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Synthesis and characterization of Cu-doped ZnO nanorods chemically grown on flexible substrate

R. Shabannia

Department of Physics, College of Science, Babol University of Technology, Babol, Iran

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ABSTRACT

Vertically aligned undoped and Cu-doped ZnO nanorods array were successfully grown on flexible substrate by chemical bath deposition method at a low 0074emperature. The fabricated materials were characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and photoluminescence (PL) spectroscopy. XRD analysis showed that Cu doping improves the crystallinity of the fabricated ZnO nanorods. The mean diameter and bending of the ZnO nanorods increase with an increase of Cu doping, but the density of Cu-doped ZnO nanorods almost unchanged. Room temperature PL measurement displayed increased intensity in UV peak and decreased visible peak after Cu doping.

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1. Introduction

ZnO nanostructures with a wide band gap (3.37 eV) and a large exciton binding energy (60 meV) at room temperature have good characteristics pertaining to their optical and electronic properties due to quantum confinement effect, which have been used as a functional material for optoelectronic devices such as UV light emitting diodes (LEDs) and UV laser diodes (LDs) [1,2]. Various synthetic approaches have been developed for ZnO nanorods, such as hydrothermal [3], chemical bath deposition [4], and chemical vapor deposition [5]. Among those methods, the chemical bath deposition (CBD) method is the most appropriate for the synthesis of ZnO nanorods because of its low temperature, simplicity, affordability, and potential for large-scale production. It has been reported that the morphology, structural and optical properties of ZnO nanostructures are depended to the preparation methods and conditions, post-processing, and doping. Many physical and chemical properties of Cu are similar to Zn. Therefore, Cu doping into ZnO nanostructures can be changed the morphological and optical properties of ZnO nanostructures [6–8]. Consequently, thorough understanding of the effects of Cu doping on the properties of ZnO nanostructures are essential. For moving objects, flexible polymer substrates are a suitable substrate for nanoscale optoelectronic devices based on ZnO nanorods because of the lightweight, low cost, high flexibility, good transparency, and portable characteristics. To the best of my knowledge, Cu doped ZnO nanorods grown on flexible polyethylene naphthalate (PEN) substrate have not been reported in the literature. In this study, undoped and Cu-doped ZnO nanorods were synthesized by simple low temperature CBD method. The structural and optical properties of the obtained ZnO nanorods on seed-layer ZnO/PEN substrate were then examined.

2. Experimental

The flexible PEN wafer utilized as substrate for growing undoped ZnO and Cu-doped ZnO nanorods by CBD method. The PEN substrates ultrasonically cleaned in a glass beaker consisting of an isopropyl alcohol solution at 50 °C for 20 min [9]. The ZnO seed layer was deposited on the prepared PEN substrates by a radio-frequency magnetron sputtering system for the growth of the vertically aligned ZnO nanorods. The growth solution of undoped and Cu-doped ZnO (with nominal fraction values of 0 and 2 at.%) were prepared by dissolving zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 0.05 M), Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 0 and 0.001 M), and hexamethylenetetramine ($C_6H_{12}N_4$, 0.05 M) in deionized (DI) water by vigorous stirring it for 3 min at 80 °C, respectively. Then they were mixed in a glass beaker, and the prepared PEN substrates were vertically dipped inside the

E-mail address: rezash56rami@gmail.com.

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beaker. For growing the ZnO nanorods, the beaker was transferred inside an oven at 90 °C for 5 h.

The structure and orientation of the undoped ZnO and Cu-doped ZnO nanorods were determined by X-ray diffraction (PANalytical X'Pert PRO MRD PW3040). Surface morphology and elemental analysis of the synthesized materials were examined by field emission scanning electron microscopy and energy dispersive X-ray spectroscopy (model FEI/Nova NanoSEM 450). The room temperature PL spectra of the undoped ZnO and Cu-doped ZnO nanorods were analyzed using a photoluminescence spectroscopy system (Jobin Yvon HR 800 UV, Edison, NJ, USA).

3. Results and discussion

Fig. 1 shows the XRD spectra of undoped and Cu-doped ZnO nanorods grown on PEN substrates. The diffraction peak i.e. (002) for pure and Cu-doped ZnO nanorods was in good agreement with the wurtzite hexagonal phase of the standard data for ZnO (ICSD 01-080-0074). A sharp and intense of ZnO (002) diffraction plane in XRD patterns, indicating that the growth of ZnO nanorods was perpendicular to the PEN substrate with the preferred c-axis orientation due to the lowest surface free energy. The intensity of the (002) peak increases going from undoped to Cu-doped ZnO nanorods, displaying that Cu doping improves the crystallinity of the fabricated ZnO nanorods. The (0 0 2) peak position of Cu-doped ZnO nanorods compared to the undoped ZnO nanorods was shifted to a higher 2θ angle from 34.325° to 34.375°.

The shift in the (0 0 2) peak is in good agreement with previous studies, and supports the evidences for the successful Cu doping in the hexagonal lattice of ZnO crystal structure [10,11]. The calculated lattice constant 'c' from the (002) diffraction peak for undoped and Cu-doped ZnO nanorods were 5.2205 Å and 5.2132 Å, respectively. The decrease in lattice constants in Cu-doped ZnO nanorods may be due to the successful substitution of Zn^{2+} ions site by smaller radii Cu^{2+} ions (The effective ionic radii of Zn^{2+} ion and Cu^{2+} ion are 0.074 nm and 0.073 nm, respectively). The grain size of undoped and Cu-doped ZnO nanorods grown on PEN substrate along the (002) peak were 55.4 nm and 83.2 nm, respectively. In addition, the strain of undoped and Cu-doped ZnO nanorods synthesized on PEN substrate along the c-axis of the (002) planes were 0.1035% to −0.0364%, respectively. The low compressive strain, and higher intensity of the (002) peak of the Cu-doped ZnO nanorods indicate better crystal quality compared with undoped ZnO nanorods.

The top view of the undoped ZnO nanorods and Cu-doped ZnO nanorods grown on the PEN substrates are shown in Fig. 2a and b, respectively. It can be observed from Fig. 2(a) and (b) that the vertically well-aligned ZnO nanorods with hexagonal shape and flat surface grown throughout the PEN substrates. The mean diameter and bending of the ZnO nanorods increase with an increase of Cu doping, but the density of Cu-doped ZnO nanorods almost unchanged, as shown in Fig. 2. The average diameter of the undoped ZnO nanorods and Cu-doped ZnO nanorods grown on the PEN substrates were 66 nm and 124 nm, respectively. Babikier et al. [12] have been explained that Cu impurity can be increased the density of nucleation site, which enhance the growth rate and hence coalescence process for nanorods, this leads to formation of larger-diameter nanorods in during the growth of ZnO nanorods.

The chemical composition of the synthesized materials was measured by EDX analysis. A typical EDX spectrum of Cu doped ZnO nanorods grown on PEN substrate is demonstrated in Fig. 3 which confirmed the presence of Cu in ZnO nanorods. It was also found that the measured concentrations of Cu in ZnO nanorods were lower than that of nominal values, which might indicate that Cu atoms did not distribute homogenously in the ZnO nanorods.

The room temperature photoluminescence measurement is an effective method of characterizing the optical properties and electronic band structure. Fig. 4 illustrates the PL spectra of undoped and Cu-doped ZnO nanorods grown on PEN substrate in the wavelength range of 350–750 nm using He–Cd laser with the excitation wavelength 325 nm. Fig. 4 exhibits two different emission peaks, which consisted of a sharp transition peak in the UV region and deep level broad emission band in the visible region. The UV emission band was attributed to a near band edge transition of ZnO, namely, the recombination of the free excitons (376 nm). The exact energy position of UV peak depends on the contribution between the free exciton and the transition between free electrons to acceptor bound holes [13,14]. The deep level emission band was related to several defects in the crystal structure of ZnO such as oxygen and zinc vacancies [15,16], oxygen and zinc interstitials [17], as well as extrinsic impurities such as substitutional Cu [18]. Fig. 4 displayed that the relative intensity of the UV emission increased with Cu doping in ZnO nanorods but that of the visible emission decreased. Previous reports of Cu-doped ZnO nanostructures

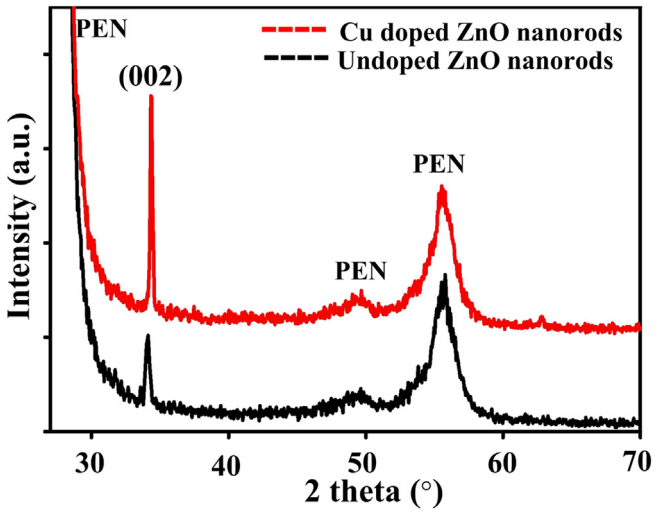

Fig. 1. XRD patterns of the undoped and Cu-doped ZnO nanorods grown on PEN substrates.

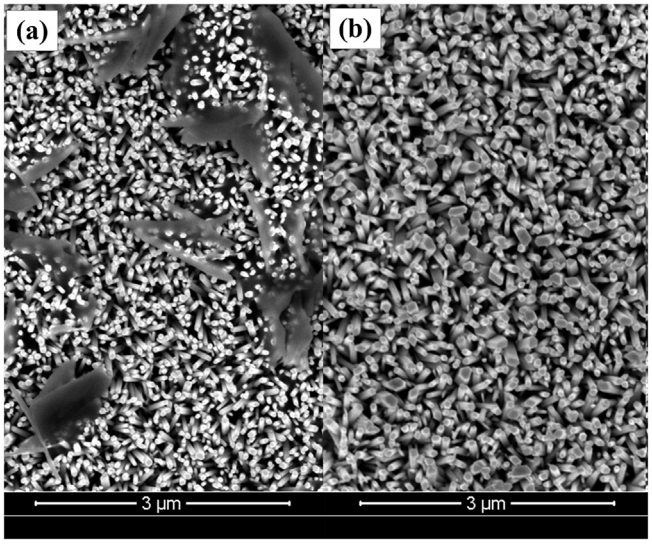

Fig. 2. Surface FESEM images of (a) undoped and (b) Cu-doped ZnO nanorods grown on PEN substrate.

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