



Three-dimensional interconnected nanowire networks of ZnO

Pu Xian Gao, Chang Shi Lao, William L. Hughes, Zhong L. Wang *

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, United States

Received 24 March 2005; in final form 1 April 2005

Abstract

In this Letter, three-dimensional (3D) interconnected networks of ZnO nanowires and nanorods are synthesized by a high temperature solid–vapor deposition process. The nanorods and nanowires have diameters of 20–100 nm and they grow along the *c*-axis. Due to the diverse orientation of the nanowires grown from a polycrystalline substrate, the networks are formed by a sintering process of the crossed nanowires during growth. The thickness of the multilayer nano-network could be as thick as ~30 μm. The sharp nanowire tips, the high degree of networking, and high surface area of these unique nanonetworks make them a potential candidate for field emission, ultra-sensitive gas sensing, catalysts and filtering.

© 2005 Elsevier B.V. All rights reserved.

Wurtzite structured ZnO is of great importance due to its versatile applications in optoelectronic, photovoltaics and sensors [1,2]. Quasi-one-dimensional nanostructures of ZnO, such as nanowires, nanobelts and nanotubes have been a relevant research topics in nanotechnology for their unique properties and potential applications [3–11]. The non-central symmetric crystallographic structure and spontaneous surface polarization characteristics make ZnO one of the most exciting oxide nanostructures for investigating nanoscale physical and chemical phenomena [12]. Unique structural configurations such as nanojunction-arrays [13–15], piezoelectric nanobelts [16], nanosprings [17], nanorings [18,19], nanobows [20] etc., have been reported. In this Letter, we report a new nanostructure of ZnO: three-dimensional (3D) interconnected nanowire network. The structure and growth process of the nanonetworks will be presented. The high temperature ‘welding’ and sintering effect on the formation of networks will be elaborated. The structure reported here could find potential applications in field emission, gas sensing, catalysis and filtering.

The interconnected networks of ZnO nanowires were grown via a high temperature solid–vapor deposition

process [21]. The experimental set-up consists of a horizontal high temperature tube furnace ~50 cm long, an alumina tube (~75 cm in length), a rotary pump system and a gas controlling system. Commercial (Alfa Aesa) ZnO powder about 2 g was ground and then loaded in an alumina boat and positioned at the center of the alumina tube as the source material. The evaporation was conducted at 1400 °C for 30–120 min under a constant pressure of ~300 mbar throughout the heating, high-temperature synthesis and cooling processes. The Ar carrier gas flow rate was controlled at 50–100 sccm (standard cubic centimeters per minute) after the temperature had reached 800 °C. The 3D networks of ZnO nanowires were grown on either a polycrystalline Al₂O₃ substrate or on a (1 1 0) Si wafer in a temperature zone of 700–800 °C.

Scanning electron microscopy (FE-SEM) (field emission LEO 1530 FEG at 5 & 10 kV) and transmission electron microscopy (TEM) (field emission TEM Hitachi HF-2000 at 200 kV), and energy-dispersive X-ray spectroscopy (EDS) attached to the SEM and TEM, respectively were used to investigate the morphology, crystal structure and composition of the as-grown nanostructures.

Fig. 1a is a typical low magnification SEM picture of the as-grown networks of ZnO nanowires and

* Corresponding author. Fax: +1 404 894 8008.

E-mail address: zhong.wang@mse.gatech.edu (Z.L. Wang).

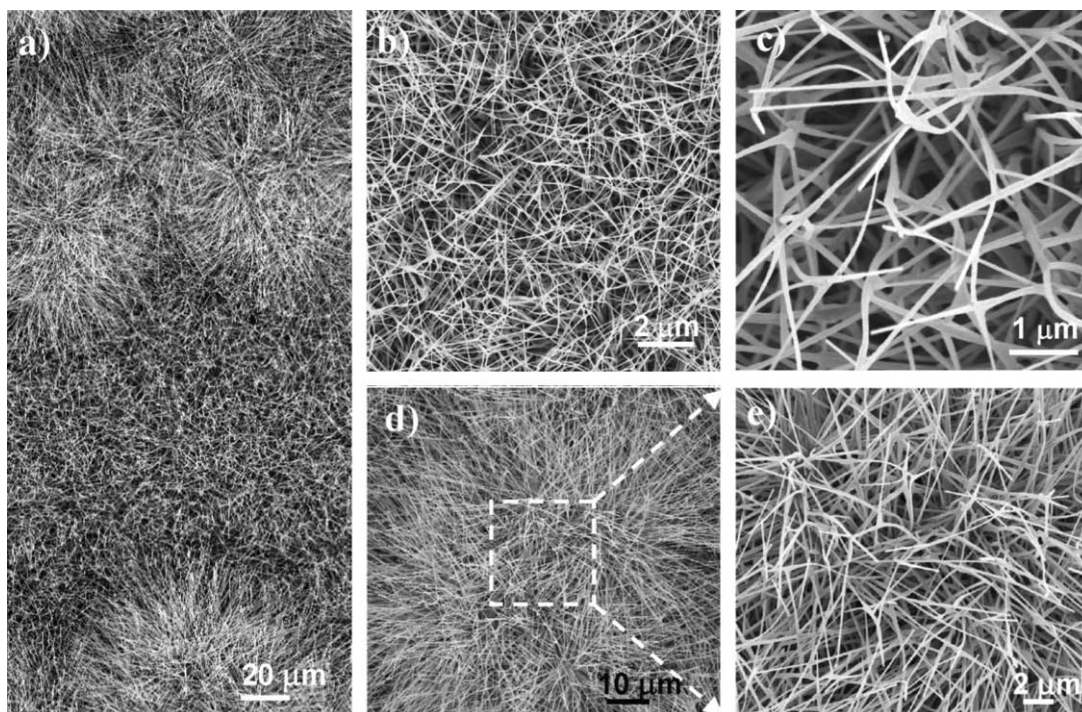


Fig. 1. (a) A typical low magnification SEM image of the as-grown networks of ZnO nanowires and nanorods consisting two types of morphologies, as indicated by area b (b,c) and c (d,e). (b,c) Enlarged SEM images of uniform networks of ZnO nanowires and nanorods. (d,e) Enlarged SEM images of clumps of nanowires showing the interconnected nanowires and nanorods.

nanorods. Two typical morphologies were found: one shown in the top of the figure is the area with distinct clumps of nanowires; the other in the middle area is a uniform layer of nanowires networks. The respectively enlarged SEM pictures of the two areas are described in Fig. 1b & c, and Fig. 1d & e. From Fig. 1b, the network feature is clearly displayed for which the mesh element is composed of nanowires with diameters around 100 nm. The further magnified picture in Fig. 1c, describes the structure of the networks with certain 3D void spaces confined by adjacent nanowires and nanorods. Fig. 1d and e depicted four clumps of radially grown

nanowires joining with each other, forming interconnected networks.

Fig. 2 shows three typical SEM images of the uniform networks of ZnO nanowires respectively, from top view (Fig. 2a), 45° tilted view (Fig. 2b), and cross section view (Fig. 2c). The top view image indicates the interconnected and periodically spaced features of the network. The tilted view picture in Fig. 2b gives a description that these interconnected nanowires and nanorods have a tendency to align along a specific direction. The cross-sectional image in Fig. 2c clearly proves that these network nanowires and nanorods are quasi-aligned normal

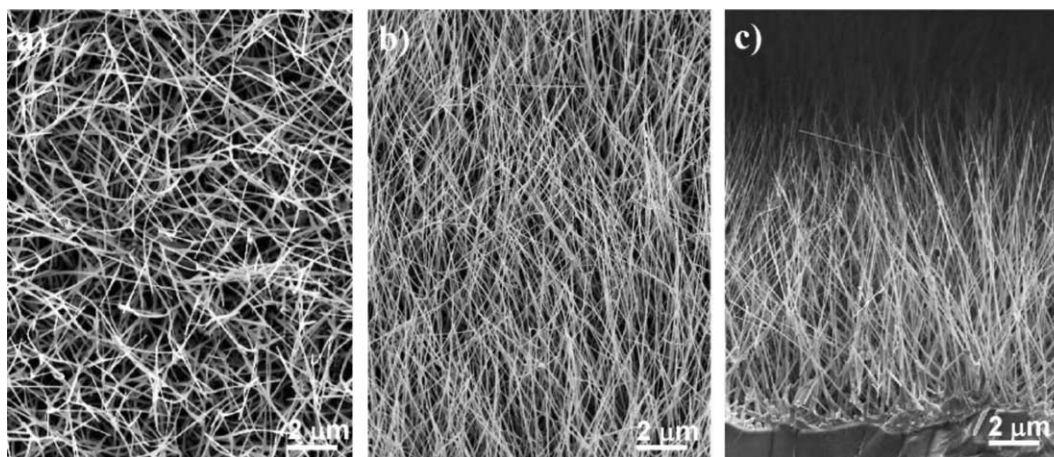


Fig. 2. Three typical SEM images of the uniform networks of ZnO nanowires: (a) viewed from top; (b) viewed at 45° tilt; and (c) cross section view.

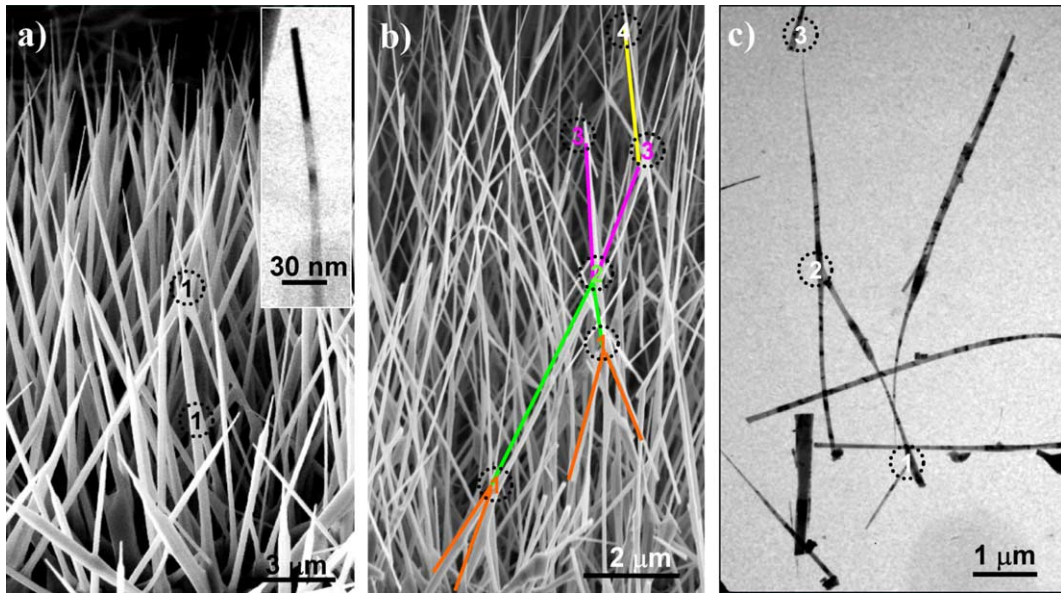


Fig. 3. A series of cross-sectional SEM and TEM images of the 3D network structures of ZnO. (a) A cross-sectional SEM image showing the beginning layer of the network. (b) A comparatively dense network cross-sectional SEM image. (c) A TEM image of a broken network, three dotted circles depicted atleast three-layer interconnected network of ZnO nanowires.

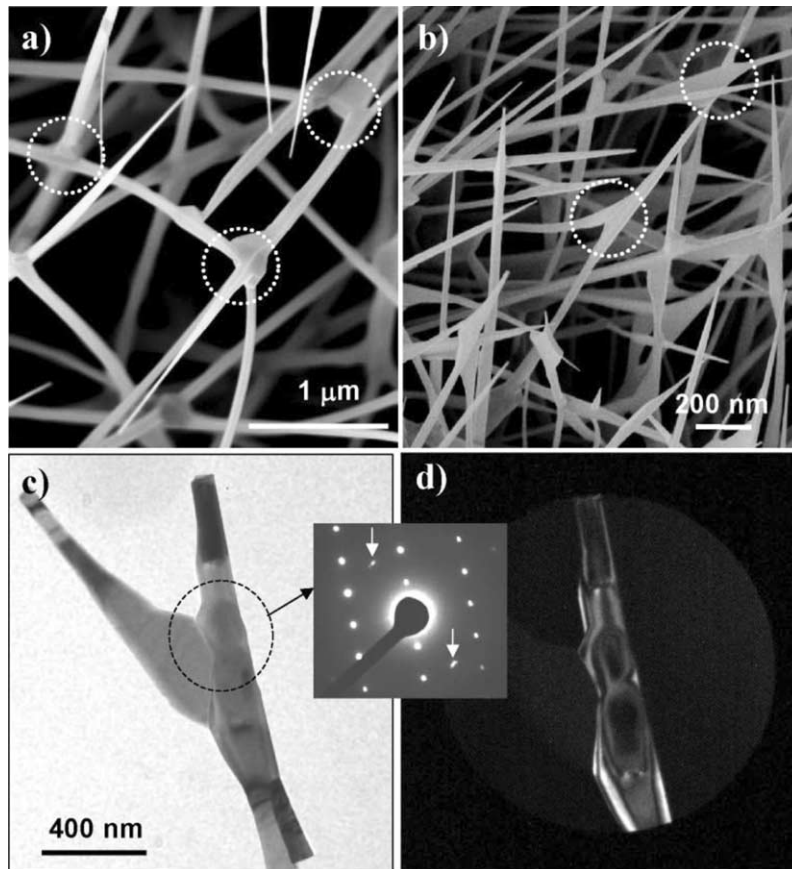


Fig. 4. (a,b) Interconnection types of ZnO nanowires in the nano-network. (c,d) Bright-field and dark-field TEM images of two nanowires interconnected with each other, indicating that the two nanowires are single crystals but they have no orientation relationship. The circle area is used for recording the selected area electron diffraction pattern (inset).

to the polycrystalline Al_2O_3 substrate with a uniform height of around 15–20 μm . In addition, Fig. 2c indicates several periodic layers of interconnected features along the height direction.

To further investigate the extent of network structure, higher magnified cross-sectional SEM and TEM images are comparatively studied. Fig. 3a is an SEM image showing the cross section at the beginning of a network. As indicated by circles, the first interconnection between the nanowires and nanorods occurs at around 5–10 μm along the length; a common sharp tips as thin as 10 nm is formed after the first merging at around 5 μm . The cross section view of a comparatively dense network is described in Fig. 3b. Along the two nanowires for about 15 μm , four orders of joining nodes were clearly identified, as indicated by dotted circles 1, 2, 3 and 4. The circle 4 represents the beginning of the fourth layer of interconnecting network of ZnO nanowires.

Then the question is how could these nanowires meet and interconnect with each other to form a network? Under SEM, it is found that two nanowires can join if their tips are close enough. As shown in Figs. 4a and

b, a joint node is formed if the two nanowires come to a cross or if one terminates at the joint point. The images appear to suggest that the joint is a ‘welding’ rather than a simple physical contact. This result has been confirmed by TEM analysis. Fig. 4c shows a bright field TEM image at the joint point of two nanowires. Electron diffraction pattern recorded from the nanowires shows that the right-hand side nanowire is single crystal and oriented along $[01\bar{1}0]$ with a growth direction of $[0001]$, while the nanowire on the left-hand side is at an arbitrary orientation whose diffraction spots are indicated by two arrowheads in the pattern. Dark-field TEM image (Fig. 4d) using one of the diffraction spot from the $[01\bar{1}0]$ oriented nanowire indicates that it has no orientation relationship with the nanowire on the left-hand side, but two of them join together with a clear grain boundary.

To track the formation process of the nanowire network, several samples were grown for different lengths of times. Fig. 5a is the initial stage of the nanowire growth, which suggests that large crystals are formed first, from which the nanowires are nucleated but with

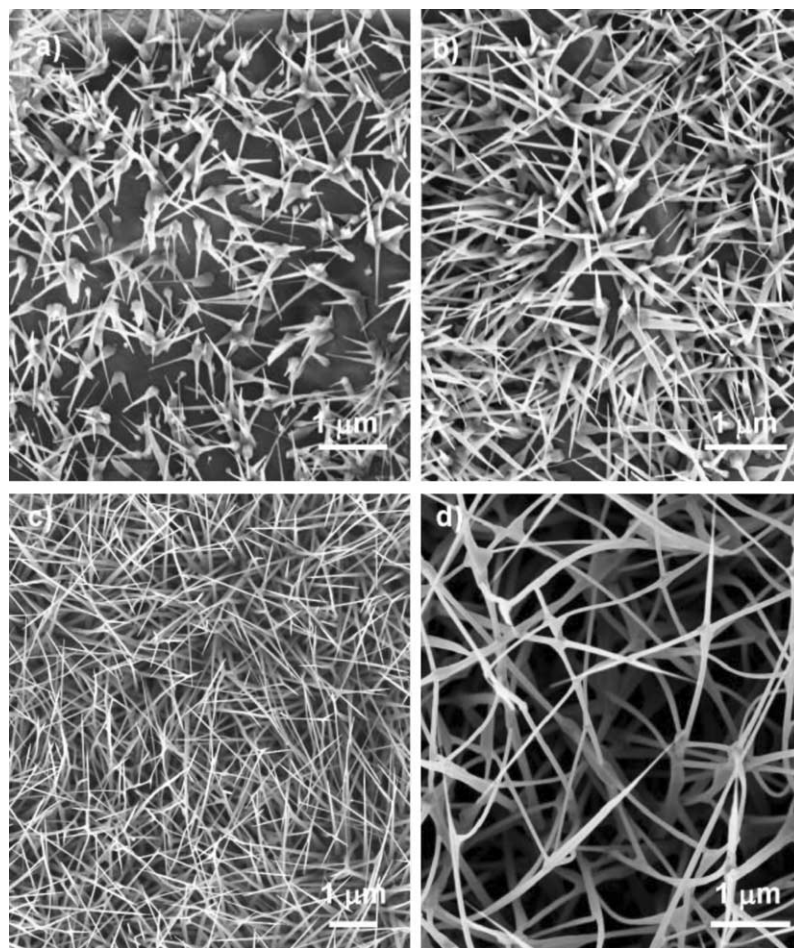


Fig. 5. Formation process of the 3D network. (a) The initial stage of interconnected nanorods growth. (b) The first layer of networking between short nanowires and nanorods. (c) The beginning of the second layer of networking. (d) Highly magnified SEM image giving a clear description about the 3D ZnO networks with mesh space around $2 \times 2 \times 2$ (μm).

a diversity of orientations. As the growth continues, the lengths of the nanowires increase, and they start to contact with each other (Fig. 5b). Under the growth temperature of 700–800 °C, sintering of nanowires is possible [18,19], forming the ‘welded’ joints among the nanowires (Fig. 5c). This is likely to be the first level of networking. The crossed nanowires continue to grow until they meet the branches of other nanowires, another welded sintering forms the second nodes of the network. Such a process continues and finally forms a 3D network of nanowires (Fig. 5d). The density of the nanowires should be high enough to increase the chances of nanowire meeting in order to make the sintering possible. The high local growth temperature of 700–800 °C at the substrate makes sintering possible for nanowires.

In summary, three-dimensional (3D) structures of interconnected ZnO nanowires and nanorods were synthesized by a high temperature solid–vapor deposition process. The nanorods and nanowires have diameters of 20–100 nm. With increasing the duration of deposition time at high temperature, the thickness of 3D networks increase, as well as the increased degree of networking. The thickness of the multilayer fish-network could be as thick as $\sim 30 \mu\text{m}$. The nanowires and nanorods row along the *c*-axis of ZnO; and the networks are formed by sintering of crossed nanowires. It is suggested that by controlling the growth parameters such as pressure, temperature and duration time, different 3D-mesh size of nano-networks could be fabricated. The quasi-aligned sharp nanowire tips, interconnecting structure characteristics, high degree of networking and high surface area of these unique nano-networks make them a potential candidate for field emission, ultra-sensitive gas sensing, catalysts and filtering.

Acknowledgments

Thanks the support from NSF, the NASA Vehicle Systems Program (URETI) and Department of Defense

Research and Engineering (DDR & 1E), and the Defense Advanced Research Projects Agency (Award No. N66001-04-1-8903).

References

- [1] Z.L. Wang (Ed.), Nanowires and Nanobelts – Materials, Properties and Devices, Metal and Semiconductor Nanowires, vol. I, Kluwer Academic Publisher, Dordrecht, 2003.
- [2] Z.L. Wang (Ed.), Nanowires and Nanobelts – Materials, Properties and Devices, Nanowires and Nanobelts of Functional Materials, vol. II, Kluwer Academic Publisher, Dordrecht, 2003.
- [3] E. Comini, G. Faglia, G. Sberveglieri, Z.W. Pan, Z.L. Wang, Appl. Phys. Lett. 81 (2002) 1869.
- [4] M.H. Huang, S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P.D. Yang, Science 292 (2001) 1897.
- [5] J.J. Wu, S.C. Liu, C.T. Wu, K.H. Chen, L.C. Chen, Appl. Phys. Lett. 81 (2002) 1312.
- [6] J. Hu, T.W. Odom, C.M. Liber, Acc. Chem. Res. 32 (1999) 435.
- [7] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, Adv. Mater. 15 (2003) 353.
- [8] X.D. Bai, P.X. Gao, Z.L. Wang, E.G. Wang, Appl. Phys. Lett. 82 (2003) 4806.
- [9] C. Yu, Q. Hao, S. Saha, L. Shi, X.Y. Kong, Z.L. Wang, Appl. Phys. Lett. 86 (2005) 063101.
- [10] S. Mao, M. Zhao, Z.L. Wang, Appl. Phys. Lett. 83 (2002) 993.
- [11] W. Hughes, Z.L. Wang, Appl. Phys. Lett. 82 (2003) 2886.
- [12] Z.L. Wang, X.Y. Kong, Y. Ding, P.X. Gao, W.L. Hughes, R. Yang, Y. Zhang, Adv. Funct. Mater. 14 (2004) 943.
- [13] P.X. Gao, Z.L. Wang, J. Phys. Chem. B 106 (2002) 12653.
- [14] P.X. Gao, Z.L. Wang, Appl. Phys. Lett. 84 (2004) 2883.
- [15] J.Y. Lao, J.G. Wen, Z.F. Ren, Nano Lett. 2 (2002) 1287.
- [16] X.Y. Kong, Z.L. Wang, Nano Lett. 3 (2003) 1625.
- [17] X.Y. Kong, Z.L. Wang, Appl. Phys. Lett. 84 (2004) 975.
- [18] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science 303 (2004) 1348.
- [19] P.X. Gao, Z.L. Wang, J. Appl. Phys. 97 (2005) 044304.
- [20] W.L. Hughes, Z.L. Wang, J. Am. Chem. Soc. 126 (2004) 6703.
- [21] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 209 (2001) 1947.