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Fabrication and characterization of ZnO comb-like nanostructures

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Abstract

High quality ZnO comb-like nanostructures have been fabricated in high yields through oxidative evaporation of pure zinc powder without catalyst at 600–650 °C. SEM, FE-SEM and HRTEM observations showed that the resulting ZnO nanostructures have two main types of single crystal morphology. Investigations through HRTEM and XRD revealed that the growth of the synthesized ZnO nanostructures was controlled by a vapor–solid (VS) mechanism. Room temperature photoluminescence (PL) spectra of the nanocombs showed a UV emission at ~385 nm and a broad green emission at ~495 nm. Such novel structures are promising for applications in some special fields.

Keywords: ZnO nanostructures; Crystal growth; Vapor–solid mechanism; Photoluminescence

1. Introduction

Zinc oxide has a hexagonal structure, lattice constants $a = 0.324$–0.326 nm and $c = 0.513$–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) [6,11,17–20]. 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

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without catalyst at lower temperature. The structures and photoluminescence (PL) property of the nanomaterials were also investigated.

2. Experimental procedure

The ZnO comb-like nanostructures were fabricated by the following procedure. The silicon substrate (15 mm × 15 mm) was placed face down on an alumina ceramic boat loaded with metal zinc powder (99.9%) with thickness of 1–3 mm. The vertical distance between the zinc source and the substrate was about 5–8 mm. The boat (10 mm × 10 mm × 100 mm length) was inserted into a quartz tube (30 mm inside diameter and 1000 mm length) of a tubular furnace under a constant flow of argon and oxygen. The total flow rate was 200–300 standard cubic centimeters per minute (sccm), and the fraction of oxygen was 2–5% according to the different conditions. The gases were fed and mixed by a Y-shape tube and controlled respectively by mass flowmeter. The quartz tube was heated up to 600–650 °C for 20–40 min. After evaporation finished, the exposed substrate surface (15 mm × 10 mm) showed full of white wax or fluffy-like materials. No catalyst was utilized in all the deposition process.

The deposited products were characterized by scanning electron microscopy (SEM) [Cambridge S360], field emission scanning electron microscopy (FE-SEM) [JEOL-6700F], X-ray diffraction (XRD) [Rigaku DMAX-RB] and high-resolution transmission electron microscopy (HRTEM) [JEOL-2010]. The PL spectrum was measured by a HITACHI 4500-type VIS-UV spectrophotometer with a Xe lamp as the excitation light source at room temperature.

3. Results and discussion

The uniform ZnO comb-like nanostructures (or nanocombs) were fabricated by controlling the flow rates and partial pressures of argon, oxygen and Zn vapor at 600–650 °C. The temperature was far lower than that in our previous work at 850 °C in the similar method [6,11,18], and no other lower temperature was found in our obtained references while the 1D ZnO nanostructures were synthesized by evaporation and deposition without catalyst. XRD measurements were made on all the fabricated products to assess the structure and phase purity. The investigations show that all the deposited materials on the silicon substrate are pure ZnO with the wurtzite structure. No diffraction peaks from Zn or other impurities were found in the samples. The diffraction peaks can be indexed to a hexagonal wurtzite structure with cell constants $a = 0.3242$ nm and $c = 0.5194$ nm. Fig. 1 shows the XRD spectra of the nanocombs and the indexing.

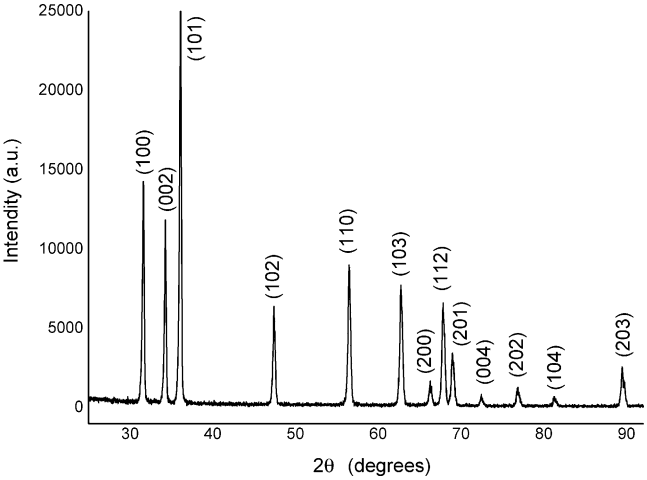

Fig. 1. XRD pattern of ZnO nanocombs.

In different fabrication conditions, the shapes of ZnO nanostructures differed. Typically fabricated combs exhibited two kinds of morphologies, i.e. nanocombs-I type (as seen in Fig. 2) and nanocombs-II type (as seen in Fig. 3). The usual width of the backbones of the nanocombs is about 400 nm to 1 μm, and the thickness is around 50–100 nm,

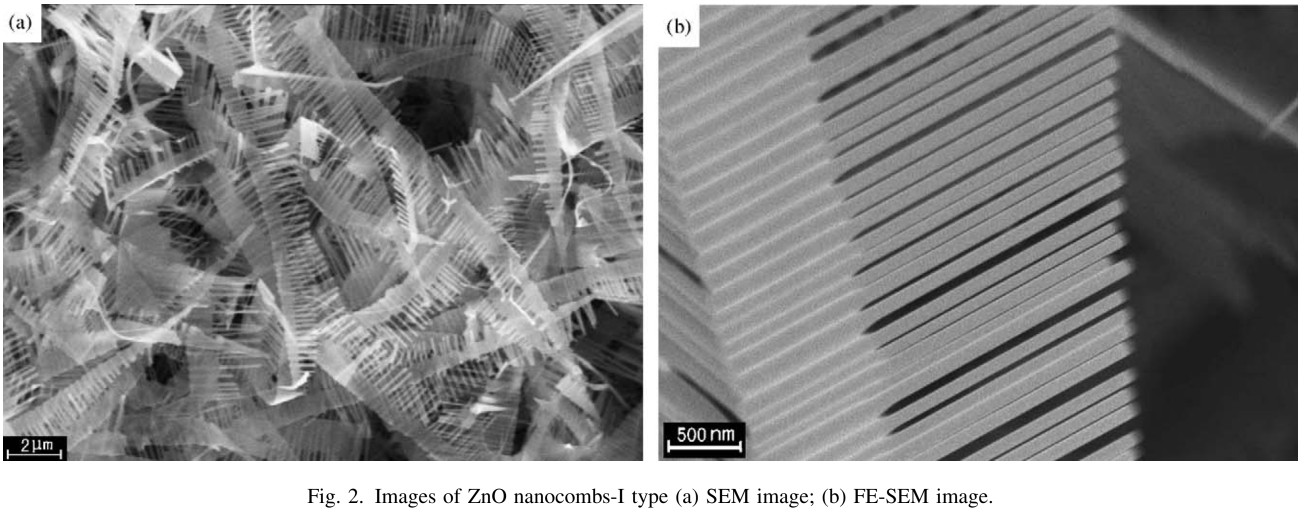

Fig. 2. Images of ZnO nanocombs-I type (a) SEM image; (b) FE-SEM image.

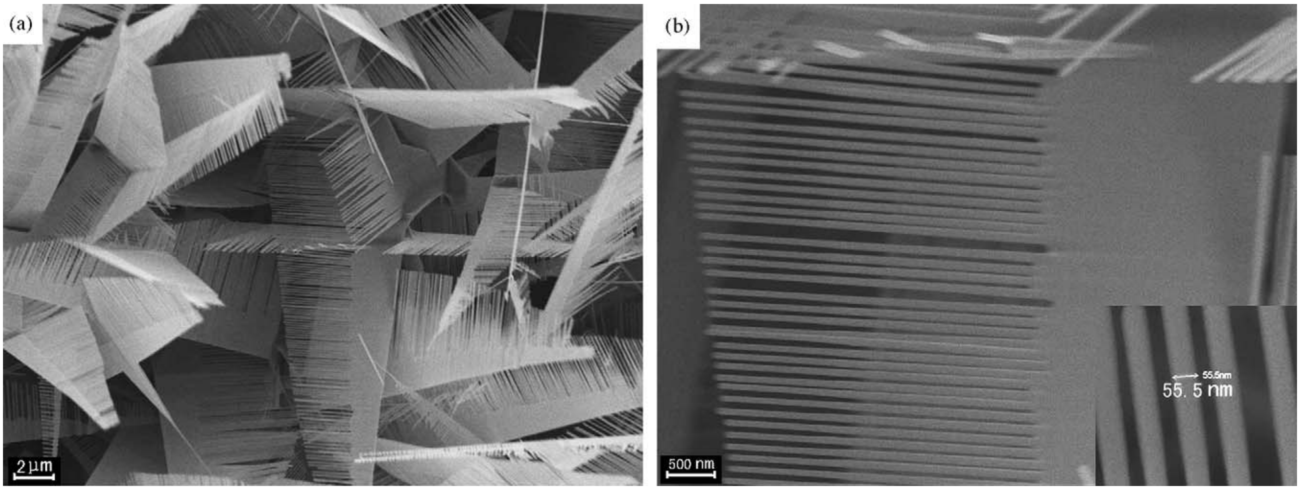

Fig. 3. FE-SEM images of ZnO nanocombs-II type.

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. The backbones of nanocombs-I are uneven like a washboard (Fig. 2b), while the backbones of type-II are smooth and have the same thickness as the teeth, Fig. 3b. The teeth of the combs exhibit regular diameter, length and spacing.

In our experiments, the ZnO nanocombs-I, Fig. 2 grew at the total flow rates of 220–260 sccm, oxygen partial pressures of 3%–5%, and 600 °C; while the combs-II, Fig. 3, grew at the total flow rates of ∼250 sccm, oxygen partial

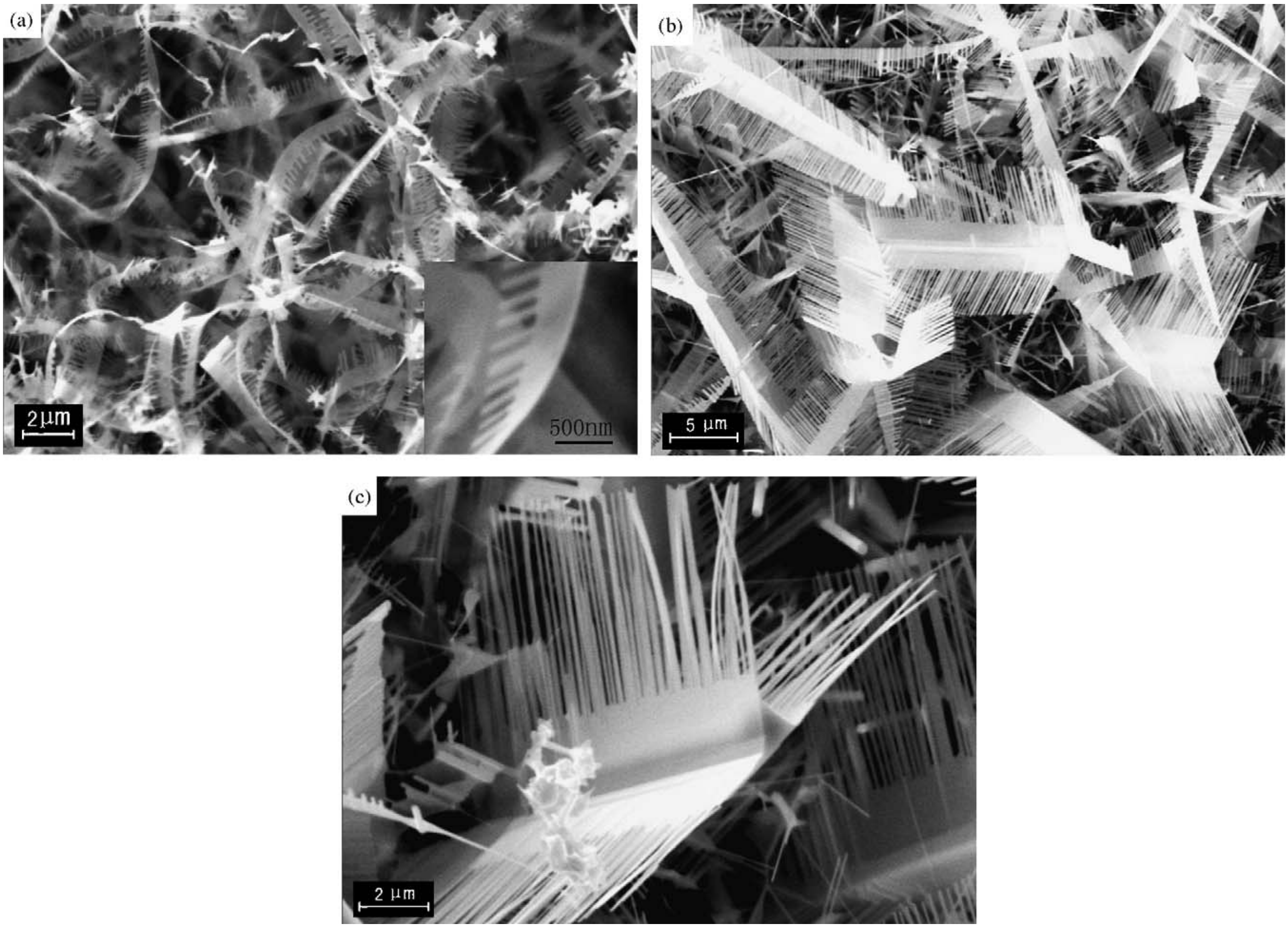

Fig. 4. SEM images of ZnO nanostructures (a) nanosaws; (b) two-edged nanocombs; (c) three-edged nanocombs.

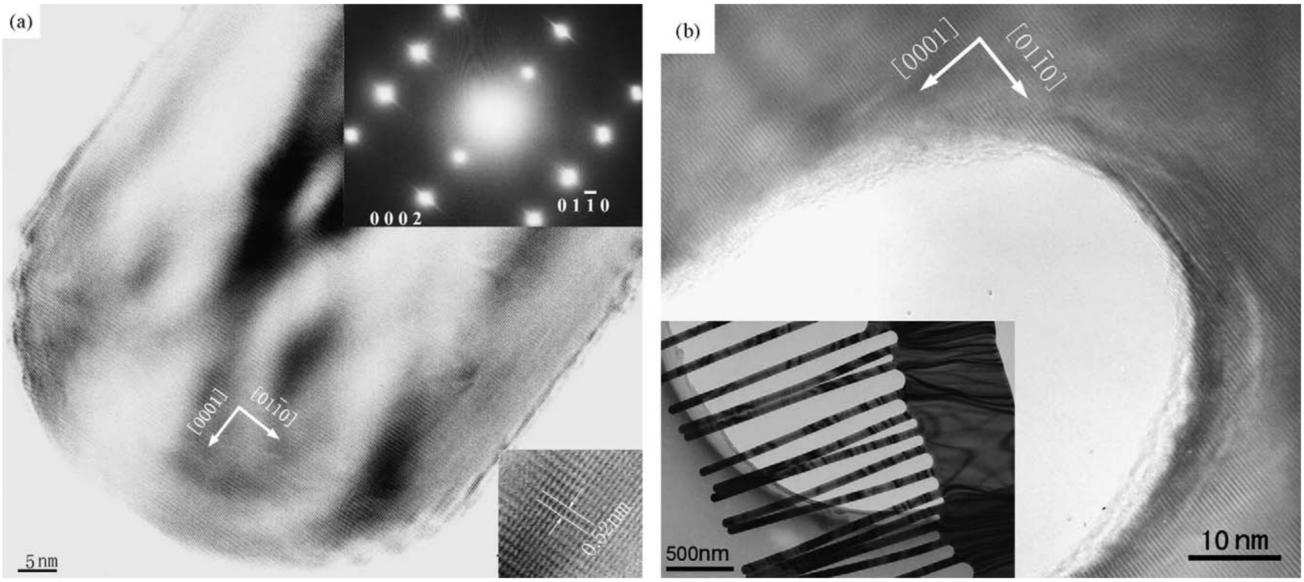

Fig. 5. HRTEM image and SAED pattern of ZnO nanocomb-II type (a) image of the tip of the tooth; (b) image of the joint of the tooth and backbone.

pressures of 2%–3% and 650 °C. The key to the fabricating method is to control the flow rates of gases, partial pressures of argon, oxygen and zinc vapor. The flow rates and partial pressures influence the size of nanostructures, and more remarkably determine the shape. Experiments revealed that the synthesis temperature influences the shape by changing the partial pressures of Zn; this also affects the size. As the temperature or partial pressure Zn vapor increases and the flow of gases are invariable, both teeth and backbones of the nanostructures become thicker and shorter. The nanostructures with smaller ratio of length to diameter and the thicker structures form most readily at the areas where the gas flow is blocked, or as the gas flow decreases.

In some conditions, nanosaws, two-edged or three-edged nanocombs have been prepared. The nanosaws, Fig. 4a, grew at lower flow rate and oxygen partial pressure while the total flow rate of Ar and O_2 was 200–230 sccm, partial pressure of O_2 was about 2% and the temperature was around 600 °C. The two-edged or three-edged nanocombs as Fig. 4b and c occurred accidentally near the interface where the silicon substrate met with ceramic boat when nanocombs-II were synthesized. The synthesis conditions at the irregular interface are very complicated since the gas flow is unexpectable and incontrollable in the area. This resulted in the peculiar and variable species.

Fig. 5 showed the HRTEM images and the selected area electron diffraction (SAED) pattern of the nanocomb-II type. SAED pattern and HRTEM image reveal that the ZnO nanocombs are structurally uniform and single crystalline. In zinc oxide crystal with hexagonal structure, $[0\,0\,0\,1]$, $[2\,\bar{1}\,\bar{1}\,0]$ and $[0\,\bar{1}\,1\,0]$ are preferential growth directions. The presented images also suggested that the tooth growth occurs along the $[0\,0\,0\,1]$ direction and the backbone along $[0\,\bar{1}\,1\,0]$. But in our observations, some teeth grew along $[2\,\bar{1}\,\bar{1}\,0]$ and the backbones along $[0\,0\,0\,1]$. The results revealed that the nanocombs may grow in two different directions.

Contrasting with VS growth, VLS growth requires the existence of a liquid. The presence of solidified spherical droplets at the tips of the nanowires or others are commonly considered to be evidence for the operation of the VLS mechanism [12–13]. The growth process can be divided into two stages: the nucleation and growth of eutectic alloy droplets and the growth of nanowires through the liquid droplets due to supersaturation. At the initial nucleation stage, Zn vapor might condense. The uniform geometry of the nanowire suggests that the growth front develops in the liquid state during growth, which is energetically favorable, and serves as the stable sites for the rapid stacking of incoming atoms. The growth front experienced a rapid oxidation after the temperature dropped and the nanowire exposed to an oxygen atmosphere [11]. On the contrary, no

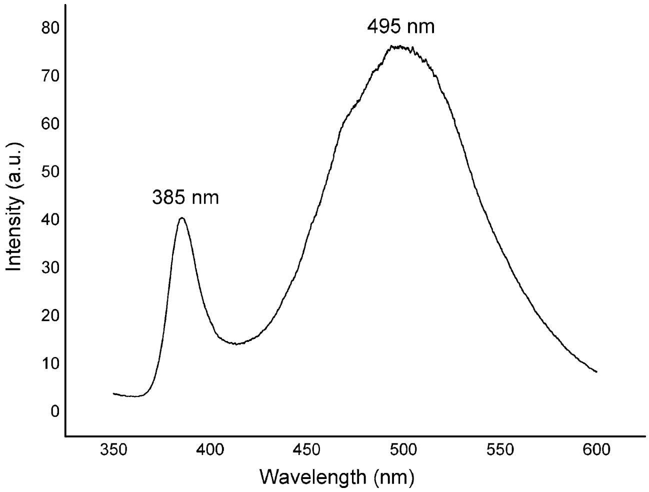

Fig. 6. PL spectrum of ZnO nanocombs-II type at room temperature.

catalyst is utilized and no solidified droplet is at the tip of any nanostructure when the growth is governed by a VS process. Such nanomaterials can be formed by oxidation of evaporated zinc vapor in gas phase [6]. In our process, some metallic zinc was in its vapor state. The gaseous zinc diffused and was immediately oxidized in the environment of oxygen. The oxidation reaction at our processing temperature is as follows: $2Zn(g) + O_2 = 2ZnO(s)$. The process of the initial nucleation includes diffusion, collision of atoms and reaction between the vapor molecules (including vapor Zn and O_2). When the supersaturation increases to a level at which nuclei formed, the produced ZnO nuclei grow to sizes larger than the critical size. The ZnO nuclei formed in the alumina crucible are homogeneous as carried by the gas phase. The investigations through HRTEM and XRD indicated that nothing except the ZnO crystal occurred at the tip of tooth or around the structures, i.e., the growth of the fabricated ZnO nanocombs is controlled by VS mechanism.

The PL spectrum of ZnO nanocombs-II type was measured at room temperature and is shown in Fig. 6. The excitation wavelength was 310 nm. Two typical emission peaks at ~385 nm and at ~495 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 to singly ionized oxygen vacancies in the ZnO; emission results from the radiative recombination of a photogenerated 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 [21–23]. 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, FE-SEM and HRTEM observations showed that such ZnO nanostructures have two typical kinds of morphologies, and both of them are single crystalline. Other nanostructures, such as nanosaws, two-edged or three-edged nanocombs have been prepared in some conditions. Investigations through HRTEM and XRD revealed that the growth of the synthesized ZnO nanostructures was controlled by vapor-solid mechanism. Room temperature photoluminescence spectra of the nanocombs showed a UV emission at ~385 nm and a broad green emission at ~495 nm. Such structures with regular dimension and arrange are promising for applications in some special fields.

Acknowledgements

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