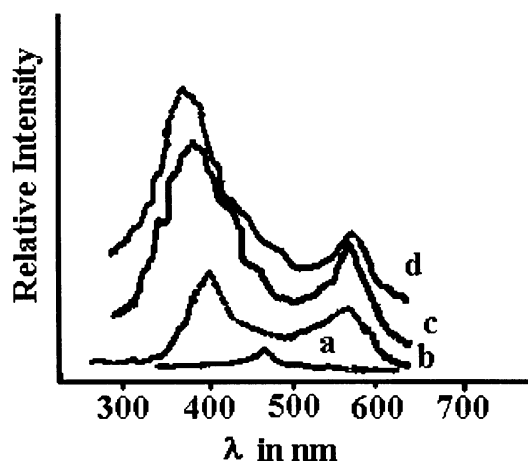| Samples	Excitation wave-length (I)	I_1	Peak positions (nm)		
			Energy	I_2	Energy
ZnS	220	480	2·576	–	–
Mn : ZnS–D_0	220	405	3·179	580	2·131
Mn : ZnS–D_2	220	382	3·236	582	2·124
Mn : ZnS–D_3	220	375	3·296	582	2·124

Figure 3. PL spectra of unirradiated **a**. polymer embedded undoped ZnS, and **b**. Mn doped ZnS, and ion irradiated **c**. 5×10^{11} ions/cm^2 and **d**. 5×10^{12} ions/cm^2 Mn doped ZnS nanoparticles.

effect studied for different substrate conditions (Pal *et al* 2000). The resulting intense emission may be suggested as net luminescence contributed by all the surface states, when the particles become fully free standing (for highest dose). Because for heavily dosed samples, the nanoparticles are supposed to be free from matrix encapsulation.

4. Conclusion

In conclusion, we claim that embedded polymer system is advantageous to observe regular grain growth process under ion irradiation. The size of the grains can be tuned by selecting proper ion fluence. The samples irradiated with highest dose are free standing and that is why strong surface emissions are visible in PL spectra which arise from the surface states. The surface emission energy are calculated to be 3·179 eV, 3·236 eV and 3·296 eV for fluences 0, 5×10^{11} and 5×10^{12} ions/cm^2, respectively. Moreover, the Mn^{+2} emission peak of irradiated samples does not shift appreciably but intensity improves because heavily exposed nanoparticles overcome barrier encapsulation. However, surface emission shifts towards blue due to size effect. Therefore, sensitivity of the optical sensors supposed to be made of ion irradiated and doped semiconductors can be tuned by proper choice of ion dose.

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