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Growth Mechanism, Structural and Optical Properties of Hexagonal Cone-shaped ZnO Nanostructure

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Abstract: Using a hydrothermal method, the single-crystalline ZnO nanowires with a hexagonal cone-shape were synthesized with zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and hexamethylenetetramine(HMT). The morphology of the hexagonal cone-shaped ZnO was investigated by selected area electron diffraction (SAED) and scanning electron microscopy (SEM) measurements. The photoluminescence (PL) spectrum of the synthesized ZnO nanowires shows a strong ultraviolet (UV) emission at 379 nm and some weak emission peaks at the visible wavelength region. In addition, the formation mechanism of the hexagonal cone-shaped ZnO is discussed.

Key words: cone-shaped ZnO; hydrothermal; growth mechanism; optical property
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1 Introduction

ZnO is an important semiconductor with a wide band gap of 3.37 eV and a large excition binding energy of 60 meV at room temperature[1]. Due to its unique electrical and optical properties[2], ZnO could have many applications such as ultraviolet (UV) lasers, photodetectors, photodiodes, solar cells[3~6] *etc*. Over the past decade, many methods have been developed for the preparation of ZnO, like vapor-liquid-solid (VLS) growth process, sol-gel, molecular beam epitaxy (MBE), and so on[7~11]. The synthesized ZnO is in various morphologies such as nanobelts, nanowires, nanorods, and nanotubes[12,13], *etc*. Recently, Fang *et al*. successfully synthesized well-aligned ZnO nanowire arrays on Si substrate by a vapor transport process[14], and flower-like ZnO nanorods were synthesized by Chen *et al*. with a sonochemical method[15]. Up to now, there still is a great interest in finding a simple, reliable and rapid method to synthesize ZnO with specific morphologies and properties.

In this paper, we report the successful fabrication of the hexagonal cone-shaped ZnO nanostructures by a hydrothermal method only using zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and hexamethylenetetramine(HMT). The room temperature photoluminescence (PL) spectrum of the synthesized ZnO shows a strong UV emission, therefore it is expected to have a new application in UV emission fields. We also discuss the formation mechanism of this hexagonal cone-shaped ZnO.

2 Experimental Details

The ZnO nanostructures with hexagonal cone-shape were grown by a hydrothermal method. All the reagents we used are analytically pure. A 100 nm-thick (002) oritented ZnO film deposited on a Si

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substrate by magnetron sputtering was used as the seed film. $Zn(CH_3COO)_2 \cdot 2H_2O$ of 0.1 mol/L and HMT of 0.1 mol/L were dissolved in aqueous solution. The mixed solution was transferred into a teflon-lined stainless autoclave, then the prepared ZnO film/Si substrate was put into the solution. Initially the tank was warmed up to 90 ℃ and kept at this temperature for 6 h. Then the temperature was directly increased to 150 ℃ and kept at this temperature for 12 h. Finally, the sample was washed with the deionized water and dried in the air at 60 ℃ for several hours.

The field-emission scanning electron microscopy (FESEM) images of our sample were carried on a Hitachis-4800 equipment, the energy-dispersive X-ray spectroscopy (EDS, GENE SIS 2000 XMS 60S, EDAX, Inc.) attached to the SEM, a transmission electron microscopy (TEM) and a D/max-RA X-ray spectrometer (Rigaku). Photoluminescence (PL) measurement was performed using a He-Cd laser line of 325 nm as the excitation source.

3　Results and Discussion

In Fig. 1 we present the X-ray diffraction (XRD) pattern of the as-grown sample. All the observed diffraction peaks can be indexed to the ZnO wurtzite structure. The dominant (002) diffraction peak indicates that the sample has a preferred orientation along the *c*-axis direction[16].

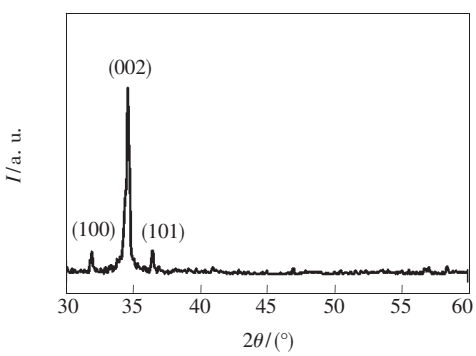

Fig. 1　XRD patterns of the as-grown ZnO sample

Fig. 2(a) shows a SEM image of as-grown ZnO nanostructures. The ZnO is a typical hexagonal cone-shaped structure with a rough surface which is seen clearly in the inset of Fig. 2(a). The range of diameters are 500 nm to 100 nm (from top to bottom), the lengths of hexagonal cone-shaped structure ZnO are about 3 μm. And some of them are grown vertically on the substrate.

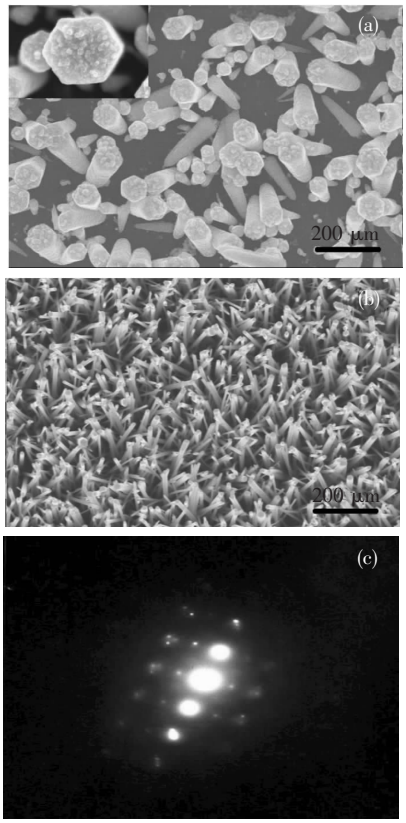

Fig. 2　(a) SEM image of hexagonal cone-shaped ZnO nanostructure; (b) SEM image of ZnO nanowires; (c) SAED pattern of hexagonal cone-shaped ZnO nanostructure.

In our experiments, we also find the morphology and the size of ZnO nanostructures are strongly depended on the reaction time and temperature. When it is prepared at 90 ℃ for 6 h, most of the products are small nanowires with a broad distribution of size as seen in Fig. 2(b). Correspondingly, when the temperature is gradually increased to 150 ℃ and kept for 12 h, a large scale of ZnO hexagonal cone-shaped nanostructure is appeared. Thus, the growth of the crystals could be controlled by the external conditions such as reaction time and temperature.

The selective area electron diffraction (SAED) pattern of hexagonal cone-shaped ZnO nanostructure is shown in Fig. 2(c). From the image, we can see spots are basically regularly arrayed. But it is obviously observed that spots in each group are not a single diffraction spot on two sides, which are com-

posed of several electron diffraction spots. As we know, diffraction spots of single crystal ZnO nanostructure are regularly arrayed. Here, it appears combination of electron diffraction spots, which may be caused by non-uniform size of cone-shape nanostructure.

The possible growth mechanism at this experiment conditions is supposed as two processes. The possible schematic diagram is shown in Fig. 3, which indicates two stages of the formation of ZnO. Finally, it can be seen clearly that we get specific ZnO structure. This supposition may account for the formation of the as-prepared hexagonal cone-shaped nanostructure.

First, different growth rates of ZnO crystal planes result in the formation of cone-shape structure. As we known that higher growth temperature is conducive to the decomposition of HMT, so the growth rate of ZnO could increase[17]. From previous reports we also know that, the growth rate (R) of the ZnO crystal planes is $R(0001) > R(10\bar{1}0) > R(10\bar{1}0)$, and (0001) crystal plane represents the polarity and is metastable[18], this polar top plane could attract more hydroxyl ions, which means that with the reaction temperature increasing, more hydroxyl ions would be applied for the growth system due to the decomposition of HMT, so the polar top plane of ZnO could further increasd than other crystal planes, at last, this hexagonal cone-shape nanostructure could be formed.

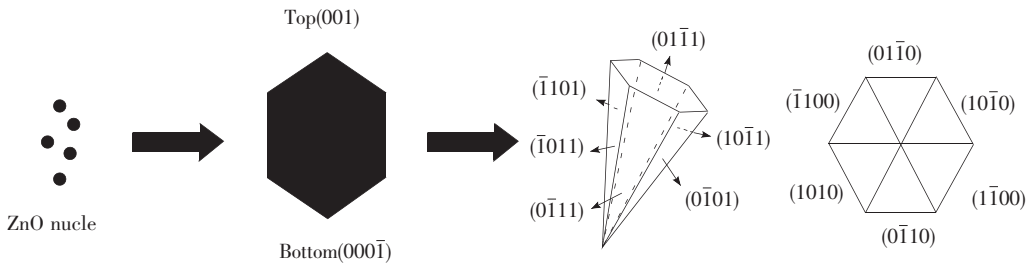

Fig. 3 Scheme of the growth of hexagonal cone-shaped ZnO

Second, the rough surface of cone-shape nanostructure is attributed to the nuclei on the surface. It can be seen that the surface of the nanostructure is roughness, especially the top crystal plane. Based on that mentioned above, the top plane could attract more hydroxyl ions, and these hydroxyl ions could erode the planes. Then, after initial experiment process, Zn^{2+} and OH^- were consumed, leading to the reduction of pH value of solution, all these could cause the heterogeneous nucleation, ZnO nanocrystal nuclei is formed on the surface of ZnO[19]. So, after reaction, we get the hexagonal cone-shape nanostructure with rough surface.

Fig. 4 shows the photoluminescence spectrum of the as-grown ZnO sample at room temperature. A strong ultraviolet emission peak is found at 379 nm. This peak belongs to the near band-edge emission of the wide band gap of ZnO due to the recombination of exciton[20]. Generally speaking, the ZnO with better crystallization and higher purity will have a

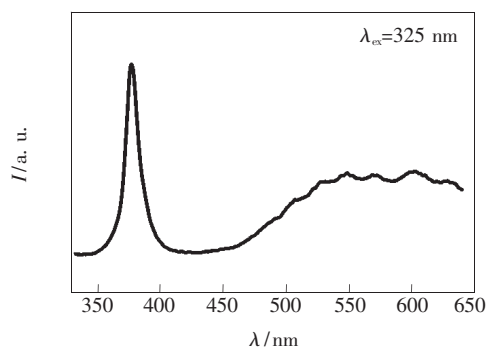

Fig. 4 Room temperature PL spectra of the ZnO samples

stronger UV emission. However, the visible emission peaks that we observe between 500 nm and 650 nm may be caused mainly by the surface defects[21].

4 Conclusion

In summary, we fabricate hexagonal cone-shaped ZnO nanostructure via the two step hydrothermal method. We discuss the growth mechanism of the hexagonal cone-shaped ZnO structure. We suggest that the formation of the hexagonal cone

shaped structure is ascribed to the different growth rates on the different crystal faces, and the growth rates of the crystal faces are depended on the growth time and temperature. Moreover, a higher deep-level emission is observed from the PL spectrum, which indicates that the ZnO samples have many surface defects.

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六角锥状 ZnO 纳米结构的生长机理、结构及光学性能

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摘要： 利用醋酸锌[$Zn(CH_3COO)_2 \cdot 2H_2O$]和六次甲基四胺($C_6H_{12}N_4$)以一定比例配置成反应溶液，通过水热合成法制备了六角锥状 ZnO 纳米结构。同时，使用了扫描电子显微镜(SEM)、X 射线衍射和选区电子衍射(SAED)，对样品的形貌与结构进行了分析。结果表明，样品形貌成六角锥状结构，并且在[002]方向择优生长。通过对样品的光学性能测试，由 PL 光谱分析可知，样品在 379 nm 处有一个较强的紫外发光峰，并且在可见光区域产生了一些较弱的可见光发射峰，表明制备的六角锥状 ZnO 纳米结构的晶体质量不是很好。除此之外，对六角锥状 ZnO 的生长机理也进行了讨论。

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