

# Research on the preparation and growth mechanism of ZnO micro/nano nails

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High quality zinc oxide (ZnO) micro/nano nails were prepared through thermal evaporation on the Si (100) substrate. Scanning electron microscopy (SEM) image shows that the bottom of the nanometer nails present hexagonal structure. The tip diameter of the micro/nano nails is about 319.9 nm, and the length is over 20  $\mu\text{m}$ . X-ray crystal diffraction (XRD) pattern shows that the sample has a hexagonal wurtzite structure and preferred orientation in (002) direction obviously. Photoluminescence (PL) spectrum shows a strong ultraviolet (UV) luminescence peak near the wavelength of 346 nm. Finally, the growth mechanism of the ZnO micro/nano nails is analyzed and studied.

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Zinc oxide (ZnO) has good photoelectric and piezoelectric properties, gas and pressure sensitive features because of the wide band gap (3.37 eV) and high exciton binding energy (60 meV). So ZnO has been widely used in solar cells<sup>[1]</sup>, light-emitting devices<sup>[2,3]</sup>, nano generator<sup>[4]</sup>, gas sensor<sup>[5]</sup> and other fields. ZnO has many different morphology of nanostructures, such as nanorods<sup>[6]</sup>, nanobelts<sup>[7]</sup>, nanotubes<sup>[8]</sup>, tetrapod-like structure<sup>[9]</sup> and nanonails<sup>[10]</sup>. The one-dimensional (1D) micro/nano nails especially show excellent properties in ultraviolet (UV) light<sup>[11,12]</sup> and unique superhydrophobic property used for self-cleaning applications fields<sup>[13,14]</sup>, such as solar panel coatings, self-cleaning automobiles, solar absorber surfaces electronic devices and self-cleaning windows. But at present, the preparation of ZnO micro/nanometer nail structure has been rarely reported.

In recent years, several approaches have been widely employed in the preparation of ZnO nanostructures, such as thermal evaporation, solution based approaches, radio frequency (RF) magnetron sputtering, metal-organic chemical vapor deposition (MOCVD) and ink-jet printing technique. However, despite proactive efforts on fabrication, there were a number of unsolved challenges associating with these processes, including small-scale, unaffordable and non-duplicated actuality. In this paper, 1D ZnO micro/nano nails with high quality were prepared through thermal evaporation which was orientated growth to the substrate under the condition of 1 100 °C on the Si substrate (100). The gas and seed layer were not used, and the micro/nano nails were prepared. To our surprise, the as-synthesized micro/nano nails are found to be catalyzed but there is no problem of impurity residue.

It is well-known that the size, shape, surface topology and composition of ZnO can drastically alter their physical and chemical properties. 1D ZnO structure with high aspect ratio has been found to significantly boost up the water splitting efficiency due to its excellent charge-carrier dynamic properties, resulting from efficient electron-hole separation<sup>[13]</sup>. The nanonails prepared in this paper have the aspect ratio of 62. The normal UV luminescence of ZnO nanostructures are usually near the wavelength of 380 nm, while the luminescence of the sample at 346 nm is blue shifted about 30 nm. Accordingly, these structured ZnO shows very good UV luminescence properties. A possible mechanistic explanation for the growth mechanism of the ZnO micro/nano nails is proposed in this study. The properties of the ZnO micro/nano nails are determined through field emission scanning electron microscopy (SEM), X-ray crystal diffraction (XRD) and photoluminescence (PL).

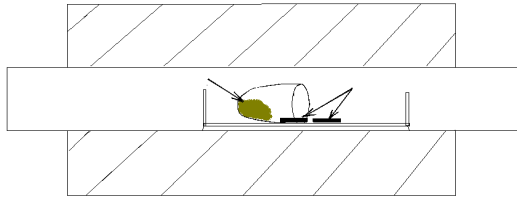
In the experiment, OTF-1200X open vacuum tube furnace with the highest temperature of 1 200 °C, YB-1A vacuum drying oven with the temperature range of 30—150 °C, KH2200DB CNC ultrasonic cleaning device, zinc powder with quality score of 90.0%, activated carbon with analytical pure, single crystal silicon with n type (100) orientation were used.

0.2 g carbon and 0.3 g zinc powder were evenly distributed on the bottom of the crucible. Ethanol, acetone and deionized water were used to ultrasonically clean Si(100) for 20 min, respectively, and then Si was dried in nitrogen atmosphere.

The crucible containing the zinc powder and carbon mixture was placed in the quartz boat, and the Si slices

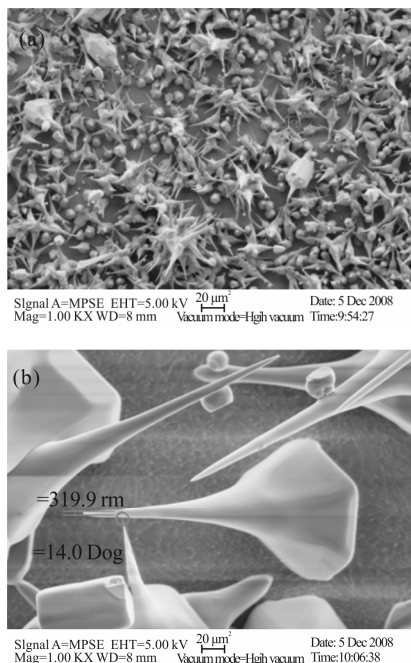
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were placed at a distance of 30 cm from the opening of the crucible. The entire quartz boat was pushed into the open tube furnace, where Zn powder is in the center of heat source. The whole device is shown in Fig.1. Tube furnace was heated with a rate of 30 °C/min from room temperature to 1 100 °C gradually. The temperature was kept at 1 100 °C for 0.5 h, and then was cooled down to room temperature naturally. After pulling out, the Si pieces were scattered with different thicknesses of white powder.



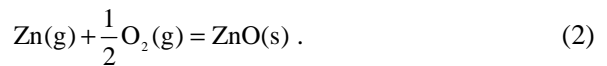
**Fig.1 Schematic diagram of experimental device**

In the experiment, ZnO micro/nano nails were synthesized in air with high temperature of 1 100 °C used zinc and carbon powder. The SEM images of ZnO morphology are shown in Fig.2. The bottom of structure is hexagonal shape with side length of 6 μm. The diameter becomes smaller with growth, and the tip diameter is about 319.9 nm. The length of the micro/nano nails is over 20 μm, and the ratio of length to diameter is about 62.



**Fig.2 SEM images of ZnO under different magnifications of (a) 1 000× and (b) 10 000×**

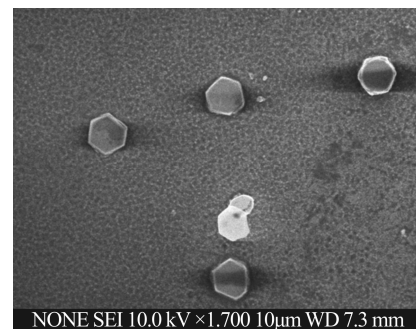
ZnO micro/nano nails were synthesized at high temperature in air. The reaction of this process can be expressed as



In this study, the growth of ZnO micro/nanometer nail structure was followed by the growth model of self-catalyzed gas-liquid-solid (VLS). Solid zinc powder will become gaseous state when the temperature is higher than its melting point (419.5 °C). It is easy to oxidize ZnO when they meet the oxygen in the air at this moment. Because of the high melting point (1 975 °C) of ZnO, they were deposited on the substrate in solid state. We speculate that the growth process of ZnO micro/nanometer nail structure has the following two stages.

The first stage is the formation stage of ZnO crystallization phase. Since the structure of ZnO is hexagonal fiber zinc ore, ZnO initially forms a positive hexagonal structure, as shown in Fig.3.

The second stage is the formation stage of ZnO micro/nano nails. Cutting edge appears perhaps due to the tube furnace cooling gradually from 1 100 °C. In this case, the zinc vapor can be reduced gradually as the decrease of temperature, so the growth of the hexagonal structure is slowed down gradually, but a small amount of zinc can continue to combine with O for generating ZnO which continues along the C axis growth, as shown in Fig.2(b). As the temperature continues to decrease, the tip diameter becomes smaller and smaller until it stops growing.

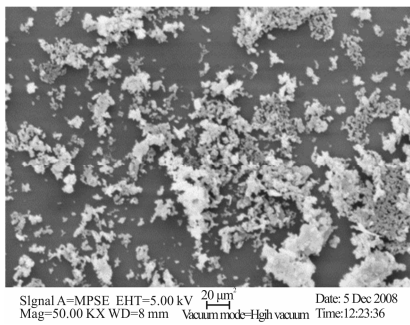


**Fig.3 SEM image of ZnO crystal nucleus**

Carbon plays an important role in the growth of ZnO micro/nano nails. As mentioned above, we got nail-like ZnO nanostructures under certain conditions, as shown in Fig.2(a). If there is no carbon in the experiment, we get the product in the same experimental conditions as shown in Fig.4. The experiment result is not ideal obviously, which is only clutter distribution of particles or lumps. Undisputedly, carbon plays an important role in the experiment.

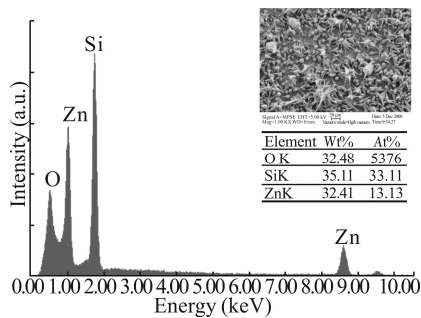
If only zinc powder is used for reactants in the experiments, zinc powder covered with the density ZnO layer is located on the surface in the heating process, which is likely to prevent the oxygen from reacting with zinc powder below. A very small amount of ZnO is

deposited on the silicon substrate, forming the morphology as shown in Fig.4. When carbon is added because of its strong adsorption, it is easy to combine with oxygen to form CO/CO<sub>2</sub>. CO/CO<sub>2</sub> gas flows from the mixture surface of the ZnO and zinc powder, which prevents the formation of dense ZnO layers. At the same time, after the carbon is oxidized to the gas, it becomes empty in the original position, and the reactant becomes very loose. CO/CO<sub>2</sub> also acts as a carrier gas, and the continuous ZnO nanostructures is deposited on the silicon substrate, forming the ZnO micro/nano nails as described previously.



**Fig.4 Samples synthesis with zinc only**

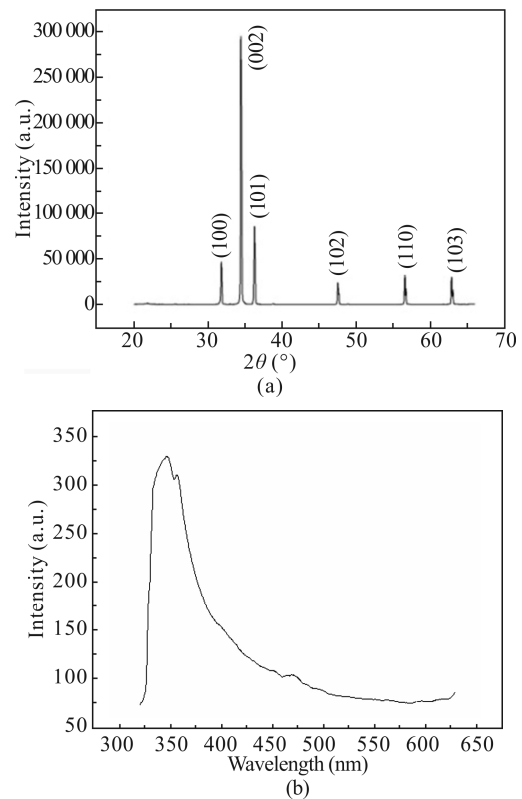
Adding catalyst is often accompanied by a problem that the catalyst appears as impurities in the product, and it is difficult to be removed. The energy dispersive X-ray (EDX) spectrum analysis shown in Fig.5 shows that there are only Zn and O peaks (Si elements are substrate peaks) without other impurities. Therefore, the catalyst of carbon is not introduced into the product in the experiment, and the prepared product is the high purity ZnO micro/nano structures with no problem of removing the catalyst.



**Fig.5 EDX spectrum of ZnO micro/nano nails**

ZnO crystal structure by XRD measurement is clearly shown in Fig.6(a). Diffraction peaks appear at  $2\theta=31.80^\circ$ ,  $34.46^\circ$ ,  $36.30^\circ$ ,  $47.56^\circ$  and  $56.66^\circ$ , which are corresponding to the ZnO crystal (100), (002), (101), (102), (110) and (103), respectively. It can be derived that the ZnO micro/nano nail has a lattice constants  $a_0=0.327$  nm

and  $c_0=0.521$  nm. And the structure has a more obvious preferential orientation in the (002) direction.



**Fig.6 (a) XRD pattern of ZnO micro/nano nails; (b) Room temperature PL spectrum of the ZnO nanonails**

As shown in Fig.6(b), PL spectrum of ZnO micro/nano nail measured at room temperature is used to compare the emission properties. The strong UV light emitting peak at wavelength of 346 nm is observed, which is caused by the near band edge emission of ZnO. The green emission of ~500 nm associated to oxygen vacancies doesn't appear in the PL spectrum, indicating that ZnO micro/nano nails have good crystal quality. The normal UV luminescence of ZnO nanostructures are usually near the wavelength of 380 nm, while the luminescence of the sample is at 346 nm which is blue shifted by about 30 nm. Accordingly, ZnO micro/nano nails obtained from the experiment have good UV luminescence properties.

This study demonstrates a simple approach to synthesize ZnO micro/nano nails with high quality through thermal evaporation on the Si (100) substrate at 1 100 °C. The XRD pattern shows that the sample has a hexagonal wurtzite structure and preferred orientation in (002) direction obviously. The PL spectrum indicates that ZnO micro/nano nails have a strong UV luminescence peak near the wavelength of 346 nm. The carbon powder has the effect of catalysis and carrier gas, while there is no problem of impurity residue.

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