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# Synthesis of Ordered Ultrathin ZnO Nanowire Bundles on an Indium–Tin Oxide Substrate

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Ultrathin ZnO nanowire bundles have been synthesized on an indium–tin oxide substrate without any catalyst by using a simple thermal evaporation method, where self-organized ZnO nanowire bundles were grown on the hexagonal heads of ZnO nanocolumns. The nanowires obtained typically have diameters of 8 nm, with lengths extending to 0.25 $\mu$m. The size is the same order of magnitude as the ZnO exciton Bohr radius ($a_B$). Room-temperature photoluminescence measurement shows a prominent peak at 374 nm (3.32 eV), which is about 100 meV blue-shifted from the bulk ZnO emission.

The applications of nanostructured materials in microelectronic and optoelectronic devices are one of the major focuses on recent nanoscience researches.[1−3] Among these, the one-dimensional (1D) ZnO nanostructures have attracted particular attention because of their unique properties (a direct band gap of 3.37 eV and a large excition binding energy of 60 meV at room temperature) and diverse nanostructures. The latter relies on the anisotropic structure of ZnO and variation of the growth rate on different facets.[4,5] The potential applications rest with both the size and the shape of 1D nanostructures. Because of the quantum confinement effect, the low-dimensional nanostructured ZnO offers the possibility of further improving lasing conditions. Therefore, several methods[6−11] have been used to synthesize ZnO nanostructures. Among these methods, thermal evaporation provides a simple but highly effective approach for fabricating 1D small-diameter ZnO nanowires both in large quantities and at reasonably cost. For example, patterned thin gold dots have been successfully used as catalysts to direct the growth of 1D ZnO nanowires with diameters of 10−15 nm on sapphire substrates by a vapor−liquid−solid (VLS) process.[12] It is well-known that the quantum confinement effect has become evidence for nanostructures with sizes comparable to the exciton Bohr radius.[13] Unfortunately, up to now, little has been reported on the synthesis of aligned ultrathin ZnO nanowires (<10 nm) by this classical method. Although Wang's group has obtained 6 nm ZnO nanobelts by solid−vapor deposition,[14] those nanobelts are randomly oriented. How to effectively synthesize well-aligned ultrathin ZnO nanowire arrays is a challenging problem.

In this work, we report a simple synthesis of ultrathin ZnO nanowire bundles on an indium−tin oxide (ITO) substrate by using the thermal evaporation method at a relatively low growth temperature (560 °C), where self-organized ZnO nanowire bundles were grown on the hexagonal heads of ZnO nanocolumns. The small nanowires typically have a diameter of 8 nm and lengths of around 0.25 $\mu$m. The size is on the same order of magnitude as the ZnO exciton Bohr radius ($a_B$), which shows evidence of quantum confinement in optical properties. Room-temperature photoluminescence (PL) measurement shows a prominent peak at 374 nm (3.32 eV), which is about 100 meV blue-shifted from the bulk ZnO

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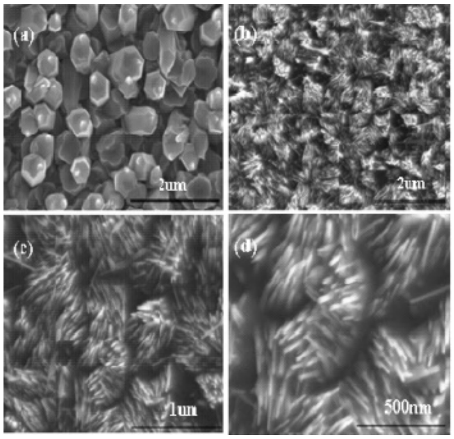

**Figure 1.** FESEM images of (a) the top view of the ZnO nanocolumn substrate and (b−d) top views of ultrathin ZnO nanowire bundles with different magnifications.

emission (3.24 eV and 383 nm).[15] In addition, it should be emphasized that the reaction was carried out at a relatively low temperature without any catalysts (Au, Sn, Cu, and so on), which not only may open a door to many opportunities for fabricating ZnO nanodevices onto various low-temperature endurance substrates but also may avoid contamination from the second-phase catalysts.

The ZnO nanowire bundles were fabricated via a simple vapor-phase transport process in a horizontal tube furnace. Instead of conventional thermal evaporation, we used a catalyst-free method. Zinc powder (99.99%) was loaded into a quartz boat serving as a source material. The ITO substrate was laid above the source material with a vertical distance of 4 mm. Before being loaded, the ITO substrate was cleaned by an organic solvent and washed with deionized water. The furnace was heated under a constant flow (150 sccm) of high-purity Ar ($\geq$99.999%). When the temperature reached 560 °C, normal nitrogen gas ($\geq$98.5%) replaced pure Ar gas. After heating at 560 °C for 30 min, the substrate was naturally cooled down to room temperature in the furnace. The as-grown sample was then investigated by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and TEM/selected-area electron diffraction (TEM/SAED). PL measurement was performed using a He−Cd laser line of 325 nm as the excitation source. In order to detect the initial growth process, another sample was grown under the same growth conditions but with a shorter growth time of 5 min.

The morphologies of as-grown samples were examined by FESEM. Figure 1a shows the sample with a 5 min growth, in which a layer of ZnO nanocolumns covers the whole substrate. Each ZnO nanocolumn has a diameter of hundreds of nanometers with a hexagonal-shaped flat surface. Some nucleation sites were observed at the second growth stage (the bright dot on the surface of the nanocolumn). Parts b−d of Figure 1 are top views of the sample (30 min growth) with different magnifications, showing lots of nanowires forming bundles. All nanowires (typically a diameter of 8 nm and lengths of around 0.25 $\mu$m) grown on the same nanocolumn are vertically aligned to the surface of the ZnO nanocolumn. Because no catalyst is used in our experiment, we suggest that the nanocolumn layer is the key factor for the formation of ZnO nanowire bundles.

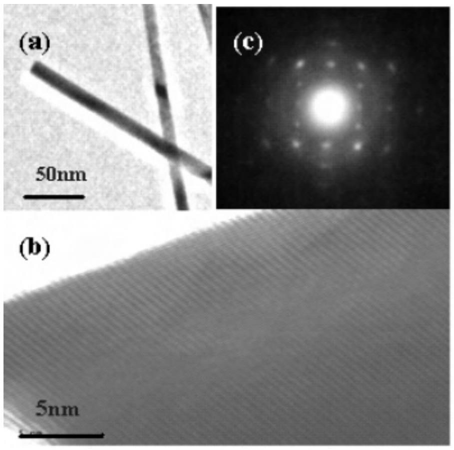

**Figure 2.** (a) Low-magnification TEM image of the ZnO nanowire bundles and (b) high-resolution TEM image from a single nanowire. (c) SAED pattern of the same nanowire as shown in part b.

To further investigate the structural characteristics of the nanowires, a TEM image of a single ZnO nanowire is given (Figure 2a). Clear lattice fringes showing from high-resolusion TEM (HRTEM) image (Figure 2b) indicate the single-crystalline structure of the ZnO nanowires, which is in accordance with the SAED pattern shown in the inset of Figure 2c. The lattice spacing is approximately 0.26 nm between adjacent lattice planes; this further confirms that the growth direction is along the [0001] plane.

Vapor−solid (VS) and VLS) mechanisms have been proposed to explain the growth of ZnO nanostructures by the vapor-phase transport process. Without using any catalysts in our experiment, we suggest that the formation of ZnO nanowires on the ITO substrate can be enucleated by the VS mechanism. Before nitrogen gas was introduced into the quartz tube, the substrate surface was covered with a Zn layer. Although the growth temperature of 560 °C was higher than the melting point of Zn, 419 °C, the absorbed Zn adatoms were deposited exactly where they landed, creating a certain number of atom clusters. Then, with nitrogen gas being led into the reaction tube, those metal Zn grains were oxidized by the residual oxygen in the nitrogen gas. Combined with the fact that [0001] is the preferred growth direction of ZnO, a thin layer of ZnO nanocolumns with hexagonal heads was formed on the substrate. The analysis is in well agreement with the FESEM results (Figure 1a). During the first stage, though the top (0001) surface of each nanocolumn is macroscopically flat, nanoscale roughness may still be formed because of adsorption−desorption kinetics and nonlinear diffusion of atoms.[16] Such a surface of each ZnO nanocolumn can provide the preferential nucleation sites for further growth of the nanowire bundles

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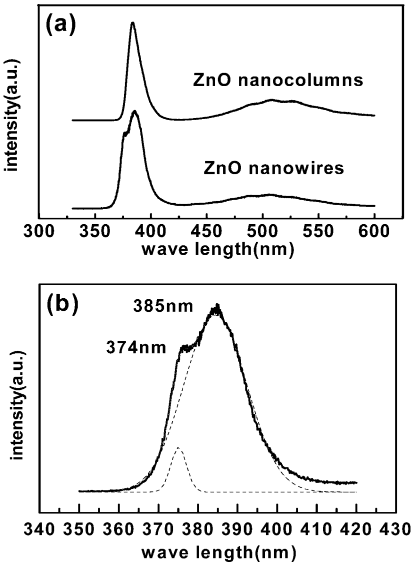

**Figure 3.** (a) Room-temperature PL spectrum of the ZnO nanocolumn substrate and ultrathin ZnO nanowire bundles. (b) UV peak of ZnO nanowire bundles (the solid line) fitted with two Gaussians (dashed lines) peaked at 374 and 385 nm.

through a self-catalyst process.[17] Most likely is the island nucleation of the second generation of nanowires on the first generation of nanocolumns responsible for yielding thinner nanowires. This is general knowledge derived from classic crystal growth, which, in turn, is based on atomistic models. Because of the limit from each ZnO nanocolumn, the density of the nucleation sites is close to that of the nanowires on nanocolumns. So, the morphology of the as-grown sample exhibits ultrathin ZnO nanowire bundles well-distributed on each nanocolumn. Also, because the first generation is grown along [0001], consequently, the second generation would follow this trend. Therefore, only vertically aligned ZnO nanowire bundles are expected to carry on and dominate, whereas growth along other directions could not continue in such a crowded condition and would be suppressed.

It is known that the Bohr exciton radius of ZnO is 2.34 nm;[13] quantum confinement effects are expected to be shown in these nanoscale entities when approaching this size region. Indeed, a blue shift of the exciton emission has been observed for ZnO nanobelts or nanofibers, with the dimension being less than 10 nm.[14,15] To examine the size-dependent property of our ultrathin ZnO nanowires, we also recorded the PL spectrum at room temperature (shown in Figure 3a). Both samples show strong UV emission peaks, which can be attributed to the near-band-edge emission of ZnO. The ultrathin ZnO nanowire bundles exhibit an asymmetric UV emission peak. It can be deconvoluted into two Gaussians located at 374 nm (3.316 eV) and 385 nm (3.221 eV), exhibited in Figure 3b. It is proposed that the interference signal from the layer underneath the nanowires could not be blocked off. Combined with single PL results of the ZnO nanocolumn substrate, the emission peak at 385 nm corresponds to the layer of ZnO nanocolumns; the emission peak located at 374 nm corresponds to ZnO nanowire bundles. Compared with the PL spectra of bulk ZnO crystals at room temperature, a blue shift of about 100 meV is observed in nanowire bundles, which possibly indicates quantum confinement arising from the reduced size of the ultrathin nanowires.

The deep-level green emission is very weak compared with the UV peak. The origin of the deep level in ZnO is not yet clearly understood but is generally attributed to structural defects, single ionized vacancies, and impurities.[18] Because we used a thin-film ZnO nanocolumn layer as the self-catalyst, the unintentional incorporation of metal impurities into nanowires can be avoided. Furthermore, ZnO was single crystalline without observable structural defects as determined from the TEM study. It is suspected that oxygen vacancies, which exist commonly in ZnO nanowires as point defects, led to the deep-level emission.[19] In contrast to the strong green emission from ZnO hierarchical nanostructures reported by Liu's group,[16] strong and sharp excitonic emissions with weak deep-level emission revealed that the synthesized ZnO nanowires were of high optical quality.

In conclusion, low-temperature growth of aligned and ultrathin ZnO nanowire bundles was accomplished by a catalyst-free thermal evaporation method. The ZnO nanowire bundles (typically the diameter is 8 nm) grown on the hexagonal heads of ZnO nanocolumns are well self-organized. This method can also eliminate contamination from the catalyst. The PL measurements at room temperature revealed a significantly blue-shifted near-band-edge emission at 374 nm, which was due to quantum confinement originating from the reduced size of the ultrathin ZnO nanowires. The excellent optical properties indicate that the crystal orientation-ordered ultrathin ZnO nanowire bundles are promising candidates for multichannel optoelectronic devices.

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