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Preparation of Free-Standing Nanowire Arrays on Conductive Substrates

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As a kind of building block for constructing nanodevices by a "bottom-up" method, nanowires hold huge promise for applications in optoelectronics, sensors, and electronic circuits.[1] Hierarchical assembly of nanowires in a controlled manner is a critical step toward accomplishing these goals.[2−5] In particular, vertically aligned nanowire arrays on a conductive substrate are expected to have high performance in solar cells and luminescent diodes because of their well-defined channels for carriers.[6−8] Though an evaporation and condensation procedure was recently employed to align ZnO nanowires vertically,[9] the insulating or semiconducting substrates (for example, Al_2O_3 or single-crystal Si) required for oriented growth greatly restrict the applications of these nanowire arrays in electrical-driven devices.

Template-assisted synthesis has been a common approach to prepare aligned nanowires.[10−16] As the nanowires grow, the nanopores of the template, typically anodized aluminum oxide (AAO), are filled. Because the nanopores, perpendicular to the AAO membrane surface, are uniform in diameter and hexagonally packed, the nanowires embedded in the template form highly ordered and vertically aligned nanowire arrays.[12] However, after the template was removed, the embedded arrays of nanowires with a high aspect ratio normally collapse into an entangled mess due to the surface tension force exerted on the nanowires during the evaporation of the liquids.[11,13−15] This makes template-assisted synthesis greatly limited when vertically aligned nanowire arrays are desired for devices. To avoid the liquid−gas interface, and thus to eliminate surface tension force during the evaporation of the liquids, supercritical drying is widely used in preparation of aerogel and highly porous silicon with a skeleton of interconnected Si nanodots and nanowires.[17−19] In this work, we make use of the supercritical drying technique to prepare noncollapsed, vertically aligned, and free-standing nanowire arrays. This new approach ensures that the nanowires in the arrays are in direct contact with the conductive substrate and provide a continuous pathway for carrier transport. Finally, we demonstrate that these vertically aligned and free-standing nanowire arrays can be feasibly used for fabricating nanowire-based electrical-driven devices.

The first step of our approach involved the electrodeposition of semiconductor CdS nanowires into the nanopores of the AAO templates decorated with a conductive Au back layer.[14] After deposition, AAO was completely removed by dissolving in 1 M NaOH aqueous solution for ~10 h, and then it was washed several times with distilled water and ethanol (during all of these steps, the sample was kept in the solution). The nanowire samples were then quickly transferred to a 0.5 L autoclave filled with ethanol. The ethanol in the pores was replaced by liquid CO_2 (T_c = 31.1 °C and P_c = 73.8 bar). After the autoclave was filled with liquid CO_2 and the residual ethanol was at or below the 10 ppm level, the temperature of the autoclave was increased to 45 °C in 2 h, reaching a pressure of about 100 bar. The samples were maintained at 100 bar and 45 °C for 3 h. Finally, CO_2 underwent a transformation from the supercritical phase to the gas phase by decreasing the pressure to atmospheric pressure at the same temperature.

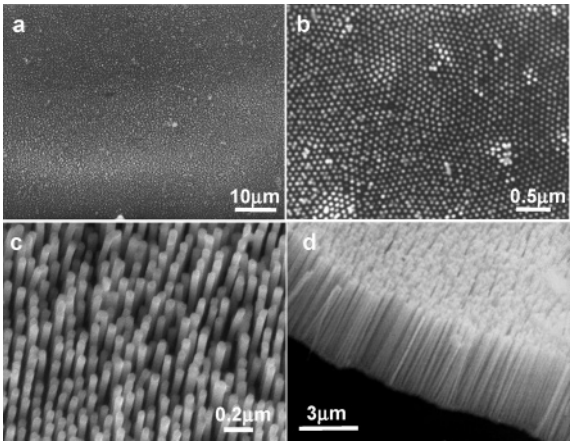

Figure 1. SEM images of the samples dried in supercritical CO_2: (a) lower magnification, (b and c) higher magnification, and (d) side view.

Scanning electron microscope (SEM) images of the samples naturally dried in air (denoted as natural drying process) showed that the nanowires bent and clustered into disordered domains after the template was removed (see Supporting Information). Normally, the nanowire arrays created by the natural drying process congregated into bundles of 1−2 μm in size and of 2−4 μm in spacing. The reason is that the nanowires, after their environmental liquids are naturally evaporated, are exposed to air, and the surface tension force exerted on each nanowire, which can be determined by the Beam Sway model,[20] leads to the congregation. It was noted during the experiments that the disorder extent of the arrays increased with the evaporation rate of the environmental liquid. In some cases, the nanowires completely detached from the Au substrate or broke into shorter pieces along their long axis. These observations are in agreement with the theoretical prediction or the earlier experimental observation for individual nanowires prepared by the natural drying process.[21] In addition, the arrangement of the nanowires after template removal also strongly depends on the nanowire diameter or aspect ratio. Data reported in the literature indicated that the nanowire arrays retain the alignment for nanowires of 200 nm in diameter,[22] but the alignment deteriorated for nanowires with small diameters.[11,23]

By using the drying process in supercritical CO_2, we successfully tamed the surface tension force in all steps, including AAO dissolution, ethanol-exchange, and phase transformation of CO_2 from liquid to supercritical and to gas state. Figure 1 displays the SEM images of the samples by the supercritical CO_2 drying process. It can be seen that large-area, noncollapsed, and vertically aligned nanowire arrays are formed. These nanowire arrays do not

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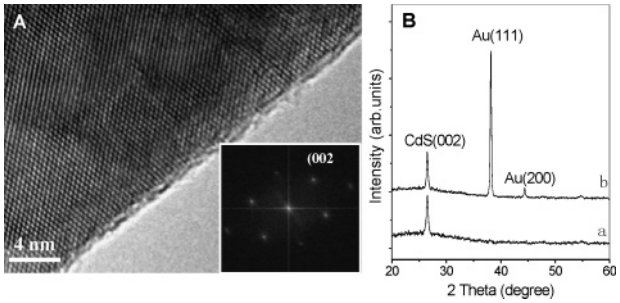

Figure 2. (A) HRTEM image of the CdS nanowire dried in supercritical CO_2. The inset in Figure 2A shows the corresponding Fourier transformation of the entire HRTEM image. (B) XRD patterns of the CdS nanowires embedded in the AAO template (curve a) and the free-standing nanowire array on the Au substrate (curve b).

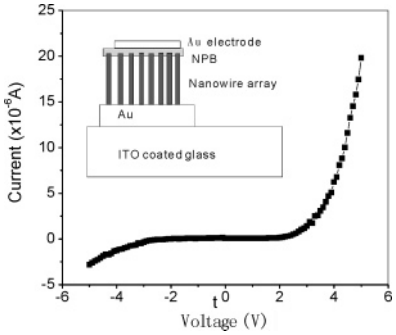

Figure 3. $I-V$ curve of an inorganic nanowire/organic NPB hybrid device. The inset shows the configuration of the device. The forward bias corresponds to a positive potential applied on the semitransparent Au electrode. The electrode area is ~1 mm^2.

aggregate, and the nanowires keep their hexagonally packed pattern after the removal of the template as if they were still embedded in the template (panels b and c of Figure 1). The side view image (Figure 1d) indicates that the AAO has been completely dissolved, and the nanowires are vertically aligned on the Au film substrate, which ensures a conductive contact between the nanowires and the substrate.

Figure 2A shows the higher-resolution transmission electron microscopy (HRTEM) image of an individual CdS nanowire, which gives a single crystalline wurtzite structure. The corresponding Fourier transformation of this HRTEM image (the inset in Figure 2A) indicates [001] as the growth direction for the nanowire. The overall crystallinity of the nanowire arrays is examined by X-ray diffraction (XRD) patterns, as shown in Figure 2B. It is found that the (002) peak of wurtzite CdS is dominant in the XRD patterns. This result confirms that, for both the nanowires embedded in the AAO template (curve a) and the free-standing nanowire array on the Au substrate by supercritical drying (curve b), the *c*-axis of the hexagonal crystal is preferentially aligned along the direction normal to the substrates.

The high performance of inorganic materials combined with the diversity of organic materials makes the inorganic−organic hybrid device attractive for optoelectronics. It was recently reported that the charge conduction channel might be crucial for the performance of hybrid devices.[24] As the first step toward elucidating the inherent charge conduction channel of the vertically aligned nanowires, we evaporated a p-type organic layer of *N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NBP) onto the vertically aligned nanowire array prepared by the supercritical drying process to form a nanowire/NBP junction. The asymmetrical $I-V$ curve displayed in Figure 3 clearly shows a rectification effect [25] of a good p−n junction, while the sample by the natural drying process only shows a normal Ohmic $I-V$ feature. The above data demonstrate that the nanowire arrays prepared by the supercritical CO_2 drying process are nearly defect-free, and the nanowires are in direct contact with the conductive substrate.

In conclusion, by combining the supercritical CO_2 drying process with AAO template-assisted electrodeposition, we have successfully developed an approach to preparing noncollapsed and free-standing nanowire arrays on a conductive Au film and demonstrated their potential use for inorganic−organic hybrid devices. For the application purpose in optoelectronics, the used material is the semiconductor CdS, but this approach can be apparently extended to prepare many materials for other applications. Significantly, this approach offers a potential technique platform for high-performance nanowire-based electrical-driven devices and might enable one bottom-up strategy for future nanotechnologies.

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Supporting Information Available: Details of the experimental methods, SEM images of the AAO template used, and the nanowires by the natural drying process. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, Y. *Adv. Mater.* **2003**, *15*, 353−389.
(2) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630−633.
(3) Melosh, N. A.; Boukai, A.; Diana, F.; Gerardot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112−115.
(4) Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255−1259.
(5) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano Lett.* **2003**, *3*, 1229−1233.
(6) Nelson, J. *Phys. Rev. B* **1999**, *59*, 15374−15380.
(7) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427.
(8) Miao, Z.; Xu, D. S.; Ouyang, J. H.; Guo, G. L.; Zhao, X. S.; Tang, Y. Q. *Nano Lett.* **2002**, *2*, 717−720.
(9) (a) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897−1899. (b) Geng, C.; Jiang, Y.; Yao, Y.; Meng, X.; Zapien, J. A.; Lee, C. S.; Lifshitz, Y.; Lee, S. T. *Adv. Funct. Mater.* **2004**, *14*, 589−594.
(10) Martin, C. R. *Science* **1994**, *266*, 1961−1966.
(11) Routkecitch, D.; Tager, A. A.; Haruyama, J.; Almawlawi, D.; Moskovirts, M.; Xu, J. M. *IEEE Trans. Electron Devices* **1996**, *43*, 1646−1658.
(12) (a)Prieto, A. L.; Sander, M. S.; Martin-Gonzalez, M. S.; Gronsky, R.; Sands, T.; Stacy, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 7160−7161. (b) Yin, A. J.; Li, J.; Jian, W.; Bennett, A. J.; Xu, J. M. *Appl. Phys. Lett.* **2001**, *79*, 1039−1041.
(13) Xu, D.; Xu, Y.; Chen, D.; Guo, G.; Gui, L.; Tang, Y. *Adv. Mater.* **2000**, *12*, 520−522.
(14) Xu, D.; Xu, Y.; Chen, D.; Guo, G.; Gui, L.; Tang, Y. *Chem. Phys. Lett.* **2000**, *325*, 340−344.
(15) Barbic, M.; Mock, J. J.; Smith, D. R.; Schultz, S. *J. Appl. Phys.* **2002**, *91*, 9341−9345.
(16) Liu, C.; Zapien, J. A.; Yao, Y.; Meng, X.; Lee, C. S.; Fan, S.; Lifshitz, Y.; Lee, S. T. *Adv. Mater.* **2003**, *15*, 838−841.
(17) Kistler, S. S. *Nature* **1931**, *127*, 741.
(18) Namatsu, H. *J. Vac. Sci. Technol., B* **2000**, *18*, 3308−3312.
(19) (a) Canham, L. T.; Cullis, A. G.; Pickering, C.; Dosser, O. D.; Cox, T. I.; Lynch, T. P. *Nature* **1994**, *368*, 133−135. (b) Xu, D.; Guo, G.; Gui, L.; Tang, Y.; Zhang, B.; Qin, G. *J. Phys. Chem. B* **1999**, *103*, 5468−5471.
(20) Tanaka, T.; Morigami, M.; Atoda, N. *Jpn. J. Appl. Phys., Part 1* **1993**, *32*, 6059−6064.
(21) (a) Quere, D.; di Meglio, J.-M.; Brochard-Wyart, F. *Science* **1990**, *249*, 1256−1260. (b) Sun, Y.; Mayers, B.; Xia, Y. *Nano Lett.* **2003**, *3*, 675−679.
(22) (a) Klein, J. D.; Herrick, R. D.; Palmer, D.; Sailor, M. J.; Brumlik, C. J.; Martin, C. R. *Chem. Mater.* **1993**, *5*, 902−904. (b) Jiang, K.; Wang, Y.; Dong, J.; Gui, L.; Tang, Y. *Langmuir* **2001**, *17*, 3635−3638.
(23) (a) Kolmakov, A.; Zhang, Y. X.; Cheng, G. S.; Moskovits, M. *Adv. Mater.* **2003**, *15*, 997−1000. (b) Gao, T.; Meng, G.; Zhang, J.; Liang, C.; Fan, J.; Zhang, L. *Appl. Phys. A* **2001**, *73*, 251−254
(24) Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800−803.
(25) Sze, S. M. *Semiconductor Devices, Physics and Technology*; Wiley: New York, 1985.

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