

Growth of ZnO nanotetrapods with hexagonal crown

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(Received 30 November 2005; accepted 9 March 2006; published online 10 May 2006)

ZnO nanotetrapods with hexagonal crown were synthesized on a silicon wafer by vapor transport process at a low temperature of 630 °C and normal pressure without the presence of catalysts. The results demonstrated that the as-synthesized products with slender legs and regular hexagonal crown are single crystal with wurtzite structure and preferentially grow up along (001) direction. Photoluminescence spectra revealed that the green emission originated from oxygen vacancies overwhelmed that of the near-band-edge ultraviolet peak, which suggests the peculiar-shaped nanotetrapods may have potential applications in multichannel nano-optoelectronic devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2202003]

Recently, one-dimensional (1D) or quasi-1D ZnO nanostructured materials have received special attention due to their unique properties and numerous potential applications. High chemical stability, low threshold intensity, wide band gap (3.37 eV), and large exciton binding energy (60 meV) make ZnO an excellent candidate for the fabrication of electronic and optoelectronic nanodevices. In order to obtain different ZnO nanostructured materials, varieties of methods have been developed. By far, a large number of ZnO nanostructured materials with different structures and morphologies have been synthesized, such as nanobelts,¹ nanowires,² nanospring,³ nanorods,^{4,5} nanocombs,⁶ tetrapodlike nanostructures,⁷ nanotubes,⁸ nanonails,⁹ nanosheets,¹⁰ and nanohelices;¹¹ their characteristics and potential applications have been studied intensively.

Considering the quantum confinement effect, peculiar properties of ZnO nanostructure may be expected to be obtained through controlling the shape and dimensionality of the materials. The nanotetrapods structured materials with special shape and structure which are significantly different from other ZnO nanostructures, have remarkable optical, electric, magnetic, and mechanical properties, and they possess promising applications in nanoelectronics and photonics. Thus, much effort has been devoted to the synthesis and investigation of their characteristics.

In this letter, we report a simple way to synthesize the special nanotetrapods. Compared with other nanotetrapods structured materials, the as-synthesized products have much larger surface area. The sample exhibits extraordinary strong green emissions that are related with the oxygen vacancies. This special characteristic suggests that the nanotetrapod material possesses high electrical conductivity, which indicates that they may be used for electron nanoconductors in multichannel optoelectronic devices.¹²

The special ZnO nanotetrapods were synthesized via vapor evaporation deposition at a low temperature. A quartz tube was mounted horizontally inside a high-temperature tube furnace (with 50 mm inner diameter and 1200 mm in length). A *p*-type silicon (111) wafer (pretreated by H₂SO₄:H₂O₂=7:3 for 30 min, then washed by de-ionized water and

ethanol three times, respectively, and finally dried naturally) was placed face down on an alumina ceramic boat (10 × 70 mm²) loaded with 1 g zinc powders (purity: 99.999%) and the vertical distance between the substrate and the zinc source was about 6 mm. The boat was inserted into the center of the horizontal quartz tube. Different from other methods, neither catalyst nor vacuum was needed in our experiment. For the sake of driving off the O₂ in the tube, an Ar flow with a rate of 1000 SCCM (SCCM denotes cubic centimeter per minute at STP) was turned on and kept for about 20 min and then closed before heating. Subsequently, the quartz tube was heated at a rate of 30 °C/min. When the temperature reached 630 °C, a flow of Ar at a rate of about 300 SCCM and O₂ at about 20 SCCM was switched on and kept for 10–30 min. Finally, the heating power and the flow of Ar and O₂ were turned off. After cooling down to room temperature, white material was found on the surface of the substrates.

The as-made nanostructured ZnO were examined using x-ray diffraction (XRD, D/MAX-2500), field emission scanning electron microscopy (FE-SEM, FEI SIRION), high-resolution field emission transmission electron microscopy (HR-FETEM, JEM 2010F), Raman spectrum (JY-T64000, excitation wavelength: 524 nm), and the photoluminescence (PL) property (900 nF, Xe lamp, 325 nm, as the excitation source).

The XRD analysis was employed to determine the structure and phase of the products. Figure 1 illustrates the XRD pattern of the as-prepared products. All the peaks are indexed to typical wurtzite hexagonal phase of ZnO with lattice constants of $a=3.250$ Å and $c=5.206$ Å. No peaks for Zn or other impurities were detected in the spectrum indicating that the as-grown samples are pure ZnO. Furthermore, it also implies that the nanostructured ZnO is highly crystallized.

The morphology and structure of the prepared products were analyzed by SEM. Figure 2(a) shows the typical SEM image and reveals that the products obtained are uniform tetrapodlike ZnO with regular hexagonal crown on each leg. In a perfect ZnO nanotetrapod unit, four nanopods share a common crystal facet and each leg is a uniform and regular hexagonal crown. The typical TEM image provides further information of the microstructure of the synthesized nanotetrapods with hexagonal crown. Figures 2(b) and 2(c) show that the four legs of a unit are uniform, the diameter of the

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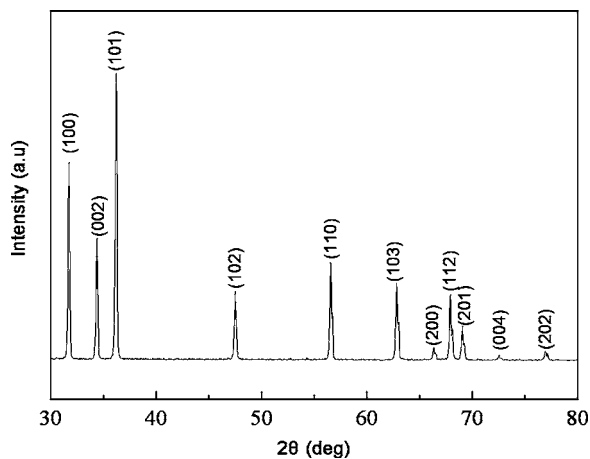


FIG. 1. XRD pattern of ZnO nanotetrapods with hexagonal crown.

four legs ranges from 50 to 100 nm and their lengths are between 1–1.5 μm . The side length of hexagonal crown is about 500 nm and around 50 nm in thick, respectively. The detailed information of the ZnO nanotetrapod was studied by HR-FETEM equipped with selected area electron diffraction (SAED). The SAED pattern as shown in Fig. 2(f) suggests that they are single crystals with wurtzite structure, which is in accord with the XRD results. The HR-TEM image [Fig. 2(e)] of the crystal corroborates that the synthesized ZnO are perfect crystalline and grown along the (001) direction.

The growth mechanism was thought to be vapor solid (VS) rather than conventionally vapor-liquid-solid (VLS) model because the synthesis was processed without any catalysts or other additives. The configuration of the grown crystal reflects its internal structure, and the growth rate of different face determines its own morphology. Generally speaking, the crystallography is dependent on the symmetry of the external structure, the bonding manner between the structural unit and the crystal defects, but the external factors play an important role in it. From Fig. 3(a), we can observe

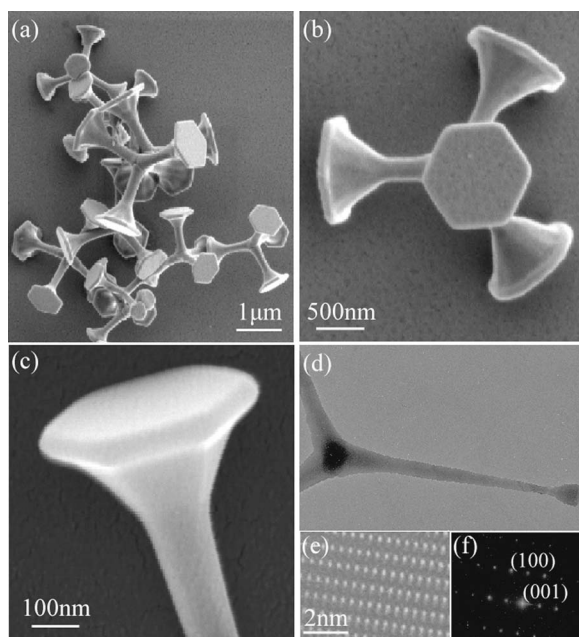


FIG. 2. (a) Low magnification SEM image of ZnO nanotetrapods with hexagonal crown. [(b) and (c)] High magnification SEM images of the nanostructured ZnO. (d) TEM image of the ZnO nanotetrapods. (e) HR-TEM image of the as-grown product. (f) The corresponding SAED pattern.

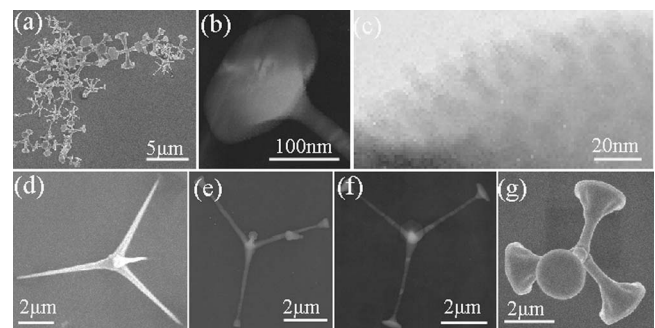


FIG. 3. (a) SEM image showing the nanotetrapods at different stages. [(b) and (c)] HR-TEM images showing the growth way of the nanotetrapods with hexagonal crown. [(d)–(g)] SEM and TEM images showing the formation process of the ZnO nanotetrapods.

that different nanotetrapods with crown were in different sizes (both in the leg and the crown) which indicates that they were in different stages of the growth process. There exists nanotetrapods with peaked leg, hexagonal bugs, little hexagonal crown, large hexagonal crown, and round crown. We can presume that the as-grown products may originate from the nanotetrapods with peaked leg. If conditions do not change, they may be grown along the same direction with long peaked leg. Actually, we found many as-said structured nanotetrapods in other regions of the boat. But when the condition changes, the growth direction will change also. Apparently, when the O_2 is just turned on, the nanotetrapods will grow along the same direction because the O_2 is enough to feed the Zn atoms to form ZnO. However, because the partial pressure of the oxygen is very low, the oxygen will consume quickly in a short period in some region of the boat where the growth of ZnO will stop, and Zn atoms (which will further be oxidized to ZnO immediately again when O_2 is available) will gather around the tip in which the surface energy is high. Although, the Zn crystal is also a hexagonal structure, there are some differences between the Zn crystal unit and that of ZnO. The marriage of the change of atmosphere and the gather of Zn atoms may cause the growth direction to change and create hexagonal crown. We speculate that the nanotetrapods ZnO with hexagonal crown may grow up into nanotetrapods with round crown in the end.

Figures 3(d)–3(g) show the growth processes of the ZnO nanotetrapods with hexagonal crown and the ZnO nanotetrapods with round crown. Figures 3(b) and 3(c) show the formation way of the crown. Intuitively, we may think they will expand along a crystal face step by step or layer by layer as reported in other literature,¹³ but it is interesting to note that there are a large number of regular protuberances sticking out from the edge around the hexagonal crown, which may further support the conclusion as mentioned above that the formation of the crown may be due to the zinc atoms gathering along the other direction.

The optical properties of the synthesized samples have been studied by using Raman and photoluminescence measurements which were performed at room temperature. According to the group theory, near the Brillouin zone, there are eight different optic modes: A_1 , $2B_2$, E_1 , and $2E_2$, among which A_1 , E_1 , and $2E_2$ modes are Raman active.¹⁴ Figure 4 shows the typical Raman scattering of the as-fabricated sample. We observe two dominated and strong intensity peaks at ~ 99.88 and ~ 438.22 cm^{-1} which are attributed to the low and high- E_2 mode of nonpolar optical phonons, re-

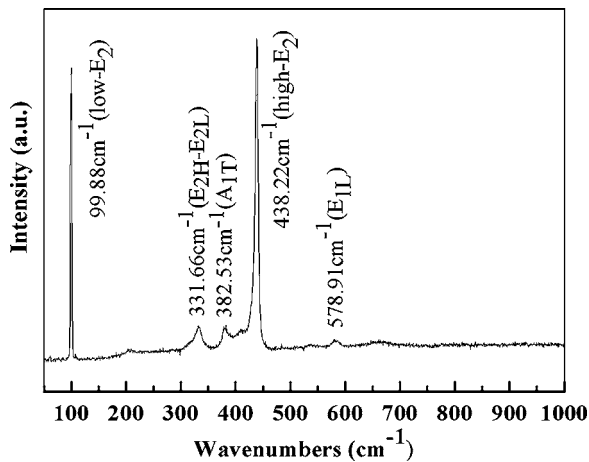


FIG. 4. Raman scattering spectrum acquired from the ZnO nanotetrapods with hexagonal crown at room temperature.

spectively, and indicating that the as-grown products are excellent single crystal with hexagonal wurtzite structure.¹⁵ Two very short peaks at ~ 331.6 and 382.53 cm^{-1} correspond to $E_{2H}-E_{2L}$ (multiphonons) and A_{1T} modes, respectively. The short and suppressed peak at ~ 578.91 cm^{-1} is assigned to E_{1L} mode which is due to the impurities and structural defects (oxygen vacancies and Zn interstitials¹⁶) of the samples.

Photoluminescence spectra of the ZnO nanotetrapods with hexagonal crown were measured at room temperature using Xe lamp as the excitation sources. From Fig. 5(a), we observe that the near-band-edge (NBE) ultraviolet (UV) peak at ~ 393 nm (3.37 eV) is considerably weak while the green emission at ~ 511 nm (2.43 eV) is very strong. It is generally accepted that the green emission is attributed to the single ionized oxygen vacancy in the ZnO, and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy, while the UV emission can be explained by the NBE emission of the wide band gap ZnO. So the surface state of the as-made ZnO determines the green emission peak. In order to prove the result, we annealed the as-deposited products under oxygen at 600 °C for 30 min. As shown in Fig. 5(b), it is noted that the peak at ~ 511 nm becomes very weak after annealing, hereby, we can infer that the green emission is due to the

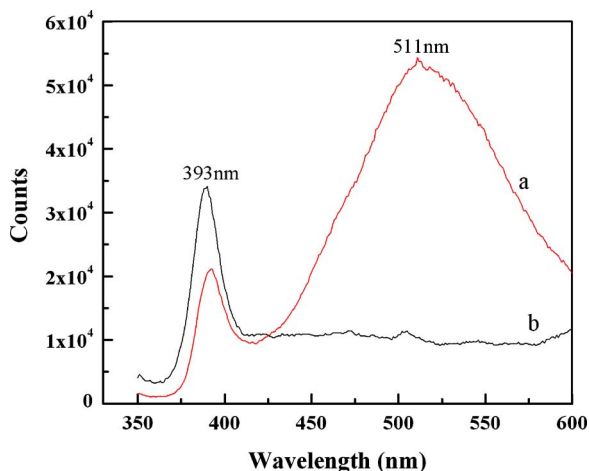


FIG. 5. (Color online) Room temperature photoluminescence spectrum for the ZnO nanotetrapods: (a) as-synthesized ZnO nanotetrapods; (b) annealed under oxygen at 600 °C for 30 min.

oxygen vacancies of the as-fabricated materials. As it is well known, the atmosphere and the configuration are important factors for the surface state of the synthesized materials, which means that both the partial pressure of oxygen in the tube and the shape of the samples play crucial roles in the green emission. Because the products have high surface-to-volume ratios for their slender legs and thin hexagonal crown with large surface area, and especially, they have been synthesized at very low oxygen partial pressure, there may exist more oxygen vacancies than other nanotetrapods. Therefore, the green emission peak at 511 nm is extraordinary strong and quite wide. It is reported that the higher density of oxygen vacancies the nanostructured materials have, the higher electrical conductivity they possess,¹⁵ therefore, the as-synthesized materials are promising candidates as electron nanoconductors in nano-optoelectronic devices. Also, the crystalline (impurity and structure defects such as oxygen vacancy) and the structure (shape, diameter, etc.) of the synthesized ZnO play key roles in the enhancement of NBE emission.

In summary, ZnO nanotetrapods with hexagonal crown have been fabricated via vapor transport process at a low temperature in argon atmosphere with a small amount of oxygen. The growth mechanism has been discussed in detail. XRD, SEM, HR-TEM, and SAED analyses show that the as-produced samples are single crystal with uniform legs and large hexagonal crown. XRD pattern, Raman measurement, and photoluminescence spectra of the nanotetrapods confirm that the as-grown products were wurtzite structured ZnO with many oxygen vacancies. The products may have potential applications for electron nanoconductors in multichannel optoelectronic devices.

This work was supported by the Distinguished Young Scholar Fund of National Natural Science Foundation of China (NSFC, Grant No. 10225209), key project from Chinese Academy of Sciences (Grant No. KJCX-SW-L2) and NSFC project (Grant No. 90305020).

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