Optical Materials 55 (2016) 73–77

Contents lists available at ScienceDirect

Optical Materials

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

Structural, photoluminescence and picosecond nonlinear optical effect of In-doped ZnO nanowires

Xiao-Yan Yan [a], Cheng-Bao Yao [a,*], Jin Li [b], Jun-Yan Hu [a], Qiang-Hua Li [a,*], Shou-Bin Yang [a]

[a] Key Laboratory of Photonic and Electric Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, China
[b] College of Information Science and Engineering, Northeastern University, Shenyang 110819, China

ARTICLE INFO

Article history:
Received 30 January 2016
Received in revised form 8 March 2016
Accepted 9 March 2016
Available online 18 March 2016

Keywords:
Nonlinear optics
Materials
Photoluminescence
Multiphoton processes

ABSTRACT

In-doped ZnO (IZO) nanowires were grown using the chemical vapour deposition method. The IZO nanowires have been characterized by scanning electronic microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and UV–Visible spectroscopy. The PL results demonstrated a larger band-gap for the IZO nanowires in comparison to the undoped ZnO. Two major emission peaks were observed for the IZO nanowires, one originated from the free exciton recombination (ultraviolet emission) and another possibly related to the deep-level emission (visible emission). Furthermore, the nonlinear optical characteristic of the nanowires was studied using picosecond Z-scan technique. The experimental results show that the two and three-photon absorption coefficient of samples were able to be observed. These studies make the promising potential applications of the samples in the development of multifunctional all-optical devices.

1. Introduction

Wurtzite zinc oxide (ZnO) is an n-type metal oxide semiconductor with a wide band-gap (3.36 eV) and large exciton binding energy (60 meV). Therefore, ZnO is widely used in various optoelectronic devices, such as ultraviolet light-emitting diodes, piezoelectric transducers, varistors, phosphors, sensors, and transparent conducting films, and solar cell [1–5]. However, the role of the nanostructure size, doping, impurities, and morphology is very important to these applications, which has driven researchers to focus on the synthesis of doped and undoped nanocrystalline ZnO in recent years. Recent papers were reported on preparation and characterization of doped and undoped ZnO with various morphology materials. Lieber and co-workers have fabricated various nanoscale electronic and optoelectronic devices using the nanowires [6,7]. To enhance its electrical and optical properties, further widen its application, ZnO is frequently doped with group III, IV, and V elements. The various elements is selected to prepare semiconductor composite with ZnO, because of their interesting optical properties in the visible range which gives rise to wide applications in optoelectronic devices [8]. Amongst the various metal elements, the group-III elements Indium (In) are excellent dopants for ZnO due to their compatible bond length with ZnO. Because of In-doped ZnO (IZO) nanomaterials have good conductivity, higher optical transmittance, high carrier density, low resistivity and large electrical mobility and excellent surface roughness than the other dopants ZnO nanomaterials [9]. Moreover, In was selected to prepare metal-semiconductor composite with ZnO, because of its transparent conductive oxides constitute a class of materials widely used in the solar cells [10] or thin film transistor (TFT) technology [11]. Thus, it can be widely used in solar cells, TFT and transparent conductors in many applications. Furthermore, In is one of the best elements for the band-gap engineering of ZnO, provided that the content is carefully controlled [12]. Many experiments have been performed to study its physical and optical properties. The field emission of IZO nanostructures was reported in Refs. [13–15]. For example, Huang et al. studied the field emission of ZnO:In nanowires [13]. Zhang et al. studied the field emission of IZO nanotips and nanowires [14]. Jung et al. investigated the field emission of IZO tetrapods [15]. However, the effect of In on the structural and optical properties of nanowires are seldom reported. Furthermore, the nonlinear optical properties of the IZO have not been reported.

In this work, we report the structure and optical properties of IZO nanowires by a chemical vapour deposition method. The obtained morphology was studied by using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The

* Corresponding authors.
E-mail addresses: yaochengbao5@163.com (C.-B. Yao), qianghua_li@163.com (Q.-H. Li).

http://dx.doi.org/10.1016/j.optmat.2016.03.016
0925-3467/

effect of In on the structural and optical properties of nanowires was investigated. The PL results demonstrated a larger band-gap for the IZO nanowires in comparison to the undoped ZnO. Furthermore, the nonlinear optical characteristic of the IZO nanowires was studied with using Z-scan technique. The experimental results show that the nonlinear absorption mechanism of IZO nanowires is exhibited by picosecond pulse laser irradiation due to the population of conduction band (CB) through multi-photon absorption.

2. Experiment

The samples were prepared by a horizontal tube furnace through a fully controlled chemical vapour deposition (CVD) process [16]. The precursor is a powder mixture of ZnO (1 g) and In_2O_3 (0.12 g) for three-edged nanowires (TENWs). The precursor was placed into an alumina boat and loaded into the tubular furnace, and the Au-coated Si (1 0 0) substrates were placed downstream from the powders. The furnace was heated to a preset temperature (1400 °C). Ar was used as carrier gas during growth at a constant flow rate and pressure: 100 sccm, 50 Pa for TENWs. Then, the furnace was naturally cooled down to room temperature. The crystal structure and morphology of the products were investigated using an X-ray diffractometer (XRD, Siemens D5000) and a field emission scanning electron microscope (SEM, Quanta 200F). The elemental contents of the products were measured using energy dispersive X-ray (EDX, Quanta 200F) and field emission Auger electron spectrometers (FEAES, Jamp-9500F). A He–Cd laser with a wavelength of 325 nm was used for the room temperature photoluminescence (PL) measurements.

The Z-scan technique is used to measure the nonlinear optical properties, which is of great advantages due to its simplicity and high sensitivity. This technique is described in detail by Refs. [17–21], the laser source used for the measurement was at the Nd:YAG laser with a pulse width of 50 ps at 1064 nm and at the second harmonic of a Nd:YAG laser with a pulse width of 50 ps at 532 nm. The pulse energy at the output of the laser system was 2.0 mJ and 1.2 mJ with linear polarization, respectively. Basically, in this technique, the nonlinear sample is scanned through the focal plane of a tightly focused Gaussian beam and the changes in the far-field intensity pattern with and without aperture are monitored. The laser stability and the beam quality have direct impact on the accuracy of Z-scan experimental results. By detecting the reference light, one can test the laser stability, and use it as the normalization reference of functional light to reduce the influence of laser energy's fluctuation on Z-scan measurement. If the quality of beam distribution isn't perfect, we can increase output energy of laser, then use keyhole to extract part of light source and expand to the limited plane wave through lens to realize the nearly Gaussian distribution. However, the too high output energy of laser may lead the nonlinear refraction and nonlinear absorbing saturation for the materials. So, to precisely test the nonlinear optical parameters, the laser intensity should keep in a proper range. Additionally, before measuring this sample, the system was calibrated using CS_2 in a quartz cell as reference. The value was measured to be 3.30×10^{-18} m^2/W, which is well accorded with the literature [19]. We performed the Z-scan measurement both on the IZO nanowires, validating that the measured NLO phenomena originate from IZO nanowires. The experiments were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows a low and high magnification SEM image of sample. The image shows evidence of the nanostructured morphology of the IZO nanowires. The diameter of single IZO nanowire is 56 nm, as shown in Fig. 1(b). The distribution of the diameter size on the nanowire was calculated, as shown in Fig. 2. And the average size of low-dimensional structure nanocrystal for the IZO nanowires was 56.21 nm. The general idea of size dispersion of low-dimensional structure nanocrystal is adopted from Ref. [22]. The results show that the size dispersion (ξ) of the IZO was 12.6%. The smaller semiconductor dopants concentration leads to finer nanowires diameter size dispersion but greater average size. Therefore, there are some coarser nanowires but also an increased number of finer nanowires, resulting in an unchanged average radius but poor size dispersion. The typical composition analysis of the sample is presented in Fig. 3(a). It is observed that the concentration of incorporated In in the samples were 3.9 at.%, and no peaks are detected from other materials. Thus, the [In]/[Zn] atomic concentration ratio varied around 1:10. In addition, the XRD pattern of the samples is shown in Fig. 3(b). The diffraction peaks at 2θ (degrees) of 32.231, 34.681, 36.381, 47.681, 57.152 and 63.841 are indexed to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) planes of ZnO, respectively. The diffraction peaks at 2θ (degrees) of 31.926 is indexed to (2 2 2) planes of In. Notably, the intensity of the (0 0 2) diffraction peak substantially decreased, which indicates that the crystallization of the IZO nanowires had changed. Moreover, XRD analysis of the IZO nanowires (Fig. 3(b)) reveals that the IZO nanowires are the wurtzite structure of ZnO with lattice constants a = 0.3258 nm and c = 0.5275 nm. And the lattice constant of IZO nanowires was larger than that of the pure ZnO (a = 0.32475–0.32501 nm, c = 0.52042–0.52075 nm [23]). Due to the difference of radius between In^{3+} ion (0.084 nm) and Zn^{2+} ion (0.074 nm), In can be incorporated in ZnO system as a substituent for Zn^{2+} to suppress the growth of ZnO. Additionally, the morphology of various In-doped ZnO nanostructures depends on the growth conditions. As shown in the inset of Fig. 1(b), the past of the single IZO nanowire was showed. The results show that

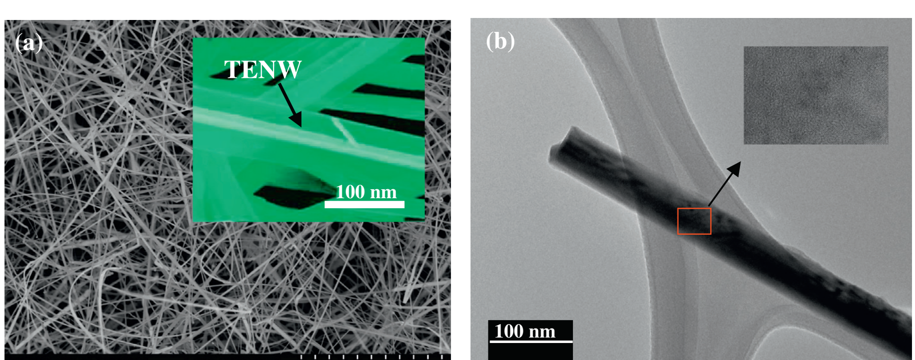

Fig. 1. SEM (a) and TEM (b) image of the IZO nanowires.