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Journal of Solid State Chemistry 177 (2004) 176–180

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

Structure-direct assembly of hexagonal pencil-like ZnO group whiskers

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Received 16 April 2003; received in revised form 26 June 2003; accepted 10 July 2003

Abstract

Hexagonal ZnO group whiskers synthesized from $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor at 145°C in a structure-directing template solvent (2.5% v/v alcohol) show strong photoluminescence at 409 and 420 nm. FE-SEM and TEM observation reveals that the ZnO group whiskers consist of uniform pencil-like whiskers with the diameter of around 1.5 μm and the length of up to 6 μm.
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Keywords: ZnO; Group whiskers; Structure-direct assembly

1. Introduction

Recently, many research efforts have been invested in the area of wide band gap semiconductor materials due to their potential applications in short wavelength optical devices [1,2]. ZnO is an II-VI compound semiconductor with a wide and direct band gap of 3.3 eV [3] and large exciton binding energy (60 meV) [4]. Recently, ZnO has been investigated as a short-wavelength light-emitting and laser diodes, transparent conducting and piezoelectric material [5–10]. Because of its rigidity and excellent chemical stability, ZnO whiskers have received great deal of attention for industrial applications as reinforced composite materials [10]. And recently, ZnO crystal whiskers with a high aspect ratio have been successfully used as probing tips to develop new precise high-resolution imaging techniques for atomic force microscopy and scanning tunneling microscopy [11–14]. The growth of single hexagonal prismatic ZnO whisker has already been achieved [10]. However, up to now, little work has been done on preparation of radial ZnO group whiskers, whose hexagonal pencil-like shape, radial tropism and inextricable union surely would give the photoelectronic devices a new future.

The growth of ZnO semiconductor whiskers recently has been demonstrated by various methods, e.g., chemical vapor deposition [15], colloidal micellar process [16], electrochemical process [17], vapor–liquid–solid (VLS) growth mechanism [18,19], oxide-assisted growth method [20–25], and direct thermal evaporation of oxide powers [26]. However, as the bulk materials the ZnO whiskers obtained from these methods exhibit regular crystallographic morphologies, such as tetrapod form, hollow structures and polyhedral crystals. Meanwhile, preparation of hexagonal pencil-like ZnO group whiskers has not been reported. In addition, for the final practical applications, the mild temperature, and low cost and easy control method with high yield is much expected. Here, for the first time, we report on a simple hydrothermal synthesis of ZnO radial group whiskers from $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor at 145°C in a structure-direct solvent of alcohol.

2. Experimental

Analytical pure $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (2.1950 g) and absolute ethanol (0.875 mL) were added into a 40 mL Teflon-lined autoclave, which was then filled with distilled water up to 75% of the total volume. Under constant stirring, the addition of 28% ammonia (5 mL) makes the clear solution turn to white and then

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transparent. The autoclave was maintained at 145°C for 12 h and then cooled to room temperature naturally. The white precipitate was collected, and washed with distilled water several times. Finally, the samples were obtained and dried at 60°C in air for 3–4 h.

The phase identification of the sample was carried out on X-ray powder diffraction (XRD) patterns employing a scanning rate of 0.02° s⁻¹, using a Rigaku D/max rA X-ray diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of the product was measured by field emission scanning electron microscopy (FE-SEM Hitachi S-4200). Further structural analysis of individual ZnO whisker was carried out using transmission electron microscope (TEM Hitachi H-800) and selected area electron diffraction (SAED). Room temperature photoluminescence (PL) spectra were recorded on a Confocal Laser MicroRaman Spectrometer (JY LABRAM-HR) with a He–Cd laser focused to $\sim 200 \mu\text{m}$ as the excitation source ($\lambda_{\text{ex}} = 325 \text{ nm}$).

3. Results and discussion

A typical XRD pattern of the ZnO product is shown in Fig. 1, in which all of the diffraction peaks can be well indexed to the known hexagonal ZnO with wurtzite structure (space group $P6_3mc$, JCPDS card No. 36-1451). Compared with the standard diffraction patterns, no characteristic peaks from impurities, such as Zn, are detected.

Fig. 2 reveals the morphology of the as-grown ZnO group whiskers recorded as the field emission scanning electron microscopy (FE-SEM) images. Fig. 2(a), the panoramic morphology of the sample, showed that the sample consists of group whiskers with hexagonal, straight and smooth whiskers. The yield of the ZnO group whiskers synthesized by this hydrothermal method is above 95%. Fig. 2(b) shows an individual ZnO group whisker in which scores of single whisker closely and firmly packed together, indicating their radial tropism growth. The image of some separated independent whiskers suggests that the whisker has smooth, well-defined crystallographic facets and regular prismatic hexagon, with width 750 nm and angles about 120°. A single whisker exhibited an awl-shaped, pencil-like morphology, as shown in Fig 2(c), with diameter around 1.5 μm and length up to 6 μm .

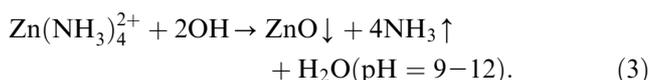
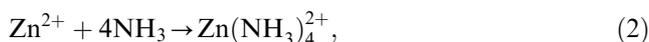
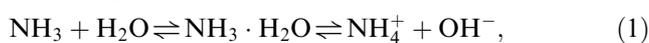
Further morphology characterization of the ZnO samples was performed using TEM as shown in Fig. 3, which agrees with the FE-SEM results. Fig. 3(a) shows two group ZnO whiskers prepared in a structure-direct solvent under 145°C, in which the group inextricably united together by dozens of single whiskers. Fig. 3(b) confirms a single ZnO whisker, which has smooth face, extending outside continuously without curving and

clearly shows awl-shaped feature, with a needle point and trapezoid end, just like the pencil-like figure. The inset SAED pattern taken on the pencil-like ZnO whisker exhibits the oriented growth direction along the c -axis. Different parts of this whisker show exactly the same electron pattern, indicating the single crystallinity of the whole single whisker. Dozens of individual whiskers have been examined using this method, and confirmed the single crystallinity.

Room-temperature photoluminescence spectrum of the ZnO group whiskers is shown in Fig. 4, in which two emission bands, including 409 and 420 nm, are contributed by the near band edge emission of the wide band gap. However, the weak and broad emission band centered at 520 nm could not be detected in our experiment although it was often observed in the previous reports [10]. The lack of green band in Fig. 4 is mainly indicative of a low surface area to volume ratio [27]. The two shoulders nearly overlapped violet emission (409, 420 nm), have slight red shift in the near band edge emission and differ from the band gap of bulk ZnO (around 380 nm) [20–22], which comes from the recombination of free exciton [23–24].

The growth of the group whiskers is suggested to follow a mechanism combined by the effect of alcohol, cleavage faces of ZnO tetrahedron and hydrothermal growth conditions.

In our approach to the formation of ZnO group whiskers, the role of ammonia is important [23–24]. Under pH = 9–12, hydroxyl OH⁻ and the tetrahedron Zn(NH₃)₄²⁺ form the initiative ZnO seed crystal according to Eqs. (1) and (3).



In this approach, appropriate amount of alcohol acts as the structure-directing reagent. When ethyl alcohol, propyl alcohol or even isopropanol was used as a substitute for the alcohol, the group whiskers cannot come forth and only single rods can be obtained. Polyol, such as glycol and polyethylene glycol, and other alcohol replacer of phenol also cannot come into being with the group whiskers. Only alcohol/water system is optimum to the group whiskers.

It has been found that systems with 1–20% (v/v) alcohol favor the growth of ZnO group whiskers. Detailed comparison experiments indicated that the yield of group whiskers is above 95% with existence of about 2.5% (v/v) alcohol in the system. The definitive factor for ZnO group whiskers is the reconstruction of the cleavage faces of tetrahedrally coordinated compound ZnO [28]. As shown in Fig. 5(a), the face of

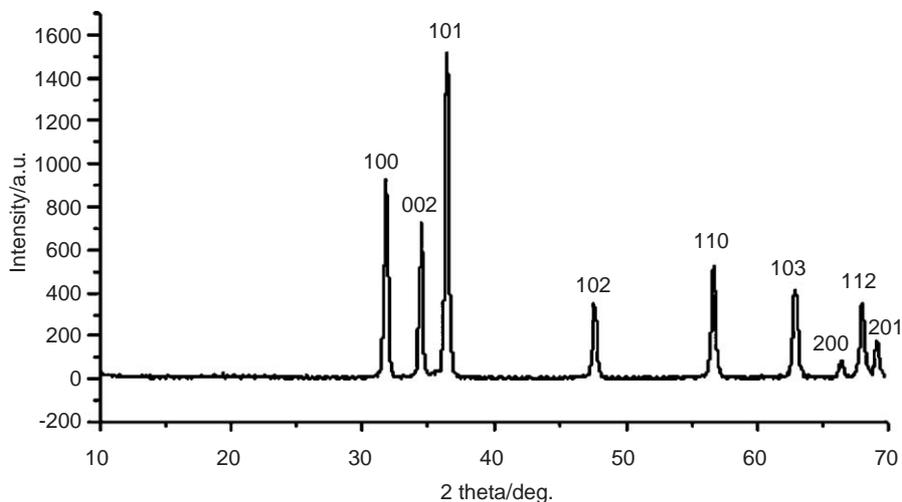


Fig. 1. XRD patterns of as-prepared ZnO.

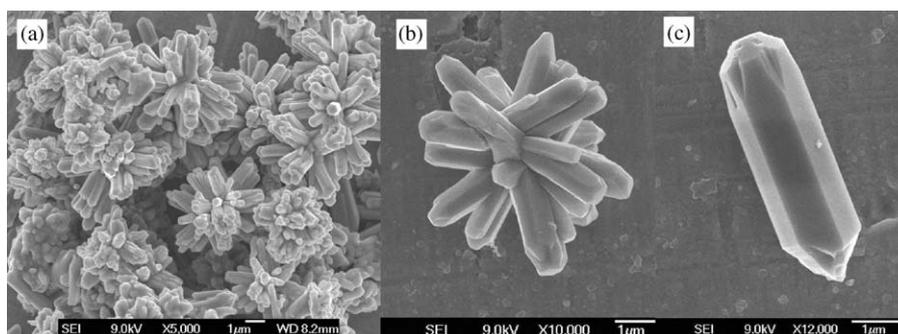


Fig. 2. FE-SEM images for the as-synthesized ZnO whiskers grown in a structure-direct solvent at a hydrothermal temperature of 145°C. (a) A large quantity of group whiskers. (b) A group whiskers. (c) One single pencil-like whisker.

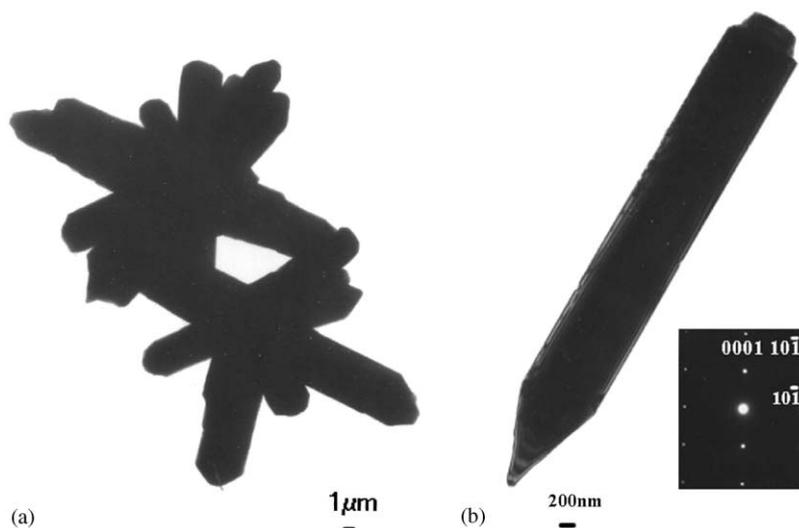


Fig. 3. TEM images of ZnO whiskers prepared in a structure-direct solvent under 145°C. (a) Two group whiskers. (b) A pencil-like whisker (inset: the corresponding SAED pattern).

tetrahedron $Zn-O_4$ is parallel to positive polar c (0001), and the vertex angle is in the face of negative polar (000 $\bar{1}$) [28]. Fig. 5(b) exhibits the projection of tetrahedron $Zn-O_4$ in $[11\bar{2}0]$. The distribution of Zn in

c is not symmetrical, which lean to (0001) but away from (000 $\bar{1}$). Zn and O are symmetrically distributed in $[\bar{1}100]$ [29–32]. Because of the crystal ZnO characteristic, many ZnO cleavage faces series, pencil-like, were formed from

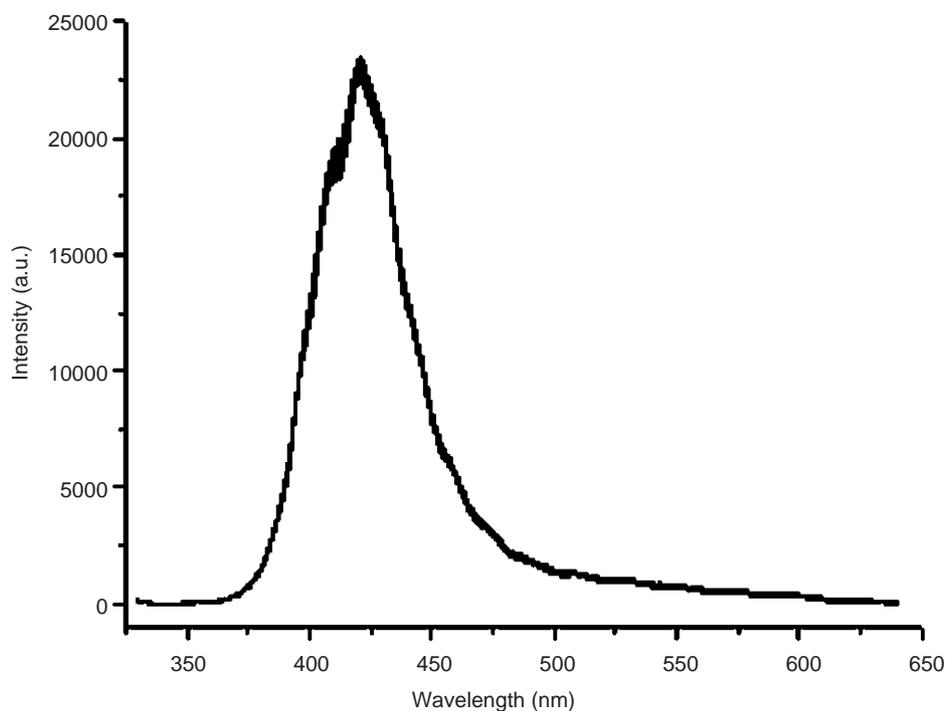


Fig. 4. Room-temperature photoluminescence spectrum of ZnO group whiskers.

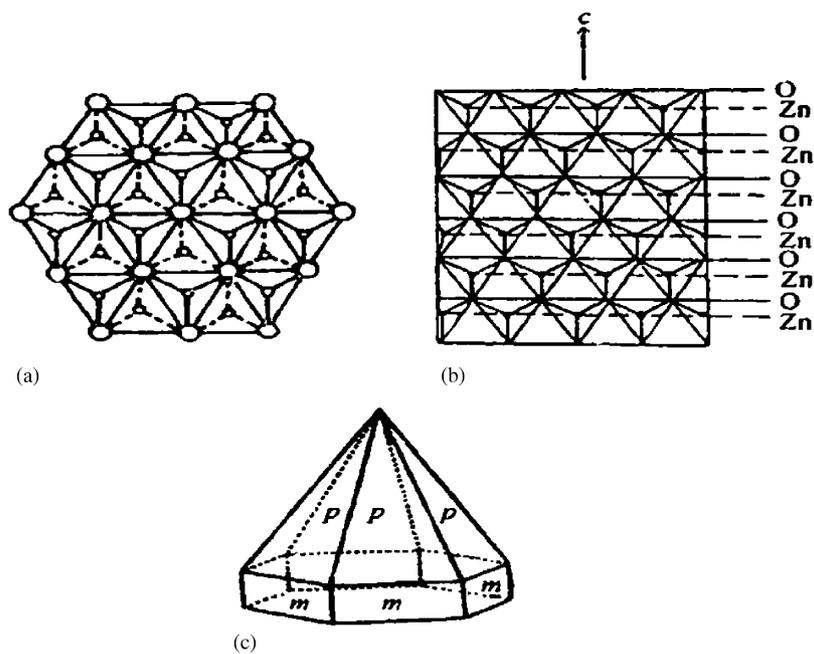


Fig. 5. Illustration of the ZnO crystal structure. (a) The projection of ZnO crystal structure in c (0001) face. (b) The projection of Zn-O₄ tetrahedron in (11 $\bar{2}$ 0) face. (c) The shape of single ZnO crystal whisker.

a seed crystal under the control of 2.5% (v/v) alcohol in radial tropism. As shown in Fig. 5(c), single whisker comes into being according the process seed crystal- p - m [29]. The experimental results suggested that 2.5% (v/v) alcohol is propitious to the ZnO cleavage and accordingly the group whiskers formed.

Under hydrothermal conditions, many seed crystals stretch forth radial orientation whiskers [33]. Single whisker's unique growth direction is explained by the favorable energy along a specific growth direction [34,35]. The hexagonal prismatic morphology and the facet outlook of the whiskers are caused by the different

growth rates of the crystalline faces [10]. At the end of growth, some whiskers show needle-like end because of the consumed OH^- .

In summary, the synthesis of ZnO group whiskers has been described via a simple mild hydrothermal method. The product consists of a large quantity of hexagonal pencil-like whiskers, with typical widths of about 750 nm and the angle of 120° , which comprise many group whiskers. Single whisker, showing awl-shaped and pencil-like morphology, has diameter around 1.5 μm and length up to 6 μm . Its photoluminescence spectrum exhibits two emission bands, including violet 409 nm band and 420 nm band, which may be contributed by the near band edge emission of the wide band gap. The growth of the group whiskers is suggested to follow a mechanism combining the effect of alcohol, cleavage faces of tetrahedrally coordinated ZnO and hydrothermal growth conditions. It is expected that the novel group whiskers may offer exciting opportunities for potential applications in photoelectronic devices. In addition, we believe that this simple process can also be applied to synthesize other group whiskers for functional materials.

Acknowledgments

Financial support from the National Natural Science Foundation of China and the Chinese Ministry of Education is gratefully acknowledged.

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