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# Growth and properties of ZnO nanorod and nanonails by thermal evaporation

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ABSTRACT

ZnO nanorods and nanonails have been synthesized on silicon wafers by a three-step catalyst-free thermal evaporation method in oxygen atmosphere. All the samples were hexagonal phase ZnO with highly *c*-axis preferential orientation. Different morphologies of ZnO nanostructures, i.e. ZnO nanorods and two kinds of nanonails, were observed at various temperature regions. Photoluminescence, transmission electron microscopy, and energy-dispersive X-ray spectroscope were employed to elucidate the reason for the formation of such different rod-like structures. The analysis results demonstrated that the caps of nanonails possess a large number of oxygen vacancies, which may play a key role in determining the formation of nanonails and the high intensity of green emission.


## 1. Introduction

One-dimensional (1D) nanomaterials have attracted much attention over the past decade due to their potential applications in nanoscale electronic and optoelectronics. Due to a wide band gap (3.37 eV) and a large exciton binding energy (60 meV) at room temperature, ZnO has been regarded as a promising material for fabricating blue/ultraviolet light-emitting devices [1,2], flat panel displays [3,4], and gas-sensors [5]. So far, various ZnO nanostructures, such as nanowires [6,7], nanobelts [8], nanoneedles [9], nanotubes [10,11], nanocages [12,13], nanorings [14], and tetrapods structures [15] have been synthesized by different methods. ZnO nanorods and nanonails are considered as good functional components for electronic and optical nanodevices [16]. Moreover, gas-sensors based on nanorods [17], ultraviolet lasing in ZnO nanonails [18], and nanoscale ZnO nanorod heterostructures [16] have been reported recently, which spurred new extensive interest in studies on ZnO nanostructure synthesis and their applications. Few reports have demonstrated the preparation of ZnO nanorods and nanonails by vapor phase growth method [19–21]. However, explain of growth mechanism of ZnO nanonails is still controversial [22,23]. In order to make the nanonail growth mechanism clear, ZnO nanonail arrays, as well as ZnO nanorod arrays for comparison, were produced by a thermal evaporation method. A new mechanism is proposed to explain the growth process of ZnO nanonails in this work.

## 2. Experiments

ZnO nanostructures were grown on Si substrates in a horizontal quartz tube furnace by evaporating zinc power (99.999%) under oxygen ambient. The schematic diagram of the furnace is shown in Fig. 1. Prior to deposition, zinc powders (about 1.5 g) were placed on the front of a quartz boat, while the Si wafers were put about 2, 4, and 6 cm far away from the source material to collect the products. The whole growth process was separated into three steps. First, when the furnace was heated to 600 °C, the quartz boat was rapidly inserted into it and kept at this temperature for 10 min with an $O_2$ gas flow rate of about 20 sccm and a $2.2 \times 10^3$ Pa oxygen pressure. Then, the growth temperature was increased from 600 to 800 °C at a heating rate of 15 °C/min. The flow rate of $O_2$ and the growth pressure were changed into 30 sccm and $2.5 \times 10^3$ Pa, respectively. Finally, the $O_2$ gas flow and the working pressure were decreased to 10 sccm and $2 \times 10^3$ Pa, respectively.

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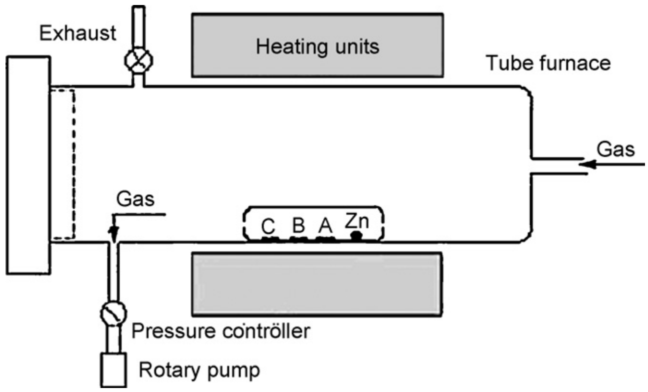


**Fig. 1.** Illustration of evaporation system for the synthesis of ZnO nanostructures.

After heating at 800 °C for 15 min, the quartz tube was drawn out from the furnace and rapidly cooled down to room temperature. Gray-white color products were found on the surface of the substrates in the temperature range of 550–750 °C.

The morphologies and structures of the as-synthesized samples were characterized by field-emission scanning electron microscopy (FE-SEM) equipped with a energy-dispersive X-ray spectroscope (EDX), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The photoluminescence (PL) measurements were performed at room temperature using Xe lamp with a wavelength of 300 nm as the excitation source.

## 3. Results and discussion

To investigate the structure and phase of the as-prepared products, XRD analyses were carried out. Fig. 2 illustrates the XRD patterns of the products by thermal evaporation of Zn powder. All the peaks can be indexed to the hexagonal wurtzite structure of ZnO. No trace of Zn or other impurities was observed in the spectra, implying that the as-grown samples are pure ZnO. Moreover, the intensity of (0 0 2) peak is much stronger than those of others, which implies that the deposited products were grown along the [0 0 2] direction. The weak (1 0 1), (1 0 3) and (2 0 1) peaks may be attributed to the imperfect vertical alignment of the nanostructures. The composition analyses of the samples were performed by EDX attached to the SEM. Fig. 3 shows the EDX spectra, only peaks of Zn and O were found, which demonstrates that the compositions of these products are ZnO with high chemical purity. This is in good agreement with our XRD results.

The morphologies of the products deposited in the different regions of the furnace are shown in Fig. 4. Three kinds of rod-like morphologies, one kind of nanorods and two kinds of nanonails, were observed, which were collected from regions A, B, and C, as shown in Fig. 1. Fig. 4(a) shows the top view of sample A obtained in the furnace temperature of about 750 °C, where a large number of ZnO nanorods were grown on the micrometer rods. From the cross-sectional view of this sample (shown in Fig. 4(b)), we can see that the diameter of the bottom rods are in the range of 1–1.5 μm, while the top nanorods have an average diameter of about 100 nm. An enlarged view of a single nanorod is shown in the inset of Fig. 4(a). Fig. 4(c) and (d) shows the top and cross-sectional views of sample B obtained at about 650 °C, respectively. The ZnO nanonail is composed of a round cap, a large diameter shaft, and a small diameter neck, which has the similar morphology to the observation in in-doped ZnO nanonails [24]. A high magnified SEM image of single nanonail (the inset of Fig. 4(c)) clearly shows that the cap of the nanonails is around 120 nm and that the shaft of the nanonail is about 1 μm and the neck is about 50 nm. Another different kind of nanonail (shown in Fig. 4(e) and (f)), with a smaller diameter shaft (300 nm), a larger diameter round cap (200 nm) and almost with similar diameter neck with that obtained at 650 °C, was grown at the temperature of 550 °C.

The detailed structure of the nanonails of sample C was investigated using TEM. Fig. 5(a) shows a low-magnification TEM image of a single nanonail. This image clearly exhibits that the nanonail has a round cap and a prismatic shaft with a small diameter neck. Fig. 5(b)–(d) shows the high-resolution transmission electron microscopy (HRTEM) of the ZnO nanonail's shaft,

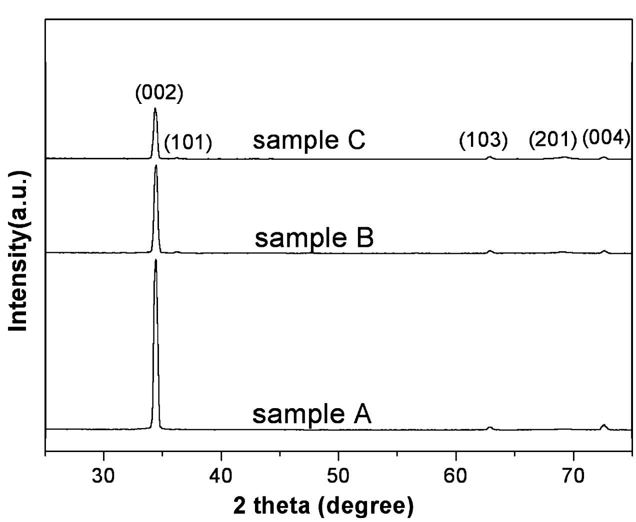


**Fig. 2.** $\theta$–$2\theta$ XRD diffraction patterns of the as-deposited ZnO nanorods and nanonails.

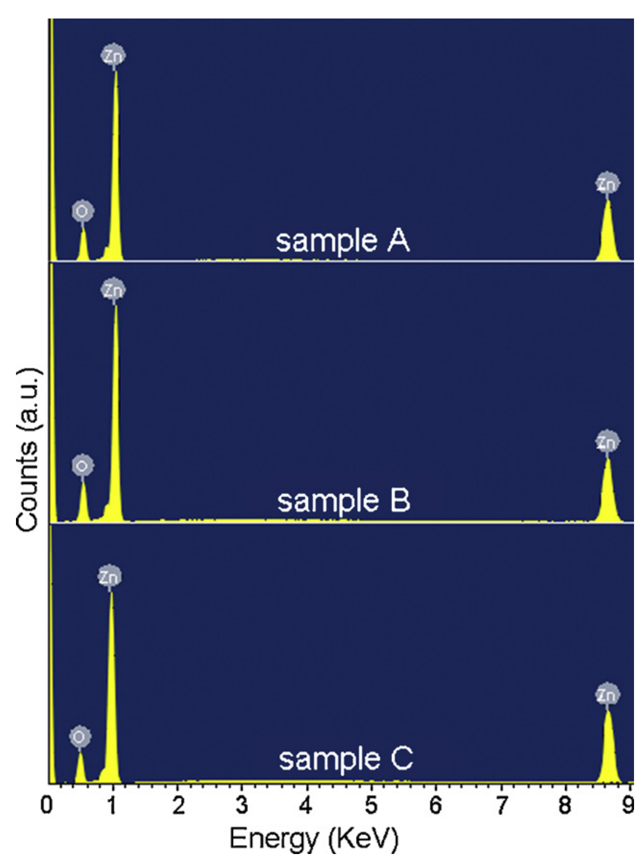


**Fig. 3.** (Colour online) EDX analysis of the ZnO nanorods and nanonails.