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Photoluminescence and field emission properties of Sn-doped ZnO microrods

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ABSTRACT

Sn-doped ZnO (SZO) microrods have been fabricated by a thermal evaporation method. Effect of Sn dopant on the microstructure, morphological and composition of as-prepared SZO microrods have been investigated by X-ray diffraction (XRD), Raman, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. The influence of the doping concentration on the morphological of the microrods has been investigated. Photoluminescence (PL) of these SZO microrods exhibits a weak ultraviolet (UV) emission peak at around 382 nm and the strong green emission peak at around 525 nm at room temperature. Field emission measurements demonstrate that the SZO possess good performance with a turn-on field of ~1.94 V/μm and a threshold field of ~3.23 V/μm, which have promising application as a competitive cathode material in FE microelectronic devices.

1. Introduction

As a wide band gap (3.37 eV of bulk material at room temperature) semiconductor with large exciton binding energy of 60 meV, ZnO is a promising material with many applications, such as chemical sensors, lithium ion electrode materials, solar cells, cathode emitters of the field emission (FE) device [1–5] and so forth. Therefore, syntheses and various properties of ZnO structures have been widely investigated. The FE measurement results of ZnO structures such as well-aligned randomly oriented, tetrapod-like, and gallium doped ZnO nanowires [6–9] show that 1D ZnO structures have promising applications in the FE device. Generally, the FE current depends on the work function of the material, the tip morphology and the density of nanostructures. It is still a challenge to develop some structures possessing a number of active emitting centers for a given emitter. Moreover, it is well known that the structural properties and dopants may determine the electronic properties of the material. Sn can serve as a doubly ionized donor with the incorporation of SnO_2 as a solute in ZnO and, consequently, provide high electron carrier concentration. Therefore, it is expected that SZO structures have higher electrical conductivity and better field emission properties.

In this work, SZO microrods were fabricated using conventional thermal evaporation method at a low temperature of 500 °C. Powder mixture of pure ZnO, Sn and graphite was employed as the source material. Room temperature PL of these SZO microrods exhibits a weak UV emission peak and a strong green emission peak. The field emission measurements confirm that the SZO microrods have a lower turn-on field, lower threshold field, and uniform electron field emission with higher emission spot density.

2. Experimental

In our experiments, all the growth was performed in a conventional horizontal tube furnace at atmospheric pressure. A quartz boat loaded with a mixed source of high-purity ZnO powder, graphite powder and Sn powder was pushed into the center of the tube. A piece of single crystal silicon substrate was then placed over the quartz boat as a substrate, 5 mm above the source powder. Meanwhile, argon at a flow rate of 800 sccm was introduced into the deposition system. After the heating process under a temperature of 500 °C lasted about 90 min, the furnace was cooled down to room temperature at the rate of 5 °C/min. A layer of white products (the SZO sample) was found on the surface of silicon substrate.

The obtained SZOs were investigated by X-ray diffraction (XRD), Raman spectra, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and photoluminescence (PL) spectra. Field emission (FE) properties were measured with diode structure in a vacuum chamber at a pressure of 5.0×10^{-5} Pa at room temperature, the sample (as a cathode) was separated from a phosphor/ITO/glass anode by Teflon spacers with thickness of 400 μm.

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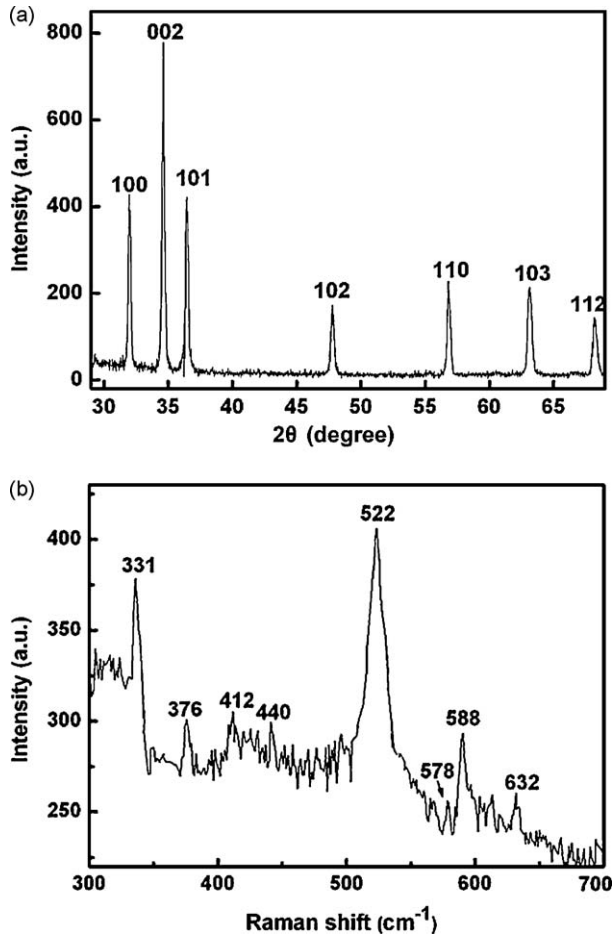

Fig. 1. (a) XRD pattern of the as-fabricated SZO microrods. (b) Raman spectra of the SZO microrods.

3. Results and discussion

Fig. 1(a) shows the XRD (D/max 2550 V) patterns of as-fabricated SZO. All of the diffraction peaks of the sample exhibited a common exactly wurtzite hexagonal crystallized of ZnO (JCPDS Card no. 80-0074) with lattice constants $a = 0.325$ nm and $c = 0.521$ nm. The main sharp diffraction peaks at 31.6°, 34.4°, and 36.3° fit well with the (1 0 0), (0 0 2), and (1 0 1) planes, respectively. No peaks for tin oxide or other impurities were detected within the sensitivity of XRD measurements, revealing the phase purity of the products. Fig. 1(b) shows the room temperature Raman spectra of samples. As shown in Fig. 1(b), the peaks at ~331, ~376, ~412, ~440, ~578 and ~588 cm^{-1} are consistent with the A_1 (TO), E_2 (high)–E_2 (low), E_1 (TO), E_2 (high), A_1 (LO) and E_1 (LO) vibration modes of ZnO, respectively [10,11]. These peaks show that the SZO possess the main characteristic of the ZnO wurtzite hexagonal structure, which is in good agreement with the results of XRD. In addition, the Raman peak at 632 cm^{-1} is attributed to SnO_2 and the peak at 522 cm^{-1} is originated from Si substrates [12].

The thermal evaporation method is widely used in the control synthesis of nanostructure materials. The stability and repeatability of nanostructure growth is determined by all the technology conditions such as temperature grads, flow rate of carrier and/or reaction gas, source material and substrate, etc. But it is still a challenge to be used in controlling the doping concentration of nanosturctures. The morphologies and composition of as-prepared products were examined by SEM and EDX, respectively. Fig. 2 gives the general morphologies of the SZO microrods. It can be seen that

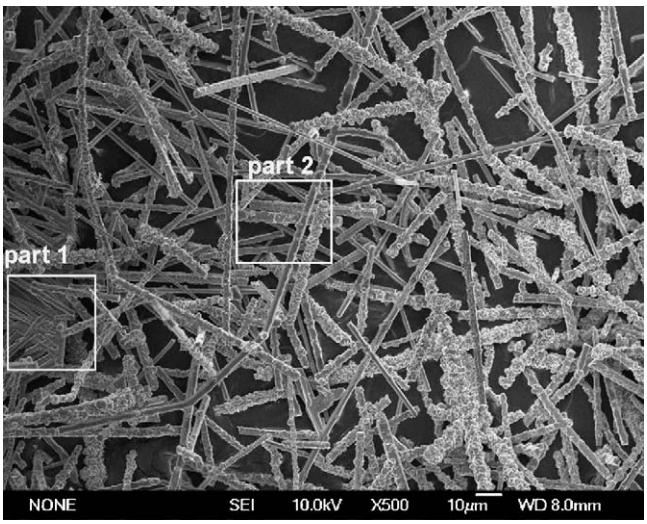

Fig. 2. SEM image of the SZO microrods.

there are large percentage of the products with interesting rod structures covering the surface of the substrate on a large scale. Careful observation reveals that the morphologies are quiet different between part 1 and part 2 of the sample. As shown in Fig. 3(a), the SZO (part 1) contains lots of quasi one-dimensional microstructures, which are about dozens micrometres in length and ~1.5 μm in width. Inset of Fig. 3(a) shows typical sidewalls of the microrods, from the hexagonal prism structure we can conclude that the ZnO microrods grow in [0 0 0 1] direction and the micro architecture is constructed from slips perpendicular to the growth direction. Corresponding EDX analysis of the part 1 is shown in Fig. 3(b). Measurements on 6 different microrods from part 1 were carried out, and doped microrods in this investigation have an average Sn concentration of ~0.5%. The concentration variation range of these microrods is 0.4%–0.6%. Fig. 3(c) shows the geometrical appearances of SZO microrods (part 2) with about 2 μm in diameter, and the micro architecture is constructed from slips with an acute angle to the growth direction. Inset of Fig. 3(c) is the corresponding high magnification SEM image of a single microrod with many sharp tip structures on the surface, which are very effective to improve the field emission properties. The EDX analysis of part 2 (Fig. 3(d)) reveals that the average Sn atomic concentration measured from 6 different microrods in part 2 is ~1.2%, much larger than that of part 1. The concentration variation range of these microrods is 1.1%–1.3%. This indicates that the fraction of Sn to Zn can influence the morphologies of the SZO microrods. Fig. 3(e) shows a schematic illustration of the SZO microrods structures with different molar fractions of Sn. Such an acute angle may be attributed to larger compressive stresses generated in higher Sn concentration microrods arising from the difference in thermal expansion coefficients as a result of the smaller ionic radii of Sn^{4+} (0.069 nm) in comparison with that of Zn^{2+} (0.074 nm), and the higher number of Zn vacancies existing in higher Sn-doped microrods. Therefore, the variation of mole fraction of the dopant Sn would influence the internal stress resulting in different slip structures of the SZO microrods [13].

The PL spectrum of the SZO microrods is shown in Fig. 4, using a He–Cd laser at 325 nm as the excitation source. It exhibits a UV emission centered at about 382 nm and wide green emissions at around 525 nm. The former is in good agreement with the typically reported free exciton peak position, and could be explained by the near-band edge emission [14] while the latter is attributed to the singly ionized oxygen vacancy in the ZnO microstructures, and results from the radiative recombination of a photo generated hole