

Structure and Photoluminescence Properties of ZnO Nanocombs Synthesized from Metal Zn Powder

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High quality ZnO nanocombs have been fabricated in high yields through oxidative evaporation of pure zinc powder without catalyst at 600–650 °C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations showed that the resulting ZnO nanostructures have one main type of single crystal morphology. Investigations through XRD revealed that the growth of the synthesized ZnO nanostructures was controlled by a vapor–solid (VS) mechanism. The band gaps of the products are ~3.26 eV determined from UV/visible absorption spectral results. Room temperature photoluminescence (PL) spectra of the nanocombs showed a UV emission at 388 nm and a broad green emission at 520 nm. Such novel structures are promising for applications in some special fields.

Keywords: ZnO Nanocombs, Crystal Growth, Vapor–Solid Mechanism, Photoluminescence.

1. INTRODUCTION

Zinc oxide has a hexagonal structure, lattice constants $a = 0.324\text{--}0.326$ nm and $c = 0.513\text{--}0.543$ nm, a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature.^{1–3} This one dimensional (1D) or quasi 1D zinc oxide nanomaterials are promising materials for applications in blue light-emitting diodes (LEDs), field-effect transistors (FET), ultraviolet laser diodes (LD), sensors, acousto-electrical devices, and detectors. Owing to numerous fundamental studies as well as for applications in one-dimensional nanodevices and other functional materials, ZnO nanostructures have received considerable attention. In addition to nanowires, nanobelts, tetrapod-like nanorods and nanotubes,^{4–7} other interesting nanostructures such as nanopropellers, nanosprings and nanorings have also been synthesized.^{8–10}

Conventionally, according to growth mechanism, the main fabrication methods of 1D ZnO nanostructures are vapor–solid (VS) growth, vapor–liquid–solid (VLS) growth and polar-surface dominated growth.^{10–12} The VLS growth involves the existence of a liquid-forming (or so-called catalysts) additive.^{12–13} Catalysts such as copper, gold, cobalt or other transition metal nanoparticles/film can often be used. In this method, the usual synthesis temperature is in the range of 850–950 °C,^{2,3,12–15} and the lowest preparation temperature for ZnO nanowires temperature

was reported as 450 °C (NiO catalyzed).¹⁶ The synthesis temperature for ZnO nanostructures by VS growth is from 850 °C (Zn-powder evaporation) to 1400 °C (zinc oxide powder evaporation).^{6,11,17–19} The temperature by VLS growth is much lower, but catalysts in the nanomaterials may affect purity and possibly properties.

In this paper, we report some novel quasi 1D ZnO nanostructures, nanocombs fabricated by an improved method. Such nanostructures were prepared onto a silicon substrate by metal zinc powder evaporation and deposition without catalyst. The structures and photoluminescence (PL) property of the nanomaterials were also investigated.

2. EXPERIMENTAL TECHNIQUE

The growth processes were carried out in a quartz tube, 4 cm in diameter, and 100 cm in length. The pure metal zinc powder (99.99%) as source materials was put in an alumina crucible and several pieces of Si substrates were positioned over the boat to collect the products. Then the crucible was inserted into the center of the quartz tube in a horizontal tubular furnace. Under a constant flow rate (260 sccm in total) of the gas mixture of Argon (97% in vol concentration) and oxygen (3% in vol concentration), the temperature of crucible was raised to 650 °C at a rate of about 20 °C/min and kept at this temperature for 45 min, then cooled to room temperature. The morphology and crystal structure of the synthesized nanostructures were characterized by X-ray diffraction (XRD)

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using a DRON 4 utilizing Cu K α radiation, scanning electron microscopy (SEM) employing a JSM-6380LV instrument and transmission electron microscopy (TEM) on a Philips EM 420 120 kV instrument. UV/visible absorption measurements were carried out on the ZnO nanocombs using a spectrophotometer (UV-210 A, Shimadzu) in a range between 190 and 900 nm. The Photoluminescence (PL) spectra were using for excitation a 337 nm ILGI 503 N2 laser.

3. RESULTS AND DISCUSSION

XRD measurements were performed for the as-deposited materials to examine the structure and phase purity. A typical XRD pattern of the nanomaterials was shown in Figure 1(a). all diffraction peaks can be indexed to wurtzite ZnO (lattice constants: $a = 0.3248$ nm and $c = 0.5205$ nm, JCPDS 89-0510). The results also show that all the deposited materials on the silicon substrate are pure ZnO and no diffraction peaks from Zn or other impurities were

found in the samples. In addition to this, the energy dispersive spectroscopy (EDS) confirmed that the as-grown nanocombs are made with almost 1:1 stoichiometry of zinc and oxygen Figure 1(b). Figures 2(a) and (b) shows typical scanning electron microscopy (SEM) images of nanocombs. The usual width of the backbones of the nanocombs is about 400 nm to 1 μ m, and the thickness is around 50–100 nm, while the length is up to several tens of microns. The teeth of the combs have diameters ranging from about 50 to 100 nm and length ranging from hundreds nanometers to several microns. Further structural characterization of the grown products was made using the transmission electron microscope (TEM). Figure 3 shows the low magnification TEM image of the nanocombs, which reveals the full consistency with the SEM observation in terms of morphology and dimensionality. Clearly, it is seen in the TEM image that the branches of the nanocombs are attached along one side of the ribbon-like stem.

It is well known that ZnO is a degenerate semiconductor with band gap energy (E_g) in the range of 3.3–3.77 eV.²⁰ This scatter in band gap energy (E_g) of ZnO may be due to varied extent of non-stoichiometry of the deposited layers. The dependency of the band gap energy on the carrier concentration has been explicitly given in the literature.²¹ It has been apprehended that band gap energy increases linearly with the increase in carrier concentration to the power 2/3. High-energy shift of an absorption

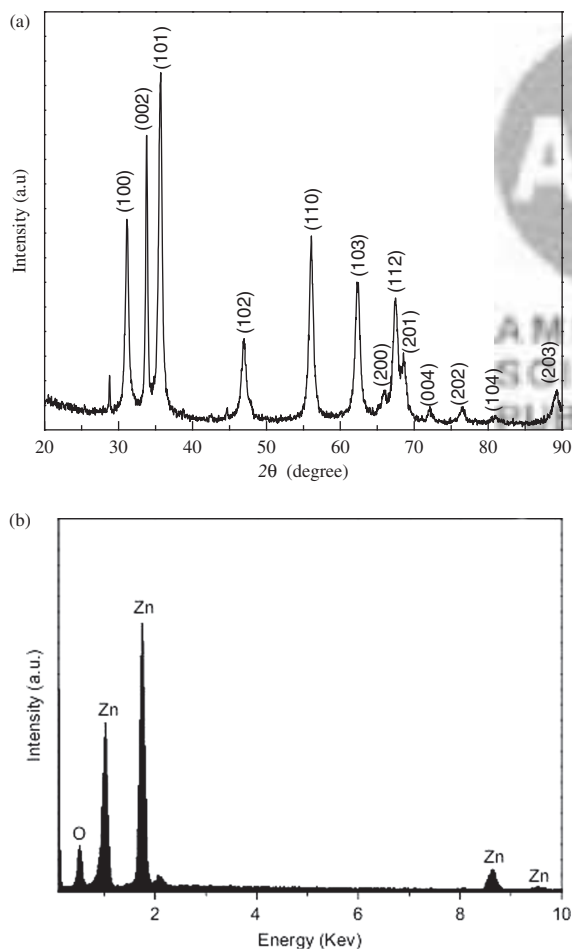


Fig. 1. (a) X-ray diffraction patterns of ZnO nanocombs. (b) EDS spectrum of high density ZnO nanocombs.

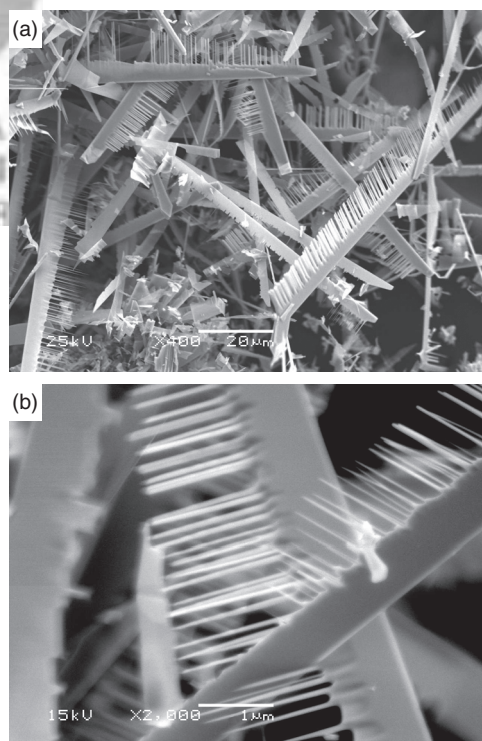


Fig. 2. (a) Scanning electron microscopy images of the synthesized ZnO nanocombs at magnifications of $\times 400$ (a) and $\times 2,000$ (b).

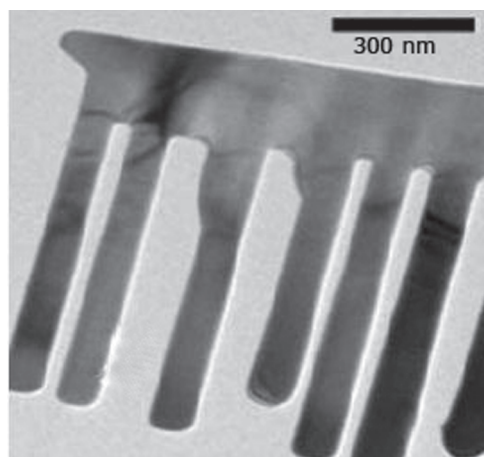


Fig. 3. Transmission electron microscopy image of ZnO nanocombs.

edge is generally expected for nanocrystalline materials. In order to confirm this, absorption spectra were acquired from the ZnO nanocombs, and the results are depicted in Figures 4(a) and (b). The optical transition of ZnO crystals is known to be a direct type.²² In this case, the absorption coefficient α is expressed as $\alpha(h\nu) \propto (h\nu - E_g)^{1/2}/h\nu$.²³ Plots of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Figure 4(b). From the intercept and slope of the tangent to the plot gives a good approximation of the band gap energy of the direct band gap materials. It was found that the E_g for sample is ~ 3.26 eV and in good agreement with previously reported data of ZnO nanostructures.^{24–25}

The PL spectrum of ZnO nanocombs was measured at room temperature and is shown in Figure 5. Two typical emission peaks at ~ 388 nm and at ~ 520 nm were observed, which were assigned to UV emission and green emission, respectively. It was reported that the improvement of crystal quality (decrease of impurities and structure defects) can result in detectable UV emission at room temperature, while the green transition is attributed

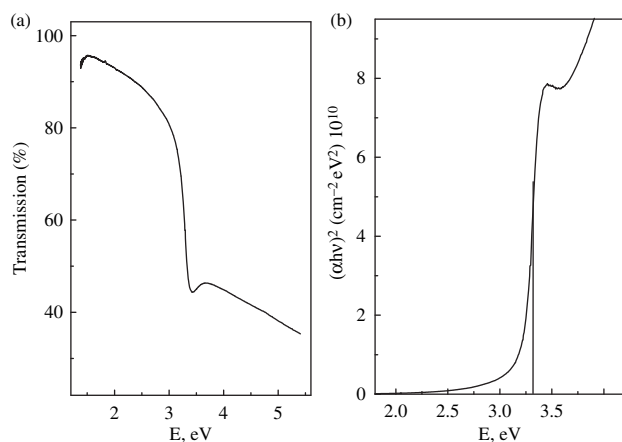


Fig. 4. (a) Spectral variations of transmittance (T) for ZnO nanocombs; (b) $(\alpha h\nu)^2$ ($\text{cm}^{-2} \text{eV}^2$) versus photon energy curve for ZnO nanocombs.

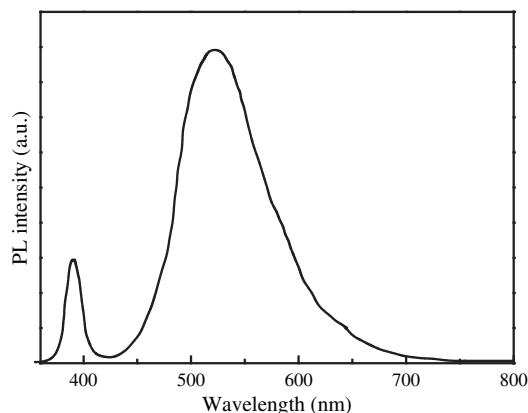


Fig. 5. Photoluminescence spectrum of ZnO nanocombs.

to singly ionized oxygen vacancies in the ZnO; emission results from the radiative recombination of a photo generated hole with an electron occupying the oxygen vacancy. The green light emission intensity increases relative to the UV emission as the wire diameter decreases, which suggested that there is a greater fraction of oxygen vacancies in the thinner nanostructures.^{26–29} Therefore, it is reasonable to believe that some oxygen vacancies exist in the ZnO nanocombs and the green light emission from the ZnO nanocombs could be attributed to the single ionized oxygen vacancy.

4. CONCLUSIONS

By controlling the gases flow rates, partial pressures of argon, oxygen and zinc vapor, uniform and high-yield ZnO comb-like nanostructures have been fabricated successfully through pure zinc powder evaporation without catalyst at 600–650 °C. The synthesis temperature, gases flow rates and vapor partial pressures determine the shape and size of the ZnO nanostructures. SEM observations showed that such ZnO nanostructures have one typical kinds of morphologies, and both of them are single crystalline. Investigations through XRD revealed that the growth of the synthesized ZnO nanostructures was controlled by vapor-solid mechanism. The optical direct band gap lies in range ~ 3.26 eV. Room temperature photoluminescence spectra of the nanocombs showed a UV emission at ~ 388 nm and a broad green emission at ~ 520 nm. Such structures with regular dimension and arrange are promising for applications in some special fields.

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