



OPTICAL PROPERTY OF Eu DOPED ZnO NANOWIRE PREPARED BY WET CHEMISTRY METHOD ON GLASS SUBSTRATE

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ABSTRACT

This work presents controllable growth of Eu doped ZnO nanowires (Eu:ZnO NWs) by Chemical bath deposition (CBD) methods. The structural and morphological properties are investigated by X-ray diffraction (XRD), SEM and EDS. The particle size, dislocation density and strain are calculated from XRD. The absorption spectra of (Eu:ZnO) nanowires have been investigated by UV-visible at room temperature.

Keywords: ZnO Nanowires, Eu Doping, Absorption Spectra

I. INTRODUCTION

ZnO possesses the wurtzite structure and a wide band gap of 3.37 eV.[1,2]. It is a low cost, environmental friendly semiconductor material, and shows high thermal and optical stability at room temperature (RT). It has an exciton binding energy of 60 meV, which is much larger than the room-temperature (RT) thermal energy (25 meV).[3-5]. Due to its wide band gap at room temperature (RT) it is suitable for optically active impurities like rare-earth ions. It has been extensively used, in both the thin film and powder forms, for photonic and optical applications.[6-8] ZnO doped with rare earth (RE) elements such as Eu, Er, and Tb have been pursued because of their important applications in optoelectronics as emitters at visible region[9]. Rare-earth doped semiconductors have been studied for their potential use in integrated optoelectronic devices like visible and infrared luminescent devices [10,11]. In these materials, the excitation of the RE cations occur by the recombination of photogenerated carriers of the semiconductor and energy transfer from the semiconductor to the RE ions [12,13]. The optical properties of pure and doped ZnO nanostructures strongly depend on the property of dopant, the intrinsic defect and crystallinity. One main obstacle imparting the ineffective Eu doping is the giant mismatch between the ion radius of Eu (0.095 nm) and Zn (0.060 nm). Various techniques are used for the synthesis of Eu:ZnO NWs. In this paper, we report these simple, facile and cost effective technique for preparing Eu:ZnO NWs.

II. MATERIALS AND METHOD

All the reagents involved in the experiments were of analytical (AR) grade and were utilized without further purification. The microscopic glass substrates were cleaned by first immersing them in the mixed solution of hydrogen peroxide (H₂O₂) and concentrated hydrochloric (HCl) acid (1:3) for 20h, washed with deionized water



under ultrasonication and then dried in air. ZnO:Eu NWs were grown on glass slides via a two-step chemical process. In the first step, a thin seed layer of ZnO was prepared on glass substrate by sol-gel method. For this, 100ml ethanolic solutions composed of 0.375M zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as precursor and 2 ml of monoethanolamine (MEA) solution as stabilizer. ZnO sol was stirred on a magnetic stirrer at $60^\circ C$ for 30 min. at 600 rpm, resulting in a homogeneous and transparent ZnO seed solution. The blank glass slides were weighed first, so that the thickness of the seed layer could be determined gravimetrically later. Seed layer was prepared on the glass slides by dipping the slides about 10 to 15 times into the ZnO seed solution. The seed layer was then annealed and weighed. The seeded films were annealed at $350^\circ C$ for 1 h to remove the organic compounds and solvents from the films. After a uniform coating of the ZnO nanoparticles on the glass substrate, ZnO: Eu NWs were obtained through different wet chemical processes as mentioned above. The growth solution consisted of an aqueous solution of 25 mM zinc nitrate hexahydrate as a zinc source and 25 mM hexamethylenetetramine (HMTA) act as a bidentate Lewis base [14] that coordinates and bridges two Zn^{2+} ions and it also acts as a weak base [15] and pH buffer in molar ratio 1:1. For Eu doping zinc nitrate: europium oxide (97%:3%) were mixed in deionized water (DI), the resultant solution was stirred on a magnetic stirrer for 30 min. at RT. The ZnO: Eu NWs were grown by immersing the seeded substrate upside down in the prepared aqueous solution by CBD method. In this method seeded glass substrates were immersed into the above mentioned precursor solution for 5h at temperature $95^\circ C$. After deposition, the substrates were rinsed with deionizer water, dried in air and preserved in desiccator. The crystal structure of ZnO:Eu NWs was characterized by XRD, Bruker/Lynx Eye 1D-PSD, Cu $K\alpha$ radiation. X-ray diffraction data were recorded with Cu $K\alpha$ radiation (1.5418 \AA). The intensity data were collected over a 2θ range of $10^\circ - 70^\circ$. SEM images and EDS were taken on a JEOL JSM-5600.

III. RESULT AND DISCUSSION

3.1 X-ray diffraction[XRD]: XRD is used to investigate the phase structure and lattice parameters of the undoped and ZnO:Eu NWs. Fig.1 shows the X-ray diffraction pattern recorded in the $10^\circ - 70^\circ$ range. The pattern matches the lattice spacing of crystalline ZnO in the wurtzite structure (space group: P63mc). The high intensity of the ZnO peaks relative to the background clearly indicates good crystallinity of the undoped and doped samples. To confirm the possible substitution of Zn ions with Eu ions in ZnO:Eu NWs, the angle shift of 2θ theta for the ZnO (101) peak as a function of doping was observed. This shift in the diffraction peaks towards a lower 2θ or in other words the increase of the lattice parameters could be observed due to the doping of the bigger size Eu^{3+} ions having ionic radii $r_i = 0.947 \text{ \AA}$ and coordination number $CN=VI$ compared to that of the smaller size Zn^{2+} ion having ionic radii $r_i = 0.74 \text{ \AA}$ and $CN=VI$ [16]. This peak shifting may be attributed to the lattice mismatching, lattice distortion, strain of the crystal. Partical size, strain, dislocation density and some other physical quantities are calculated by XRD for undoped and ZnO:Eu NWs are given in table 1.

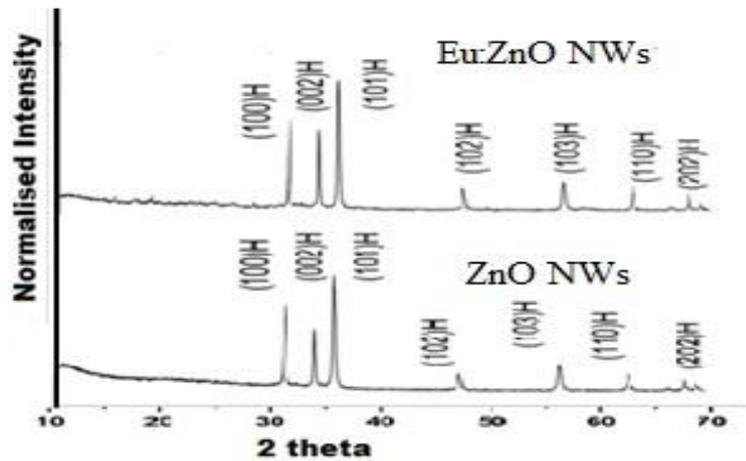


Fig.1 XRD of undoped and Eu doped ZnO NWs

Table 1: Value of particle size, strain, dislocation density for undoped and ZnO:Eu NWs

Sample	2(theta)	hkl	d(A ⁰)	A(A ⁰)	FWHM (Degree)	Crystalline size D (nm)	Strain	Dislocation density
Eu:ZnO NWs	36.355	(101)H	2.47E-6	3.5E-6	0.305	26.8	0.0047	4.3E+12
Undoped ZnO NWs	36.399	(101)H	2.47	3.49	0.5	16.3	0.0066	3.57E+15

3.2 Morphological properties through SEM

SEM micrographs of undoped and Eu:ZnO NWs films prepared by CBD method are shown in Fig.2. Scattered Eu grains having a distinct cubical morphology can be observed in the given micrographs. One main obstacle in effective Eu doping is the giant mismatch between the ionic radii of Eu (0.095 nm) and Zn (0.060 nm). To tackle this problem, we developed a two-step growth method for Eu doping. The anion-rich environment inherent to the sol-gel route significantly benefits the doping process by suppressing the “self-purification” mechanism, leading to the enhanced Eu doping in the fig. 2 (B). In order to measure the concentration of europium in Eu:ZnO NWs we took EDS pattern of doped nanowire sample. In these cases, the concentration of europium was maximum up to 0.35 atomic %. In fig.2(C) EDS shows that 0.35atomic% Eu doped by CBD method.

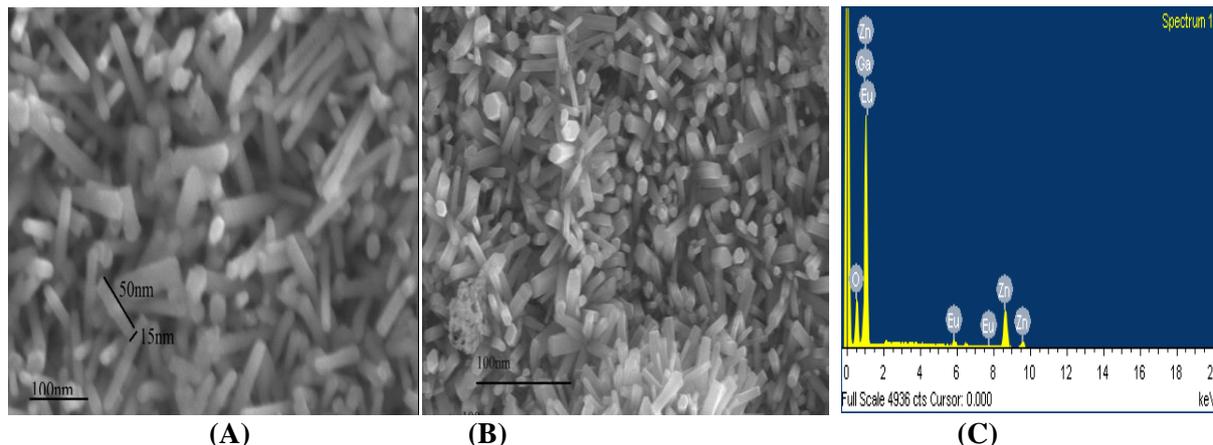


Fig:2: (A) SEM of Undoped ZnO NWs (B) SEM of Eu:ZnO NWs(C) EDS of Eu:ZnO NWs

3.3 UV-Vis Absorption Spectra

UV-Vis absorption spectra of pure and Eu:ZnO NWs by CBD method are shown in fig.3.

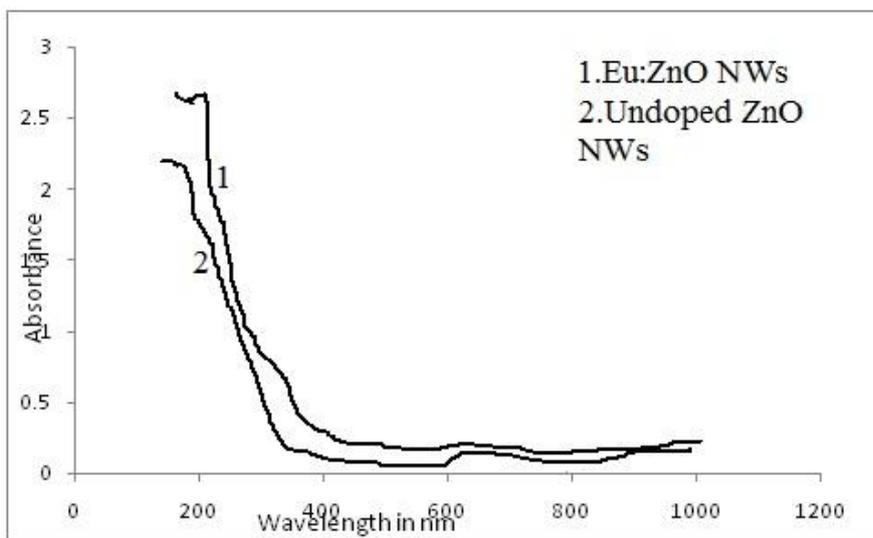


Fig.3: Absorption spectra of pure and Eu:ZnO NWs

The Eu:ZnO NWs showed a remarkable absorption band edge shifted towards the longer wavelength region, which indicates a decrease of the band gap energy. It becomes 3.32eV to 3.19eV for Eu:ZnO NWs. The band gap energy (E_g) of semiconductor material was calculated by using the following equation

$$E_g = 1240 / \text{wavelength}$$

IV. CONCLUSION

Eu:ZnO NWs were grown on glass substrate by CBD method. Compared with the undoped counterpart, the lattice parameters were increased by europium doping because of the bigger size of Eu^{3+} cations. The nanowires are single crystalline with $\pm[0\ 0\ 0\ 1]$ growth direction. The concentration of Eu^{3+} in the nanowires was less such a small amount of the dopant (Eu^{3+}) concentration is very useful for studying their optical absorption. The study of the optical properties of Eu^{3+} in the ZnO host and also the energy transfer mechanism from the host ZnO to the dopant europium are under progress.



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