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One-pot reaction to synthesis and characterization of two-stage zinc oxide hexagonal microprism on nickel thin films

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ABSTRACT

A novel two-stage zinc oxide (ZnO) hexagonal microprisms was successfully synthesis *via* a hydrothermal route on a nickel (Ni) thin films. The Ni thin films are deposited by using magnetron sputtering onto Si (100) substrate. The formation of the secondary structure and optical properties of ZnO microprism have been investigated and the formation mechanism has been discussed. The results illustrate the Ni substrate is a key factor to grow the two-stage ZnO, and the photoluminescence (PL) emission peak at 389 nm reveals that the high crystal quality of these nanorods. ZnO with its excellent luminescent properties and the controllable nanostructures will hold promise for the development of photonic devices. Copyright © 2013 VBRI press.

Keywords: Zinc oxide; hexagonal microprisms; nanostructure.

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Introduction

Though enormous progress has been made in producing transition metal oxides micro- or nanocrystals with controllable morphologies, it is still a key goal in modern materials chemistry and has attracted substantial interest in recent years [**1, 2**]. Moreover, as a result of requirement and rapid advancements in material science, high symmetric structures with novel morphology and characteristics are demanded urgently. Until now, template methods as the general approach for fabricating high symmetric structures have involved the use of various removable or sacrificial templates [**3**]. For overcoming the above disadvantages and the other limitations such as material compatibility and process complexity, newer template-free methods under one-pot conditions are expectative for synthesizing desired nanomaterials [**4**].

ZnO is a direct, wide band gap semiconductor material with many promising properties for blue/ultraviolet (UV) optoelectronics, transparent electronics, spintronic devices and sensor applications due to its wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [**5-7**]. Microstructured ZnO materials have received broad attention owing to their distinguished performance in electronics, optics and photonics [**8, 9**]. Furthermore, when the size and microscopic morphology of

ZnO have changed, novel chemical and physical properties are introduced correspondingly.

Additionally, various symmetric structures of ZnO, such as rings, helix, bridges, cages, screws and cables have already been synthesized by a variety of methods, including thermal evaporation, chemical vapor deposition, electrodeposition, and template-directed growth [**10**-**13**]. Recently, Zhang et al have reported well-faceted hexagonal ZnO microprisms with regular interior space have been successfully prepared by a template-free hydrothermal synthetic route [**14**]. However, the fabrication process needs to prepare a complex flower-like hierarchical precursor with the formula of $ZnO{\cdot}0.33ZnBr_2{\cdot}1.74H_2O$. To our best knowledge, there are scarcely reports on the fabrication of two-stage ZnO hexagonal microprism, and as a consequence, the optical properties of microprism are limited. Herein, we describe a simple solution-phase route to produce uniform two-stage ZnO hexagonal microsprim by a hydrothermal reaction at the presence of hexamethylenetetramine (HMTA) on a nickel (Ni) thin films.

Experimental

Materials

Hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, AR) was purchased from Aladdin Chemical Reagent CO., Ltd., zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, AR) was purchased from Sinopharm Chemical Reagent CO., Ltd., and all regents used as received without further purification.

Preparation of Ni prelayers on Si substrate

Ni thin film prelayers were deposited on the Si substrate by ultra-high vacuum dc magnetron sputtering (Japan ULVAC ACS-4000-C4) from a 2 inch target of Ni (purity 99.99%) in argon (Ar) with a flow rate of 25 sccm. Before deposition, the sputtering chamber was evacuated to a base pressure of 2.5E-5 Pa. The sputtering took place at a pressure of 7.2E-1Pa, an input power of 100 W. The films were deposited onto 4 inch Si substrates and with a rotation speed of 10 rpm, which were placed about 150 mm over the target. The substrate temperature was about room temperature. The deposition time was 2553 s, which was controlled by a computer.

Synthesis of two-stage ZnO hexagonal microsprim

In a typical process, 20mM HMTA (10 ml) and 50 mM $Zn(CH_3COO)_2{\cdot}2H_2O$ (10 ml) were mixed together under ultrasonic condition at room temperature. The mixture solution was then transferred into a 25 ml Teflon-lined tube reactor. Then, as-prepared Ni film substrates were added in the bottom of the tube, and were kept at 90 °C for 5 h. The autoclave, once removed from the furnace, was allowed to cool down to room temperature. The substrate will present white color after the reaction.

Characterization

The surface morphologies and compositions of the films were analyzed by field emission scanning electron microscopy (FE-SEM) using a FEI Nava NanoLab with an energy dispersive X-ray (EDX) detector (ICNA, Oxford Instrument). Powder X-ray diffraction (XRD) patterns of the samples were recorded on a D8 Advance X-ray diffractometer (Germany) using Cu Kα radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA and at a scan rate of 0.05° 2θ s^{-1}. The optical properties were evaluated using photoluminescence (PL) measurements by HORIBA Jobin Yvon UV-VIS-NIR Lab RAM raman spectroscopy.

Results and discussion

The average thickness is obtained as 128.2 nm by a surface profiler (Form Talysruf Profiler, Taylor Honson S4C-3D). The FESEM photographs of as-deposited Ni thin films deposited at room temperatures are shown in **Fig. 1a**. The grain sizes of as-deposited films are found to be fine and the average diameter was 37.1 nm (the insert is size distribution, and the result was statistically analyzed with JEOL SmileView software, analyzing more than 200 grains) and the standard deviation (σ) was 4.9 nm, indicating that the as-deposited film was in a good crystallization state with a uniform and smooth surface. To confirm the composition of the as-deposited films, EDX spectra in situ composition analysis were collected and the result was shown in **Fig. 1b**. EDX indicated the presence of nickel and silicon element from the sample. The silicon is from the substrate, and the spectrum validates only Ni element exist in the films, confirming that the as-deposited films was Ni thin films.

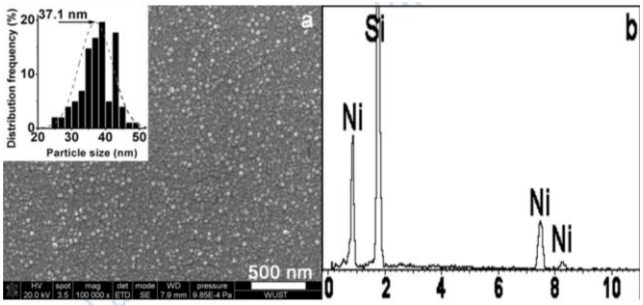

Fig. 1. "Field emission scanning electron microscopy **(**FESEM) micrographs (a), the inert is the size distribution histogram) and *in situ* EDX spectrum, (b) of as-deposited Ni films".

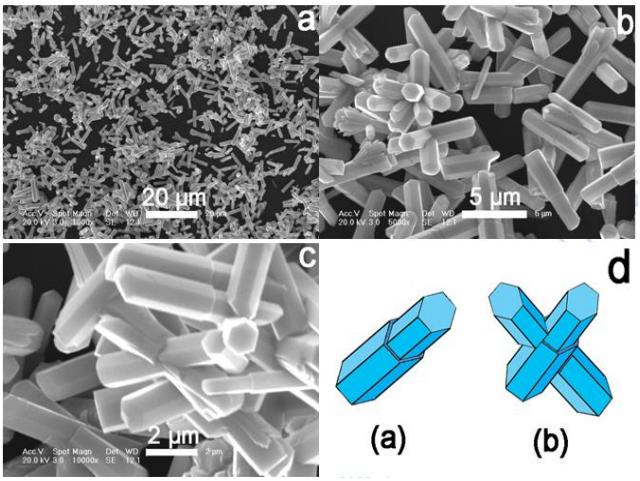

Fig. 2. FESEM images at different magnification and model of two-stage ZnO hexagonal microprisms.

Typical morphology of as-synthesized two-stage ZnO hexagonal microprisms (the bottom subunit larger than the top subunit, the modle as shown in **Fig. 2d** (a)) at different magnification are presented in **Fig. 2a-2c**. From the FESEM pictures of typical ZnO nanostructure, it is clear that high yield of uniform hexagonal microprisms with closed-end and nanometer-size edge is almost the exclusive products in our synthetic result. The well faceted hexagonal microprisms have a diameter of top-stage about 1 μm and a length of up to 5 -6 μm. And the length of bottom subunit and top subunit is almost equal. Additionally, some crossed ZnO hexagonal microprisms (the modle as shown in **Fig. 2d**(b)) also present in the product. In our synthesis route, Zn^{2+} ions will hydrolysize to form the transition complex of $Zn(OH)_2$, which will decompose to form the final product of ZnO microrods. The reactions is as follow,

$$Zn(Ac)_2+2H_2O \rightarrow Zn(OH)_2\downarrow+2HAc,\ Zn(OH)_2 \rightarrow ZnO\downarrow+H_2O.$$

The small ZnO nanocrystallines have a tendency to form crystal nucleus through oriented attachment mechanism. In the reaction process, the HMTA hydrolyzes to form ammonia and formaldehyde above 70 °C. Meanwhile, OH^- concentration increases because of the hydrolysis of HMTA [**15**]. However, when the substrate is glass, large-scale ZnO micro-dumbbells have been fabricated (**Fig. S1**). Each has two heads, which were not exactly the same. Interestingly, it was found that the morphology of the synthesized ZnO dumbbell was the nanorod aggregates and the length can be up to 10 μm. Many approaches have been employed to fabricate different shapes of ZnO nanostructures. Hydrothermal method is a simple way to control the morphology and size of the synthesized materials by changing the reaction conditions. In the current reaction processes, a novel two-stage ZnO hexagonal microprism has been prepared when the Ni prelayers present. The results reveals that the Ni prelayers should be as an important factor in the reaction, we would do a series of further experiments focusing on the influence of the Ni prelayers.

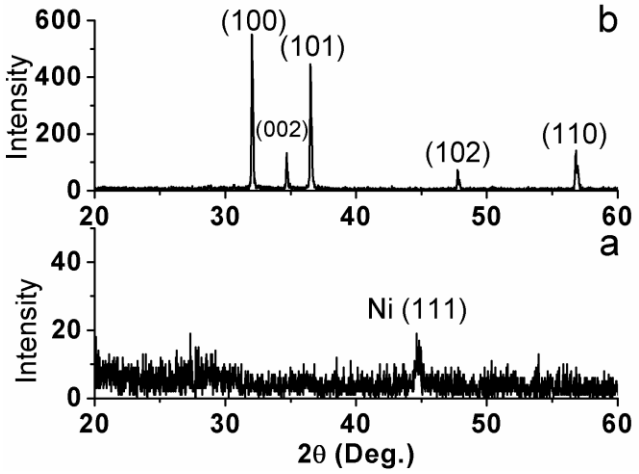

Fig. 3. XRD patterns of Ni prelayers (a) and two-stage ZnO hexagonal microprisms (b).

Fig. 3a shows the XRD patterns of the as-deposited Ni thin films. From this figure, it can be seen that there is one diffraction peak which is located at about 44.51°, it proved that cubic structural Ni film with strong preferred orientation along the (111) direction perpendicular to the substrate surface. XRD data further confirmed the crystal structure information of the ZnO microprisms. As shown in **Fig. 3b** the diffraction lines coincide with the (100), (002), (101), (102), (110) planes of the hexagonal-wurtzite ZnO (JCPDS PDF #36-1451).

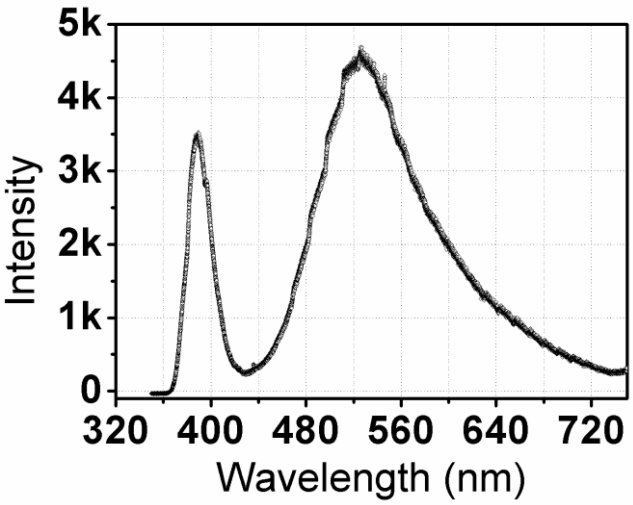

Fig. 4. Room temperature PL of two-stage ZnO microprisms

Photoluminescence (PL) is an important property, which provides information on the optically active defects and relaxation pathways of excited states. The study is useful to identify the origin of sub-band-gap luminescence. **Fig. 4** plots the room-temperature PL spectra of the two-stage ZnO hexagonal microprisms. Only two emission peaks at 389 nm (3.190 eV, corresponded to the emission from the free exciton and supports the high crystal quality of these nanorods) and 525 nm were observed. It was found that UV emission intensities lower than the visible emission, suggesting that the native defects needs to be reduced by the subsequent annealing.

Conclusion

In summary, we have demonstrated that two-stage hexagonal ZnO microprisms can be facile fabricated with large-scale yield via a template-free hydrothermal synthetic route on the Ni prelayers. Although the substrate is an important factor for obtaining the ZnO microprisms, we still believe the morphologies of products also depend on the other experimental conditions and the details are under investigated. This type of microsprims shows unique PL characteristics, which might be potentially useful material in future optoelectronic applications.

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Supporting information

Materials

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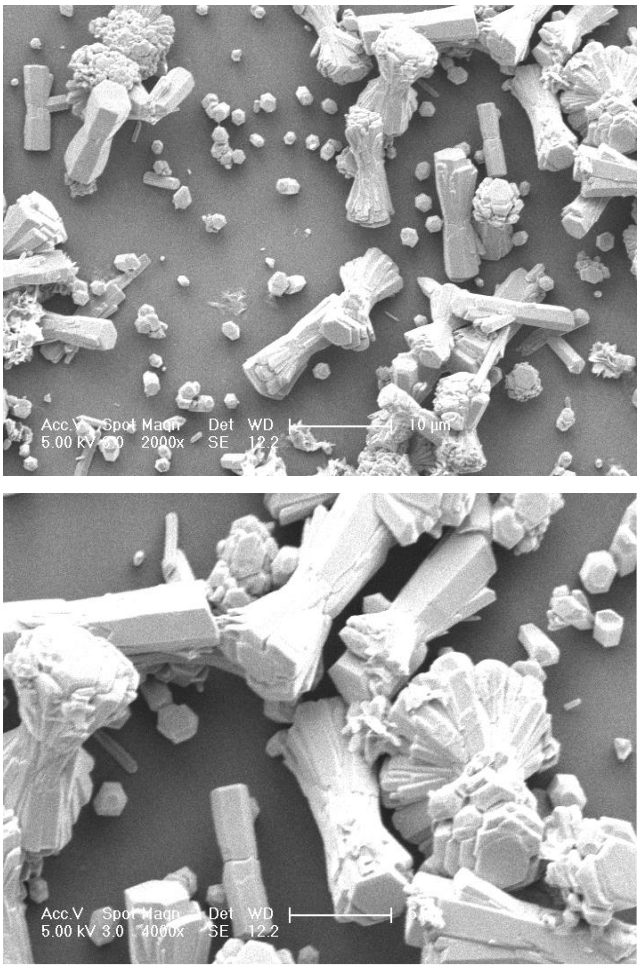

Fig. S1. FESEM images at different magnification of two-stage ZnO dumbbell microprisms.