ZnO microbowls grown on ITO glass substrate through thermal evaporation*

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Novel ZnO microbowls are successfully synthesized by thermal evaporating of a mixture of ZnS powder and Zn powder. The morphologies of the as-synthesized products can be adjusted by changing the temperature and the type of substrate. The morphologies, microstructures, and photoluminescence properties are investigated by X-ray diffraction, Raman spectroscopy, scanning electron microscope, and photoluminescence spectroscopy respectively. The growth mechanism of the as-synthesized ZnO microbowls is proposed based on the experimental results. ZnO microbowls presented here can be used as building blocks to fabricate optical and optoelectronic micro/nano devices.

Keywords: microbowls, thermal evaporation, ZnO, growth mechanism

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1. Introduction

ZnO, as an important wide band gap semiconductor material with a large exciton binding energy (60 meV) at room temperature, has been used as the optical and electronic material.[1−8] On micro/nano scale, many fantastic physical and chemical properties can be demonstrated due to the quantum size effect and the surface effect.[9−12] Yu *et al.*[13,14] reported ZnO nanowindmills and nanocubes synthesized using the hydrothermal route and found a blue shift in the ultraviolet region. Cao *et al.*[15] synthesized large scale quasi-aligned ZnO stacking nanoplates through a solution strategy, and the results revealed that the double and the multilayer stacking nanoplates had a very large photocatalytic activity in the decomposition of methylene blue compared with the common nanowire arrays. Lee *et al.*[16] found that ZnO nanorod arrays displayed the broadband reflection suppression compared with the SiN single layer antireflection coating. And the syringe-like ZnO nanorod arrays as the light harvesting layers of the InGaN-based multiple quantum well solar cells were synthesized.[17]

Bowl-like micro/nano structures are novel, and can be used in solar cell, photocatalysis, and photovoltaic technology.[18] However, many reports concentrate on nanobowls in which polystyrene (PS) spheres or the other polymers are used as the scaffold templates. For example, Wang *et al.*[18] synthesized TiO_2 nanobowl arrays using polystyrene spheres as the template for atomic layer deposition of a TiO_2 layer. Zhang *et al.*[19] reported the synthesis of C_{60} single crystalline hollow nanobowls using a sonophysical strategy in a binary organic solution. Ge *et al.*[20] synthesized PS nanobowls by controlling the weight ratio of monomer to silica. So far, there are few reports dealing with the ZnO bowl-like structures. Wang *et al.*[21,22] reported ZnO nanobowls synthesized using polymer films with spherical nanowell arrays as the sacrificial templates. Tao *et al.*[23] prepared ordered ZnO nanobowl arrays by magnetron sputtering using the self-assembled polystyrene sphere arrays as the templates. Guo *et al.*[24] synthesized bowl-like ZnO nanodiscs by film deposition and thermal oxidation. The above mentioned methods for preparing ZnO bowl-like structures involve complex procedures,

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sophisticated equipments, or rigid experimental conditions. Herein, we report a novel ZnO microbowl structure obtained through a simple thermal evaporation method. Morphologies, microstructures, and optical properties of the as-synthesized products are investigated by using different characterization techniques, and the effects of the experimental parameters on the morphologies are also investigated.

2. Experiment details

The samples were synthesized in a conventional horizontal tube furnace. First, a slice of indium tin oxide (ITO) glass (purchased from Shenzhen Nanbo Company, China) was immersed into an acetone solution, ultrasonically cleaned for 30 min, rinsed with the de-ionized water, and then dried in air. The mixture of ZnS powder (Alfa Aesar, 99.99% purity) and Zn power (Alfa Aesar, 99.99% purity) with the mole ratio of 5:1 was put into an alumina boat, then the boat and the prepared ITO glass were loaded together into a ceramic tube inserted in the furnace. After the system was sealed, the furnace was pumped by a mechanical pump for 2 h to eliminate the residual oxygen. Then the furnace was heated to 1200 °C at a rate of 20 °C/min, and kept at that temperature for 2 h. The argon carrier gas was kept flowing at a rate of 100 sccm throughout the experiment. The chamber pressure was kept at 0.04 MPa. After the furnace was cooled down to room temperature, a layer of white fluffy powder was deposited on the surface of the ITO glass substrate. The as-synthesized products were characterized by X-ray diffraction pattern (Rigaku Dmax-rB, Cu $K\alpha$ radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA), scanning electron microscope (SEM, Hitachi-4800), Raman scattering spectrum (HR800), and photoluminescence spectrum (HORIBA JY- Fluoro Max 4).

3. Results and discussion

The morphology of the as-synthesized product is characterized first by SEM. Figure 1(a) shows a low magnification SEM image, revealing the large quantity of hemispheric products formed. A further observation reveals that these products possess bowl-like shapes and coarse surfaces (Figs. 1(b) and 1(c)). The average diameter of the microbowls is about 4 μm. Raman spectrum and XRD analysis are utilized to study the microstructure of the as-obtained microbowls. Figure 2(a) shows a Raman spectrum of the as-synthesized product at room temperature. Four major vibration bands positioned at 215.5 cm^{-1}, 336.5 cm^{-1}, 436.2 cm^{-1}, and 565.3 cm^{-1} can be found. In general, the ZnO crystal with a hexagonal wurtzite structure belongs to the C_6V_4 ($P63mc$) space group. According to the selection rule of phonon mode, the Raman active modes of the wurtzite ZnO are $A_1 + 2\ E_2 + E_1$.[25] Among them, A_1 and E_1 modes are polar and can be split into transverse (TO) and longitudinal (LO) optical components. For the sample, vibration peaks can be clearly observed at 215.5 cm^{-1}, 336.5 cm^{-1}, 436.2 cm^{-1}, 565.3 cm^{-1}. Among these peaks, the strongest one centered at about 565.3 cm^{-1} corresponds to the LO phonon of A_1. The peak at 436.2 cm^{-1} is the characteristic of the high-frequency E_2 mode of the wurtzite structure.

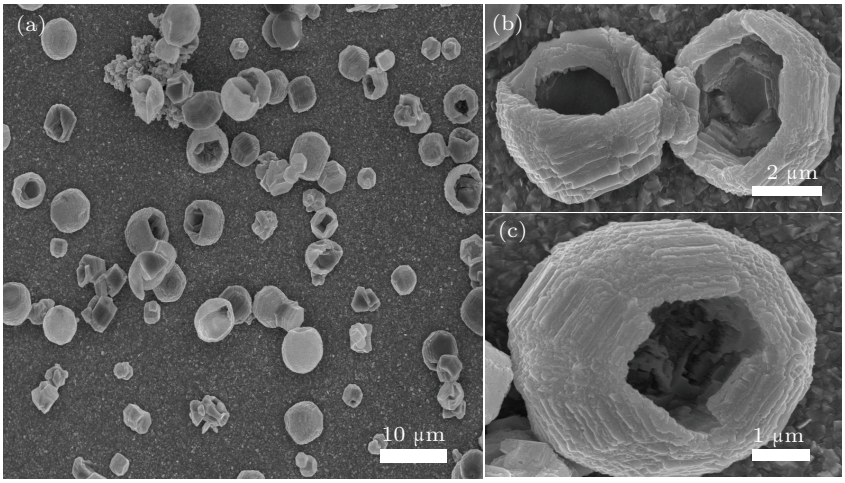


Fig. 1. (a) Low and ((b), (c)) high magnification SEM images of the as-synthesized ZnO microbowls.

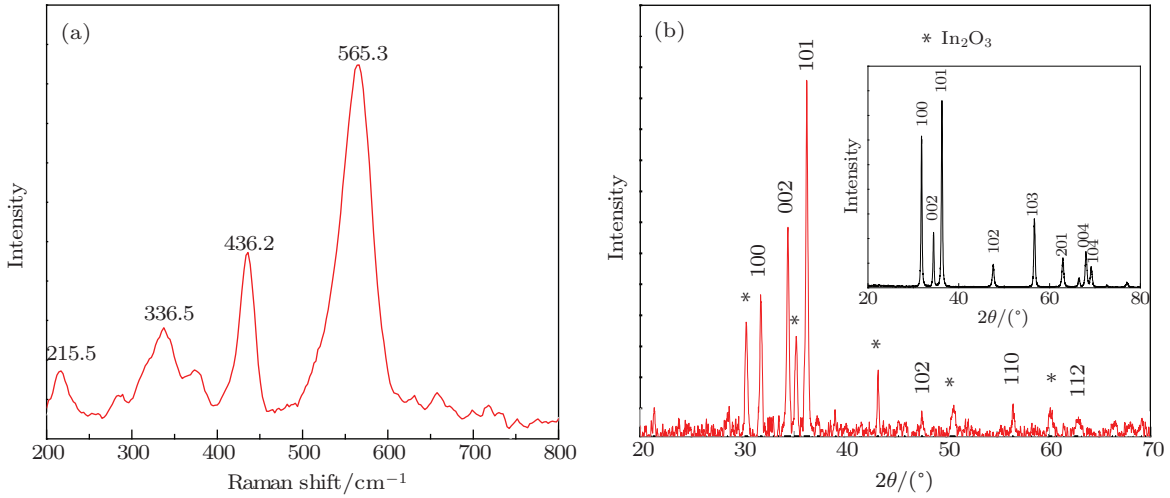


Fig. 2. (colour online) (a) Raman spectrum and (b) XRD pattern of the as-synthesized ZnO microbowls.

Besides these typical Raman modes, the Raman spectrum also shows two other modes with frequencies of 215.5 cm^{-1} and 336.5 cm^{-1}. These additional peaks cannot be explained within the framework of the bulk single phonon modes, and are attributed to the multiphonon scattering processes.[26] Figure 2(b) demonstrates the XRD pattern of the as-synthesized ZnO microbowl. All diffraction peaks can be indexed to the wurtzite phase of ZnO (JCPDS Card No. 36-1451, see the inset of Fig. 2(b)). The asterisk marked peaks are from the ITO substrate.

To investigate the growth mechanism of the as-synthesized ZnO microbowl, temperature- and substrate-controlled experiments are conducted. When the substrate temperature is elevated to 700 °C (the microbowls grow at 600 °C deposition zone), some nanowires each with a diameter of 50 nm and a length of several micrometers appear (see Figs. 3(a) and 3(b)), revealing that the temperature located at the nucleation sites can seriously influence the morphologies of the resulting products. High temperature can cause the nuclei to move fast and not to deposit easily, making many nuclei joint into a wire-like structure. This explanation is consistent with the growth of ZnO nanohelices.[27] Keeping other growth parameters unchanged, using the copper foil instead of the ITO substrate, we only obtain irregular microcrystals (Figs. 3(c) and 3(d)). It shows that different substrates have different interfaces with the as-synthesized products, which determine the nucleation rates of the nanoparticles and then the final morphologies of the as-synthesized products. Therefore, for the synthesis of nanostructures by thermal evaporation method, the deposition substrate is also important for obtaining the desired nanostructures.

Based on the above experimental results, a possible growth mechanism of ZnO microbowl structure can be proposed as follows. The ZnS powder is decomposed first into Zn vapor and S vapor, and they are carried downward by the carrier gas. At the same time, the Zn power is also evaporated into Zn vapor. With the reaction proceeding, the Zn vapor can nucleate and further aggregate into large Zn spheres. Then the surfaces of these spheres can be oxidized into ZnO films due to the residual oxygen inside the ceramic tube. Because of the low melting point (419 °C) of metal Zn, the Zn vapor inside the ZnO spheres overflows from the gaps of the ZnO films, inducing the fractures of the ZnO spheres, thereby forming the microbowls.

The investigation of optical properties of semiconductor micro/nano structures is very important for the optoelectronics micro/nano devices.[28–30] Here the photoluminescence (PL) properties of the as-synthesized ZnO microbowls at room temperature are studied. Figure 4 shows a PL spectrum of the as-grown ZnO microbowls, where an ultraviolet (UV) emission band centered at 389 nm and two visible emission bands at around 435 nm and 596 nm are seen. The intrinsic emission peak locates at 380 nm for the ZnO powder, therefore the emission band at 389 nm can be attributed to the near band edge emission of the ZnO crystal. The as-synthesized product possesses abundant defects due to the growth condition. Visual emission peaks at 435 nm and 596 nm are probably the defect state related luminescence. The visible lu-

minescence is related with the defect states, such as Zn interstitials and oxygen vacancies.[31] Zeng *et al.*[8] ascribed the emission at 435 nm to an interstitial zinc defect level. Besides, oxygen vacancies can also act as luminescence centers, the defect peak at 596 nm may originate from the interstitial oxygen ions.[32]

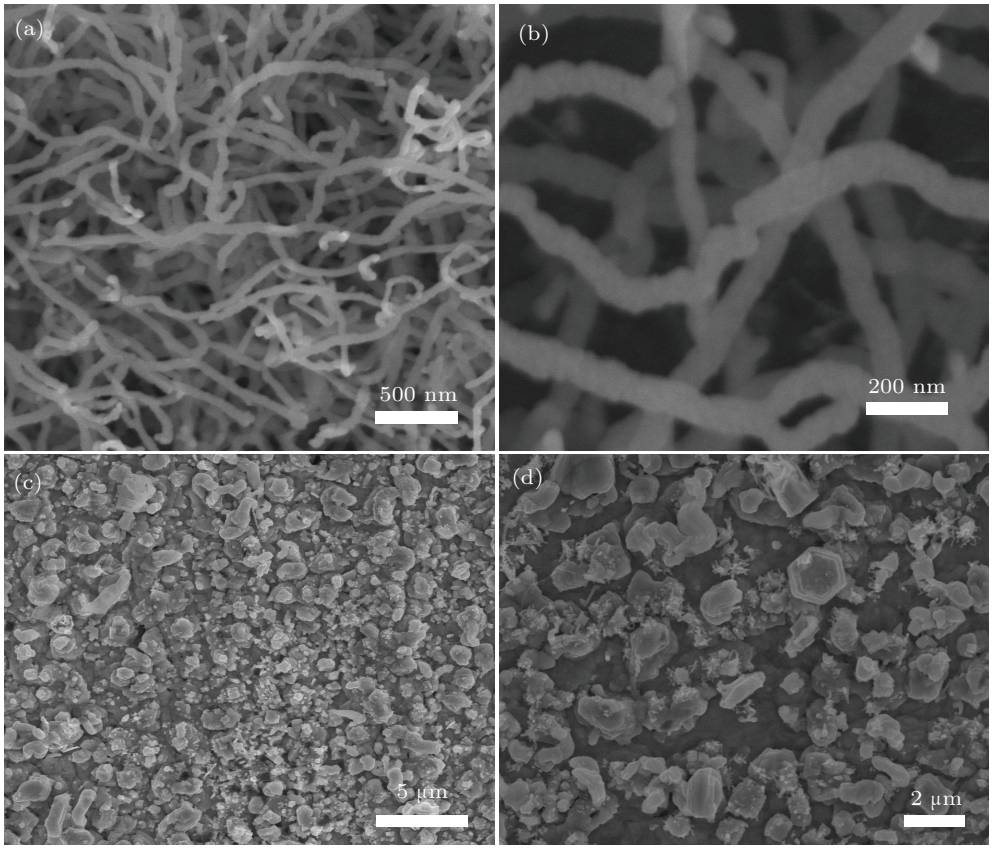


Fig. 3. SEM images of the as-synthesized products at ((a), (b)) high temperature and ((c), (d)) on the copper substrate.

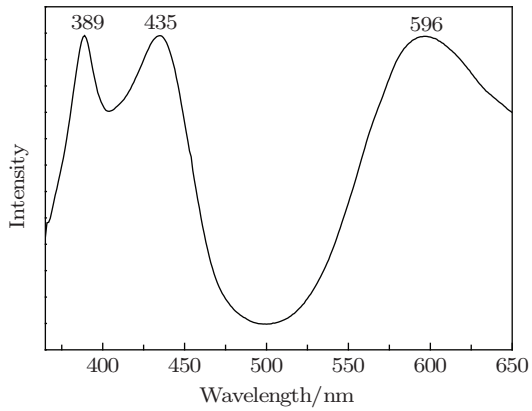


Fig. 4. PL spectrum of the as-synthesized ZnO microbowls.

4. Conclusion

In the present paper, we synthesize ZnO microbowls by using a thermal evaporation approach. The average diameter of the ZnO microbowls is about 4 μm. The effects of temperature and substrate on the final morphology are investigated. The photoluminescence spectrum shows that there is an ultraviolet emission peak at 389 nm and two visual emission peaks at 435 nm and 596 nm. The former is attributed to the recombination of free excitons, the latter two are related to the defect states such as Zn interstitials and oxygen vacancies. ZnO microbowls reported here may be used as building blocks in solar cell, photocatalysis, and photovoltaic technology.

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