ZnO Well-Faceted Fibers with Periodic Junctions

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ZnO well-faceted microfibers with periodic junctions were prepared by an evaporation and deposition process. The junctions with spacings of 5−30 μm presented concavo−concave morphologies, and the spacings could be changed with the growth conditions. The anisotropic growth mechanism was investigated by X-ray diffraction (XRD), energy-dispersive X-ray (EDX) analysis, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD). The photoluminescence (PL) and PL microscopy studies showed the structure-related optical character and that the well-faceted and modulated fibers could serve as microscale waveguides and emit enhanced green lights at the junctions under UV excitation. These functional structures should make possible the creation of microscale light-emitting arrays as well as bar codes used in biotechnology and electronics.

Recently, much effort has been focused on the fabrication of inorganic mesostructures by controlling the sizes, shapes, crystal structures, and surface structures,[1] because these feature parameters contribute much to the variety in applications[2]. An efficient way to achieve controlled growth is to apply the anisotropies of crystals. It has been extremely successful in different growth systems, such as the solution-based route for growing shaped nanocrystals[3], vapor-phase growth of quasi-one-dimensional mesostructures with well-defined cross sections and surface polarities, as well as some other exotic configurations through a vapor−liquid−solid (VLS) or vapor−solid (VS) process.[4] These structure-controlled materials have exploited a wide range of technological applications in chemical, optic, electronic, and mechanical fields. For example, the well-faceted ZnO or SnO_2 nanowires/belts are usually used as natural resonance cavities for emitting nanolasers.[5] Moreover, new types of functional mesostructures with modulated sizes and shapes have also been prepared, such as Si/Ge heterostructures,[6] metallic micro-bar codes,[7] and helical nanosprings of SiO_2 and ZnO.[8]

Herein, on the basis of the anisotropic nature of wurtzite ZnO, we have synthesized a novel configuration of well-faceted microfiber with periodic junctions via a simple vapor growth process. ZnO is an important functional material with semiconducting and piezoelectric dual properties, and it has been widely used in luminescence, photocatalysts, sensors, piezoelectric transducers, and surface acoustic wave devices.[9] The modulated and well-faceted microfibers of ZnO prepared here should have more promising applications, due to the embodiments of some structure-related characters and the microscale feature size suit for integration for functional devices. The anisotropic growth of these modulated structures was investigated by X-ray diffraction (XRD), energy-dispersive X-ray (EDX) analysis, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD). The micro-photoluminescence (PL) and PL microscopy studies further indicate the potential application of the fiber in light excited technology at the microscale.

The well-faceted microfibers with periodic junctions were synthesized by an evaporation and deposition process. Zinc powders (5 g, 99.9% purity) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 g, 99.99% purity) as the starting materials were loaded into the center of a quartz tube with a length of 30 cm and a diameter of 20 mm. The tube was sealed, leaving one small open end, and then put into a furnace heated to ∼800 °C. The reaction of zinc with oxygen taking place in the tube resulted in a white and fluffy product containing a high yield of microfibers. The general morphology of the product was examined by scanning electron microscopy (SEM, JSM-5900). The crystal structure and the phase composition were analyzed by powder X-ray diffraction (XRD, Rigaku D/Max-RA) using Cu Kα radiation. The orientation measurements were performed on a scanning electron microscope (LEO-1530VP) equipped with an EBSD system (EDAX OIM). The micro-PL was measured by an UV Labran Infinity spectrophotometer (JY Company) excited by the 325 nm He−Cd laser, and the PL microscopy was charactered by a fluorescence microscope (Nikon E800) excited by the 380 nm halogen lamp.

SEM observations reveal that the as-synthesized products are composed of microfibers with periodic junctions at a significant percentage (over 95%) of the yield and over 80% reproducibility from run to run (Figure 1a). Most of the fibers consist of strings of nearly hexagonal prisms (Figure 1b). The fibers with very thin junctions usually grow parallel to each other, and the roots appear to be compressed and broad (indicated by arrows in Figure 1b). The junctions with spacings of 5−30 μm exhibit concavo−concave morphologies. The side surfaces of the fibers are well-faceted (Figure 1c). EDX microanalysis results show Zn and O species without any other impurities. Powder XRD results show that the fibers are wurtzite structured ZnO with

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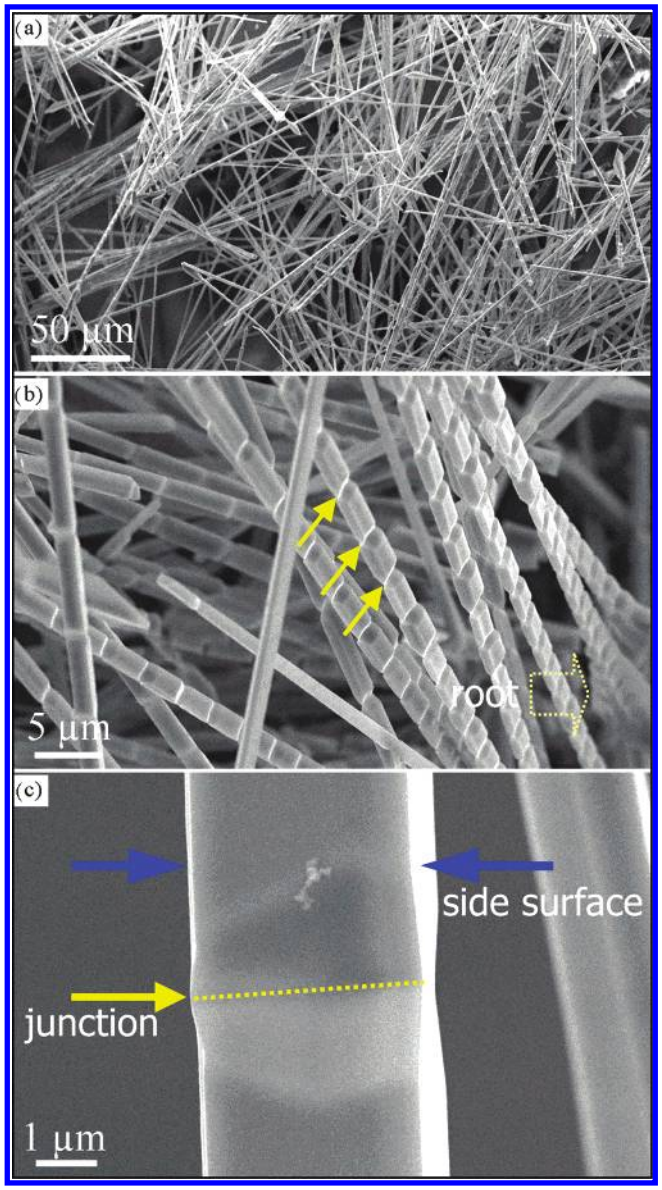

Figure 1. SEM images of the ZnO microfibers at (a) low magnification, (b) higher magnification, and (c) high magnification.

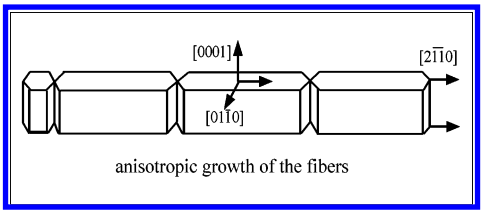

Figure 2. Microfiber crystal model.

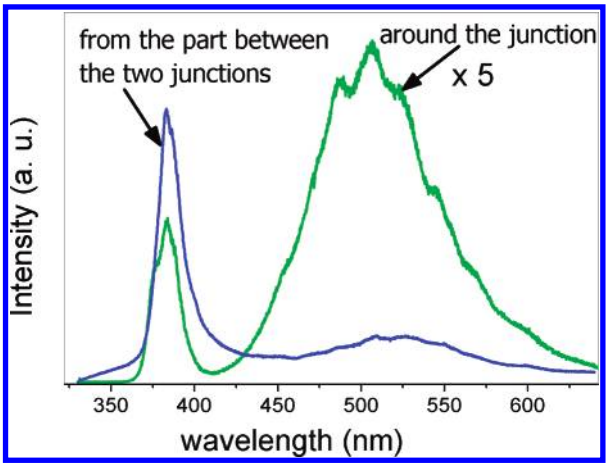

Figure 3. PL spectra obtained from a microfiber denoting the enhancement of the green light emission around the junction.

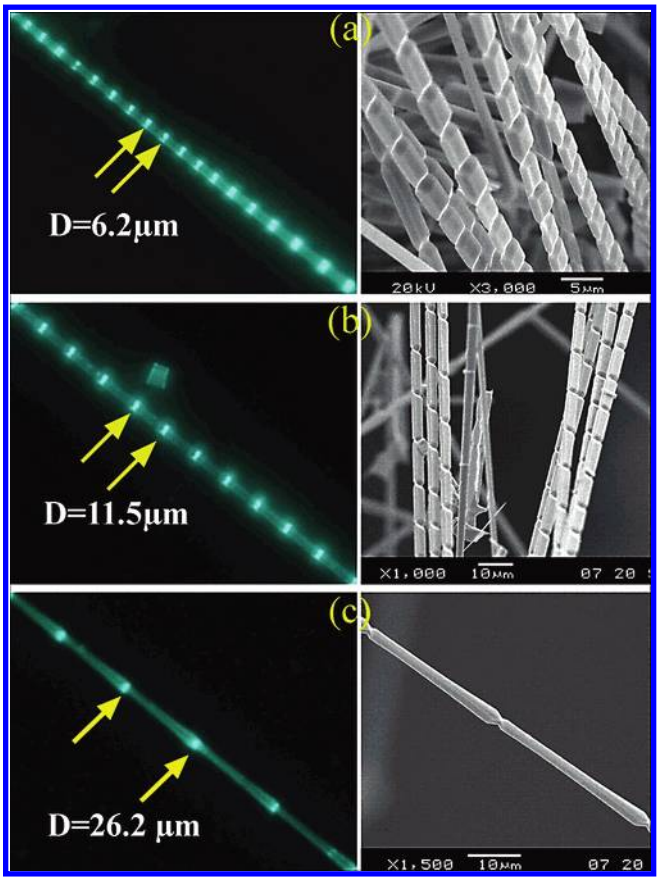

Figure 4. PL micrographs (left panel) corresponding to the same scale products shown in the SEM images (right panel) of the ZnO fibers revealing the enhancement of green light emission at the junctions.

lattice constants of $a = 3.249$ Å and $c = 5.206$ Å (Supporting Information Figure S1). Crystallographic orientations of the fibers obtained by EBSD (see Supporting Information Figure S2 for details) confirm the growth model (Figure 2). The growth direction of the microfiber is [2$\bar{1}\bar{1}$0] (a axis), and the side surfaces (indicated by blue arrows) are $\pm$(0001).[10] The broad top and bottom surfaces are parallel {01$\bar{1}$0} planes. The growth patterns observed in the experiments reveal that the microfiber growth may be guided by the nickel via the VLS mechanism, and an anisotropic growth process is shown as follows: a nanobelt base was formed by fast catalysis growth along [2$\bar{1}\bar{1}$0], followed by slow growth along [0001], forming the separate units of nearly hexagonal prisms. Developing on the nanobelt, these small units merged and formed junctions (see Supporting Information Figure S4 for details).

The room-temperature micro-PL spectra shown in Figure 3 indicate the enhancement of the green light emission at the junction. The spectrum obtained from the part between the two junctions consists of an intensive UV peak at 383 nm and a weak green band around 510 nm. Note the spectrum around the junction indicates that the green band is very strong. This was further demonstrated using a PL microscope. The PL microscopy images (Figure 4, left) show the fibers emitting strong green light at the junctions.

It is generally accepted that the UV peak at 383 nm resulted from free excitonic emission of ZnO,[11] while the green band

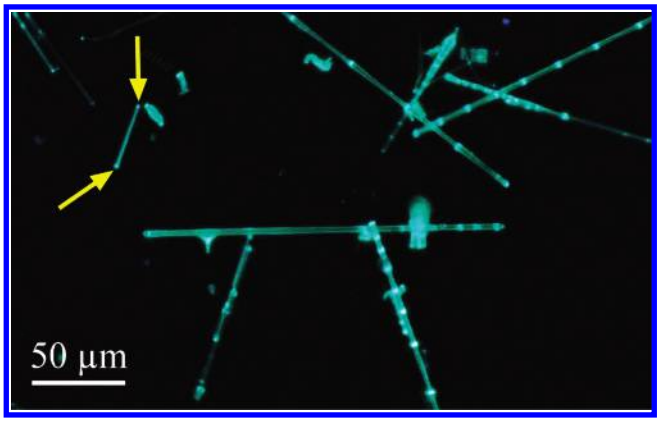

Figure 5. PL micrograph of the ZnO fibers. Note that the enhancement of green emission at the ends of a single segment (indicated by the yellow arrows) should be related to the optical waveguide property.

arises from the recombination of a shallowly trapped electron within a deeply trapped hole.[12] Note that two neighboring units form one thin junction and the V-like slots upon/below the junctions are not suitable as a platform (substrate) for uniform epitaxial growth of the crystals; thus, the intrinsic defects such as oxygen vacancies easily develop, resulting in the enhancement of the green light emission.[13] However, our results suggest that the inhomogeneous PL emission of green light along the fiber stem, which was characterized by the periodic enhancement at the nearly isometric junctions, should be mainly attributed to the waveguide property of the well-faceted fibers (Figure 4). When the fibers were excited by UV light,[14] a major portion of the green fluorescence reflected and was transported along the well-faceted stems and then emitted out from the junctions and ends.[15] This was further evidenced in Figure 5. Note that the enhancement of green emission at the ends of a single rod (which was broken off from a fiber, indicated by the arrows) should be related to the optical waveguide property.[5] Therefore, the origin of the periodic enhancement of the green emission should be structure-related rather than induced by quantum confinement effects.[16]

In short, we have prepared the modulated and well-faceted ZnO microscale fibers in high yield. Micro-PL and PL microscopy studies demonstrate that the fibers could serve as microscale waveguides and emit strong green light at the nearly isometric junctions under UV excitation. By varying the growth conditions, it may be possible to construct bar-code-like structures with specific spacings between neighboring junctions. Note that anisotropic growth is a common phenomenon in the fabrication of wurtzite structured materials[17] and the extended methods for the growth control of ZnO and CdSe;[3,18] it should be possible to synthesize the well-faceted fibers with periodic junctions preferring a different axis (rather than here) or develop similar structures from other wurtzite semiconductor materials for further fabrication of light-emitting arrays sensing to different wavelengths. Therefore, this may be an effective way to fabricate microscale light-emitting arrays[19] as well as the bar codes[20] used in biotechnology and electronics.

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Supporting Information Available: XRD and detailed discussions on the growth mechanism (Supporting Information Figures S1−S4, in PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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