Large-quantity free-standing ZnO nanowires

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(Received 15 May 2003; accepted 11 July 2003)

Large-quantity (grams) one-dimensional ZnO nanowires of different sizes have been synthesized by a simple thermal evaporation of ZnO powder in a tube furnace at a temperature controlled to 1000–1200 °C and pressure to 1–2 Torr air. A mixture of ZnO and graphite powder was used as the source. Fine graphite flakes were used to promote the growth. The graphite flakes are the key for large-quantity yield and were easily removed by oxidation in flowing O2 at about 700 °C for 1–3 h. The scanning- and transmission-electron-microscopic studies show that the diameter and length of the nanowires vary from 20 to 100 nm and 0.5 to 10 μm, respectively. Room temperature photoluminescence studies found that the luminescent intensity depends on the processing conditions. A reduced band edge ultraviolet (380 nm) and deep-band green (520 nm) emission have been observed for these nanowires. Most importantly, the method can be extended to any other oxide nanowires that will be the building block of future nanoscale devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609036]

Recently one-dimensional (1D) nanowires have received extensive attention because of their potential applications in various fields. They can not only play a crucial role in improving future optoelectronic devices,1,2 data-storage,3,4 biochemical and chemical sensors,5 but also can be used to enrich our understanding of basic quantum mechanics.6,7 Zinc oxide (ZnO), a semiconductor with wide direct band gap (3.36 eV) and large exciton binding energy (60 meV), becomes a natural candidate for studies in modern nanoelectronics2 and photonics.8,9 Zinc oxide (ZnO), a semiconductor with wide direct band gap (3.36 eV) and large exciton binding energy (60 meV), becomes a natural candidate for studies in modern nanoelectronics and photonics.8,9

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ZnO nanowires and nanorods were synthesized by thermally vaporizing a mixed source of commercial ZnO powder (Alfa-Aesar, particle diameter ~10 μm) and graphite powder (Alfa-Aesar, particle diameter 5–10 μm) with an atomic ratio of 1:4 in a horizontal tube furnace. The source material was located in the higher temperature region (1000–1200 °C) of a quartz boat covered by another similar boat. In the same boat, graphite flakes (Pennsylvania Microscics, size 5–10 μm2) were spread uniformly in the lower temperature region (700–850 °C) to collect the ZnO nanowires. The sharp temperature gradient (from 1000–1200 down to 700–850 °C over a distance of 6–7 cm) had been chosen deliberately to ensure high quality and better yield of ZnO nanowires. During growth, the source was maintained at a pressure of 1–2 Torr air. After 30–45 min growth, the original black graphite flakes turned into a gray color indicating the deposition of a significant amount of ZnO. Under SEM examination, large quantity 1D hexagonal ZnO nanowires (5–10 μm in length and 20–50 nm in diameter) and nanorods (0.5–5 μm in length and 60–100 nm in diameter) are observed. A weight increase of hundreds of milligrams versus the original graphite flakes has been achieved, which converts into as high as 200% of the original graphite flakes, and 35% of the ZnO powder in the source in each experimental run.

The as-made samples were studied by SEM. SEM sample specimens were collected from different regions that have different condensation temperatures. The SEM images of the as-made ZnO nanowires and nanorods containing the graphite flakes are shown in Fig. 1. Mainly three kinds of morphologies have been observed. In the high temperature zone (800–850 °C), close to the source material, long (5–10 μm) and thin (20–50 nm) nanowires were grown as shown in Figs. 1(a), 1(b), and 1(c) in different magnifications, respectively. In the medium temperature region (700–800 °C), short and large diameter nanorods of 0.5–5 μm in length and 60–100 nm in diameter are abundant as shown in Figs. 1(d), 1(e), and 1(f) in different magnifications, respectively. Generally, these nanorods have prominent hexagonal structure with a blunt head, whereas the nanowires have a sharp tip with a smooth round surface. At the low temperature region
furnace with O$_2$ gas flowing through it at different tempera-

with unit cell constants of $a \approx \frac{5.206}{\text{Å}}$ and $c \approx \frac{3.248}{\text{Å}}$, respectively, whereas (d), (e), and (f) show nanorods of length 0.5–5 μm and diameter 60–100 nm in different magnifications, respectively.

(600–700 °C), far away from the source, only nanoparticles were observed (SEM images are not shown here).

In order to remove the graphite flakes in the as-made ZnO nanowires, the samples were oxidized for 2 h in a tube furnace with O$_2$ gas flowing through it at different temperatures. After oxidation, the as-made gray powder turned white, which indicates that the graphite flakes are removed (clearly indicated by the x-ray spectra discussed in the next paragraph) from the ZnO nanowires. Figures 2(a), 2(b), and 2(c) show the typical morphology of the nanorods after oxidation in different magnifications. It is worth noting that the images are not as clear as those shown in Fig. 1 due to the charging during SEM image recording, which resulted from the poor electrical conductivity due to the extra oxygen incorporated during the removal of graphite flakes. In addition to the electrical conductivity change, the morphology of the nanowires has also changed: most of the nanowires and nanorods become very sharp at the tip with a diameter of 2–4 nm after oxidation. Fortunately, the conductivity can be restored by further annealing at 500 °C in vacuum. The most convincing evidence of the removal of graphite is the observation of voids mimicking the shape of the graphite flakes, as indicated by arrows in Figs. 2(a) and 2(b).

The crystallinity of the ZnO nanowires, the existence of graphite flakes in the as-made sample and the removal of graphite flakes by oxidation were studied by x-ray diffraction. The spectra are shown in Fig. 3. Clearly, the ZnO nanowires are highly crystallized. In the as-made samples, a very strong graphite peak (002) at $2\theta = 26.6^\circ$ is observed indicating the existence of a significant amount of graphite. With oxidation at 600 °C for 2 h, the graphite peak intensity was reduced substantially. The graphite peaks are completely disappeared for the samples annealed at 700 °C. From these spectra, it is found that both as-made and oxidized samples show a typical wurtzite hexagonal structure like bulk ZnO with unit cell constants of $a = 3.248$ Å and $c = 5.206$ Å.

The typical TEM images of the microstructure of ZnO nanowires are shown in Fig. 4. Figure 4(a) is a general morphology of the nanowires. The diameter of these nanowires varies from a few nanometers to 100 nm, and the length is generally a few micrometers. The nanowires with larger diameter are straight, and their tips can be sharp or blunt, while those with smaller diameter are generally bent and end up with very sharp tips (shown in the inset). The diameter of all the nanowires is gradually reduced from the root to the tip. A ripple-like contrast in the TEM image is caused by strain resulting from the bending of the nanowires. A high-resolution TEM (HRTEM) image in Fig. 4(b) indicates that the growth direction is along [0001], and the surface is enclosed mainly by {1100} facets and possibly by other high index lattice planes parallel to the c axis. The tip is usually not sharp at the atomic scale. For example, the tip shown in the HRTEM image ends up on a (0002) plane with a diameter of about 4 nm. The surface of these nanowires is clean and free from amorphous shells as shown in Fig. 4(e). This is in contrast to similar samples before oxidation, in which the surface is always wrapped by amorphous carbon or turbostratic graphite, as shown in Fig. 4(d). The structure of these nanowires is perfect, free from any kind of defects, such as dislocations, stacking faults, etc. An electron diffraction pattern from a nanowire is shown in Fig. 4(c), which exhibits hexagonal structure. The appearance of the extinction diffraction spots such as (0 0 0 2n + 1) (n is an integer) is due to a double diffraction effect. For example, the (0001) diffraction spots between (0002) and the central spot are re-

FIG. 1. SEM images showing morphologies of the large quantity ZnO nanostructure grown on fine graphite flakes. (a), (b), and (c) show nanowires of length 5–10 μm and diameter 20–50 nm in different magnifications, respectively, whereas (d), (e), and (f) show nanorods of length 0.5–5 μm and diameter 60–100 nm in different magnifications, respectively.

FIG. 2. SEM images showing morphology of ZnO nanostructures after oxidation. (a) and (b) show the voids left by flakes (indicated by the arrows) and (c) shows the sharpened tips of the nanorods after oxidation.
results of the double diffraction of (10\,\bar{1}0) and (\bar{1}011). The streaks along the (10\,\bar{1}0) diffraction spot series are caused by the shape effect of the nanowires.

The different surface structures between the as-made [Fig. 4(d)] and oxidized samples [Fig. 4(e)] provide a key clue to understand the different photoluminescence properties of these samples. These ZnO nanowires have a weak UV PL peak at 380 nm and a strong green band peak at 520 nm depending upon the processing conditions. It has already been shown\textsuperscript{14} that the deep-band green light emission is due to the radiative recombination of the photogenerated holes with electrons belonging to the oxygen vacancy of the surface. Obviously, the greater the oxygen vacancy on the surface, the stronger the green band peak should be (Fig. 5). That is why samples annealed in vacuum showed a stronger green band peak. Although our x-ray diffraction (XRD) and TEM data showed the disappearance of graphite in the sample, we believe there is still a trace amount of graphite left at the roots which caused the kink around 360 nm in the photoluminescence spectra indicated by arrows.

High surface area of the graphite flakes is the key to the large quantity growth of ZnO nanowires, although the hexagonal structure of graphite also played a role since both the graphite foils and other nano powders such as Al\textsubscript{2}O\textsubscript{3} did not yield similar quantities. It is important to point out that the graphite flakes can certainly be extended to grow many other nanowires in large-quantity such as In\textsubscript{2}O\textsubscript{3}, Ga\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2}, Cdo, etc., which will be the building blocks of the future nanoscale devices.

In summary, large quantity (grams) 1D hexagonal ZnO nanowires have been synthesized via thermal evaporation of commercial ZnO powder. Fine graphite flakes in the collection zone were the key to yield the large quantity due to their high surface area. After growth, the graphite flakes were easily removed through oxidation at 700 °C for about 2 h. The SEM and TEM analysis showed that the average length and diameter of the nanowires are 5–10 \,\mu m and 20–50 \,\textmu m, respectively, and 0.5–5 \,\mu m and 60–100 \,\textmu m for nanorods. These nanowires showed a weak UV band (380 nm) and green band (520 nm) PL. These graphite flakes certainly will lead to the possibility of growing other nanowires in large quantities.

The authors would like to thank Dr. Jean Herbert at Natick Soldier Systems Center for her idea-stimulating discussions. The work performed by one of the authors (J.Y.L.) is supported by the US Army Natick Soldier Systems Center under Grants No. DAAD16-02-C-0037 and DAAD16-00-C-9227. The work done by another author (Z.F.R.) is supported by DOE under Grant No. DE-FGO2-00ER45805 and by NSF under Grant No. CMS-0219836.