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Photoluminescence decay kinetics of ZnO:Mn nanobelts

D. KUMAR*, S. KUMAR[a], A. GUPTA[b], H. S. BHATTI
Department of Physics, Punjabi University, Patiala-147 002, India,
[a]School of Physics & Materials Science, Thapar University, Patiala –147 004 India,
[b]Department of Physics, School of Manufacturing and Materials Technology, Caparo(PTU), Village Khera, Kapurthala-144601, India

Zinc oxide Mn doped nanobelts have been synthesized by chemical precipitation technique using zinc acetate and manganese acetate as a starting material. Electron microscopy observations indicate that the length of nanobelts are ranging from 100μm to 200μm. X-Ray diffraction pattern confirms the wurtzite structure. Nitrogen laser having high peak power (1MW), pulsed (5-7ns) and (λ =337.1nm) has been used for the time resolved luminescence studies and spectroflourometer for steady state photoluminescence measurements. From the decay curves of time resolved laser induced photoluminescence various important optical parameters such as excited state life time, trap depth value, decay constant and integrated cross section and dipole moment have been calculated and reported in this paper. Einstein's spontaneous and stimulated coefficient values obtained from decay curves indicate the probability of transitions from various traps. Selective excitation of the levels can make ZnO a best suited laser medium. Various parameters have been calculated from recorded luminescence decay curves. Crystallographic and morphological characteristics have been studied using X-Ray diffraction (XRD) and electron microscopy (SEM and TEM).

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Keywords: Nanobelts, Photoluminescence, Laser, Time resolved

1. Introduction

Zinc oxide have been widely used for various functional devices including surface acoustic wave devices, gas sensor, photocatalysts, solar cells, chemical sensor, piezoelectric transducers, transparent electrodes [1,2], electroluminescent devices and ultraviolet laser diodes [3,4]. Compared to other II-VI compound semiconductors, ZnO has a wide band gap of 3.37 eV and rather large exciton binding energy, (60 meV), which makes exciton state stable even at room temperature. Further more, ZnO is an environmentally friendly material, which is desirable especially for bio-application. Various chemical methods have been employed to synthesize the nanostructures such as solvothermal, hydrothermal, self assembly and template assisted sol gel [5,6]. However in this paper very simple and low temperature fabrication methods for long nanobelts of ZnO are mentioned. Mn doped materials are of great interest because of possible applications in the field of short–wave magneto optical devices [7]. Furthermore, researchers predicted that Mn doped ZnO would show ferromagnetic behaviour with a curie temperature T_c above room temperature [8]. When ever semiconductor is irradiated with radiations there are trapping levels at different depths with in the forbidden gap of the material, leading to transition from the various traps.

Diluted magnetic semiconductors (DMS) have attracted great deal of attention in the past few years as enabling materials in the emerging field of "spintronics"[1]. DMS are semiconductor solid solution, where a small percentage of cations are replaced by magnetic impurities such as Mn. Due to the host sp-Mn d interactions in these DMSs, unusual magneto-transport and magneto-optical phenomena like large Faraday rotations, giant magnetoresistance, and magnetic field induced metal-insulator transitions have been observed [2]. Among the DMSs, Mn –doped II-VI compounds are so far studied [3]. However, most of the II-VI compounds studied are chalcogenides: the corresponding oxides are comparatively less investigated.

The fabrication of nanometer –sized one –dimensional materials has attracted considerable attention because of their fundamental importance in the understanding of mesoscopic phenomena as well as their potential in the development of nanodevices. Although many approaches have been used to prepare nanorods or nanowires, the exploration of novel and simple method is still a challenging research area. However low temperature wet chemical synthesis method have many advantages and it is easy to synthesize nanomaterials. Earlier, Jun Zhang etal. fabricated semiconducting ZnO nanobelts [9] using a halide source and their photoluminescence properties have been measured. Manganese-doped ZnO nanobelts [10] for spintronics have been fabricated by C. Ronning etal using thermal evaporation technique. Temperature-controlled growth of ZnO Nanostructures of branched nanobelts and wide nanosheets [11] was done by QingWei. et al. Xianghua Kong etal [12] synthesized ZnO Nanobelts by Carbothermal Reduction and their photoluminescence properties were studied. Aurangjeb Khan et al. studied the steady state photoluminescence [13] behavior of ultrafine ZnO nanobelts synthesized by thermal evaporation and condensation techniques. XY Zhang etal conducted

hydrothermal synthesis [14] of oriented ZnO nanobelts and studied their temperature dependent steady state photoluminescence. So far work has been done regarding the synthesis of pure and doped ZnO nanobelts by different workers but no one has tried to see the time resolved behavior of these ZnO:Mn nanobelts. In our previous paper [15] we have reported the preparation and the characterization of undoped ZnO nanobelts. In this paper we are reporting the time resolved behavior of these ZnO:Mn nanobelts, as for any optoelectronic application response time is a very important parameter. In the present paper, Einstein's spontaneous and stimulated coefficients, oscillator strength, life times and dipole moment of ZnO:Mn doped nanobelts have been calculated. The optical parameters obtained from the time resolved laser induced photoluminescence decay curves indicate the possibility of ZnO:Mn as a active medium for laser oscillations. ZnO is a wide band gap semiconductor compound exhibiting the phenomenon of a wide band gap semiconductor compound exhibiting the phenomenon of phosphorescence, which has potential industrial applications such as coating material for fluorescent lamps, vacuum displays, picture tubes etc.

2. Experimental

Synthesis of long length Mn-doped ZnO nanobelts were carried out using chemicals zinc acetate and absolute ethanol. The synthesis method was initially based on the experimental procedure as adopted by Spanel and Anderson [1,3]. Alcohols are commonly used because the solvent also act as a reagent. However, the solvent does not participates in the reaction forming ZnO from Zinc acetate [1,4]. 0.1M Zn^{2+} prepared from Zinc acetate in absolute ethanol was refluxed for 3 hours under magnetic stirring at 80 ^{0}C. Next two routes have been opted for obtaining nanobelts from precursor which are as follow.

1. In the first method the precursor obtained was mixed with 0.1M LiOH prepared in 100ml triply deionized water. Precipitates were formed immediately and separated out using centrifugal machine at room temperature. Finally, precipitates were dried in oven at 100^0 C.
2. In the second method, the precursor was mixed with 0.14M LiOH prepared in 100ml triply deionised water, immediately precipitates start forming, which were kept at 4^{0}C for three hours. And then the precipitates are dried in the vacuum oven at 80^{0}C.

3. Morphological characterizations

X-ray Diffraction data for structural characterization of various prepared samples of ZnO were collected on an X-ray diffractometer(PW 1710) using Cu-K α radiation (1.541 the Å). Scanning electron microscope (SEM) images of samples were obtained from JSM-6100 type microscope.

4. Photoluminescence measurements

Nitrogen laser is employed here as an excitation source (337.1 nm, 10 ns) for phosphorescence studies. The short lived phosphorescence (life time in microseconds) from the sample at an angle of 90^o to the laser beam was collected by a fast photo multiplier tube (Fig. 3a) through an assembly of monochromator (wavelength selective element) and glass slab (UV radiation filter). The PL decay signals from the phosphors were recorded and analyzed to calculate Einstein's spontaneous and stimulated coefficients. The hyperbolic decay curves have been peeled off into three components by the peeling off methods of bube using advanced computer simulation. Steady state Photoluminescence emission spectrum (PL) of ZnO nanobelts at room temperature was obtained using spectrofluorometer.

5. Results and discussion

The morphological characterization of the prepared samples were examined by XRD and SEM. Typical SEM images of the products synthesized by method 1 and 2 are shown in Fig. 1 [16, 20] (a, b) and 2 (a, b). Typical XRD pattern of ZnO nano belts are shown in fig-3 with lattice constant (a=b=0.32 nm and c=0.52 nm). Diffraction peaks corresponding to the planes <100>, <002> and <101> obtained from X- ray diffraction data are confirming wurtzite crystal structure of Zinc Oxide. (consistent with those of bulk ZnO and JCPDS) nanobelts. Fig. 3 (b) represent the hyperbolic decay curves for the nanobelts of ZnO synthesized by method 2. Fig. 4 shows the steady state luminescence of ZnO nano belts. The yellow emission at 620nm is identified as radiative transition due to recombination of electrons in shallow donors with the trapped holes in singly ionized oxygen vacancies and interstitial oxygen. Blue emission is related to the intrinsic defects which arise due to O and Zn vacancies or interstitials and their complexes.

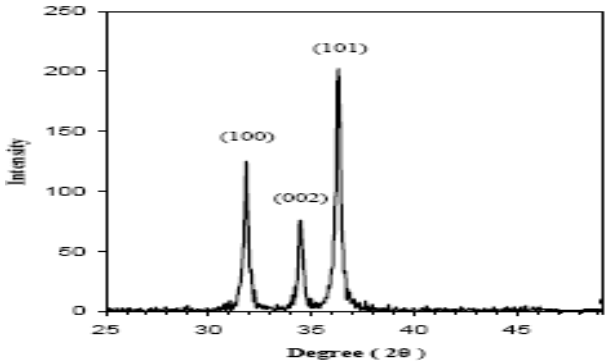


Fig. 3. XRD pattern of ZnO nanobelts.

Table 1 represents the data of life –time values for the synthesized doped ZnO phosphors at room temperature. The excited state life time values at room temperature vary from 50 to 1100 ns. The trap depth

values vary from 0.1012 to 0.1812 eV. Einsteins stimulated coefficients ($\times 10^{17}$) varies from 4.495 to 98.984. Oscillator strength values vary from 626.41 to 13780 $\times 10^{-6}$. Integrated cross-section ranges from 0.608 to 13.398 $\times 10^{-9} m^2 s^{-1}$. Dipole moment values varies from 25.189 to 49.105 $\times 10^{-31}$ C m.

It is clear from the SEM Fig. 1 that the nano belts are not of good quality, but in Fig. 2 the products consists of a long nanobelts like structures with typical lengths in the range of several hundreds of micrometers to a few millimeters. Addition of Mn in to the ZnO helps in obtaining the long length nanobelts. The reflux of precursors containing Zinc acetate and ethanol for long time results in long nanobelts of ZnO. Addition of catalyst stops the isotropic agglomeration of particles instead of the occurring of the anisotropic agglomeration, that results in nanowires or nanobelts [11]. The yellow emission is due to the radiative recombination of the electrons from shallow donor with the trapped holes from singly ionized oxygen vacancies and interstitial oxygen [21, 26] whereas blue emission is due to the intrinsic defects.

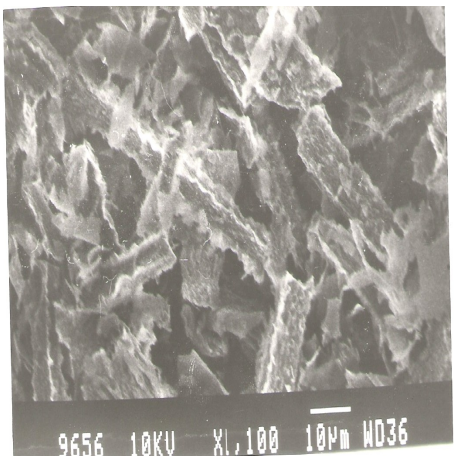


Fig.1. ZnO:Mn nanobelts fabricated by method-1.

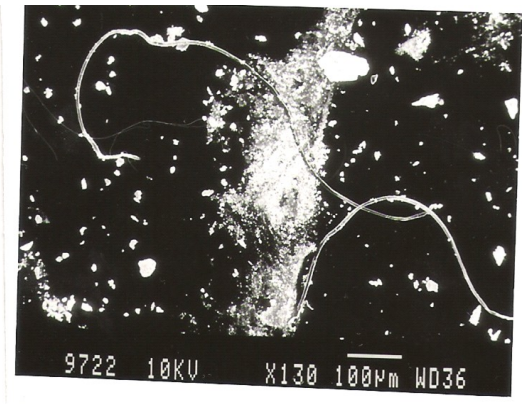
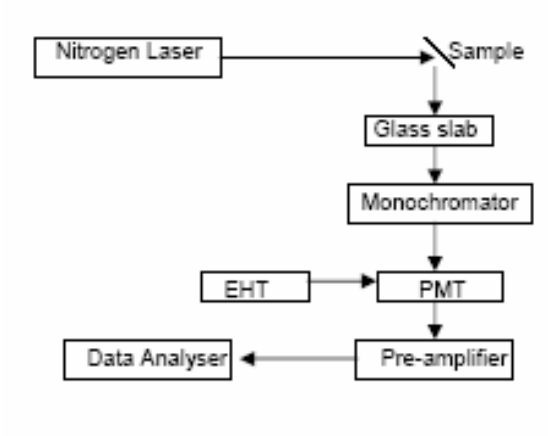
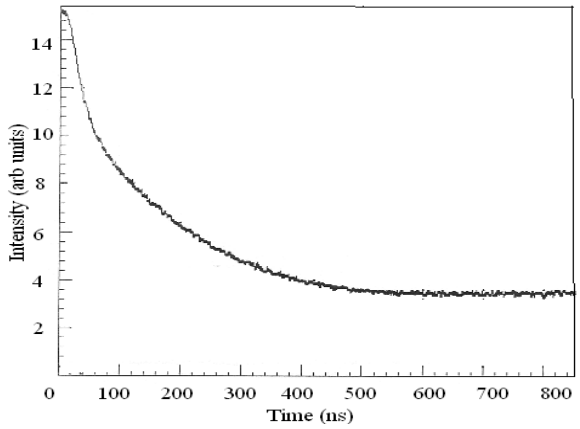


Fig. 2. ZnO:Mn nanobelts fabricated by method-2.



(a)



(b)

Fig. 3 (a) Experimental set- up for Nitrogen Laser Induced Photoluminescence decay measurements and (b) hyperbolic decay curve of ZnO nanobelts synthesized by method 1.

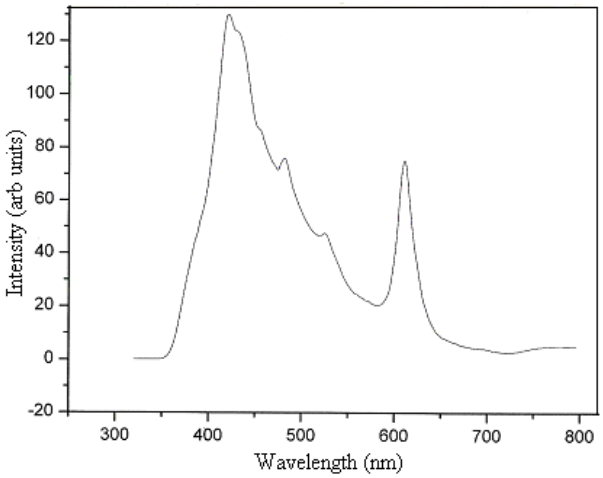


Fig. 4. PL emission spectrum for ZnO nanobelts.

Table 1. Life-time and trap-depth values for synthesized nano belts of Mn doped ZnO.

Phosphor	Life-time values (in ns)			Trap-depth values (in eV)		
	τ_1	τ_2	τ_3	E_1	E_2	E_3
ZnO:Mn(0.1%)	150	190	1100	0.1296	0.1358	0.1812
ZnO:Mn(0.3%)	120	175	1080	0.1224	0.1336	0.1807
ZnO:Mn(0.5%)	90	145	900	0.1165	0.1288	0.1760
ZnO: Mn(1%)	80	339	679	0.1133	0.1508	0.1687
ZnO:Mn(1.5%)	74	100	876	0.1114	0.1192	0.1753
ZnO:Mn(2.0%)	50	85	806	0.1012	0.1144	0.1732

Table 2. Oscillator strength and Integrated cross section values of Mn doped nanobelt.

Doped Phosphors	Oscillator strength values ($\times 10^{-6}$)			Integrated cross-section values ($\times 10^{-9}$ $m^2 s^{-1}$)		
	f_1	f_2	f_3	I_{cs1}	I_{cs2}	I_{cs3}
ZnO: Mn (0.1%)	4593.3	3626.3	626.41	4.4658	3.5257	0.6080
ZnO: Mn (0.3%)	5741.7	3937.1	637.97	5.5823	3.8278	0.6202
ZnO: Mn (0.5%)	7655.7	4751.8	765.56	7.4430	4.6198	0.7443
ZnO: Mn (1%)	8612.6	2026.5	1016.3	8.3735	1.9702	0.9880
ZnO:Mn(1.5%)	9310.9	6890.1	786.5	9.0524	6.6988	0.7647
ZnO:Mn(2%)	13780.0	8100.0	854.8	13.398	7.8809	0.8311

Table 3. Dipole-moment and Einstein' stimulated coefficient values of Mn doped ZnO nanobelts.

Doped Phosphors	Dipole-moment values ($\times 10^{-31}$ C m)			Einstein' stimulated coefficient values [$\times 10^{17}$ m^3 (rad/s)/(J s)]		
	μ_1	μ_2	μ_3	E_1	E_2	E_3
ZnO: Mn (0.1%)	28.357	25.189	10.557	32.964	26.024	4.495
ZnO: Mn (0.3%)	31.697	26.249	10.568	41.205	28.255	4.578
ZnO: Mn (0.5%)	36.600	28.834	11.574	54.941	341.01	5.494
ZnO: Mn (1%)	38.826	18.831	13.335	61.808	14.54	7.293
ZnO:Mn (1.5%)	40.365	34.721	11.731	66.820	49.447	5.644
ZnO:Mn (2%)	49.105	37.661	12.230	98.894	58.173	6.134

6. Conclusions

High purity nanobelts of ZnO having lengths in the range of several hundreds of micrometers to a few millimeters have been synthesized in the laboratory. Good results are obtained by method 2. Time resolved laser induced photoluminescence studies shows that the selective excitation of the corresponding levels can make ZnO:Mn the most suited active medium for laser system and other optoelectronic applications.

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*Corresponding author: sunilkumar32@gmail.com