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Physical Properties of ZnCoO Tetrapods and Nanofibers

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In this paper the physical properties of two types of Co-doped ZnO nanostructures: tetrapods and nanofibers grown by a rapid thermal evaporation process and prepared by the electrospinning technique, respectively, were investigated and analyzed. Surface morphology of the samples was examined using scanning electron microscopy. X-ray diffraction measurements showed hexagonal wurtzite crystal structure of both types of investigated nanostructures. Both X-ray diffraction and Raman scattering data confirmed high phase purity of the samples. The magnetic properties studied with the use of the SQUID magnetometer confirmed a presence of ferromagnetic order in analyzed nanostructures. The observed photoluminescence spectra exhibited two groups of lines. The first one, in the ultraviolet spectral range, is due to the optical transitions close to ZnO band gap, the second one in the red region is most probably related to the Co^{2+} *d–d* internal transitions. The influence of native defects on the optical properties is also shown and discussed. All results reported here lead us to the conclusion that in the mixed crystal nanostructures obtained, a fraction of the Zn^{2+} ions is substituted by Co^{2+} ions.

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1. Introduction

One-dimensional (1D) semiconductor nanostructures including nanowires, nanorods, nanobelts and nanotubes [1] have recently attracted a lot of attention because of their potential application in electronic, optoelectronic, electrochemical and electromechanical nanodevices. ZnO with its wide band gap (3.37 eV at room temperature) and its large exciton binding energy of 60 meV is a very promising candidate for these applications. Moreover, according to theoretical predictions, ZnO doped with 3*d* transition metal, may show room temperature ferromagnetism [2] which is very important for future spin-based electronics and optoelectronics. Finally, ZnO based nanostructures are relatively bio-safe and biocompatible and may be used for biomedical applications [3]. In this paper we studied several physical properties of two types of Co doped, ZnO-based nanostructures: tetrapods and nanofibers.

2. Experimental details

$Zn_{1-x}Co_xO$ (the nominal value $x = 0.08$) tetrapods were grown by rapid thermal evaporation process of mixture of metallic zinc, cobalt acetate, and aluminum acetate. The growth process took place in a horizontal tube furnace in an open quartz tube under ambient atmosphere and lasted about 5 min. The evaporation temperature was 915 °C. It is modification of the method [4–6] which results in a large scale production of ZnO nanostructures. The $Zn_{1-x}Co_xO$ (the nominal value $x = 0.1$) nanofibers were prepared by the electrospinning technique followed by high-temperature (about 500 °C) calcination in the air [7]. The poly(vinyl alcohol) (PVA) or poly(ethylene oxide) (PEO) zinc acetate, and cobalt acetate were applied as precursors, the final nanofibers were deposited onto quartz, silicon, or aluminum substrates.

The surface morphology of the nanostructures was examined by using a scanning electron microscopy (SEM). The Zeiss Neon 40 microscope was applied for that purpose. The X-ray diffraction (XRD) measurements were carried out using a Philips X'Pert PRO Alpha1 diffractometer (Cu K_{α_1} radiation) equipped with a strip detector and Johansson monochromator. The Raman scattering measurements were performed using a Jobin-Yvon U1000 double monochromator in the spectral range from 0 to 750 cm^{-1} with a spectral resolution close to 1 cm^{-1}. The Ar^+ 514.5 nm laser line was applied for the excitation. For the low temperature spectra, several dozens of randomly distributed tetrapods were irradiated by the laser spot (diameter of the order of 150 μm). In the case of room temperature spectra, the use of a microscope allowed to focus the laser onto a diameter spot close to 1 μm so that only a few isolated nanostructures were excited. Magnetic properties were studied by using a su-

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perconductor quantum interference device magnetometer (SQUID) in the temperature range $T = 5$–250 K and in external magnetic fields up to 1500 Oe. Photoluminescence (PL) spectra were measured in the temperature range from 10 to 300 K using a Jobin-Yvon SPEX 270 M spectrometer with a CCD detector. The PL was excited using the 325 nm laser line from the He–Cd laser operating at 50 mW.

3. Results

Representative SEM images of the investigated nanostructures are shown in Fig. 1. The diameters and the lengths of the tetrapods arms lie in the ranges of 20–300 nm and 0.3–8 μm, respectively. Moreover SEM measurements revealed that the nanofiber's diameters varied from 100 to 300 nm and consisted of nanocrystalline grains with a size of 10–50 nm. The XRD patterns, taken for both types of nanostructures, demonstrated their hexagonal wurtzite structure and a good phase purity. No additional peaks resulting from possible precipitates or other crystal phases were observed. Figure 2 shows typical XRD pattern of $Zn_{1-x}Co_xO$ nanofibers.

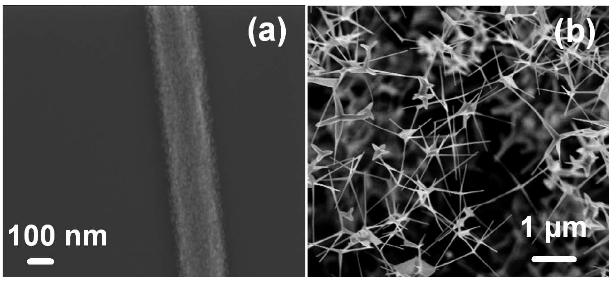

Fig. 1. Typical SEM images of the samples: (a) $Zn_{0.9}Co_{0.1}O$ (nominal composition) nanofiber and (b) $Zn_{0.92}Co_{0.08}O$ (nominal composition) tetrapods.

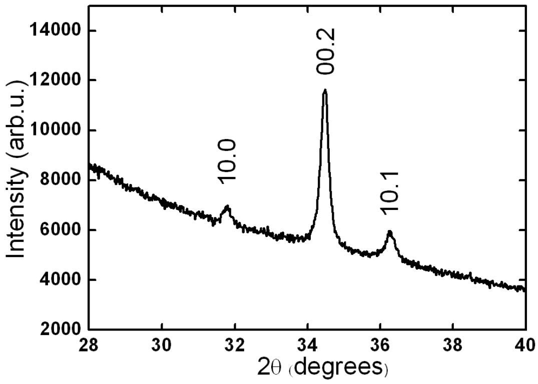

Fig. 2. Part of X-ray diffraction pattern of the nanofibers deposited on quartz substrate.

For $Zn_{1-x}Co_xO$ tetrapods the principal structures resulting from the first–order Raman scattering on the optical ZnO phonons are well seen at both, room and low temperatures. The main first-order Raman modes are identified, their frequencies and widths are similar to that observed on bulk ZnO. Some traces of two-phonon excitations may also be observed in the spectra. It should be mentioned that possible disorder-activated structures are absent in the spectra accumulated at room temperature, which is another evidence of the excellent crystalline structure of the investigated tetrapods.

The magnetization measurements (the results are not shown here) confirmed ferromagnetic order in both nanofibers and tetrapods structures. Hysteresis loops were observed in both cases with a coercive field ranging from 200 to 250 Oe.

Low temperature PL spectra taken for the $Zn_{1-x}Co_xO$ tetrapods (see Fig. 3) exhibited two groups of lines. The first in the ultraviolet (at 3–3.4 eV) region, due to the near-band-edge emission and the second in the red region (at 1.9 eV), related to the Co^{2+} d–d internal transitions [8]. PL investigations of the sample grown by using twice as much of metallic zinc, cobalt acetate, and aluminum acetate revealed also additional green defect band emission (at 2.3 eV), most probably connected to the presence of oxygen vacancies [9]. For this sample red emission was not observed.

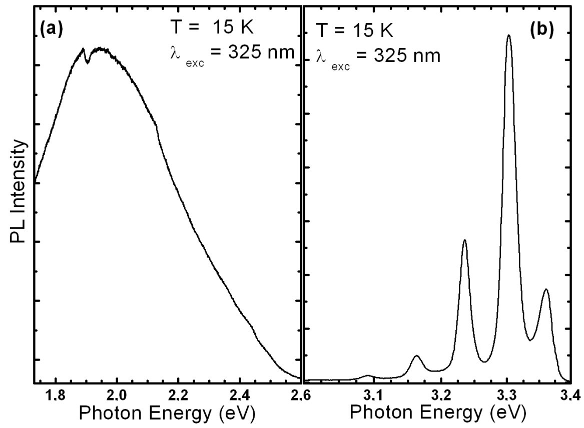

Fig. 3. PL spectra of the $Zn_{0.92}Co_{0.08}O$ (nominal composition) tetrapods at a temperature of 15 K: (a) emission lines in the red region assigned to the radiative transitions within the Co^{2+} ions occupying the Zn sites in the wurtzite host lattice (trigonal symmetry) and (b) group of ultraviolet lines in the spectral range close to the ZnO energy gap. The maximum intensity ratio for (a) and (b) type of emission lines $I_a/I_b \approx 0.01$.

Room temperature PL measurements for nanofibers, which were obtained by using PVA as a precursor, revealed a red emission which can be related to the electronic transitions of Co^{2+} ions. There was no PL emission from samples obtained by using PEO as a precursor. The frequency of the red emission observed for the tetrapods and the nanofibers which is expected for Co^{2+} ions occupying cation sites in ZnO crystal lattice is an optical evidence of the achievement of good quality $Zn_{1-x}Co_xO$ mixed crystals.

4. Conclusions

The ZnO-based tetrapods and nanofibers containing Co were grown and investigated by SEM, XRD, PL, Raman scattering, and magnetization (SQUID) measurements. The evidence of single phase, $Zn_{1-x}Co_xO$ mixed crystal character of the analyzed nanostructures was shown, the presence of a ferromagnetic order at low temperatures was demonstrated.

Acknowledgments

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