Fabrication and microstructure analysis on zinc oxide nanotubes

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**Abstract.** Well crystallized aligned zinc oxide nanoscale tubular structures have been fabricated via vapour phase growth on large area substrates. The ZnO nanotubes have regular polyhedral shapes, hollow cores with diameters of 30–100 nm, lengths over a few tens of micrometres and wall thicknesses of 4–10 nm. In morphology, the nanotubes were either straight or twisted with several straight parts. The microstructure of the tubular material was investigated in detail by using high-resolution transmission electron microscopy (HRTEM), Z-contrast imaging and compositional line profile analysis. The chemical composition of individual tubular structures was found to be stoichiometric ZnO using selected area energy dispersive x-ray spectroscopy and electron energy loss spectroscopy. X-ray diffraction (XRD) and selected area electron diffraction results indicated that the ZnO nanotubes had wurtzite crystal structure. XRD analysis and HRTEM investigations indicated the ZnO nanotubes were grown along the [001] direction. The growth of the tubular ZnO nanostructures was found to be closely related to the hexagonal nature of the ZnO crystal and the peculiar growth conditions used.

Nanoscale tubular structures have stimulated intensive research interests because of their exceptional physical properties [1, 2], i.e. ballistic transport or Luttinger liquid behaviour in the molecular regime [3, 4], and potential applications in constructing nanoscale devices [5, 6]. However, compared to the recent research on nanotubes with lamellar structures (BN [7], BCN [8], WS\textsubscript{2} [9], MoS\textsubscript{2} [10]), the study of direct growth of nanotubular structures from solid-state materials is more demanding, due to difficulties in the preparation techniques. ZnO has been recognized as one of the most promising optoelectronic materials in the ultraviolet (UV)

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region because of its wide bandgap (3.37 eV) and large exciton binding energy (60 meV). Various methods have been developed to synthesize ZnO nanostructures including nanoparticles, nanorods and nanowires, as well as nanobelts \[11\]–\[14\]. However, there are few reports on synthesis of ZnO nanotubes \[15, 16\], and analyses of the microstructure and growth mechanism of the ZnO nanotubes are far from being well understood. In this paper, we will provide comprehensive transmission electron microscope (TEM) experimental evidence for the existence of nanoscale zinc oxide tubular structures from three-dimensional (3D) materials, which would extend the knowledge of nanosized tubular structures from lamellar to 3D materials.

The ZnO crystals used in the study were grown using thermal evaporation of Zn/ZnO powder mixture. Powders of zinc oxide (1.0 g) and zinc (0.3 g) were well mixed and put into the central zone of an alumina tube in a tube furnace evacuated to about 300 Torr and filled with argon. The furnace was heated to about 1300 °C under flowing Ar atmosphere (40 sccm) for 1 h. The products were collected with regularly placed Si substrates (5 mm × 20 mm). A wet oxidation ambient is essential for the growth of the ZnO nanotube with an appropriate amount of water held in a glass vessel upstream of the alumina tube.

The structural and chemical natures of the zinc oxide tubular materials were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM, DB-235 focused ion beam (FIB) system, FEI Company), high-resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDS), and scanning transmission electron microscopy (STEM) as well as electron energy loss spectroscopy (EELS) attached to a transmission electron microscope (TEM, Tecnai F30 with field emission gun (FEG) and accelerating voltage of 300 kV, FEI Company). TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping onto a porous carbon film supported on a copper grid, and then drying in air.

The structure of the products was first characterized using XRD, which proved that the as-grown products were wurtzite crystalline ZnO. In the XRD spectrum shown in figure 1(A), no peaks corresponding to the Si substrate can be observed, indicating formation of a substantive number of nanotubes on the substrate. Figure 1(B) shows a typical SEM image of the sample, and it is visible that large quantities of tubular materials were formed in large areas on the silicon substrates. The diameters of the tubular materials are around 30–100 nm, with a mean value around 60 nm. The lengths can be over a few tens of micrometres. It can also be seen that some of the nanotubes appear straight in morphology, while many of them were usually twisted with several straight parts. In order to analyse the tubular structure clearly, the tubular materials were mechanically ground and plenty of open ends can be clearly observed, as shown in figure 1(C). Detailed SEM analysis revealed that the nanotubes had distinctive hollow cores with well defined polyhedral or cylindrical shapes. Most of the open ends of the nanotubes are found to have typical hexagonal shapes (marked with ‘1’ in figure 1(C)), providing strong evidence of the [001] growth direction (the c-axis) of the hexagonal ZnO nanotubes. The other open ends demonstrate rectangular (marked with ‘2’) and round shapes (marked with ‘3’). In figure 1(D), a zinc nanoparticle is found to exist at the end of the nanotube with brighter contrast (marked with the white arrow), which is indicative of a growth controlled by the vapour–liquid–solid (VLS) mechanism \[17\].

Analytical TEM investigations provide further insight into the nanostructures and the chemical compositions of the nanotubes. Figure 2(A) shows a typical bright field TEM image of the nanotubes, exhibiting tubular structures with uniform wall thickness for most of the nanostructures. The thickness of the sidewalls is measured in the range 4–10 nm. For each
**Figure 1.** Large area aligned nanoscale tubular structures of zinc oxide (with wurtzite crystal structure). (A) XRD pattern recorded from the ZnO nanotubes indicates excellent [001] growth direction. (B) Typical SEM image of the as-synthesized materials revealing a large number of hollow ZnO nanotubes on Si substrate; (C) SEM image of ZnO nanotubes with broken ends. The nanotubes marked with ‘1’ have well defined hexagonal shapes while the nanotubes marked with ‘2’ and ‘3’ reveal rectangular and round shapes. (D) High magnification SEM image of a single ZnO nanotube. The brighter contrast at the tip of the nanotube (marked with a white arrow) reveals the existence of zinc nanoparticles at the ends of the nanotubes, which is indicative of a growth controlled by the VLS mechanism.
nanotube, the wall thickness remains almost constant during high angle tilting along the tube axis, which confirms that the investigated nanostructures are tubular. Selected area electron diffraction (SAED, inset in figure 2(A)) analysis from the nanotubes in figure 1(A) also indicated that the nanotube was wurtzite ZnO (space group \( \text{P}_{6_3} \text{mc} \), \( a = 0.325 \text{ nm} \) and \( c = 0.521 \text{ nm} \)), which was in coincidence with the result of XRD (figure 1(A)). The only difference between the SAED pattern and XRD spectrum is the relative intensities between the diffraction peaks. The (00\(l\)) diffraction peaks (002 and 004) of wurtzite ZnO in the XRD spectrum are much stronger than the standard values for the bulk ZnO, which indicates excellent [001] growth direction for the ZnO nanotubes. However, the aligned growth direction was destroyed in the preparation of TEM samples. The intensities of the circles in the SAED pattern are comparable with the standard values for the bulk ZnO. Both EDS (figure 2(B)) and EELS (figure 2(C)) analysis indicated stoichiometric ZnO formation during vapour phase growth.

As shown in figure 2(A), twisted structures with several straight parts can be observed frequently in TEM. Straight nanotubes can also be observed at times in TEM. Figure 2(C) shows a bright field TEM image of a straight nanotube (or perhaps the straight part of a twisted nanotube), revealing representative hexagonal open end in morphology. In order to observe the nanostructures more visually, STEM images collected by a high angle annular dark field detector (HAADF) attached to a TEM were recorded. It is well known that the STEM image with an HAADF is a Z-contrasted one, that is, the contrast of the STEM image comes from the inelastic forward Rutherford electron scattering by the nucleus of the elements and thereby is proportional to \( Z^2 \), where \( Z \) represents the atomic number of the elements. In contrast to that, in the diffraction contrast bright field TEM images, the sidewalls of the nanotubes in the STEM images demonstrate brighter contrast due to the relatively larger number of atoms than the other parts of the nanotubes, as shown in figure 2(E). The sidewalls with brighter contrast can be easily distinguished from the other parts of the nanotube. Compositional line profiles probed in EDS mode shows well correlated zinc and oxygen signals across the tube walls (figure 2(F)). The spot size and distances between every two adjacent spots are about 1 nm. The scan position is also illustrated in figure 2(E) as the black double-arrow-line.

Figure 3 shows typical HRTEM images of the ZnO tubular structures. In figure 3(A), both the top and bottom walls are visible at the broken end of a single nanotube, as indicated by two white arrows. The nanotube is straight in morphology and the thicknesses of the sidewalls are measured to be about 8 nm. Fast Fourier transformation (FFT) of the digitalized 1024 \( \times \) 1024 HRTEM image analysis reveals that the nanotube is a single crystal and the walls are as solid as the bulk ZnO. FFT analysis also indicated that the HRTEM was taken along the [010] zone axis. A lattice spacing of 0.28 nm for (100) planes of the wurtzite ZnO structure along the nanotube can be readily resolved on HRTEM images of both the tube surfaces (figure 3(B)). Figure 3(C) illustrated a HRTEM image of twisted nanotube. The open tip of the nanotube was parallel to the incident electron beam and the lower part of the nanotube was perpendicular to the incident electron beam. The morphology of the open end was hexagonal, which is consistent with the symmetry of the wurtzite ZnO along [001] direction. Two-dimension lattice spacings of 0.52 nm for (001) planes and 0.28 nm for (100) planes of the ZnO structure can be readily resolved on the magnified HRTEM image of the tube wall (figure 3(D)). Inset in figure 3(D) was an FFT diagram of the nanotube in figure 3(C), which is similar to that in figure 3(A), confirming the aligned growth direction (c-axis).

As to the formation mechanism of the zinc oxide nanotubes, the nuclei at proper nucleation sites and unidirectional growth of the nuclei are key factors responsible for it. In general,
Figure 2. Analytical TEM investigations on the ZnO nanotubes. (A) Typical bright field TEM image of the nanotubes exhibiting tubular structures with uniform wall thickness. The inset is the SAED pattern of the ZnO nanotubes showing diffraction circles corresponding to 100, 002, 101, 102, 003 and 110 planes of the wurtzite ZnO. (B), (C) EDS and EELS spectra from the same single nanotube reveal stoichiometric ZnO. (D) High magnification TEM image of a straight part of a single ZnO nanotube with one open end. (E) STEM image of a single ZnO nanotube. (F) The compositional line profiles probed by EDX along the black double-arrow line in (E), showing well correlated zinc and oxygen signals across the tube walls.
ZnO nanostructures tend to form hexagon-faceted nanowires along the c-axis. The observed hexagonal end of the nanotubes is thus a macroscopic reflection of its hexagonal nanostructure. Distinguished from other ZnO nanowire growth conditions, a wet-oxidation atmosphere and the mixing of metallic zinc with zinc oxide were introduced during the formation process of the ZnO nanotubes. As demonstrated in figure 1(D), the metallic zinc-rich alloy plays a crucial role in the nucleus formation of the ZnO nanotubes, similar to the catalyst effect in the growth of carbon nanotubes. During heating of the source materials, zinc with relatively lower melting point will initially wet the substrate to form nanoscale liquid nuclei at proper nucleation. The zinc oxide will be continuously absorbed into those nanoscale liquid zinc droplets, and become supersaturated. Then the ZnO nanotubes start to grow out of the supersaturated droplets. Compared with that for synthesis of ZnO nanowires/nanobelts [12, 13], the wet-oxidation ambient used here played a very important role in the formation of tubular nanostructures.

In summary, well crystallized aligned nanoscale zinc oxide tubular structures have been synthesized. This opens a new and quick way to produce non-lamellar semiconductor compound nanotubes. The novelty and the unique features of the ZnO nanotubes will have wide applications in optics and optoelectronics as well as in biology.

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References

[1] Iijima S 1991 *Nature* **354** 56
[2] Lieber C and Yang P 2002 *Nature* **319** 553
[3] Yao Z, Postma H W Ch, Balents L and Dekker C 1999 *Nature* **402** 273
[4] Cheung C L, Hafner J H and Lieber C M 2000 *Proc. Natl Acad. Sci.* **97** 3809
[5] Kim P and Lieber C M 1999 *Science* **286** 2148
[6] Bachtold A, Hadley P, Nakanishi T and Dekker C 2001 *Science* **294** 1317
[7] Nath M and Rao C N R 2001 *J. Am. Chem. Soc.* **123** 4841–2
[8] Weng-Sieh Z, Cherrey K, Chopra N G and Blase X 1995 *Phys. Rev. B* **51** 11229
[9] Tenne R, Margulis L and Genut M 1992 *Nature* **360** 444
[10] Margulis L, Salitra G, Tenne R and Talianker M 1993 *Nature* **365** 113
[11] Kong Y C *et al* 2001 *Appl. Phys. Lett.* **78** 407
[12] Pan Z W, Dai Z R and Wang Z L 2001 *Science* **291** 1947
[13] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897
[14] Guo L, Ji Y L, Xu H B, Simon P and Wu Z Y 2002 *J. Am. Chem. Soc.* **124** 14864
[15] Zhang J, Sun L D, Liao C S and Yan C H 2002 *Chem. Commun.* **3** 262
[16] Wu J J, Liu S C, Wu C T, Chen K H and Chen L C 2002 *Appl. Phys. Lett.* **81** 1312
[17] Wagner R S and Ellis W C 1964 *Appl. Phys. Lett.* **4** 8