Fabrication of Metal Cadmium Nanowires by an Assistant Thermal Decomposition Method

Jian-wei Zhao,* Chang-hui Ye, Xiao-sheng Fang, Peng Yan, and Li-de Zhang

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences,

Hefei, Anhui 230031, P. R. China

(Received July 22, 2005; CL-050949)

Using a simple assistant thermal decomposition method, metal cadmium nanowires were large-scale fabricated from CdS powders in an argon atmosphere. Investigation results demonstrate that the Cd nanowires have lengths of several microns and diameter of about 70–150 nm.

Over the past decade, numerous efforts have been employed in controlling the sizes and shapes of inorganic nanomaterials because these parameters represent key elements that determine their electrical and optical properties.^{1,2} In particular, different morphologies, such as wire-like, rod-like, belt-like, tube-like, and scroll-like, may have different properties with unique applications.3–5 Thus, one of the most important researches on nanomaterials is to develop the techniques for the fabrication of quasi-one dimensional (1D) nanomaterials. It is well known that cadmium metal is an important material used in metal plating and coating operations. Cadmium is also used extensively in nickel–cadmium and solar batteries and in pigments. Although cadmium metal is an important material but most research about cadmium nanomaterials were focused on the cadmium chalcogenides. $6-11$ Because of the relatively low melting point, cadmium metal (melting point: 321 °C) nanostructrue is difficult to prepare by vapor process. Recently, Hu et al. have prepared singlecrystalline cadmium nanotubes by the pyrolysis of CdS powder in inert gas.¹² In our previous works, we fabricated cadmium nanosheets and a polycrystalline CdS thin layer on surface was found as the determining factor for its formation.¹³ But if this thin layer is lost at the formation process, what would be formed finally? Herein, some zinc powder was used to adsorb sulfur chemically in experiment and single crystal cadmium nanowires were fabricated. Their growth process and mechanism have also been discussed.

The apparatus used for the thermal decomposition of CdS powers is also the conventional horizontal tube furnace with a 2-cm inner-diameter alumina tube mounted inside. CdS powders (ca. 50 nm, 6 g, self-made by the direct reaction of CdCl and Na2S in aqueous solution) were placed in an alumina boat that covered with a quartz plate and then put into the center of the alumina tube. A little of zinc powders were placed in another boat and put downstream in the alumina tube (12 cm away from the source materials). The tube furnace was purged with highpurity argon for 2 h prior to heating to eliminate oxygen in the furnace. Under a constant flow of Ar (20 sccm), the furnace was rapidly heated to $1000\,^{\circ}\text{C}$ in 8 min and kept at this temperature for 40 min. After the system was cooled down to room temperature, a soft and silvery-white product was collected on the inner wall of the alumina tube at a temperature of $200-300$ °C.

The as-prepared products were characterized and analyzed by scanning electron microscopy [(SEM) JEOL JSM 6700F], X-ray diffraction $[(XRD)$ PW1710 instrument with Cu K α radiation], and transmission electron microscopy [(TEM) JEOL 2010, operated at 200 kV].

Figure 1 shows the XRD pattern of the as-prepared products. All of its peaks can be indexed to those of hexagonal-phased cadmium with lattice constants of $a = 2.963 \text{ Å}$ and $c = 5.591$ Å. It should be noted that no diffraction peaks from CdO or other impurities have been found in our samples. Different from the XRD pattern of the Cd nanosheets, the (002) peak was not sharp and strong and it suggests that Cd nanowires may have different plane of the surface. The morphology of the products was examined using SEM. A typical SEM image for cadmium nanowires is shown in Figure 2a. The image shows that the products consist of a large quantity of wire-like nanostructure with lengths in the range of several to several tens of micrometers. As shown in Figure 2b, it is a high-magnification SEM image and reveals that the wires have a diameter of about 70–150 nm.

Figure 1. XRD pattern of as prepared products.

The morphology and structure of individual Cd nanowires have been characterized in further detail using TEM and selected area electron diffraction (SAED). A representative TEM image shown in Figure 3a reveals that the produced Cd nanowires are curved and similar with the reported Cd nanotubes.10 Some linear nanowires with a diameter of about 100 nm were also found as shown in Figure 3b. The SAED pattern (Figure 3c) recorded perpendicular to the nanowire long axis could be

Figure 2. The morphology of the Cd nanowires. (a) A lowmagnification SEM image, (b) a high-magnification SEM image.

Figure 3. (a) and (b): The TEM images of the Cd nanowires, (c): the corresponding SAED pattern of Cd nanowires, (d) EDS data shows that composition of the nanowires is metal cadmium, the Cu peaks come from the TEM grid.

indexed for the $[01 - 10]$ zone axis of single crystalline Cd and suggested that the nanowires growth occurred along the $\langle 0002 \rangle$ direction. EDS attached to TEM analysis demonstrated that composition of the nanowires is cadmium metal as shown in Figure 3d. Because some zinc powder was used in experiment, the trace sulfur element is not seen in the EDS data of Cd nanowires.

The formation process of Cd nanowires involves a vapor– solid mechanism similar to the growth of Cd nanotubes reported by Hu et al.¹² and Cd nanosheets reported by Zhao et al.⁶ But different from the formation of the Cd nanosheets, the S_2 gas was generated from the decomposition of the CdS and then was adsorbed chemically by the Zn powders at high temperature before reacting with the Cd products in experiment. As a result, the polycrystalline CdS thin layer on the surface could not be formed and its restriction on the further growth along [0001] direction was lost. It is known that, from thermodynamic point of view, the (0002) surface is a high-energy plane for hexagonal crystal owing to the closed packing effect. As a result, the [0001] direction would be an optimized growth direction in vapor growth. So at low gas flow rate and relatively low vapor pressure of Cd, the crystals grow along this optimized direction and finally form the Cd nanowires. The relatively low melting point of metal cadmium, small diameters of the wires, and the equivalent growth temperature may explain the curve morphologies of the nanowires.

Through controlling the heating time, we can obtain Cd wires with different diameters. As an example, when the heating time was extended to 100 min, cadmium microwires would be formed. A typical SEM image (Figure 4a) shows that the products consist of a large quantity of wire-like structures with lengths of several hundreds of micrometers. The diameter of these wires, seen from the image of Figure 4b, was in the range

Figure 4. The morphology of the Cd microwires. (a) A lowmagnification SEM image, (b) a high-magnification SEM image.

of one to two micrometers. These microwires were the result of the continued growth of the nanowires. It should be noted that these microwires were almost linear. That may be the result of increase of the diameter and so the effect of the temperature decreased in the experiment.

In conclusion, metal cadmium wires were large-scale fabricated from CdS powders by a simple thermal decomposition method with some zinc powder used to adsorb sulfur chemically in experiment. The as-prepared Cd nano-wires have lengths of several microns and diameter of about 70–150 nm. The formation of the wires could be ascribed to the lost of restriction on the further growth along [0001] direction. These Cd wires may be used as precursors to synthesize the cadmium chalcogenides or other cadmium-related compounds nanostructures.

This work was financially supported by the National Major Project of Fundamental Research: Nanomaterials and Nanostructures (Grant No. 2005CB623603).

References

- 1 X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Liber, Nature, 409, 66 (2001).
- 2 Z. L. Wang, ''Nanowires and Nanobelts. Vols. 1 and 2,'' Kluwer, Boston (2003).
- 3 Y. Y. Wu and P. D. Yang, Chem. Mater., 12, 605 (2000).
- 4 X. F. Duan and C. M. Liber, Adv. Mater., 12, 298 (2000).
- 5 Y. W. Wang, L. D. Zhang, G. W. Meng, C. H. Liang, G. Z. Wang, and S. H. Sun, *Chem. Commun.*, **2001**, 2632.
- 6 Z. W. Pan, Z. R. Dai, and Z. L. Wang, Science, 291, 1947 (2001).
- 7 X. S. Peng, X. F. Wang, Y. W. Wang, G. Z. Wang, G. W. Meng, and L. D. Zhang, J. Phys. D, 35, L101 (2002).
- 8 C. H. Ye, G. W. Meng, Y. H. Wang, Z. Jiang, and L. D. Zhang, J. Phys. Chem. B, 106, 10338 (2002).
- 9 X. C. Jiang, B. Mayers, T. Herricks, and Y. N. Xia, Adv. Mater., 15, 1740 (2003).
- 10 J. Zhang, F. H. Jiang, and L. D. Zhang, J. Phys. Chem. B, 108, 7002 (2004).
- 11 T. Gao and T. H. Wang, J. Phys. Chem. B, 108, 20045 (2004).
- 12 P. A. Hu, Y. Q. Liu, L. Fu, L. C. Cao, and D. B. Zhu, Chem. Commun., 2004, 556.
- 13 J. Zhao, C. Ye, X. Fang, P. Yan, and L. Zhang, J. Cryst. Growth, 277, 445 (2005).