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Original Research

Effect of nitrogen doping on structural and optical properties of ZnO nanoparticles

Renu Kumari[a,1], Anshuman Sahai[b,1], Navendu Goswami[b,*]

[a]Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India
[b]Department of Physics and Materials Science and Engineering, Jaypee Institute of Information Technology, A-10, Sector-62, Noida 201307, India

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Abstract

Influence of nitrogen doping on structural and optical properties of ZnO nanoparticles has been studied. Undoped and N doped ZnO nanoparticles were synthesized via chemical precipitation approach. The prepared samples were characterized through X-ray diffraction (XRD), Transmission electron microscopy (TEM) equipped with Energy dispersive X-ray (EDAX) spectroscopy, UV–visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy (μRS). Wurtzite phase of undoped as well as 0.5–10% N doped ZnO nanoparticles was confirmed through characteristic XRD patterns. The particle size expansion due to N incorporation in ZnO was further revealed by TEM and EDAX analysis where 11 nm size undoped and 18–22 nm size 0.5–10% N doped ZnO (N:ZnO) nanoparticles without any impurity were ascertained. Slight blue-shift in band gap energy, as observed in our case, symbolized weak quantum confinement of the prepared nanoparticles. The alterations in vibrational modes of ZnO due to N incorporation, remarkably H substituting at O site and subsequently causing the passivation in N:ZnO nanoparticles, were detected through FTIR analysis. Finally, the effect of the nano-size of crystallite and gradual prominence of N into ZnO lattice due to increase of N doping concentration in prepared nanoparticles was meticulously expatiated though μRS analysis.

Keywords: II–VI Semiconductors; Infrared spectra; Raman spectra; Optical properties of low-dimensional; Mesoscopic; Nanoscale materials and structures

1. Introduction

The need for blue and UV solid-state emitters and detectors has propelled the investigation of several wide band gap semiconducting materials in recent years [1–3]. Zinc oxide, due to its direct band gap (3.2 eV) and large exciton binding energy (60 meV), is considered a good candidate for optoelectronic devices like photodetectors, ultra-violet laser diodes and visible light emitting diodes [2,3]. Because of wide band gap, ZnO is transparent in the visible part of the electromagnetic spectrum, and hence it can be used as a transparent conducting oxide [4], blue/UV solid-state emitters [3], shield against high-energy radiation, organic light-emitting diodes (OLED) and transparent thin-film transistors (TTFT) [5]. As a crucial advantage, synthesis of ZnO is more cost effective than various other alternate semiconductors, such as III–V semiconductors [6].

ZnO exhibits broad range of properties that depend on doping, including a range of conductivity from metallic to insulating (including *n*-type and *p*-type conductivity), high transparency, piezoelectricity, wide-band gap semi conductivity, room-temperature ferromagnetism and huge magneto-optic and chemical-sensing effects [3]. Therefore, to realize the applications of ZnO for applications/devices, it is very important to fabricate both *p*-type and *n*-type semiconductors. Usually undoped ZnO shows *n*-type conductivity due to the presence of native point defects [6]. Usually the photoluminescence of ZnO includes near-band-edge ultraviolet emission and deep-level emission, where the latter is related to structure defects and impurity [2,3]. Theoretical investigations has concluded that shallow acceptor

*Corresponding author. Tel.: +91 120 2594364; fax: +91 120 2400986.
E-mail address: navendugoswami@gmail.com (N. Goswami).
[1]Authors equally contributed.
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levels in ZnO can be produced upon various doping mechanisms, such as Group-I element (Li, Na) substitution on a Zn site [7,8], large-size Group-V elements As or Sb substitution on a zinc site [9] or Group-V element substitution on the O site [10]. It is also reported that very low resistance from n-type is achieved by doping ZnO with group III elements such as In, Ga, Al, B, but still, it is a challenge to dope *p*-type ZnO [11–14]. Also, many previous theoretical calculations suggested the possibility of obtaining *p*-type ZnO using acceptor and donor co-dopants, like N and Al, Ga, or In [9,15,16]. Also major chemical trends in the energy levels of sp^3-bonded substitutional deep impurities in the wurtzite semiconductors were predicted and N impurities (deposited on the anion site) appeared to be producing shallow *p*-type dopants in semiconducting materials [10]. However, growth of stable *p*-type ZnO with large hole concentrations at room temperature and the controlled production of high-quality *p*-type ZnO has been difficult to achieve [17]. So its potential applications are limited due to difficulties that come across in the determination of the proper dopant and/or suitable growth processes that result in p-type conductivity and consequently in the preparation of a *p*-type ZnO material, either in the form of thin films or bulk crystal.

Nitrogen has been demonstrated as a very good *p*-type dopant for other II–VI semiconductors [11]. Nitrogen, having an ionic radius comparable to oxygen, appears to be the most likely dopant candidate. One possible route is to substitute N on an O site (N_O) [18–22], but theoretical calculations show the hole binding energy to be around 400 meV [7] which is too large for appreciable ionization to occur at room temperature. Previously, N doped ZnO thin films has been grown by various techniques such as molecular beam epitaxy [20], ion implantation [10], pulsed laser deposition technique [23], ion beam sputtering [24], magnetron sputtering [25] etc. However, most of the basic aspects of p-type ZnO are still not well understood, and that lack of knowledge impedes further progress [26].

Driven by aforesaid motivations we aim to understand the effect of nitrogen doping on structural and optical properties of ZnO nanoparticles. A facile chemical precipitation approach was adopted to prepare Nitrogen doped ZnO (N:ZnO) nanoparticles with varied dopant concentrations. Prepared samples were subjected to a series of characterizations and the results thus obtained were systematically discussed.

2. Experimental details

2.1. Synthesis procedure

The synthesis of N:ZnO nanoparticles was attempted adopting chemical precipitation route [27–33]. All chemicals used for synthesis were of AR grade. Aqueous solutions of 0.4 molar concentrations of zinc acetate dihydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$), monoethanolamine (MEA) and isopropyl alcohol (IPA) were prepared separately in doubly de-ionized (DI) water. In order to obtain a homogeneous mixture MEA and IPA solutions were added drop wise to the base solution of zinc acetate. The undoped ZnO nanoparticles were obtained through this mixture. In this precipitation technique, composition of solvent was modified in such a way that ZnO nanoparticles formed, which has a significantly lower solubility than the concentration in solution [28–30]. Further, to achieve different percentages of N doping to ZnO i.e., 0.5%, 1%, 5% and 10% N doping, calculated respective amounts of 0.4 molar concentration of ammonium acetate (CH_3COONH_4) aqueous solution was added into previous mixture. Mixing of these solutions was performed along with continuous and slow speed magnetic stirring, as it is crucial for obtaining precipitate of N:ZnO nanoparticles. The precipitate of N:ZnO was thoroughly washed with DI water and then dried at 200 °C for 8 h in an electric oven. The powder samples finally produced are basically undoped and N:ZnO nanoparticles, obtained through 0.4 molar concentration of differing N doping amounts and therefore, 0.5% is referred as 4MN05, 1% is referred as 4MN10, 5% is referred as 4MN50 and 10% is referred as 4MN100 respectively.

As per the established literature on a chemical precipitation method, the growth mechanism is critical in controlling and designing the undoped and doped ZnO nanoparticles [28–32]. The formation of nanoparticles proceeds step by step from seeds (primary particles) to larger particulates [28]. In order to achieve mono-disperse nanoparticles, it is crucial here that the seed formation rate or nucleation rate be faster than the growth rate of particles [28–30,34,35]. Due to this reason, the slow mixing of reactants in our methodology is expected to increase nucleation rate and decrease growth rate.

2.2. Characterizations

To study the structural, electronic and optical properties, powder samples of undoped and 0.5%, 1%, 5% and 10% N:ZnO were subjected to various characterization techniques. To identify the crystalline phase and associated parameters of prepared material, XRD analysis was performed using a *Bruker D8 Advance X-ray diffractometer* (XRD) with a Cu anode, generating K_α radiation of wavelength 1.544 Å and operating at 40 kV and 40 mA. XRD $\theta-2\theta$ patterns of all samples were recorded with scan rate of 3°/min. In order to study finer structural details, real space images of prepared materials were captured employing a *JEOL JEM-2100F High Resolution Transmission Electron Microscope* (HRTEM) operating at 200 kV. Utilizing same instrument, EDAX analysis was carried out and chemical composition of prepared materials were estimated quantitatively. Micro-Raman spectra were collected through *InVia Raman microscope, Renishaw, UK system* consisting of Ar^+ laser with 514.5 nm wavelength and 50 mW in the scanning range of 100–800 cm^{-1}. IR active vibrational modes of undoped and N:ZnO nanoparticles were examined by recording their IR spectra employing a *Perkin-Elmer BXII FTIR spectrophotometer*. FTIR spectra were acquired scanning the powder samples embedded in KBr matrix in the transmittance mode for frequency range of 400–4000 cm^{-1}. Room temperature UV–visible reflectance mode spectra of prepared material were recorded in wavelength range 250–800 nm using *Perkin-Elmer Lambda-35 UV–visible spectrophotometer*.