Low-Temperature Growth of ZnO Nanowire Array by a Simple Physical Vapor-Deposition Method

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Received August 14, 2002. Revised Manuscript Received April 14, 2003

Well-aligned single-crystalline wurzite zinc oxide (ZnO) nanowire array was successfully fabricated on an Al_2O_3 substrate by a simple physical vapor-deposition method at a low temperature of 450 °C. The diameter and growth rate of ZnO nanowires increased as a function of growth temperature. TEM observation showed that the ZnO nanowires were synthesized along the *c*-axial direction of the hexagonal crystal structure. We demonstrate that ZnO nanowires followed the self-catalyzed growth mechanism on the ZnO nuclei. Besides high-quality ZnO nanowires, sometimes a fascinating hierarchically ordered ZnO structure was also observed.

Introduction

Since the first discovery of carbon nanotubes, one-dimensional semiconductor materials have attracted extensive interest because they exhibit curious structures and various remarkable physical, chemical, and electrical properties distinctive from those of conventional bulk materials.[1−6] Among the various semiconductor nanowires, zinc oxide (ZnO) nanowire having a direct band gap of 3.37 eV and large exciton binding energy of 60 meV can promise practical applications in the area of nanoscale laser diodes and ultraviolet (UV) sensors. Because of the radial quantum confinement effect of nanowires, ZnO nanowires possess high density of states at the band edge. Recently Huang et al. reported that UV lasing nano-devices working at room temperature with a low-lasing threshold based on ZnO nanowires would be quite potentially feasible.[7,8]

ZnO nanowires can be synthesized by various methods such as arc discharge, laser vaporization, pyrolysis, electrodeposition, and chemical or physical vapor deposition.[7−17] To date, well-aligned ZnO nanowire arrays, which have the well-faceted hexagonal structure, were synthesized on a sapphire substrate by a carbon thermal-reduction vapor transport method at 880 °C.[7,8] In addition, ZnO nanobelts were also obtained by evaporating ZnO powder at a high temperature of 1400 °C.[18] These previously reported ZnO nanowires or nanobelts had high purity and high-crystalline structure, but the growth temperature was too high to allow use of low-temperature-endurance substrates. To apply ZnO nanowires to many nanoscale devices, it is very desirable to have synthesized those nanowires at low growth temperature. Recently, ZnO nanorods were grown directly on silica or silicon substrate at a temperature of 500 °C in a two-temperature-zone furnace using evaporated zinc acetylacetonate hydrate ($Zn(C_5H_7O_2)2{\cdot}xH_2O$) as a reaction source.[15] But in that work, the produced ZnO nanowires had poor morphology and a low growth rate. More recently, Park et al. reported vertically well-aligned ZnO nanowires on sapphire substrates or ZnO nanoneedles on silicon sub-

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(1) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Hu, Y. D. *Science* **1997**, *277*, 1287.
(2) Wong, S. S.; Joselevich, E.; Woolley, A. T.; Cheung, C. L.; Lieber, C. M. *Nature* **1998**, *394*, 52.
(3) Cui, Y.; Wei, Q. Q.; Park, H. K.; Lieber, C. M. *Science* **2001**, *293*, 1289.
(4) Huang, Y.; Duan, X.; Cui, Y.; Lauhon, L. J.; Kim, K. H.; Lieber, C. M. *Science* **2001**, *294*, 1313.
(5) Kim, J. R.; So, H. M.; Park, J. W.; Kim, J. J.; Kim, J.; Lee, C. J.; Lyu, S. C. *Appl. Phys. Lett.* **2002**, *80*, 3548.
(6) Lee, C. J.; Lee, T. J.; Lyu, S. C.; Zhang Y.; Ruh, H.; Lee, H. J. *Appl. Phys. Lett.* **2002**, *81*, 3648.
(7) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. D. *Science* **2001**, *292*, 1897.
(8) Huang, M. H.; Wu, Y. Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. D. *Adv. Mater.* **2001**, *13*, 113.
(9) Duan, X. F.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298.
(10) Li, Y.; Meng, G. W.; Zhang, L. D.; Phillipp, F. *Appl. Phys. Lett.* **2000**, *76*, 2011.
(11) Konenkamp, R.; Boedecker, K.; Lux-Steiner, M. C.; Poschenrieder, M.; Zenia, F.; Clement, C. L.; Wagner, S. *Appl. Phys. Lett.* **2000**, *77*, 2575.
(12) Liu, R.; Vertegel, A. A.; Bohannan, E. W.; Sorenson, T. A.; Switzer, J. A. *Chem. Mater.* **2001**, *13*, 508.
(13) Kong, Y. C.; Yu, D. P.; Zhang, B.; Fang, W.; Feng, S. Q. *Appl. Phys. Lett.* **2001**, *78*, 407.
(14) Hu, J. Q.; Li, Q.; Wong, N. B.; Lee, C. S.; Lee, S. T. *Chem. Mater.* **2002**, *14*, 1216.
(15) Wu, J. J.; Liu, S. C. *Adv. Mater.* **2002**, *14*, 215.
(16) Park, W. I.; Kim, D. H.; Jung, S.-W.; Yi, G.-C. *Appl. Phys. Lett.* **2002**, *80*, 4232.
(17) Yao, B. D.; Chan, Y. F.; Wang, N. *Appl. Phys. Lett.* **2002**, *81*, 757.
(18) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.

10.1021/cm020465j CCC: $25.00
Published on Web 07/09/2003

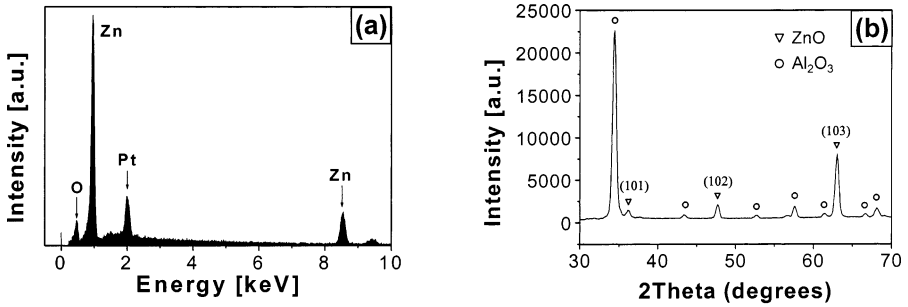

Figure 1. EDX analysis of the ZnO nanowires on the Al_2O_3 substrate (a) and XRD spectra (b).

strates at low-temperatures ranging from 400 to 500 °C using metal−organic chemical vapor deposition.[16,19] In their method, a very thin ZnO epitaxial layer was grown on the sapphire substrates prior to ZnO nanowire growth. Despite much progress on the synthesis of ZnO nanowires, it is still difficult to produce high-quailty ZnO nanowires at low temperature using a simple growth technique. Currently, a large-scale synthesis of high-quality ZnO nanowires at low temperature remains a great challenge.

In this paper, we demonstrate fabrication of a high-quality single-crystalline ZnO nanowire array on the Al_2O_3 substrate using a simple physical vapor-deposition method at a low growth temperature of 450 °C. The ZnO nanowires were synthesized along the *c*-axis growth direction and followed the catalyst-free growth mechanism. We emphasize that our simple growth technique employs a much lower growth temperature for the synthesis of high-quality ZnO nanowires. Such a low-temperature growth method may open up the opportunities for fabricating ZnO nanowires onto various low-temperature-endurance substrates and extend the realm of ZnO-based nanoscale devices. We also discovered that some nanowires have a hierarchically ordered ZnO structure, the so-called fractal nanofern. These fractal structures of ZnO nanowires are caused by structural defects at low growth temperature.

Experimental Section

High-quality ZnO nanowires were synthesized on NiO-nanoparticle-deposited Al_2O_3 substrates. The Al_2O_3 material used consists of grain structure, resulting in mound morphology on the surface. In a typical process, a solution (0.01 M) of nickel nitrate (Sigma-Aldrich 99.999%) and ethanol was dropped onto the Al_2O_3 substrate (10 mm × 5 mm). After drying the Al_2O_3 substrate at 400 °C in ambient air, NiO particles were evenly formed on the Al_2O_3 substrate. The substrate was put on the top of a quartz boat loaded with metal zinc powders (100 mesh, 99.999%, Sigma-Aldrich) and inserted into a quartz tube furnace. The vertical distance between the zinc source and the Al_2O_3 substrate was about 3−5 mm. To synthesize ZnO nanowires, the furnace was heated to reaction temperature under an Ar flow rate of 500 sccm. The Zn source was physically vaporized to synthesize the ZnO nanowires in atmospheric pressure under an Ar (99.99%) flow rate of 500 sccm for 60 min at the temperature range of 450−600 °C. After the reaction, the substrate surface appeared as a layer of white waxlike material. The as-deposited products were characterized by scanning electron microscopy (SEM; Hitachi, S-4700), transmission electron microscopy (TEM; Hitachi, H-9000), energy-dispersive X-ray spectroscopy (EDX; Hitachi, S-4700), and X-ray diffraction (XRD; Rigaku, DMAX 2500).

(19) Park, W. I.; Yi, G.-C.; Kim, M. Y.; Pennycook, S. J. *Adv. Mater.* **2002**, *14*, 1841.

Results and Discussion

Figure 1 shows EDX analysis and XRD spectra of the synthesized white waxlike material. EDX indicates that the products consist of zinc and oxygen elements exactly as shown in Figure la. The element of Pt was from the coating layer used for SEM imaging of the products. XRD measurement demonstrates that the produced ZnO materials have a single-crystalline wurtzite structure as shown in Figure 1b. Only (10*l*) peaks (l = 1,2,3) are observed in the XRD spectra, implying that the ZnO materials have some tilted alignment degree toward the vertical direction. The strong intensities of ZnO diffraction peaks indicate that the products have a high-purity ZnO wurtzite phase.

Figure 2 shows the SEM images of the ZnO materials synthesized at 450−600 °C. In the SEM image, high-purity ZnO nanowires are synthesized on the Al_2O_3 substrate at a low growth temperature of 450 °C. This result indicates that for zinc metal (mp 419 °C) vapor pressure at 450 °C is high enough to sustain the growth of ZnO nanowires. Figure 2a−d shows low-magnification SEM images, indicating that vertically aligned ZnO nanowires have a radial direction on the substrate with a high density. It is suggested that the tilted alignment of ZnO nanowires is caused by the surface morphology of the Al_2O_3 substrate material. In the SEM images, one can find that the alignment of the ZnO nanowire advances as the growth temperature increases from 450 to 600 °C. Further study is necessary to elucidate the alignment dependence of ZnO nanowires on growth temperature. The growth rate of ZnO nanowires also increases as a function of growth temperature. The growth rates of ZnO nanowire for the growth temperatures of 450, 500, 550, and 600 °C are 2.6, 4.8, 5.4, and 7.2 μm, respectively. High-magnification SEM images indicate that the straight ZnO nanowires have a uniform diameter and clean surface as shown in Figure 2e−h. The average diameters of ZnO nanowires grown at 450, 500, 550, and 600 °C are 55, 65, 84, and 100 nm, respectively. The higher growth temperatures will be in favor of formation of ZnO nanowires with larger diameters. Higher growth temperature is also beneficial to synthesizing ZnO nanowires possessing perfect hexagonal crystal morphology as shown in the SEM images.

We employed NiO nanoparticles on the Al_2O_3 substrate to synthesize ZnO nanowires. In our experiment, NiO nanoparticles sized several tens of nanometers are produced on the Al_2O_3 substrate by adopting a simple baking process at 400 °C in the ambient air as shown in Figure 3a. The SEM image shows that the Al_2O_3

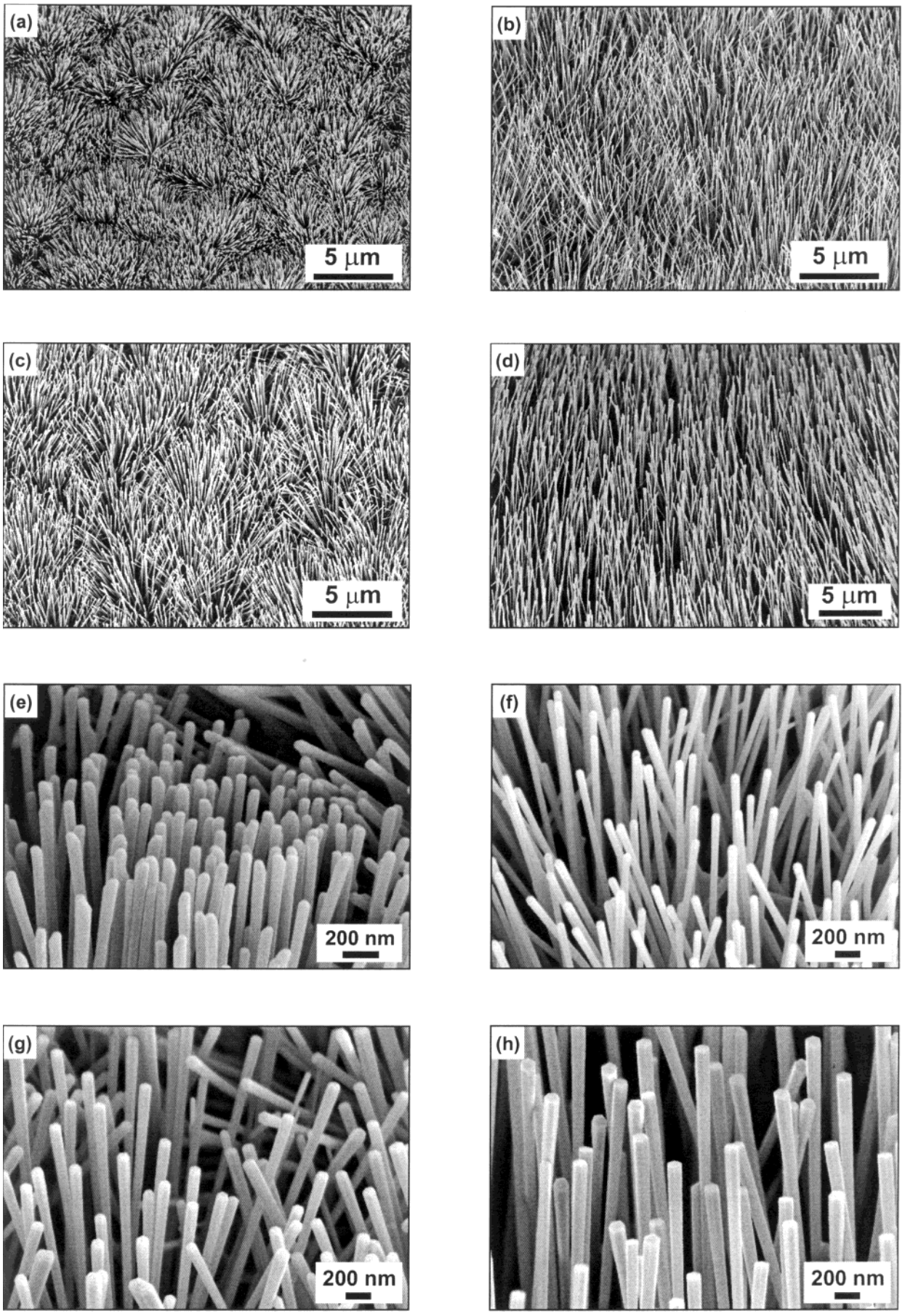

Figure 2. SEM images of aligned ZnO nanowires on the Al_2O_3 substrate: at low magnification (a−d), at high magnification (e−h). The growth temperatures are 450 (a, e), 500 (b, f), 550 (c, g), and 600 °C (d, h).

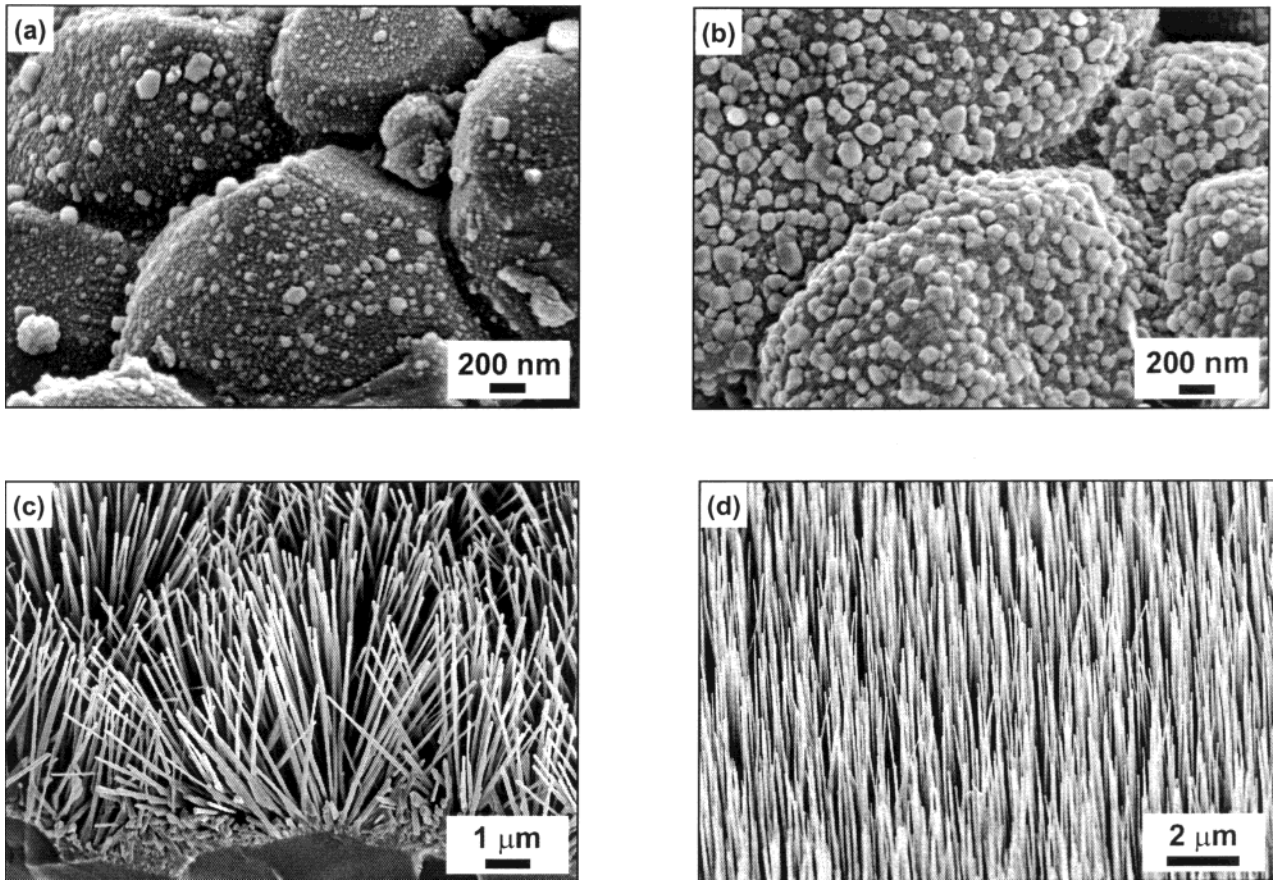

Figure 3. SEM image of NiO nanoparticles produced on the Al_2O_3 substrate (a) and SEM image for the initial growth stage of ZnO nanowires on the NiO-nanoparticle-deposited Al_2O_3 substrate (b). Cross-sectional SEM image of the synthesized ZnO nanowires at 550 °C (c) and SEM image of well-aligned ZnO nanowires synthesized on the silicon substrate at 550 °C (d).

substrate surface reveals isolated grain morphology because the Al_2O_3 material used has a bulk crystal structure. Figure 3b shows an SEM image for the initial growth stage of ZnO nanowires on the NiO-nanoparticle-deposited Al_2O_3 substrate, in which the ZnO nanowires were synthesized for 3 min at 550 °C. The laterally grown ZnO layer, which is originated from the NiO nanoparticles, perfectly covers the NiO catalyst particle on the Al_2O_3 substrate. As a result, it would be impossible to supply a Zn source into the NiO nanoparticles during the ZnO nanowire growth. Figure 3c is the cross-sectional SEM image of the ZnO nanowires synthesized on the Al_2O_3 substrate at 550 °C, indicating the surface of the Al_2O_3 grain covered with a ZnO layer. From SEM observation, we suggest that the ZnO nanowires are directly synthesized not on the NiO nanoparticles but on the laterally grown ZnO layer. Park et al.[16] announced the catalyst-free growth of ZnO nanowire, in which a thin ZnO epitaxial layer was grown on the sapphire substrates before ZnO nanowire growth. Figure 3d shows the SEM image of well-aligned ZnO nanowires synthesized on the silicon substrate at 550 °C. Compared with ZnO nanowires grown on the Al_2O_3 substrate, the synthesized ZnO nanowires have vertical direction because the used substrate has a plane surface.

It is well-known that transition metal oxides, such as NiO and FeO, have a similar catalytic effect on the VLS growth of semiconductor nanowires as well as metal catalysts.[20] Our experimental result shows that the NiO nanoparticles are fully covered with a laterally grown ZnO layer and no metal catalyst particles are observed on the ZnO nanowire tip. Moreover, the ZnO nanowires could be synthesized on the Al_2O_3 or the silicon substrate without catalyst nanoparticles. Therefore, we suggest that the ZnO nanowires follow a catalyst-free growth model in our method. In the initial stage, NiO nanoparticles on the Al_2O_3 substrate are covered with the ZnO layer; and then the nucleation can occur at any of the sites on the ZnO layer. Continuous feeding of an evaporated Zn source and elemental oxygen into favorable nucleation sites of ZnO will lead to one-dimensional growth of ZnO nanowires. The oxygen element may origin from the ambient gas which is introduced into the quartz tube because the reaction pressure is atmospheric.

Figure 4 shows a TEM image of the ZnO nanowires synthesized at 450 °C. It indicates that the ZnO nanowires have uniform diameter and no catalyst particle at the tip as shown in Figure 4a. High-resolution TEM image and electron diffraction characterization indicate that the ZnO nanowire is grown along the $[\bar{2}110]$ zone axis as shown in Figure 4b. In the HRTEM analysis, the ZnO nanowire is single-crystal and follows *c*-axial growth direction ($c = 5.13$ Å). From TEM observation,

(20) Chen, X. L.; Li, J. Y.; Cao, Y. G.; Lan, Y. C.; Li, H.; He, M.; Wang, C. Y.; Zhang, Z.; Qiao, Z. Y. *Adv. Mater.* **2000**, *12*, 1432.

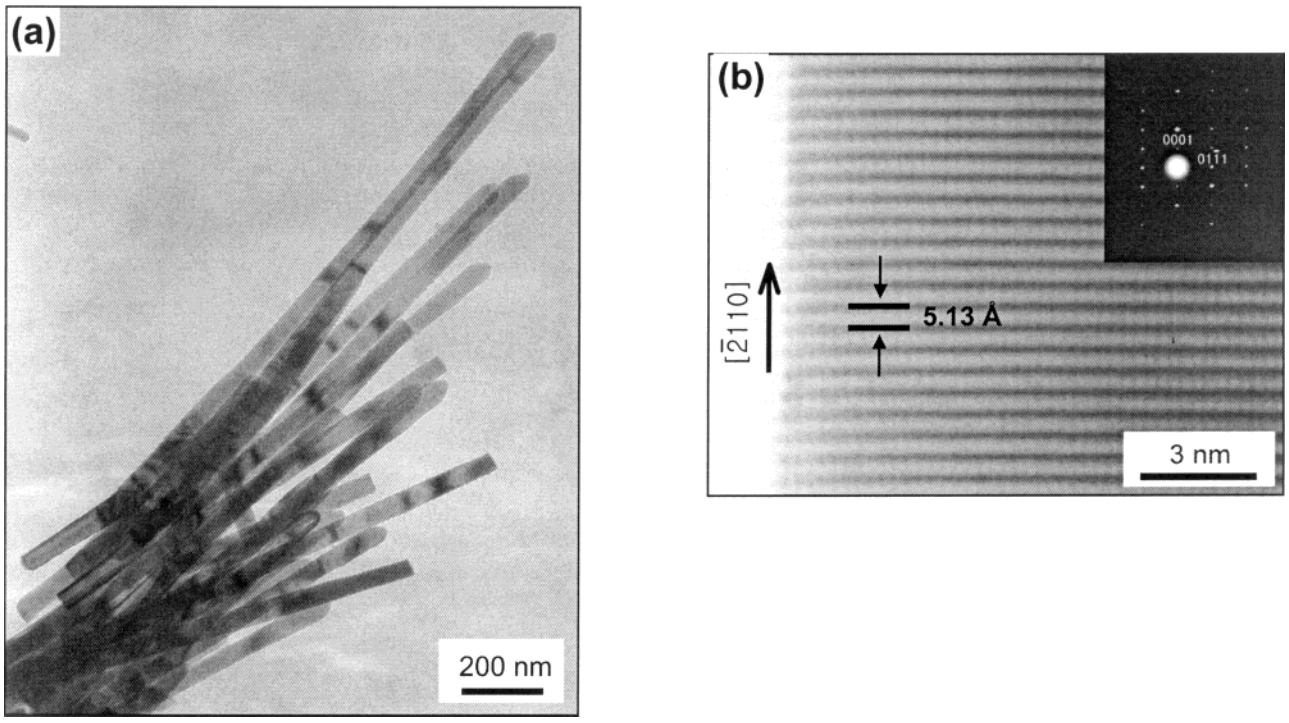

Figure 4. TEM image of ZnO nanowires synthesized at 450 °C (a) and HRTEM image of ZnO nanowire with selected area electron diffraction pattern (b).

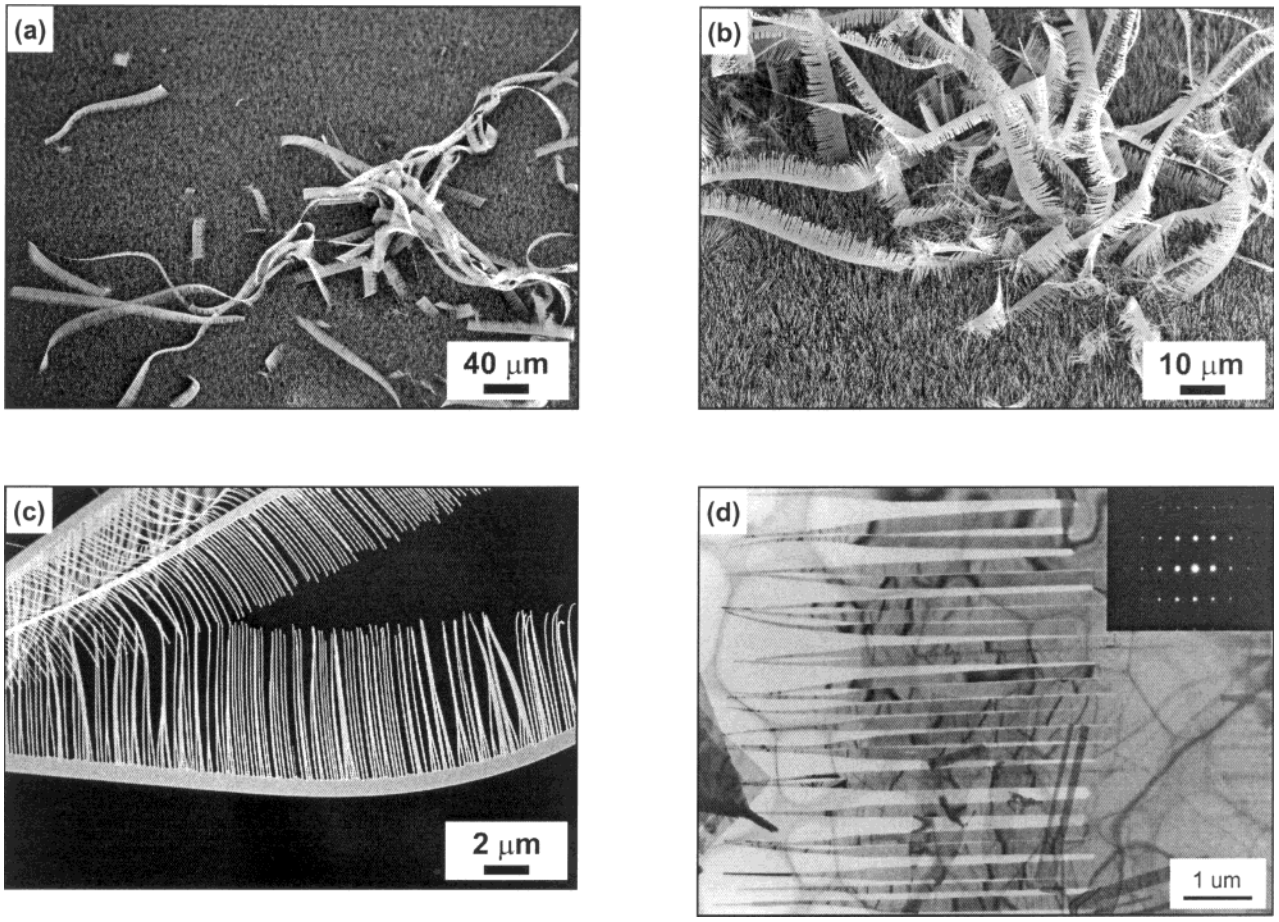

Figure 5. SEM images of novel hierarchical structured ZnO fractal nanoferns on the surface of ZnO nanowire array (a−c) and HRTEM image of a ZnO fractal nanofern with selected area electron diffraction pattern (d).

we consider that high-crystalline hexagonal structured ZnO nanowires can be successfully synthesized at low growth temperature.

During SEM observations, we could sometimes find novel hierarchical-structured ZnO fractal nanoferns on the surface of the ZnO nanowire array grown at edge

areas of the substrate where no catalyst nanoparticles were supplied (Figure 5). The HRTEM image indicates that the produced ZnO fractal nanoferns have no catalyst particle at the tip and some strain. Actually, the growth model of those curious structures could not be explained using the catalyst-assisted VLS model. It is well-known that strains and defects, which are often found in the crystalline materials with wurtzite structure, mainly influence the one-dimensional growth of whiskers or nanowires.[21] Here we suggest that the growth of ZnO fractal nanoferns originates from some structural defects within the ZnO crystal. The fractal structure of ZnO nanowires could be used to build functional nanodevices such as the tips of atomic force microscopes and scanning tunneling microscopes.

Conclusion

We demonstrated that single-crystalline wurtzite ZnO nanowire array was successfully fabricated on the NiO-nanoparticle-deposited Al_2O_3 substrate by a simple physical vapor-deposition method at a low temperature of 450 °C. The diameter and growth rate of ZnO nanowires increased as the growth temperature increased. TEM observation showed that the ZnO nanowires were synthesized along the *c*-axial direction of the hexagonal crystal structure. We demonstrate that ZnO nanowires followed the catalyst-free growth mechanism. Some fascinating hierarchically ordered structure was also observed. Our results hold promise for the fabrication of ZnO-nanowires-based nanoscale devices onto various low-temperature-endurance substrates.

Acknowledgment. We thank J. S. Joeng for helpful discussion regarding the TEM analysis. This work was supported by the Center for Nanotubes and Nanostructured Composites at SKKU and by the National R&D project for Nano Science and Technology of MOST.

CM020465J

(21) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1791.