Synthesis of Nano/Micro Zinc Oxide Rods and Arrays by Thermal Evaporation Approach on Cylindrical Shape Substrate

Yousheng Zhang, Lisheng Wang, Xiaohua Liu, Yunjie Yan, Changqiang Chen, and Jing Zhu*

Electron Microscopy Laboratory, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received: February 18, 2005; In Final Form: May 13, 2005

Nano and micro ZnO rods and arrays have been synthesized by a simple thermal evaporation approach on a cylindrical shape substrate. Most of the synthesized ZnO products are single crystalline with a hexagonal structure and grow along the [0001] direction. Individual protrusive ZnO rods and well-aligned arrays are two typical products in our work. The individual protrusive ZnO rods have diameters of 25 nm ∼ 2.1 μm and lengths from several hundred nanometers to 40 μm, while in the well-aligned arrays, the diameter and length of each ZnO rod range from 60 nm to 1.2 μm and from 4 μm to 6 μm, respectively. The heating temperature and deposition position are two key points to control the diameters of the rods. The growth mechanism is discussed and proposed. The perfect crystalline ZnO rods with different scales from nanometer to micrometer are good models for the investigation of the size effect of physical and chemical properties of one-dimensional material.

Introduction

It is a challenge to overcome difficulties in fabricating a low-dimensional material with wider scale from nanometer to micrometer under a single process. Since the new century, the study of one-dimensional nanostructural ZnO has attracted much interest owing to its low cost; its unique electrical, optoelectronic, and luminescent properties; and its many potential applications in devices, such as solar cells, luminescent devices, and chemical and biological detectors.[1−4] Different methods have been reported for fabricating ZnO nanostructures. Among them, the thermal evaporation approach is the most commonly used. In the thermal evaporation approach, ZnO nanorods have been synthesized by using Zn or ZnO powders as source materials and Au,[4,5] NiO,[6] Fe_2O_3,[7] Co,[8] Cu,[9] and Sn[10] as catalysts, which may introduce impurities into the final products. ZnO nanorod arrays have been synthesized by using sapphire[4] and any surface promoted by an aluminum precoat[11] as substrate or porous aluminum oxide[12] as template, which have many complex preprocess. Recently, well-aligned ZnO nanowire arrays have been synthesized with the assistance of undoped ZnO thin film.[13,14] In another aspect, ZnO microrod arrays have been synthesized on polycrystalline, single-crystalline, or amorphous substrates[15] from an aqueous solution of zinc salt at low temperature or on ZnO thin films which were deposited by pulsed laser ablation using a hydrothermal method.[16]

Here, we report a simple thermal evaporation approach to synthesize nano/microsized ZnO rods and arrays on a cylindrical shape substrate by heating Zn powders directly without any catalyst. The method makes it become reality to synthesize wider scale ZnO rod from nanometer to micrometer in a single process. The fabrication process, the morphology of the ZnO rods and arrays, and the growth mechanism are introduced.

Fabrication of Nano/Micro ZnO Rods and Arrays. Zinc powders (∼74 μm in diameter and 99.99% in purity) were used as the source material. A quartz tube is lying in a horizontal tube furnace without a vacuum system (Figure 1).[17] 0.2∼1 g zinc powders was spread in an alumina boat and the boat was placed at the center of the quartz tube. A unilateral flow of Ar gas was used as the carrier gas. The Ar flow can be 150∼250 sccm (standard cubic centimeter mass). A cylindrical shape substrate, such as iron, aluminum, tungsten, or nickel wire, was located upstream or downstream of the source along the quartz tube. It was used to receive the products. The exact positions of the desired products are determined by the flow of the Ar gas. In a typical procedure, the cylindrical shape substrate was cleaned in an aqueous 1.0 M HCl solution for ∼20 s, followed by repeated rinsing with distilled water. The wire was about 7∼15 cm long and 0.14 mm in diameter. In this paper, iron wire was taken as an example of the cylindrical shape substrate. The temperature at the tube center increased at a constant rate of 25 °C/min from room temperature to heating temperature (650∼850 °C) and then was preserved for 60∼120 min. During this period, zinc powders were heated, vaporized, oxidized, and deposited on the cylindrical shape substrate to form the final products.

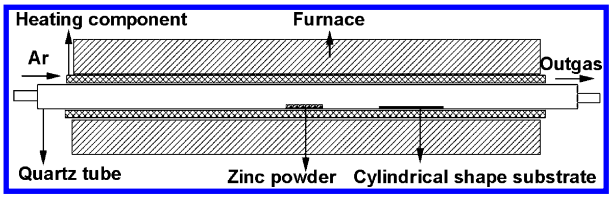

Figure 1. Experimental scheme.

Product Characterization. The synthesized products were characterized using field emission scanning electron microscopy (JSM-6301F) and transmission electron microscopy (JEM-2010F).

Figure 2 shows the SEM images of ZnO rods and arrays synthesized on iron wire substrate. Figure 2a shows a large area of individual protrusive ZnO rods with varied diameters and lengths. The upper left and right insets of Figure 2a are images

* To whom correspondence should be addressed. E-mail: jzhu@mail.tsinghua.edu.cn.

10.1021/jp050851z CCC: $30.25
Published on Web 06/16/2005

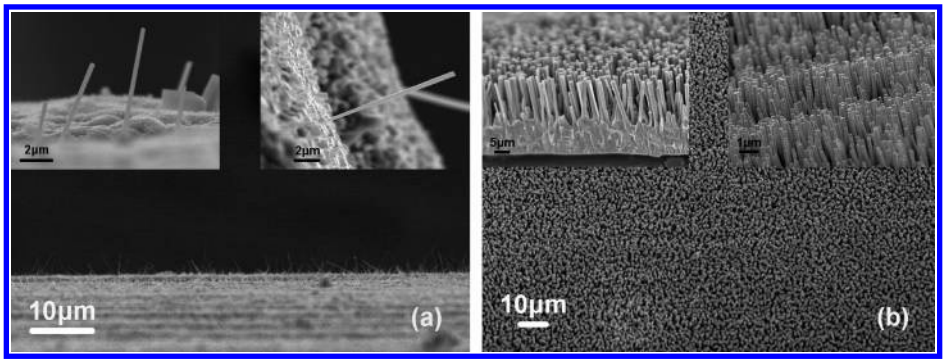

Figure 2. SEM image of the as-synthesized individual ZnO rods and arrays obtained from Zn powder thermal evaporation deposition on iron wire substrate: (a) individual protrusive ZnO nanorods, the upper left and right insets are images with large magnification at some places of the iron wire, showing areas of several individual ZnO nanorods with different lengths and one uniform rod of 400 nm in diameter with 11 μm in length, respectively. (b) Large area of well-aligned ZnO rod arrays, the upper left and right insets show areas of microsized and nanosized rod arrays, respectively.

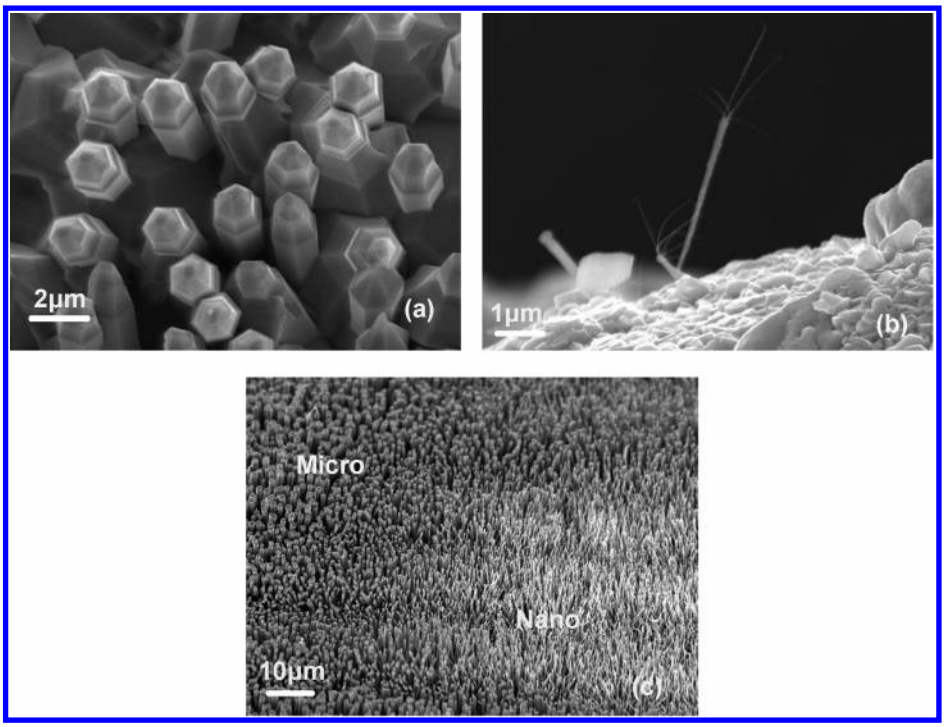

Figure 3. a and b are results of changing the heating temperature: (a) a top view of the nanorods whose diameters decrease along the growth up direction while changing the heating temperature from 650 °C (hold on about 60 min) to 710 °C (hold on about 20 min), (b) several thin ZnO nanorods grow on a thick rod as the heating temperature changes from 675 °C (hold on about 60 min) to 800 °C (hold on about 30 min), and (c) a mixture area of nano/micro ZnO rod arrays.

with large magnification at some places of the substrate, showing areas of several individual ZnO nanorods with different lengths and one uniform rod of 400 nm in diameter and 11 μm in length, respectively. Figure 2b is a top view of a large area of well-aligned ZnO nanorod arrays. Such arrays can extend about 3∼5 mm along the substrate. The upper left and right insets of Figure 2b show areas of microsized and nanosized rod arrays, respectively. Well-aligned ZnO rods can be acquired at the place about 6 cm downstream or 7 cm upstream of the source while the Ar flow is 180 sccm and the heating temperature is 675 °C. The individual protrusive ZnO rods have diameters of 25 nm ∼ 2.1 μm and lengths from several hundred nanometers to 40 μm. The lengths of the ZnO rods are in the several hundreds of nanometers to 40 μm ranges. In the well-aligned arrays, the diameters and the lengths of the ZnO rods range from 60 nm to 1.2 μm and from 4 μm to 10 μm, respectively.

The temperature dependence on the fabrication is studied. Figure 3a and 3b is the results of changing the heating temperature. Figure 3a is a top view of the nanorods whose diameters decrease along the growth direction while changing the heating temperature from 650 °C (hold on about 60 min) to 710 °C (hold on about 20 min) during the synthesis process. It can be seen in Figure 3a that ZnO structures have hexagonal cross sections, which was a typical section of the [0001] direction of a ZnO rod. Figure 3b shows several thin ZnO nanorods growing on a thick ZnO rod, which served as a substrate for the former, while the heating temperature changed from 675 °C (hold on about 60 min) to 800 °C (hold on about 30 min) during the synthesis process. The tails of the thin ZnO nanorods were blurred because of thermal vibration. It implies that the heating temperature is an important factor to control the diameters of the rods.

Besides the heating temperature, the deposition position along with the surface of the substrate can also affect the diameters of the ZnO rods and arrays. Figure 3c is a special area where the diameters of ZnO rod arrays decrease from micrometer to

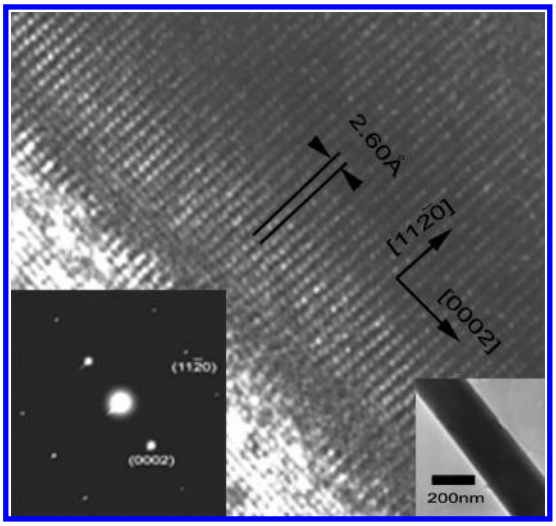

Figure 4. High-resolution TEM image along with the diffraction pattern from a ZnO rod.

nanometer. The sharp boundary has been seen often in our products. Further work can be done on how to exactly control the diameters of ZnO rods and how to fabricate varied morphologies made up of ZnO rods.

Figure 4 shows the high-resolution TEM image and diffraction pattern from a ZnO rod, which is a single crystal. The space of the lattice is about 0.260 nm corresponding to an interlayer space of the (0002) ZnO. The lower right of Figure 4 shows that the diameter of this rod is about 250 nm.

Discussion

Zinc powders were heated, vaporized, oxidized, and deposited on a cylindrical shape substrate to form the above products. The dominant source of oxygen is the residual air in the reaction tube and the ambient air entering into the quartz tube through the loose joint of rubber tube and quartz tube during the process. To interpret the growth process of ZnO rods and arrays, the VLS (Vapor−liquid−solid) mechanism[18] and the VS[19] (Vapor−solid) mechanism have been proposed. In the VLS mechanism, metal nanoparticles are always used as catalysts and there will be a metal droplet remaining at the tip of each nanowire. Since no particle was observed at the ends of or in the ZnO rods by using SEM or TEM, we proposed that the ZnO rods do not grow following the VLS mechanism. Other cylindrical substrates, like aluminum, tungsten, or nickel wire, can also be used as a substrate to synthesize the nano/microsized rods and arrays. It is shown in Figure 2 that the ZnO rods do not directly grow from the iron wire substrate but from a thick layer of ZnO polycrystalline material deposited on the cylindrical shape substrate. ZnO film then plays a crucial role for the nucleation of ZnO rods and arrays. So, it is likely that the growth process is governed by the VS mechanism. After being vaporized, oxidized, and transported to the downstream substrate, zinc particles first form a thin ZnO film on a cylindrical shape substrate and then self-catalyze during the deposition and formation of ZnO rods and arrays.[13,14] Hence, catalysts or pre-prepared doped or undoped ZnO film is not needed in our growth process of ZnO rod arrays. In the case of the individual nanorods protruding out of the rod arrays, it may be due to the temperature distribution, the substrate surface, or the probability that results in a quick growth. It hints that individual protrusive 1D nanostructures can be easily acquired, observed, and manipulated on a cylindrical substrate.

Conclusion

We have successfully developed a simple thermal evaporation approach to synthesize nano/micro ZnO rods and arrays on a cylindrical shape substrate. The ZnO rods do not directly grow from a cylindrical shape substrate but from a thick layer of ZnO polycrystalline material deposited on the substrate. The synthesized ZnO rods are single crystalline in a hexagonal structure and grow along the [0001] direction. The different sized 1D structures can help to understand fundamental concepts about the effects of dimensionality and size on, for example, mechanical, optical, and electrical properties.

Acknowledgment. This work is financially supported by the Chinese National Nature Science Foundation (Grant No. 90206046), National 973 Project of China, and National Center for Nanoscience and Technology of China.

References and Notes

(1) Wang, Z. L. *J. Phys.: Condens. Matter* **2004**, *16*, R825.
(2) Heo, Y. W.; Norton, D. P.; Tien, L. C.; Kwon, Y.; Kang, B. S.; Ren, F.; Pearton, S. J.; LaRoche, J. R. *Mater. Sci. Eng. R* **2004**, *47*, 1.
(3) Gao, P. X.; Wang, Z. L. *J. Phys. Chem. B* **2004**, *108*, 7534.
(4) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
(5) Ng, H. T.; Li, J.; Smith, M. K.; Nguyen, P.; Cassell, A.; Han, J.; Meyyappan, M. *Science* **2003**, *300*, 1249.
(6) Lyu, S. C.; Zhang, Y.; Lee, C. J.; Ruh, H.; Lee, H. J. *Chem. Mater.* **2003**, *15*, 3294.
(7) Tang, C. C.; Fan, S. S.; de la Chapelle, M. L.; Li, P. *Chem. Phys. Lett.* **2001**, *333*, 12.
(8) Lee, C. J.; Lee, T. J.; Lyu, S. C.; Zhang, Y.; Ruh, H.; Lee, H. J. *Appl. Phys. Lett.* **2002**, *81*, 3648.
(9) Li, S. Y.; Lee, C. Y.; Tseng, T. Y. *J. Cryst. Growth* **2003**, *247*, 357.
(10) Gao, P. X.; Ding, Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1315.
(11) Koh, Y. W.; Lin, M.; Tan, C. K.; Foo, Y. L.; Loh, K. P. *J. Phys. Chem. B* **2004**, *108*, 11419.
(12) Jie, J. S.; Wang, G. Z.; Wang, Q. T.; Chen, Y. M.; Han, X. H.; Wang, X. P.; Hou, J. G. *J. Phys. Chem. B* **2004**, *108*, 11976.
(13) Wang, L. S.; Zhang, X. Z.; Zhao, S. Q.; Zhou, G. Y.; Zhou, Y. L.; Qi, J. J. *Appl. Phys. Lett.* **2005**, *86*, 024108.
(14) Jie, J. S.; Wang, G. Z.; Chen, Y. M.; Han, X. H.; Wang, Q. T.; Xu, B.; Hou, J. G. *Appl. Phys. Lett.* **2005**, *86*, 031909.
(15) Vayssieres, L.; Keis, K.; Lindquist, S. E.; Hagfeldt, A. *J. Phys. Chem. B* **2001**, *105*, 3350.
(16) Henley, S. J.; Ashfold, M. N. R.; Nicholls, D. P.; Wheatley, P.; Cherns, D. *Appl. Phys. A* **2004**, *79*, 1169.
(17) Zhang, Y.; Wang, N.; Gao, S.; He, R.; Miao, S.; Liu, J.; Zhu, J.; Zhang, X. *Chem. Mater.* **2002**, *14*, 3564.
(18) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(19) Yang, P.; Lieber, C. M. *J. Mater. Res.* **1997**, *12*, 2981.