

Low-temperature growth and properties of ZnO nanowires

Cite as: Appl. Phys. Lett. **84**, 4941 (2004); <https://doi.org/10.1063/1.1760594>

Submitted: 17 November 2003 . Accepted: 13 April 2004 . Published Online: 28 May 2004

Xuan Wang, Qingwen Li, Zhibo Liu, Jin Zhang, Zhongfan Liu, and Rongming Wang



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[A comprehensive review of ZnO materials and devices](#)

Journal of Applied Physics **98**, 041301 (2005); <https://doi.org/10.1063/1.1992666>

[Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach](#)

Applied Physics Letters **78**, 407 (2001); <https://doi.org/10.1063/1.1342050>

[Ordered semiconductor ZnO nanowire arrays and their photoluminescence properties](#)

Applied Physics Letters **76**, 2011 (2000); <https://doi.org/10.1063/1.126238>

Lock-in Amplifiers
up to 600 MHz



Low-temperature growth and properties of ZnO nanowires

Xuan Wang, Qingwen Li, Zhibo Liu, Jin Zhang,^{a),b)} Zhongfan Liu,^{a)} and Rongming Wang^{c)}

Centre for Nanoscale Science and Technology (CNST), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

(Received 17 November 2003; accepted 13 April 2004; published online 28 May 2004)

ZnO nanowires were obtained through evaporation of zinc powders under a low temperature of 400 °C. These ZnO nanowires, in the diameter of ~ 10 nm, were long and curved with lengths of tens of micrometers. High-resolution transmission electron microscopy showed these ZnO nanowires were mostly crystalline structure; however, the kink parts contained dislocations and stacking faults. Furthermore, the movement of dislocations was observed in the kink parts under e-beam irradiation. Photoluminescence and Raman spectra show that there exist oxygen vacancies in the ZnO nanowires. Possible reasons for the growth and properties of ZnO nanowires were discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1760594]

Semiconducting nanowires with controlled dimension and morphology will be critical for the fabrication of electronic and optical nanodevices. ZnO is one of promising semiconducting materials for potential applications^{1–8} due to its wide band gap of 3.37 eV and exciton binding energy of ~ 60 meV. In the past decade, numerous studies have been made on both production and application of one-dimensional ZnO.^{1,2,7–18} Most recently, vapor-phase methods such as thermal evaporation and condensation,^{1,8,9,12,13} carbon thermal-reduction vapor transport,^{2,7} and evaporation of organic zinc precursors¹⁰ have been used. However, most of these processes require synthetic temperature higher than 800 °C.

In the present study, it has been shown possible to grow ZnO nanowires at 400 °C with the assistance of Au nanoparticles. These ZnO nanowires, in the diameter of ~ 10 nm, were long and curved with lengths of tens of micrometers. It was found that most of the ZnO nanowires were crystalline structure; however, the kink parts contained dislocations and stacking faults. In addition, the movement of dislocations was observed in the kink parts under e-beam irradiation. Besides the structural characterization, photoluminescence and Raman spectra of ZnO nanowires were discussed. Thus, the present work offers a mild way of producing ZnO nanowires as well as their possible applications.

The synthesis of ZnO nanowires was achieved by direct evaporation of zinc powders at 400 °C. Zinc powders (purity >90%) were loaded into a 10-cm-long glass tube ($\phi = 0.8$ cm) in order to maintain sufficient zinc vapor in the reactor. Silicon wafers with well-dispersed gold nanoparticles¹⁹ (~ 10 nm) were put ~ 2 cm downstream of zinc powders. The assembly was then placed in the middle of a quartz tube in a horizontal furnace. The furnace temperature was increased to 400 °C at a flow rate of 100 sccm N₂ (99.9%), and O₂/N₂ ($V_{O_2}:V_{N_2} = 0.5\%$) was then added at a

flow rate of 20 sccm for a further 30 min. The system was then allowed to cool to room temperature under nitrogen.

Scanning electron microscopy (SEM) was used to characterize the morphology of the products. Figure 1(a) shows a typical SEM image of ZnO nanowires grown on silicon substrates. Most of these ZnO nanowires were uniform in the diameter of ~ 10 nm. The lengths of ZnO nanowires were mainly about tens of micrometers.

In our experiments, many kinds of substrates can be used for the growth of ZnO nanowires due to a low growth temperature. As a result, the growth of nanowires could be achieved on Cu grids directly. High-resolution transmission electron microscopy (HRTEM) and energy-disperse x-ray analysis (EDAX) were used to investigate the structure and composition of as-grown ZnO nanowires. HRTEM images and EDAX spectra were collected using a FEI Tecnai F30 FEG operated at 300 kV.

Figure 1(b) shows one TEM image of ZnO nanowires grown on Cu grids. EDAX results confirmed that these nanowires were composed of Zn and O. The diameters of nanowires mainly distributed in the range of 6–12 nm, close

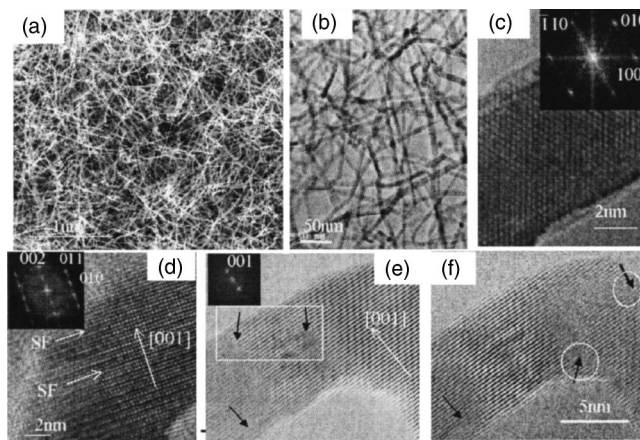


FIG. 1. SEM and TEM images of ZnO nanowires: (a) SEM image of ZnO nanowires; (b) TEM image of ZnO nanowires grown on Cu grid; (c) HRTEM image of ZnO nanowires with inset of its corresponding FFT; (d) HRTEM image of the kink part of one curved nanowire; (e) and (f) HRTEM images, recorded sequentially, of the kink part of one curved nanowire.

^{a)} Authors to whom correspondence should be addressed.

^{b)} Electronic mail: jzhang@chem.pku.edu.cn

^{c)} Also at: Electron Microscopy Laboratory and State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, P.R. China.

to sizes of Au nanoparticles. Since most of these ZnO nanowires were long and curve, consisting of straight parts and kink parts, we investigated the structure of straight parts and kink parts, respectively.

As identified by HRTEM, straight parts of ZnO nanowires were mostly highly crystallized structures. Figure 1(c) shows a HRTEM image of one straight part of ZnO nanowires. The inset is its corresponding fast Fourier transform (FFT) along the [001] zone axis. Judging from the lattice fringes and its FFT, the nanowire could be indexed to be a wurtzite structure of ZnO with lattice constants of $a = 0.32$ nm, $c = 0.52$ nm and its axis direction was [110].

The kink parts of ZnO nanowires, on the other hand, contained stacking faults and dislocations. Figure 1(d) shows a HRTEM image from one kink part of as-grown nanowires, with stacking faults indicated by arrows. The inset is its corresponding FFT. The FFT pattern was indexed as wurtzite structure of ZnO, along the [100] zone axis. Another example of kink parts was displayed in Fig. 1(e), in which dislocations were labeled with arrows. The spacing between adjacent lattice planes is ~ 2.6 Å, in agreement with the distance between two (002) crystal planes of wurtzite ZnO. Both in Figs. 1(d) and 1(e), the axial direction of nanowires was [001] (indicated with arrows).

It is noteworthy that kinking of ZnO nanowires was seemingly random, such as angles of $\sim 63^\circ$, $\sim 109^\circ$, and $\sim 125^\circ$. It has been reported that close proximity of neighboring nanowires may induce the strain, which forces nanowires to change growth direction.²⁰ However, in the present study, we found that kinking of ZnO nanowires occurred even when ZnO nanowires were short and in low density (data not shown). By examining a number of kink parts, it was found that defects generally existed in the kink parts of nanowires growing along the [001] direction. Since (001) crystal plane of ZnO is the dense-packed plane with lowest energy, stacking faults and dislocations were perhaps easily introduced.²¹ Thus, the insertion of stacking faults or dislocations may possibly result in the change of growth direction of ZnO nanowires. However, the possible reason for the introduction of defects is not known, but could be due to disturbance in the growth process such as small change of gas flow and the temperature.

The difference between Figs. 1(e) and 1(f) is that there occurred movement of dislocations. These two figures were recorded sequentially at an interval of at least 1 s. Obviously, two dislocations [indicated by a rectangle in Fig. 1(e)] disappeared from the original positions and another two dislocations appeared in the position indicated by circles in Fig. 1(f), indicating that dislocations in the kink parts were mobile under e-beam irradiation. We believe that the movement of dislocations may be induced by e-beam heating, especially in the case of nanowires in which heating dissipation is difficult.

The growth of ZnO nanowires was found sensitive to the oxygen content and temperature. When the amount of oxygen in the flowing carrier gas exceeded 0.25%, no ZnO nanowires could be obtained. Under 500 °C, similar ZnO nanowires in much higher density than under 400 °C could be synthesized by modulating the flow rate to mixture of 50 sccm N₂ (99.9%) and 20 sccm O₂/N₂ ($V_{O_2}:V_{N_2}=0.5\%$).

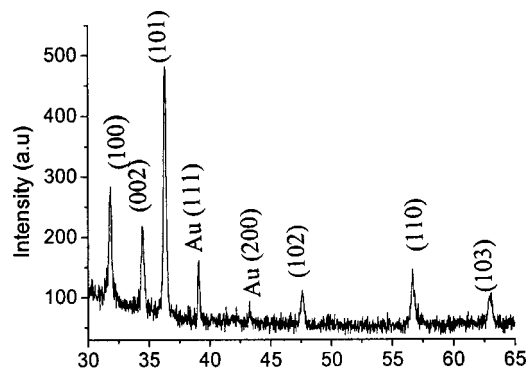


FIG. 2. XRD pattern of ZnO nanowires on a silicon substrate: indices specified above the corresponding peaks.

Figure 2 shows the x-ray diffraction (XRD) pattern of these ZnO nanowires, indicating that these ZnO nanowires were in highly crystallized structure. The diffraction peaks can be indexed to be wurtzite structure of ZnO. In addition, Au(111) and Au(200) peaks were also detected.

The achievement of ZnO growth under 400 °C was based upon a fact that Zn powder is easy to evaporate and its evaporation pressure can reach up to 10.8 Pa at 400 °C. Therefore, enough Zn vapor at 400 °C and proper oxygen in flowing nitrogen could probably allow the growth of ZnO nanowires. In the process, Au nanoparticles played a key role as catalysts and we could not obtain ZnO nanowires without Au nanoparticles.

Figures 3(a) and 3(b) show the Raman spectrum and photoluminescence of ZnO nanowires grown under 500 °C. As shown in Fig. 3(a), the peak at 437 cm^{-1} corresponds to E_2 mode of ZnO crystal, while the peak at 581 cm^{-1} corresponds to E_1 mode of oxygen deficiency.^{22,23} This indicates that there exist oxygen vacancies in the ZnO nanowires, which is consistent with the photoluminescence property of these ZnO nanowires. Room-temperature photoluminescence was measured with excitation wavelength at 340 nm, as shown in Fig. 3(b). The peak around 388 nm is attributed to the near band-edge emission and the peak around 470 nm may be associated with the singly ionized oxygen vacancy.² It has been reported that emission density corresponding to oxygen vacancy increased as the nanowire diameter decreased, probably caused by the high surface area to volume ratio for thin nanowires.²

In summary, ZnO nanowires in the diameter of ~ 10 nm could be obtained at a low temperature of 400 °C. This mild catalyzed synthesis route may promise us a way to fabricate ZnO nanowires for future application. HRTEM showed that the kinking parts of ZnO nanowires contained stacking faults

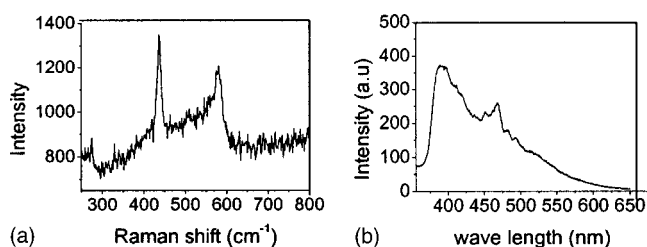


FIG. 3. Raman spectrum and photoluminescence of ZnO nanowires: (a) Raman spectrum of ZnO nanowires on a silicon substrate; (b) photoluminescence of ZnO nanowires on a silicon substrate.

and dislocations. Possible reasons for the growth and kinking of ZnO nanowires were discussed. In addition, photoluminescence and Raman spectra indicate the existence of oxygen vacancies in ZnO nanowires.

The authors are grateful for financial support from the National Natural Science Foundation of China (NSFC 30000044, 90206023), Ministry of Science and Technology of China (2001CB6105), and FOKYING TUNG Education Foundation (94012). The authors also thank Professor Ruguang Zhao for her kind help and useful discussion.

¹Z. W. Pang, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).

²M. H. Huang, Y. Y. Wu, H. Feick, N. Tran, E. Weber, and P. D. Yang, *Science* **292**, 1897 (2001); *Adv. Mater. (Weinheim, Ger.)* **13**, 113 (2001).

³H. Rensmo, K. K. Lindstrom, L. N. Wang, and M. Muhammed, *J. Phys. Chem. B* **101**, 2598 (1997).

⁴J. C. Johnson, H. Yan, R. D. Schaller, L. H. Haber, R. J. Saykally, and P. Yang, *J. Phys. Chem. B* **105**, 11387 (2001).

⁵H. J. Muhr, F. Krumeich, U. P. Schonholzer, F. Bieri, M. Niederberger, L. J. Gauckler, and R. Nesper, *Adv. Mater. (Weinheim, Ger.)* **12**, 231 (2000).

⁶S. Mann, W. Shenton, M. Li, S. Connolly, and D. Fitzmaurice, *Adv. Mater. (Weinheim, Ger.)* **12**, 147 (2000).

⁷C. H. Liu, W. C. Yiu, F. C. K. Au, J. X. Ding, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.* **83**, 3168 (2003).

⁸C. H. Liu, J. A. Zapien, Y. Yao, X. M. Meng, C. S. Lee, S. S. Fan, Y. Lifshitz, and S. T. Lee, *Adv. Mater. (Weinheim, Ger.)* **15**, 838 (2003).

⁹Y. C. Kong, W. Fang, and S. Q. Feng, *Appl. Phys. Lett.* **78**, 407 (2001).

¹⁰J. J. Wu and S. C. Liu, *Adv. Mater. (Weinheim, Ger.)* **14**, 215 (2002).

¹¹S. C. Lyu, Y. Zhang, H. Ruh, H. J. Lee, H. Wookshim, E. K. Suh, and C. J. Lee, *Chem. Phys. Lett.* **363**, 134 (2002).

¹²J. Y. Lao, J. Y. Huang, and Z. F. Ren, *Nano Lett.* **3**, 235 (2003).

¹³J. Y. Lao, J. G. Wen, and Z. F. Ren, *Nano Lett.* **2**, 1287 (2002).

¹⁴R. Konenkamp, K. Boedecker, and S. Wagner, *Appl. Phys. Lett.* **77**, 2575 (2000).

¹⁵Y. Li, G. W. Meng, L. D. Zhang, and F. Phillipp, *Appl. Phys. Lett.* **76**, 2011 (2000).

¹⁶L. Guo, S. H. Yang, C. L. Yang, J. N. Wang, and W. K. Ge, *Chem. Mater.* **12**, 2268 (2000).

¹⁷L. Guo, Y. L. Ji, and H. B. Xu, *J. Am. Chem. Soc.* **124**, 14864 (2002).

¹⁸B. Liu and H. C. Zeng, *J. Am. Chem. Soc.* **125**, 4430 (2003).

¹⁹A. Ulman, *Chem. Rev. (Washington, D.C.)* **96**, 1533 (1996).

²⁰Z. H. Wu, X. Mei, D. Kim, M. Blumin, and H. E. Ruda, *Appl. Phys. Lett.* **83**, 3368 (2003).

²¹G. W. Zhou, Z. Zhang, and D. P. Yu, *J. Cryst. Growth* **197**, 129 (1999).

²²X. L. Xu, S. P. Lau, J. S. Chen, G. Y. Che, and B. K. Tay, *J. Cryst. Growth* **223**, 201 (2001).

²³J. J. Wu and S. C. Liu, *J. Phys. Chem. B* **106**, 9546 (2002).