

On the Growth of CdS Nanowires by the Evaporation of CdS Nanopowders

Changhui Ye,* Guowen Meng, Yinhai Wang, Zhi Jiang, and Lide Zhang

Laboratory of Functional Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei, Anhui 230031, People's Republic of China

Received: January 30, 2002; In Final Form: June 19, 2002

This article describes for the first time the direct observation of the nucleation and growth process of CdS nanowires in a typical vapor–solid synthetic route. Thermal evaporating of CdS nanosized powders at 1173 K for various time durations corresponds to different growth stages and leads to varied product morphologies. Initially, CdS appeared as amorphous spherical particles, followed by nucleation of nanorods from cusps on the particle surface. Subsequently, nanorods developed to nanowires with matrix particles being consumed. Strategies could be optimized to grow CdS nanowires of varied diameters and lengths for a variety of applications.

1. Introduction

The discovery of carbon nanotubes and semiconductor nanowires has initiated an exploding research field in which enormous efforts have been invested because of their fundamental significance to the study of size- and dimensionality-dependent chemical and physical properties.^{1–3} CdS is a well-studied semiconductor with a direct band gap of 2.4 eV at room temperature and is extensively used for photoelectric conversion in solar cells and light-emitting diodes in flat panel displays.^{4–6} CdS nanorods/nanowires have been fabricated by several groups.^{6–9} Duan et al.⁷ produced thin CdS nanowires by laser ablation of CdS and a metal catalyst mixed target. Peng et al.⁶ Yan et al.,⁸ and Jun et al.⁹ all adopted organic surfactants in the synthesis of CdS nanowires/nanorods by a soft chemistry approach. However, there has been no report about the growth mechanism of CdS nanowires by the thermal evaporation of nanosized CdS powders. The growth mechanism could also give an important clue to improvement in the quality of the grown nanowires. Thus, more detailed and systematic experimental investigations are required.

In this paper, we have systematically investigated the growth process of CdS nanowires. Our results show that three steps are involved in the growth of CdS nanowires: growth of CdS spheroids, nucleation of short CdS nanorods, and growth of long CdS nanowires. Optimization of the heating duration is important in the nanowire synthesis.

2. Experimental Method

The apparatus used for the thermal evaporation of CdS nanopowders is a conventional horizontal tube furnace with a 2-cm inner-diameter alumina tube mounted inside. CdS nanopowders (ca. 50 nm, 5 g, self-made by the direct reaction of $\text{Cd}(\text{NO}_3)_2$ and Na_2S in aqueous solution¹⁰) were placed in an alumina boat and then put into the center of the alumina tube. A Si wafer (20 mm in length and 10 mm in width) was placed downstream in the alumina tube (10 cm away from the source material) to act as the deposition substrate for the material growth. High-purity argon was adopted as a protecting medium

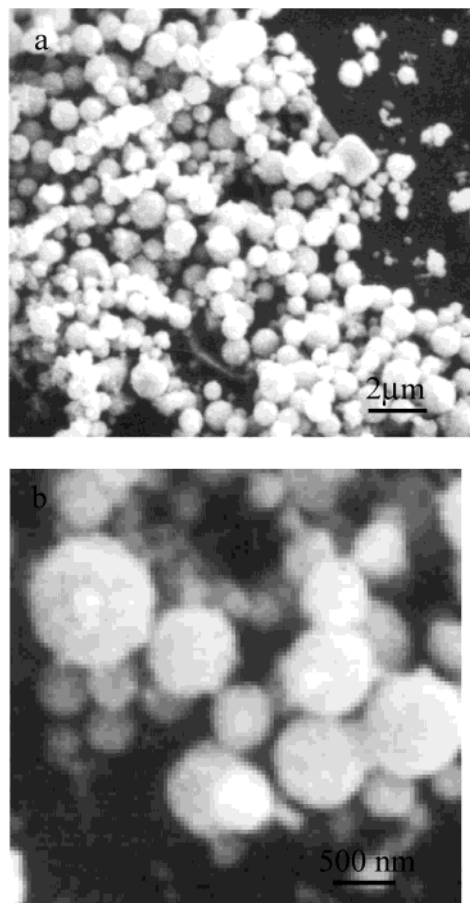


Figure 1. SEM images of the CdS amorphous particles produced in the first 15-min heating process. (a) Low-magnification view. Most of the particles are micrometer-sized spheroids, and the sizes are relatively uniform. (b) High-magnification view. The matrix particles are composed of tiny grains.

during the evaporation at a constant flow rate of 80 sccm under a pressure of 250 Torr. The furnace was heated to 1173 K in 5 min. A series of growth experiments were performed with different heating time durations of 15, 30, 45, 60, and 90 min and with other parameters essentially the same.

* Corresponding author. E-mail: chye@mail.issp.ac.cn. Tel: +86-551-5592755. Fax: +86-551-5591434.

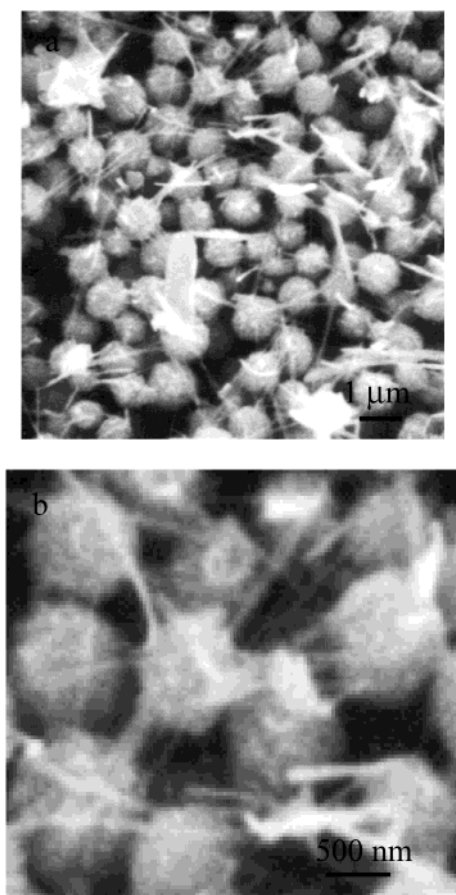


Figure 2. SEM images taken after the 30-min heating process. (a) Low-magnification view shows the nucleation of short CdS nanorods on the matrix particles. (b) High-magnification view reveals that the nanorods essentially nucleate from cusps (concaves) on the particle surface.

After evaporation, the Si wafer was removed from the alumina tube. The morphologies of the as-deposited products were examined by scanning electron microscopy (SEM) (Hitachi-X650); the microstructures were investigated by transmission electron microscopy (TEM) (JEM-200CX at 200 kV) and high-resolution electron microscopy (HREM) (JEOL-2010 at 200 kV); the crystalline state was analyzed by X-ray diffraction (XRD) (D/Max γ A using Cu K α radiation, $\lambda = 1.54178 \text{ \AA}$).

3. Experimental Results

The total heating time during the evaporation was a critical factor for the development of CdS nanostructures. Three stages were observed in the growth process.

3.1. Initial Stage (≤ 15 min): Growth of CdS Spheroids. In the first 15 min, nearly all the CdS powders are evaporated

and converted to micrometer-sized spheroids. The CdS spheroids seem to be amorphous, judging from the weak and extensive broadening of diffraction peaks in the XRD spectrum, though tiny crystallites may also nucleate in the core of the matrix particle at this stage and contribute to the broadening of the diffraction peaks. Previously, amorphous fine particles were observed largely for the typical glass-forming materials such as antimony, selenium, and gallium.^{11,12} However, CdS particles generated by thermal evaporation are generally crystalline.¹² The generation of amorphous CdS spherical particles in this work is possibly due to the rapid evaporation rate, which retards the nucleation and growth of the crystalline phase, and to spheroidization by a thermodynamic driving force. As indicated in the SEM image (Figure 1a), nearly spherical and uniform CdS particles were produced. Although the fine structure of these particles cannot be clearly resolved because of their amorphous nature, tiny hillocks appear to be embedded in the matrix particles (Figure 1b).

3.2. Second Stage (15–30 min): Nucleation of Short Nanorods. When the heating process is extended to the second stage, short nanorods will form. As noticed, no platelets were involved in the nucleation of CdS crystalline nanorods in the present work. The nucleation seems to initiate randomly on the surface of matrix particles, as shown in Figure 2a. Closer inspection reveals that the nucleation begins between fine hillocks (i.e., from cusps (concaves) on the surface of the matrix particles (Figure 2b)). This is not surprising because those sites have negative curvatures and low chemical potentials.¹³ The instability of the molecules neighboring these sites (cusps) gives them the tendency to migrate to these sites to reduce the free energy of the system and subsequently to nucleate nanorods. Kinetic barriers to migration of molecules on the surface of the matrix particles to nucleation sites would favor the growth of well-crystallized phases given that enough time is available for atom arrangement in the crystal lattice. These nanorods are completely wurtzite phase, which is in agreement with the literature (CdS nucleates as wurtzite phase when $T > 573 \text{ K}$).⁹

And more interestingly, all the nanorods grow along one single axis of the $[100]$ direction regardless of the nucleation sites they grow from. The HREM image in Figure 3 shows lattice fringes of the $(1\bar{1}0)$ plane. The selected area electron diffraction pattern is taken along the $[002]$ zone axis perpendicular to the long axis of the nanorod (inset). Although $[100]$ and $[002]$ are both favorable growth axes for CdS nanorods/nanowires,⁷ we have not observed the $[002]$ orientation in any CdS nanorods. It must be that this growth axis of $[100]$ is more favorable in the present synthesis, which needs further examination.

3.3. Final Stage (30–90 min): Growth of Nanowires. Extending the heating time elongates the nanorods and consumes matrix particles (Figure 4, examined at heating times of (a) 45,

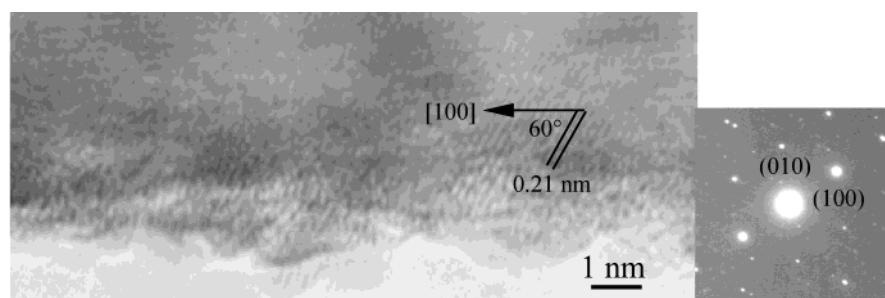


Figure 3. HREM image of a CdS nanorod. The lattice spacing of 0.21 nm corresponds to the separation between two $(1\bar{1}0)$ planes. The electron diffraction pattern was taken along the $[002]$ zone axis perpendicular to the long axis of the nanorod. The lattice image and the electron diffraction pattern indicate that the CdS nanorod grows along the $[100]$ axis.

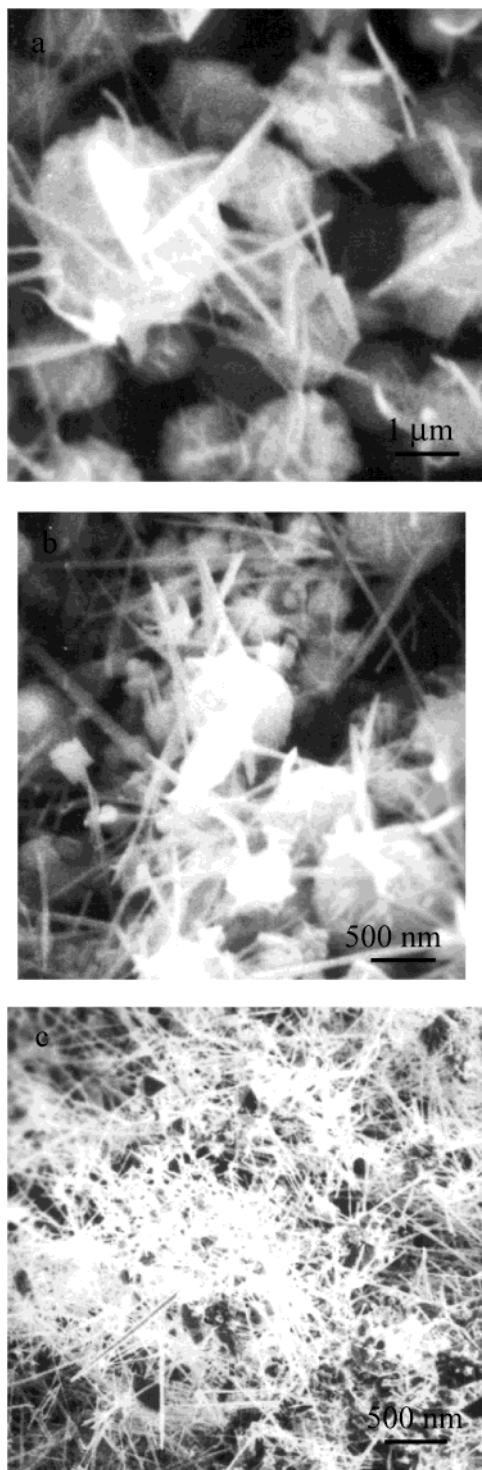


Figure 4. SEM images of CdS nanowires. Images were taken after a heating times of (a) 45 min, when the nanowires are typically several micrometers in length; (b) 60 min, when the nanowires are tens of micrometers in length; and (c) 90 min, when the nanowires are hundreds of micrometers in length. The thickness of the nanowires does not change significantly during the heating process.

(b) 60, and (c) 90 min). Typically, a 90-min heating process leads to nearly complete consumption of CdS matrix particles and generates CdS nanowires with diameters in the range of 30 to 70 nm and lengths up to hundreds of micrometers. In our experiment, neither transition metal was employed as a catalyst, and no ball of catalyst was observed on the tip of any nanorods (see Figures 2, 4 and 5a). The nature of the catalyst's free growth appears to be a vapor–solid (VS) process^{14–16} where helical

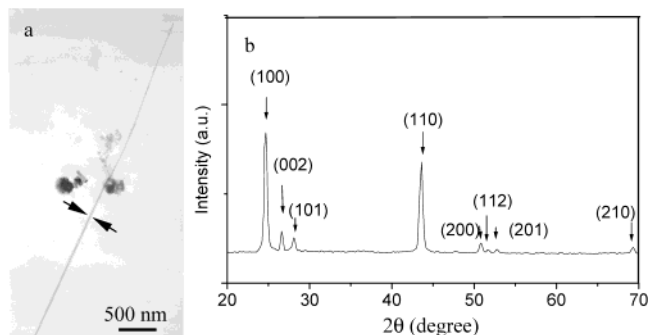


Figure 5. (a) TEM image of an ~ 40 -nm-thick CdS nanowire. The tapering tip of the nanowire without metal-particle attachment is a characteristic observation in the VS process. (b) XRD pattern of the as-grown CdS nanowires. All of the peaks can be indexed to the hexagonal phase.

dislocation was proposed to be responsible for the 1D growth, which will be discussed later. In this stage, molecular migration on the surface of matrix particles to the growth front of the nanowires is a slow process because of the increasing migration length. Considering that the temperature difference between the source material and the deposition substrate is less than 100 K, we know that CdS particles can be revaporized to build up an equilibrium partial pressure. The pressure is higher near the tips of the CdS nanowires according to the Gibbs–Thomson effect. In this context, the CdS molecules in the vapor phase will preferentially deposit on the kinks and steps present in the growth front of the nanowires, which is a typical observation for the VS growth process. We believe that kinetics rather than thermodynamics is responsible for the 1D growth of CdS nanowires.

There are several mechanisms that have been proposed to account for the growth of nanowires, including VS, VLS (vapor–liquid–solid), SLS (solution–liquid–solid), and an oxide-assisted mechanism. The VLS mechanism could be ruled out because no metal catalyst was used and no alloy particle was observed at the tips of the nanowires. The SLS mechanism is also impossible because no solution phase was used in the experiments. The growth of CdS nanowires through the oxide-assisted mechanism is less likely because the experiments were performed in an Ar atmosphere. As for the VS mechanism, it is very typical that the nanowire decreases in thickness during growth and possesses a sharp tip, which is usually accepted as an indication of the growth of nanowires via the VS mechanism. A 40-nm-thick CdS nanowire (measured near the arrow) is displayed in Figure 5a. This nanowire is not uniform along the whole length; instead, it tapers toward the growing tip. Moreover, no particle attachment is observed on the tip of this nanowire. On the basis of these reasons and experimental observations, the growth of CdS nanowires by the evaporation of nanosized CdS powders in this work via the VS mechanism is possible. However, further work to confirm the existence of helical dislocations is necessary to prove completely that the VS mechanism is responsible for the growth of CdS nanowires in the present study.

We also noticed that no phase transition occurred during the growth of the nanowires from nanorods, as revealed in the XRD pattern (Figure 5b) that CdS nanowires are in the wurtzite phase, which is the same as that of the CdS nanorods they develop from.

4. Discussion

The results described in section 3 show that, by the thermal evaporation of CdS nanopowders at 1173 K for different times

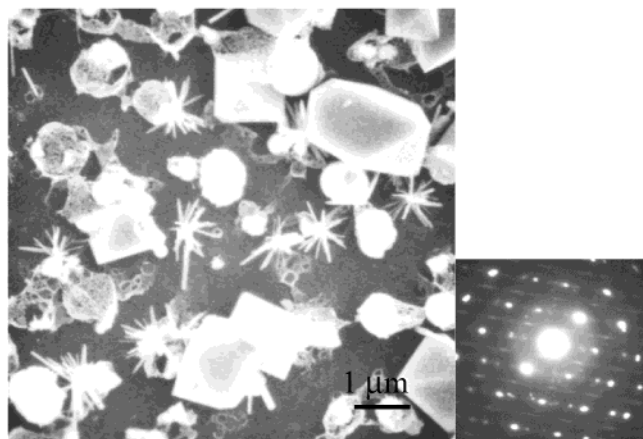


Figure 6. SEM image of the faceted CdS micrometer-sized crystals. The inset is the Fourier transform of this image.

under 250 Torr of Ar gas at a flow rate of 80 sccm, micrometer-sized amorphous CdS spheroids, short nanorods, and long nanowires can be obtained. Our extensive experiments at varied heating times (15–90 min) show that the product development was strongly related to the heating duration. With the extension of the heating process, CdS short nanorods nucleated from the cusps of matrix particles, which was then followed by the growth of long nanowires.

Nucleation of the crystalline phase out of an amorphous matrix generally initiates from near the center of the matrix, where temperature can be retained near the melting point longer than at the surface of the particle. The cusps on the surface of the matrix particles go deep into the matrix (i.e., nearer to the center of the particles than the surface of the particle does); therefore, nucleation of crystalline nanorods from the cusps inside the matrix particle is reasonable.

An account could not be taken of the growth of the CdS nanorods exclusively along the [100] axis solely on the basis of growth thermodynamics and kinetics. The growth of CdS nanorods and nanowires along the [100] axis is not favored over growth along the [002] axis in the thermodynamic sense because as for hexagonal CdS, {100} planes are energetically more stable than {001} planes. It does not fulfill the kinetics either, taking into consideration the more rapid growth rate of {001} planes compared to that of {100} planes from an energetic point of view. We assume that the confined nucleation of CdS crystalline seeds in the cusps on the surface of the CdS matrix particles induced the growth of CdS along the [100] axis.

Although only the heating process was discussed in this paper, other experimental parameters such as the heating temperature, gas flow rate, and distance between the source material and deposition substrate also have an influence on the nanostructure development. Relatively high flow rates and elevated heating temperatures promote more rapid nanostructure derivation and generally lead to thicker and longer nanowires; even platelets and large-faceted crystallites could also be generated under these conditions (Figure 6).

The growth of CdS nanowires by the evaporation of CdS nanopowders is a rather complicated process, and many issues remain open. Studies are now underway to determine the exact structure of nanorod nucleation sites and the growth kinetics for the three growth stages as well as further investigations on the formation mechanism of nanorods exclusively along the [100] axis.

5. Conclusions

CdS nanowires have been grown by the evaporation of self-made nanometer-sized CdS powders. Direct observation of the growth process of CdS nanowires indicates that the growth involves three stages: the growth of amorphous CdS particles, the nucleation of CdS nanorods, and the growth of CdS nanowires. Nanowire length depends principally on the duration of the growth cycle. This experimental mechanistic study provides explicit clues as to how CdS nanowires develop from a VS process. Finely tuning the experimental parameters will enable one to synthesize CdS nanowires with varied diameters and lengths for a variety of applications.

Acknowledgment. We thank the NSF of China (grant nos. 19974055 and 10074064) and the 973 national key project for their support of this work. Thanks are also due to Professor Weiping Cai, Professor Guanghai Li, and Dr. Guozhong Wang for valuable discussions.

References and Notes

- (1) Iijima, S. *Nature (London)* **1996**, 354, 561.
- (2) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, 32, 435.
- (3) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science (Washington, D.C.)* **1997**, 277, 1287.
- (4) McClean, I. P.; Thomas, C. B. *Semicond. Sci. Technol.* **1992**, 7, 1394.
- (5) Deshmukh, I. P.; Holikatti, S. G.; Hankare, P. P. *J. Phys. D: Appl. Phys.* **1996**, 27, 1784.
- (6) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, 119, 7019.
- (7) Duan, X.; Lieber, C. M. *Adv. Mater. (Weinheim, Ger.)* **2000**, 12, 298.
- (8) Yan, P.; Xie, Y.; Qian, Y.; Liu, X. *Chem. Commun.* **1999**, 1293.
- (9) Jun, Y.; Lee, S.; Kang, N.; Cheon, J. *J. Am. Chem. Soc.* **2001**, 123, 5150.
- (10) In a typical synthesis, 20 mL of 0.5 M Na₂S aqueous solution was added dropwise to 20 mL of 0.5 M Cd(NO₃)₂ aqueous solution under intensive stirring. Meanwhile, Ar was bubbled for 30 min. The yellow-brown precipitate was collected and cleaned thoroughly with distilled water, followed by gradually drying at room temperature. Before use, the as-prepared CdS powder was ground in a mortar and examined with XRD.
- (11) Ghosh, B.; Kothiyal, G. P. *Prog. Cryst. Growth Charact.* **1983**, 6, 393.
- (12) Kaito, C.; Saito, Y.; Fujita, K. *J. Cryst. Growth* **1989**, 94, 967.
- (13) Hooks, D. E.; Yip, C. M.; Ward, M. D. *J. Phys. Chem. B* **1998**, 102, 9958.
- (14) Pan, Z.; Dai, Z.; Wang, Z. *Science (Washington, D.C.)* **2001**, 291, 1947.
- (15) Yang, P.; Lieber, C. M. **1997**, 12, 2981.
- (16) Wu, X.; Song, W.; Zhao, B.; Sun, Y.; Du, J. *Chem. Phys. Lett.* **2001**, 349, 210.