

Growing one-dimensional ZnO nanostructures

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Using zinc foils as the only starting material, we synthesized one-dimensional ZnO nanostructures (nanorods, nanoneedles and nanowires) in air by zinc vapor condensation method at 500°C. The morphology, structure and photoluminescence of the synthesized one-dimensional ZnO nanostructures were investigated with scanning electron microscopy, X-ray diffractometry, transmission electron microscopy and spectrophotometry. It is found that the size, shape and photo luminescent properties of the one-dimensional ZnO nanostructures depend on the growth time of ZnO in the furnace. Mechanisms on the growth of the nanostructures were discussed, and controllable morphology and photoluminescence of the ZnO nanostructures were achieved by varying the growth time of ZnO in the furnace. It provides a simple, energy-saving and environment benign route to synthesize one dimensional ZnO nanostructures with controllable morphology and emission properties.

Keywords: Zinc oxide; Photoluminescence; Nanostructure; Zinc vapor evaporation

1. INTRODUCTION

Due to the large exciton binding energy (60 meV) and direct wide band gap energy (3.4 eV), ZnO nanostructures are viewed as the fundamental building blocks for constructing electronic devices such as ultraviolet nanolasers and solar cells. The synthesis of ZnO nanostructures is a key component for the fast development of the ZnO based nanotechnology; various chemical and physical methods have been reported for fabricating ZnO nanostructures [1-4]. Among the physical methods, thermal evaporation and

condensation is the most common technique to prepare ZnO nanostructures, but high temperatures (above 1000oC) and vacuum chamber are necessary to vaporize the zinc source material [5, 6]. The high temperature makes the production of ZnO nanostructures energy ineffective, while the vacuum system renders vacuum pumping auxiliaries indispensable. Here we report a simple and low-cost method to synthesize one-dimensional ZnO nanostructures in air at relatively low temperature (500oC) without usage of vacuum system. Various ZnO nanostructures (nanorods, nanoneedles and nanowires) are produced. The control on the morphology and photoluminescence (PL) is achieved by varying the growth time of ZnO in the furnace.

2. EXPERIMENTAL DETAILS

ZnO nanostructures were fabricated on zinc foils in air by vapor evaporation in a box furnace. After zinc foils (99.99%) were introduced into the furnace, the temperature of the furnace was kept at 500oC and the growth time was varied in the range of 1-20 hours. X-ray diffraction (XRD) characterization of the ZnO nanostructures was carried out on an X-ray diffractometer (D/max 2500 PC, Rigaku, Japan). A copper target was utilized to generate the X-ray ($\lambda = 0.154$ nm). Scanning electron microscope (SEM) and transmission electron microscope (TEM) (model JEM-2100, Japan Electronics Corp) were employed to characterize the morphologies of the ZnO nanostructures. The PL spectra of the ZnO nanostructures were recorded with a spectrophotometer. The 325-nm laser line from a helium-cadmium laser was utilized as the excitation source for the PL measurement.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the one-dimensional ZnO nanostructures grown in air at 500oC for 1, 3, 5 and 7 hours. Fig. 1(a) indicates that ZnO nanorods were resulted when the growth time was 1 hour. The diameter of the ZnO nanorods is about 20 nm and the length is about 400 nm, making the aspect ratio of the nanorods to be about 20. Fig. 1(b)-(d) demonstrate that the diameter, length and shape of ZnO nanostructures evolved with the growth time of ZnO in the furnace. As the growth time increased from 1 to 7 hours, the ZnO nanostructures got longer (up to 20 nm) in size and denser in population while the shape of ZnO nanostructures evolved from nanorods to nanoneedles and then to nanowires. The

aspect ratio of the nanostructures increased from 20 to 500 as the growth time was increased from 1 to 7 hours. The result in Fig. 1 demonstrate that the size and the shape of the ZnO nanostructures can be controlled by varying the growth time of ZnO in the furnace. Zinc has relatively low melting point of 419.5oC, and zinc vapor is created once the temperature in the furnace is raised to 500oC. It is thermodynamically favorable for the zinc molecules in the vapor phase to react with oxygen atoms in air to form ZnO, and ZnO nanoparticles will nucleate on substrates. Once nucleation occurs, remaining zinc vapor will be reacted with the oxygen in air to produce more ZnO nanoparticles, which will then be condensed on the resulting ZnO nuclei with the results of continuous growth of ZnO nanostructures [7, 8]. As a result, ZnO nanorods can grow longer in the form of nanoneedles and nanowires. (Fig. 1)

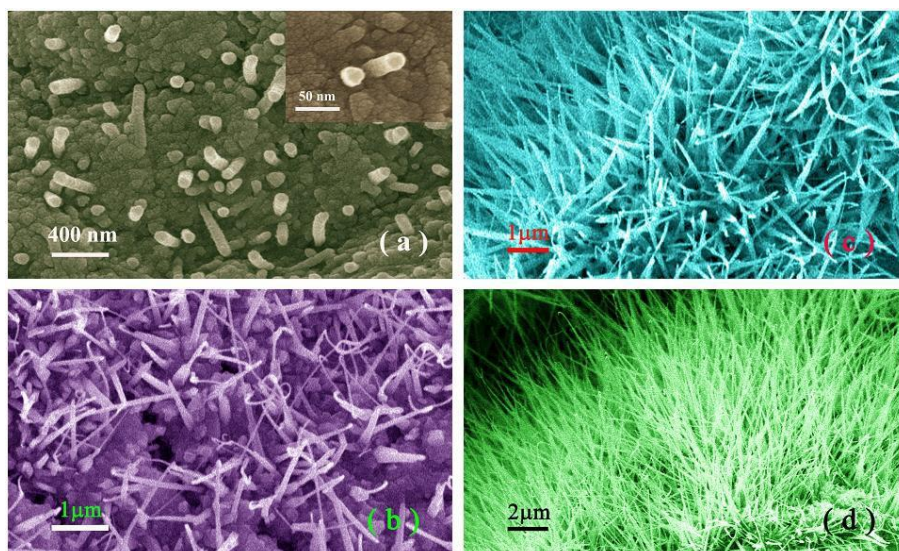


Figure 1 SEM micrographs of the ZnO nanostructures synthesized in air at 500oC for 1, 3, 5 and 7 hours.

Figure 2 depicts the XRD spectra of one-dimensional ZnO nanostructures grown on the zinc foils by the zinc vapor condensation method in air at 500oC for 1, 7 and 20 hours, respectively. The peaks at 31.8, 34.5, 36.3, 47.5, 56.6, 62.90, 68.1o in Fig. 2(a-c) can be assigned to the reflections from the 100, 002, 101, 102, 110, 103 and 112 planes of the hexagonal ZnO (JCPDS no.36–1451), while the peaks at 36.3, 38.9, 43.0, 70.1 and 77.0o in Fig. 2(a) and (b) can be assigned to the reflections from the 002, 100, 101, 103 and 104 planes of hexagonal zinc (JCPDS no.04–0831) [4]. Because the peaks of Zn (002) and ZnO (101) are located at the same diffraction angle 36.3o, it is hard to differentiate them in Fig.2(a) and (b). The co-existence of the diffraction peaks of zinc and ZnO nanocrystals in Fig. 2 reveals

that ZnO nanostructures have been formed on the zinc foil. As the growth time reached to 20 hours, only reflections from ZnO nanostructures were recorded with the results of complete disappearance of the reflections from zinc crystals because of the dense ZnO nanostructures grown on zinc foils. (Fig. 2)

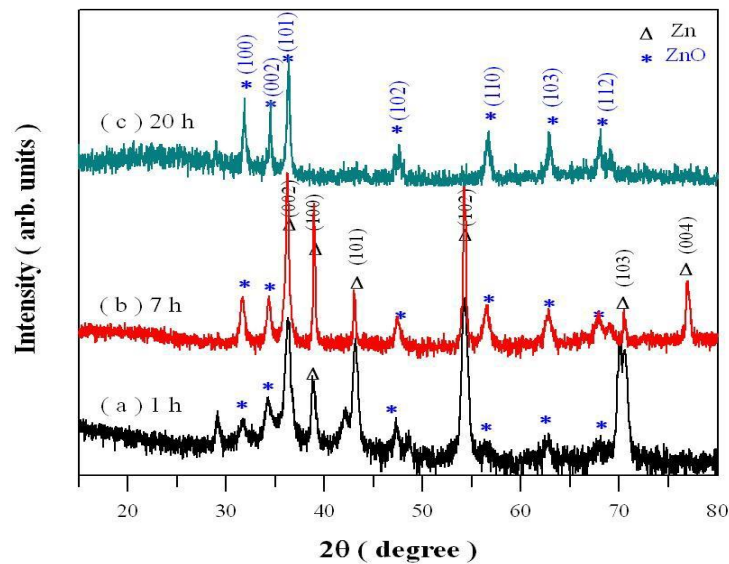


Figure 2 XRD spectra of ZnO nanostructures grown on the zinc foils by zinc vapor condensation in air at 500oC for 1, 7 and 20 hours, respectively.

Figure 3 illustrates the PL spectra of one-dimensional ZnO nanostructures grown on zinc foil in air by the zinc vapor condensation technique at 500oC for 1, 3, 5 and 7 hours, respectively. Each PL spectrum in Fig. 3 can be decomposed into an ultraviolet luminescent band with its peak wavelength at about 380 nm and a green luminescent band with its peak wavelength at about 500 nm. As the growth time increases from 1 to 7 hours, the green emission gets stronger in the meantime the ultraviolet emission gradually loses its intensity (Inset in Fig. 3). It is generally accepted that the green peak of ZnO is due to radiative recombination of a photo-generated hole with an electron attributed to an oxygen vacancy while the ultraviolet emission is attributed to the near band-edge free exciton transition [7-9]. It can be understood why the green emission gets stronger as the growth time is increased because more oxygen atoms on the surface of the ZnO nanostructures can be diffused into the nanostructures to form more surface and sub-surface oxygen vacancies. Therefore, the results in Fig. 3 indicate that the emission of the synthesized one-dimensional ZnO nanostructures can be controlled by varying their growth time in the furnace. (Fig. 3)

Figure 4 displays the high-resolution TEM image and the selected area electron diffraction pattern of the synthesized ZnO nanostructures. As shown in Fig. 4(a), the synthesized ZnO nanostructures are highly crystalline. The spacing between two adjacent planes is about 0.254 nm which is in good agreement with the distance between two (0002) crystal planes of ZnO. Fig. 4(b) shows the selected area electron diffraction pattern of the ZnO nanostructures. The hexagonal diffraction pattern verifies the wurtzite structure of the synthesized ZnO nanostructures. Our results in Fig. 4 demonstrate that wurtzite ZnO nanostructures were synthesized in air at 500°C. On one hand, our method is one of the simplest among the physical techniques to synthesize ZnO nanostructures because of one starting material and no involvement of vacuum system and inert carrier gases. On the other hand, our method is environment friendly because neither organics nor dangerous materials are used or produced in the synthesis. (Fig. 4).

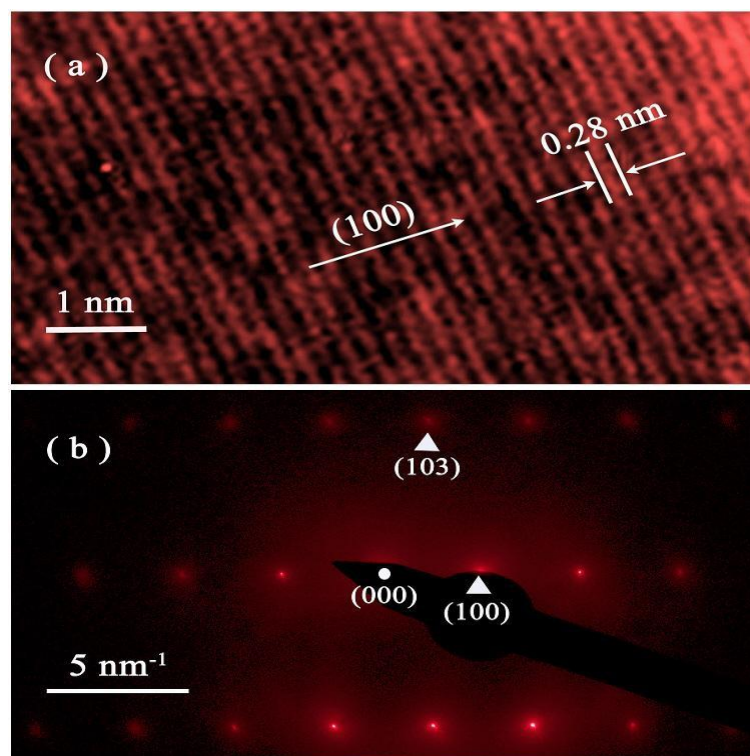


Fig. 3. High resolution TEM image and electron diffraction pattern of the synthesized ZnO nanostructures in air by zinc vapor condensation at 500 °C.

4 CONCLUSIONS

Various ZnO nanostructures have been synthesized in air by using zinc vapor condensation technique in air at 500°C. Controllable morphology and emission of the ZnO nanostructures have been achieved by varying the growth time of ZnO in the furnace. It provides a simple, low-cost and environment benign route to synthesize one-dimensional ZnO nanostructures with controllable morphology and emission properties.

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