Synthesis of Uniform Hexagonal Prismatic ZnO Whiskers

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Large-quantity growth of hexagonal prismatic ZnO whiskers was achieved via a process of first reduction and following oxidation of a ZnS powder at 1300 °C. The products were characterized using X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, and photoluminescence spectroscopy. The as-grown whiskers appear to be structurally uniform with an individual width of around 350 nm and length of up to 15 μm, and they are single crystalline in nature. All of them have hexagonal cross sections and grow along the [001] crystallographic direction. Room-temperature photoluminescence spectra of the whiskers reveal a strong and sharp UV emission band at 388 nm and a weak and broad green emission band at 515 nm. Possible growth mechanisms of the ZnO whiskers were discussed.

1. Introduction

Wide and direct band-gap semiconductors are of great interest in optical industries including blue and ultraviolet (UV) optical devices, such as light-emitting diodes and laser diodes.[1] Zinc oxide (ZnO), a II−VI compound semiconductor with a wide and direct band gap of 3.3 eV,[2] is a potential candidate for such applications. In fact, it has already been widely used in transparent conductive films, varistors, solar cell windows, and bulk acoustic wave devices.[3−6] Along with the development of nanotechnology, one-dimensional or quasi- one-dimensional ZnO may find wider applications. Because of its high-temperature strength and rigidity and excellent chemical stability, small-diameter ZnO whiskers have received great attention for industrial applications as reinforced composite materials.[7−9] Because the luminescence of ZnO is very sensitive to its surface state,[10] ZnO whiskers with a high surface-to-bulk ratio are expected to have novel practical applications in electrooptical devices and chemical sensors. Recently, ZnO crystal whiskers with a high aspect ratio have been successfully used as a probing tip to develop new precise high-resolution imaging techniques for atomic force microscopy and scanning tunneling microscopy.[11−14]

The conventional growth process of ZnO whiskers involves vapor-phase oxidation of metallic Zn powders. Examples include ZnO whiskers grown by gas-flow-ascension zinc vapor oxidation at 950−1400 °C by introducing O_2,[15] oxidizing fine Zn particles coated with a ZnO layer mixed with zeolite as a reaction catalyst,[12] and heating the Zn source and lead oxide in the presence of reducing agent carbon in air.[16] Recently, a hydrothemal method,[17] chemical vapor deposition,[7] and a shock wave technique[18] have also been applied to grow ZnO crystalline whiskers. The ZnO whiskers obtained by these routes tend to exhibit regular crystallographic morphologies as the bulk materials do, such as tetrapod forms,[12,19−22] hollow structures,[23] and polyhedral crystals.[18] In this paper, we demonstrated that structurally

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uniform hexagonal prismatic ZnO whiskers grew in a large scale via a process of first reduction and following oxidation of a ZnS powder at 1300 °C. The optical property of the as-grown whisker was investigated, and possible whisker growth mechanisms were discussed.

2. Experimental Procedure

A horizontal alumina tube (outer diameter 42 mm; length 80 cm) was mounted inside a high-temperature tube furnace. A total of 3 g of analytical-grade ZnS powder (Goodfellow; 99.99%, <10 μm) was placed on an alumina wafer (40 × 25 × 1 mm), which was loaded to the center of the tube. The tube was then sealed and evacuated by a mechanical rotary pump to a pressure of 4×10^{-2} Torr. The furnace was heated at a rate of 10 °C/min to 800 °C and maintained at this temperature for 30 min, followed by further heating to and maintenance at 1300 °C for 10 h. Except for the last 4 h of the heating period, the whole process was carried out with a constant flow of Ar mixed with 5% H_2 at a rate of 50 sccm. In the last 4 h, the Ar/H_2 was switched to O_2 at the same flow rate. During the whole heating period, the pump continually evacuated the system, and the pressure inside the tube was kept at 300 Torr. After the furnace was cooled to room temperature, a white wool-like product deposited on the inner wall of the tube was collected for characterization and measurement. The yield was calculated based on the amount of the ZnS powder used.

The morphology and phase identification of the product were characterized using scanning electron microscopy (SEM; Philips XL 30 FEG) and powder X-ray diffraction (XRD; Siemens D-500 with Cu Kα radiation and a normal $\theta - 2\theta$ scan), respectively. Further structural analysis of individual ZnO whiskers was carried using transmission electron microscopy (TEM) and selected area electron diffraction (SAED). (Philips CM20 and CM200 FEG microscopes operating at 200 kV were used for the TEM study.) Two different types of samples were prepared for the TEM characterization: one is the regular whisker sample prepared by conventional dispersing followed by carbon film fishing, so that the whiskers were held by the carbon films for transfer to the microscope; the other is a cross-sectional sample. Details of the sample preparation can be find elsewhere.[20] Room-temperature photoluminescence (PL) spectra were recorded by an image-intensified detector ICCD combined with a spectrometer (SpectraPro 500i; Acton Research Corp.), using a pulsed Nd:YAG laser (355 nm) as an excitation source with energy in the range of millijoules.

3. Results and Discussion

The yield of the ZnO whiskers was calculated to be ~40%. A powder XRD pattern of the products is shown in Figure 1. All of the diffraction peaks can be indexed as those from the known Wurtzite-structured (hexagonal) ZnO with lattice constants $a = 3.250$ Å and $c = 5.207$ Å, within experimental error (Joint Committee on Powder Diffraction Standards, Powder Diffraction File No. 36-1451; $a = 3.249\ 82$ Å and $c = 5.206\ 61$ Å). No characteristic peaks from impurities, such as ZnS and Zn, are detected.

The general morphologies and structures of the ZnO samples are shown in Figure 2. As can be seen from a low-magnification SEM image, the sample consists of a large quantity of straight and smooth solid whiskers with fairly uniform width and length. No particle is observed. Analysis of a number of the whiskers shows that each whisker has a diameter of around 350 nm and a length of up to 15 μm (the aspect ratio is about 45). A high-magnification SEM image (inset) suggests that the whisker has a hexagonal cross section and well-defined crystallographic facets. The as-grown whiskers appear to have regular hexagonal prismatic structures.

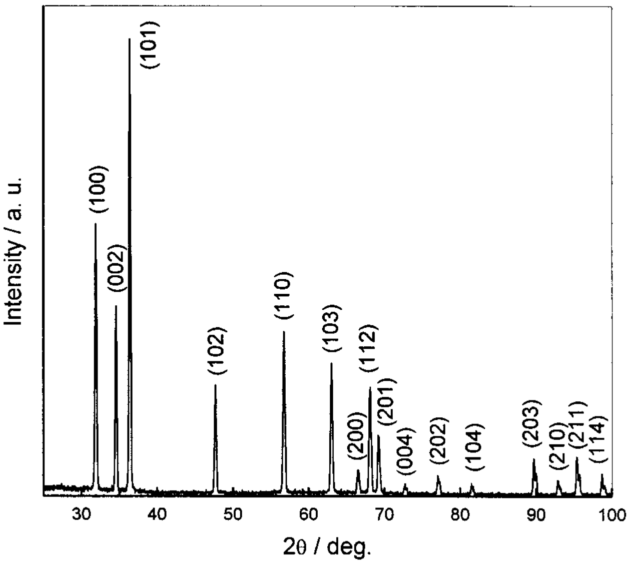

Figure 1. XRD pattern recorded from the product synthesized by the present method.

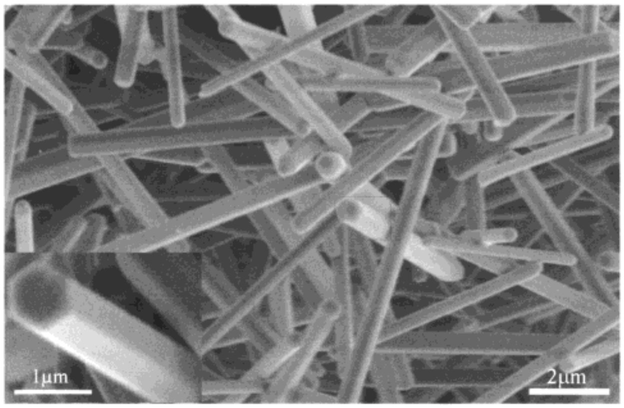

Figure 2. SEM image of the as-synthesized ZnO whiskers, with the inset showing a hexagonal cross section of one whisker.

TEM images including low-magnification images, high-resolution images, and SAED patterns of individual ZnO whiskers further confirm the structure of these materials, as suggested by both XRD and SEM. Figure 3a shows a low-magnification image of an individual ZnO whisker. It reveals that the whisker has a hemispherical-like end (the commonly observed whiskers have one flat platform-like end, as shown in Figure 5a). The inset SAED pattern was taken from the ZnO whisker shown in Figure 3a with an electron beam along its [100] zone axis. Diffraction patterns taken from different parts of the whisker show exactly the same pattern without further tilting the whisker, which indicates the single crystallinity of the whole whisker. Several tens of individual whiskers have been examined using this method, and the out-of-focus diffraction patterns suggest that all of them grow along the [001] direction. The high-resolution TEM (HRTEM) image (Figure 3b) taken from the ZnO whisker shown in Figure 3a further confirms that the whisker grows along the [001] direction (indicated with an arrow). No dislocations or stacking faults are observed in all areas examined. However, it does not indicate that there are no other types of defects in the synthesized ZnO

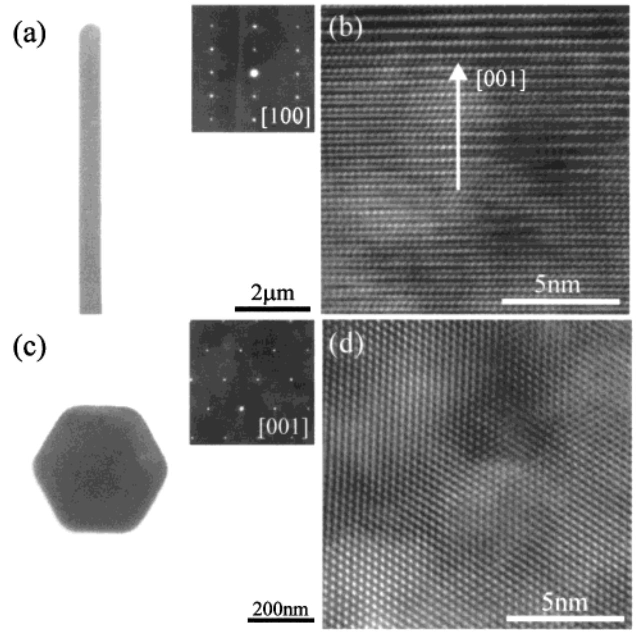

Figure 3. (a) TEM image of an individual ZnO whisker and its corresponding SAED pattern (inset). (b) HRTEM image of one whisker, with the arrow showing the growth direction of [001]. (c) Cross-sectional TEM image of a ZnO whisker and its corresponding SAED pattern (inset). (d) HRTEM image of one hexagonal cross section.

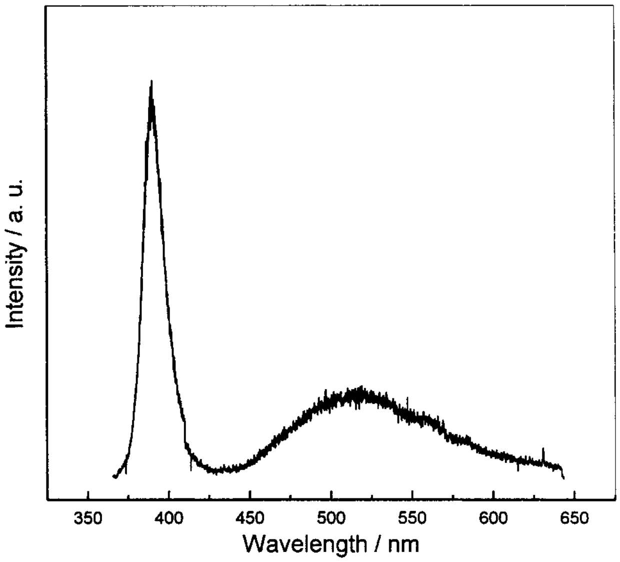

Figure 4. Room-temperature PL spectrum of the ZnO whiskers.

whiskers. Defects such as vacancy or interstitial may not be visible in the HRTEM observation.

Figure 3c is taken from a cross-sectional TEM sample. It is clear from the image that the whisker has a regular hexagonal cross section. Typical widths and angles of the hexagon are about 180 nm and 120°, respectively. This is consistent with the SEM observations. The corresponding SEAD pattern (inset) is indexed as the [001] zone axis diffraction pattern of ZnO. The corresponding HRTEM image (Figure 3d) shows two-dimensional lattice fringes of the (001) plane with Wurtzite structure.

Figure 4 shows the room-temperature PL spectrum of the as-synthesized ZnO whiskers. It is clear from the figure that the spectrum consists of a sharp and strong emission band located at 388 nm and a weak and broad emission band centered at 515 nm. The near-UV emission at 388 nm agrees with the band gap of bulk ZnO (around 380 nm),[24−26] which comes from the recombination of free excitons.[10] The green emission at 515 nm is related to the singly ionized oxygen vacancy, and this emission results from the recombination of a photogenerated hole with a singly ionized charge state of the specific defect.[27,28]

The formation process of the ZnO whiskers could be divided into two stages from a chemical reaction point of view. In the first stage, the starting material ZnS was reduced by H_2 (from the flow of Ar mixed with 5% H_2) to metallic zinc at a suitable temperature. In the second stage, oxygen gas was introduced into the tube, and the newly reduced Zn was oxidized to ZnO. Although the chemical reaction was rather simple, the formation of the ZnO whisker would involve a very complicated process. Because of the fact that the whiskers can only be formed above a certain process temperature (1200 °C) and only in a place away from the center of the tube furnace (lower temperature range), we can reasonably speculate the whisker formation process as follows: The metallic zinc is in its vapor state when reduced from ZnS by H_2 because of the high process temperature (Zn: bp of 911 °C).[29] The vaporized zinc is then carried by the processing gases and travels to lower temperature regions in the furnace tube, where it deposits in the form of a liquid droplet (Zn: mp of 419.6 °C)[29] on the inner wall of the tube. The liquidized zinc then reacts with O_2 when O_2 is introduced and forms ZnO, which further serves as some seeds for ZnO whisker growth. The above growth is most likely to be controlled by the vapor−liquid−solid (VLS) mechanisms.[30] In the present VLS growth of the ZnO whiskers, no additional transition metals are added as catalysts; it is, therefore, believed that the formation of the ZnO whiskers undergoes a self-catalyzed VLS growth process. The reduced Zn not only acts as the reactant but also provides an energetically favored site for the absorption of O_2. The newly formed ZnO functions as a whisker seed, which further grows to a ZnO whisker in the presence of Zn vapor and oxygen gas. The size and hence the uniformity of the ZnO whiskers are predecided by the size of the liquid Zn droplets.

One unique aspect of the current study was that the ZnO whiskers prepared using the above method were single crystalline with a single growth direction. The uniform hexagonal prismatic growth morphology can be simply explained by the "lowest energy" argument; i.e., the hexagonal (0001) plane of ZnO with Wurtzite structure is the closest packed plane in the crystal, and stacking along the [0001] direction therefore becomes energetically favorable. Several crystalline facets are

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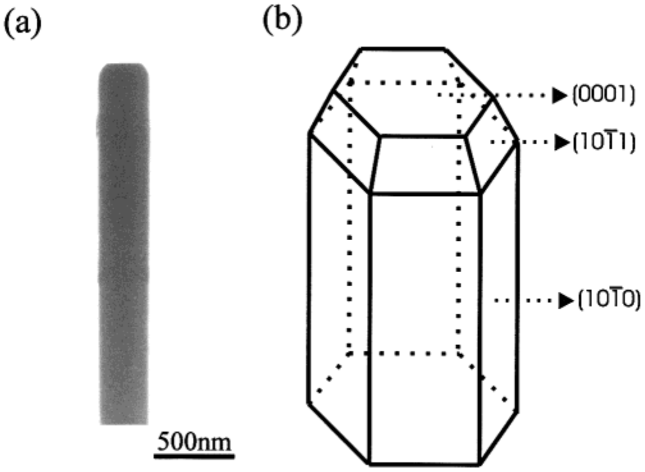

Figure 5. TEM image (a) and the growth habit schematic (b) of the commonly observed ZnO whiskers prepared using the described method.

observed for the as-grown whiskers, i.e., (0001) and (1000). In the past decade, many researchers have studied the growth mechanism of prismatic crystals and several models have been proposed.[17,31,32] Laudise et al. claimed that the growth of crystals is related to the relative growth rate of different crystal facets and the difference in the growth rates of various crystal facets results in a different outlook of the crystallite. In the model of idealized ZnO crystal growth, the growth rate along the [0001] direction is about twice as fast as that along the [1,0,−1,0] direction, whereas the growth rate in the [1,0,−1,1] direction seems to be intermediate between those along the [0001] and [1,0,−1,0] directions. Figure 5 shows the TEM image (Figure 5a) and the growth habit schematic (Figure 5b) of the commonly observed ZnO whiskers prepared using the above-described method. The (0001) and (1000) planes are the most likely remaining facet after the growth, and the (0,1,−1,−1) plane easily disappears, which is consistent with Laudise's argument. Although no dislocations or stacking faults are observed for the whiskers examined, some defects are expected to exist in the as-grown whiskers. As indicated by the PL spectrum of the ZnO whisker, the green emission at 515 nm may result from the recombination of a photogenerated hole with a singly ionized charge state of the specific defect such as oxygen vacancies.[27,28]

4. Conclusion

Large quantities of hexagonal prismatic ZnO whiskers can be grown via a process of first reduction and following oxidation of the ZnS powder. The as-grown whiskers are single crystalline and structurally uniform. All of the whiskers examined grow along the [001] crystallographic direction. Each whisker has a regular hexagonal cross section with widths of around 180 nm, angles of 120°, and length of up to 15 μm, respectively. A room-temperature PL spectrum pattern of the whiskers consists of a strong and sharp UV emission band at 388 nm and a weak and broad green emission band at 515 nm. The growth of the whiskers is suggested to follow a self-catalyzed VLS mechanism, and the unique growth direction is explained by the favorable energy along a specific growth direction. The hexagonal prismatic morphology and the facet outlook of the whiskers are believed to be caused by the different growth rates of the crystalline faces. Using the present method, the uniform structured ZnO whiskers could heighten their use in reinforced composite materials and the strong PL may suggest possible applications in optoelectronic devices. When suitable synthetic parameters, such as reaction temperature and time, are chosen, it is reasonable to expect that the method can be extended to obtain other semiconducting metal oxide whiskers.

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