Nuclear Instruments and Methods in Physics Research B 269 (2011) 374–379

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Effect of 80-MeV nitrogen ion irradiation on ZnO nanoparticles: Mechanism of selective defect related radiative emission features

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ARTICLE INFO

Article history:
Received 11 October 2010
Received in revised form 15 November 2010
Available online 20 November 2010

Keywords:
ZnO
Ion irradiation
Nanoparticles
Emission

ABSTRACT

We report on the 80-MeV nitrogen ion irradiation on spherical ZnO nanoparticles fabricated by way of solid state mixing. The structural and compositional analyses of the as-synthesized ZnO nanoparticles were done by X-ray diffraction, electron microscopy and energy dispersive spectroscopy studies. As evident from the optical absorption spectra, the energetic ion irradiation, on the nanoparticle system, is governed by evolution of new characteristic absorption features owing to modification in the electronic states. Again, in the luminescence spectra, though the near band-edge emission was not observable for pristine ZnO, it was recovered (at ~385 nm) upon irradiation. As far as the defect related emission is concerned, a competition between the formation and annihilation of different defects (especially, zinc vacancies and interstitials) at different ion fluences was realized. Correlating the luminescence spectra and the theoretical investigation, it can be understood that during irradiation the formation of zinc related defects are energetically favorable than the oxygen related counterparts. Exploration of defect related radiative features corresponding to definite structural organization/modification would help in making next generation light emitting and display devices, where a select emission response is desired.

1. Introduction

Nanoscale semiconductor systems have gained significant importance due to their size-dependent optical, electronic, and catalytic properties of plentiful technological relevance [1,2]. The wide band-gap semiconductor nanostructures, in particular, have emerged as a center of attraction for possible deployment in the field of optoelectronics and luminescence [3,4]. Zinc oxide (ZnO), a wide direct band gap (3.37 eV at 300 K), have been found to be a promising candidate for optoelectronics and display devices as it shows intense light emission characteristics from UV to visible range in the electromagnetic spectrum [5–8]. With the advancement in processing techniques like chemical vapor deposition, laser ablation, radio frequency/magnetron sputtering, chemical bath deposition, rapid thermal annealing, etc. it has been possible to fabricate quality ZnO nanoparticles as well as asymmetric structures in the form of rods, pillars, flowers, and urchins [9–11]. Undoubtedly, the concerned methods were pretty good for large scale production with controlled size distribution.

In contrast, a fast moving ion may lead to significant changes in the material leading to the track formation, implantation and other such effects [12]. Bombardment of the nanoparticle systems with suitable energetic ions leads to permanent change in the structural and morphological features like nanoparticle growth [13], nanostructure elongation [14], ripple formation [15], etc. Nanoparticle growth, splitting and directed growth are reported for ions having energy in the MeV scale, whereas ion implantation and ripple formation are observed on irradiating with ions carrying keV energies [13,15]. Controlled irradiation of the semiconductor nanoparticles, with light ions (e.g., N^{4+}, Ar^{8+}, etc.), is expected to influence the luminescence patterns by introduction or rearrangement of the nanoscale crystal defects [16].

The present work reports on the fabrication of spherical ZnO nanoparticles by a cost-effective, one-step solid-state reaction and their luminescence patterns due to the 80-MeV nitrogen ion impact at different fluences. The luminescence response and the structural modification are being correlated followed by a relevant theoretical treatment.

2. Experimental details

2.1. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized using a surfactant assisted solid state reaction method. A mixture of zinc acetate dihydrate (ZAD), a cationic surfactant cetyl trimethyl ammonium bromide (CTAB, 99.9% pure, Loba-Chemie), and sodium hydroxide (NaOH) with a molar ratio of 1:0.3:2 were ground together in an agate mortar for ~45 min at room temperature. The unidirectional soft

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doi:10.1016/j.nimb.2010.11.044

grinding led to the excess heat release as the reaction was in progress. After ultrasonication, the product was washed repeatedly with deionised water and ethanol to remove any unreacted species. Finally the ZnO nanoparticles were obtained on drying the product ~70 °C in air for 2 h.

2.2. Irradiation of ZnO nanoparticles

Polymers being protecting materials against the agglomeration of nanoparticles, polyvinyl alcohol (PVA) matrix medium was selected to disperse ZnO nanoparticles. For the irradiation purpose, the ZnO nanoparticles-dispersed PVA films were casted on laboratory glass slides (1×1 cm^2). The samples were irradiated in the Material Science chamber under a high vacuum (pressure of $\sim 10^{-6}$ mbar) condition and using 80 MeV-N^{4+} ion beams (with a beam current of ~1 pnA, particle-nanoampere), available at the 15UD tandem pelletron accelerator of Inter University Accelerator Centre, New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. The ion fluence was varied as 1.25×10^{11}, 5×10^{11}, 2×10^{12} and 8×10^{12} ions/cm^2.

2.3. Characterization techniques

The structural characterization of the ZnO nanoparticles were performed by X-ray diffraction (XRD) measurements recorded on a Rigaku D/max-2000 diffractometer employing Cu-K_α radiation ($\lambda = 1.54$ Å). Low resolution transmission electron microscopy (TEM) study was carried out by a JEOL JSM-100 CX microscope working at a beam accelerating voltage of 80 kV. In contrast, high resolution transmission electron microscopy (HRTEM) study was made with the help of a FEI, Tecnai S-twin electron microscope working under an accelerating voltage of 200 kV. The elemental analysis was performed through the energy dispersive X-ray spectroscope (EDS) attached with the scanning electron microscope (JEOL JSM: 6390 LV). The optical absorption study was performed by the UV–Visible absorption spectroscopy (UV 2450, Shimadzu Corporation). The room temperature photoluminescence spectra were revealed by using a PerkinElmer LS 55 spectrophotometer, having Xe lamp as the excitation source.

3. Results and discussion

3.1. Structural analysis

The TEM image of the as-synthesized ZnO nanoparticles are shown in Fig. 1(a). The average size of the nanoparticles is ~10–12 nm. The lattice fringes due to single crystalline planes are clearly observed in the HRTEM image of the ZnO specimen (Fig. 1(b)). The lattice spacing is found to be ~0.26 nm and it corresponds to the interplanar separation between the consecutive (0 0 2) planes of ZnO. The XRD pattern, shown in Fig. 1(c), shows hexagonal wurtzite structure of the ZnO nanoparticles (JCPDS 36-1451) [10]. No extra peak related to other byproducts e.g., $Zn(OH)_2$ was detected. The elemental constitution was obtained from the EDS spectra (Fig. 1(c)). In the EDS, the detection of a small peak corresponding to Br-element was noticed which might have arisen owing to the presence of a minor amount of CTAB surfactant used in synthesizing ZnO specimens.

3.2. Optical absorption spectra

As can be observed in the absorption spectra (Fig. 2), the pristine ZnO nanoparticle system before irradiation is characterized

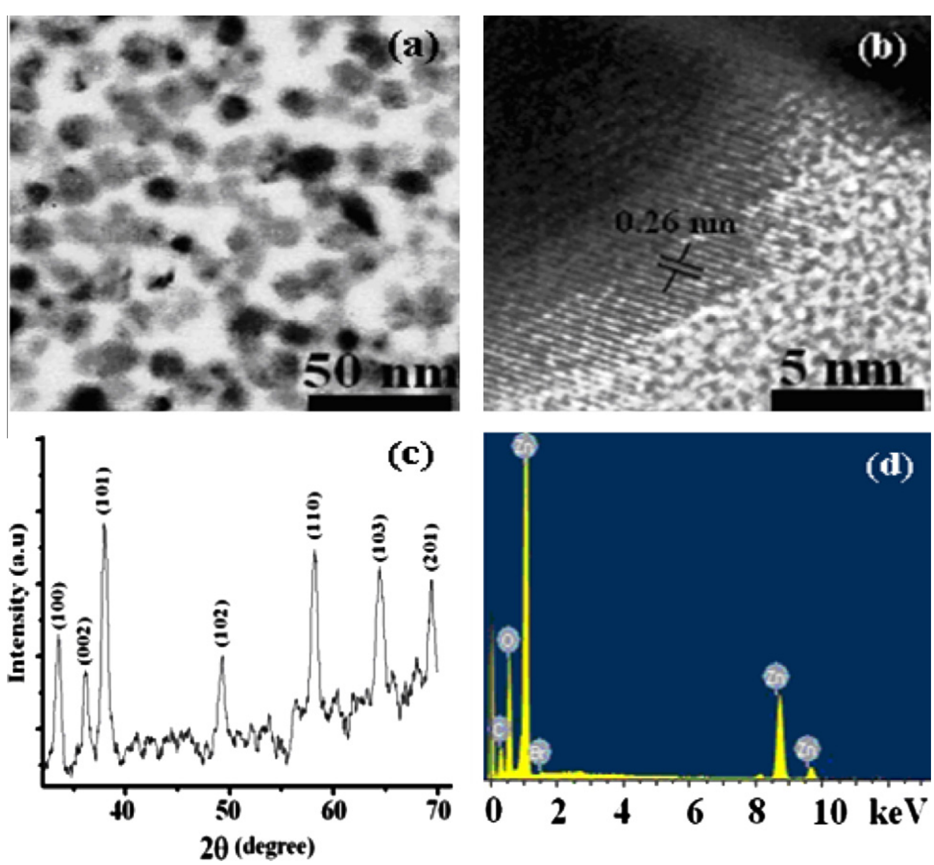

Fig. 1. (a) Low resolution TEM, (b) High resolution TEM, (c) XRD pattern, and (d) EDS spectra of the nanoparticle system.