# Low-Temperature Synthesis of Single Crystalline Ag<sub>2</sub>S Nanowires on Silver Substrates

Xiaogang Wen, Shuhua Wang, Yutao Xie, Xiao-Yuan Li, and Shihe Yang\*

Department of Chemistry, Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Received: January 8, 2005; In Final Form: March 26, 2005

We report on the successful synthesis of silver sulfide (Ag<sub>2</sub>S) nanowires by a simple and mild gas-solid reaction approach. For the nanowire synthesis, a preoxidized silver substrate is exposed to an atmosphere of an  $O_2/H_2S$  mixture at room temperature or slightly above. The resulting Ag<sub>2</sub>S nanowires are phase pure with a monoclinic crystal structure and have diameters of a few tens of nanometers and lengths up to 100  $\mu$ m. The influence of reaction conditions on the diameter, length, and morphology of the Ag<sub>2</sub>S nanowires has been studied by a number of structural and spectroscopic techniques. The nanowire growth mechanism on the Ag substrate has been discussed, which is likely characterized by continuous deposition at the tip. Additionally, we demonstrate thinning and cutting of individual Ag<sub>2</sub>S nanowires with electron beams and laser beams, which are potentially useful for nanowire manipulation and engineering.

#### Introduction

The one-dimensional (1D) nature endows nanowires unique electrical, optoelectronic, and mechanical properties with fundamental significance and practical ramifications.<sup>1-11</sup> Although several nanowire fabrication methods have been developed,<sup>12-22</sup> conventional nanowire synthesis often requires high temperature and/or various templates. We have recently found that Cu<sub>2</sub>S nanowire arrays can be grown from a copper surface by reacting with O<sub>2</sub> and H<sub>2</sub>S at low temperatures, thus avoiding the usage of templates.<sup>23,24</sup> Such a structure of nanowire array on electrode has permitted convenient measurement of the promising field electron emission properties of the Cu<sub>2</sub>S nanowire arrays.<sup>25</sup> Gold- and polypyrrole-coated Cu<sub>2</sub>S nanowire arrays have also been prepared aiming at electronic applications.<sup>26,27</sup> The facile synthesis of Cu<sub>2</sub>S nanowire arrays on Cu by the gas-solid reaction method has raised a number of important questions about the growth mechanism. For example, why does Cu<sub>2</sub>S prefer 1D growth under those conditions and how do the Cu<sub>2</sub>S nanowires grow at such low temperatures? Furthermore, can we extend this method to the synthesis of nanowires of other semiconductor compounds? It is important to address these questions so as to facilitate the generalization of the gas-solid reaction method for the synthesis of nanowire materials and the device applications of these interesting materials.

The outstanding questions mentioned above have prompted us to attempt the synthesis of Ag<sub>2</sub>S, a close fellow of Cu<sub>2</sub>S, nanowires on Ag substrates. The synthesis of Ag<sub>2</sub>S nanowires turns out to be much more difficult because of the difficulty in forming the precursor oxide phase. By varying experimental conditions, we have finally succeeded in the synthesis of Ag<sub>2</sub>S nanowires using the gas—solid reaction approach. In this paper, we present the results of the Ag<sub>2</sub>S nanowire synthesis and discuss the growth mechanism based on the experimental results. The influence of the reaction conditions on the Ag<sub>2</sub>S nanowire growth has been systematically studied. We also describe methods to tailor, reshape, and section the Ag<sub>2</sub>S nanowires by using electron beams and laser beams.



**Figure 1.** Typical SEM image of  $Ag_2S$  nanowires grown at 40 °C for 5 days. Inset: The EDX pattern in an area including many  $Ag_2S$  nanowires.

Silver sulfide is known to exist in several different allotropic forms including, e.g.,  $\alpha$ -Ag<sub>2</sub>S (achantite, monoclinic, stable up to 178 °C),  $\beta$ -Ag<sub>2</sub>S (argentite, bcc, 178–600 °C), and  $\gamma$ -Ag<sub>2</sub>S (fcc, above 600 °C). Bulk α-Ag<sub>2</sub>S is an important semiconductor with an band gap of  $\sim 1 \text{ eV}$  at room temperature and a relatively high absorption coefficient.<sup>28,29</sup> It can be used for the manufacture of optical and electrical devices such as photoconductors, photovoltaic cells, IR detectors, 30,31 solar-selective coating, 32 and photosensitive films in optoelectronical devices. Ag<sub>2</sub>S is an unusual solid ionic conductor, which operates at room temperature and conducts both electrons and ions.33 Ag<sub>2</sub>S nanoparticles have been synthesized and studied extensively,<sup>34-39</sup> and their application potential in photography<sup>37,38</sup> and luminescent devices<sup>39</sup> has been recognized. However, Ag<sub>2</sub>S nanowires seem to have been much less explored due to the lack of appropriate samples. There is a sign that this is starting to change. Very recently, Peng et al. prepared Ag<sub>2</sub>S nanowire arrays electrochemically by using anodic aluminum oxide (AAO) membrane

<sup>\*</sup> Address correspondence to this author. E-mail: chsyang@ust.hk.



Figure 2. Low-magnification TEM image (A), SAED pattern (B), and HRTEM image (C) of a single Ag<sub>2</sub>S nanowire (T = 40 °C).

as the template.<sup>40</sup> As another example, Lu et al. synthesized Ag<sub>2</sub>S nanorod arrays by a solution-growth method.<sup>41</sup> Our fabrication of Ag<sub>2</sub>S nanowires is characterized by the ambient conditions of the gas—solid reactions, the removal of the need for templates, and the high aspect ratio and good monocrystallinity of the synthesized nanowires. Moreover, there is a potential to grow uniform Ag<sub>2</sub>S nanowire arrays on silver substrates.

## **Experimental Section**

A typical synthesis is as follows. A Ag foil (Aldrich, 99%) was cleaned with a 4 M HCl aqueous solution and then deionized water in an ultrasonic bath. The cleaned Ag foil was then subjected to preoxidation. Two methods were used to oxidize the Ag foil surface. The first is simply to expose the Ag foil surface in the ambient air. The color of the Ag surface changed from shining gray to pale purple, then to yellow, and to brown black, indicating the formation of Ag<sub>2</sub>O. Because the oxidation step above is too time-consuming (up to a few months), another method was tried, which involves the electrochemical oxidation of the Ag foil. Here the Ag foil was used as a working electrode, another Ag foil was used a counter electrode, and an Ag/AgCl electrode was used as a reference electrode. The preoxidation was accomplished with a Model 600 electrochemical analyzer (CH instruments Inc. U.S.A.) by keeping the Ag foil at a constant potential ( $\sim 0.3$  V) for 5–10 min in a 0.1 M NaOH aqueous solution. Afterward, the surfaceoxidized Ag foil was taken out of the electrochemical cell, washed with deionized water, and dried in air. For the synthesis of Ag<sub>2</sub>S nanowires, the oxidized Ag foil was held on the outer wall of a test tube or a glass rod, which was then loaded into a sealed glass reactor (600 mL). The reactor was pumped to a vacuum with a rotary pump for 5 min, followed by the injection of 280 mL of H<sub>2</sub>S and 280 mL of O<sub>2</sub> (1:1) to the reactor. The reactor temperature was varied from room temperature to 40



Figure 3. XPS spectra taken from the surface with different extents of oxidation of Ag foils: (A) Ag  $3d_{5/2}$  spectra and (B) Ag MNN Auger spectra.

°C in a water bath (the reactor pressure is  $\sim 1$  atm). As the reaction progressed, a black layer was formed on the Ag foil surface. After a given reaction time, the Ag foil with the Ag<sub>2</sub>S nanowires grown on it was collected for characterization.

The structural phase of the  $Ag_2S$  nanowires was identified by powder X-ray diffraction (XRD, Philips PW-1830 X-ray diffractometer) with a 1.5405 Å Cu K $\alpha$  rotating anode point source operated at 40 kV and 40 mA. SEM images were taken with a JEOL 6300 scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDX) at an accelerating voltage of 15 kV. TEM, HRTEM, and ED analyses were conducted on Philips CM 20 and JEOL 2010 transmission electron microscopes operating at an accelerating voltage of 200 kV. For TEM characterization, the  $Ag_2S$  nanowires were transferred onto carbon-coated copper grids by gently sliding the Cu grids over the surfaces of the  $Ag_2S$  nanowire films. X-ray photoelectron spectroscopy (XPS) was performed in a Physical Electronics PHI 5600 multitechnique system with a monochromatic Al K $\alpha$  X-ray source.



**Figure 4.** SEM images of Ag<sub>2</sub>S nanostructures grown from the silver substrates (30 days) under different surface oxidation conditions (T = 25 °C). The Ag foils are oxidized in air for 2 (A), 4 (B), and 6 months (C), or oxidized by EC for ~5 s at 0.3 V (D), 5 min at 0.3 V (E), and 10 min at 0.3 V (F), respectively.

# **Results and Discussion**

A typical SEM image of the as-synthesized Ag<sub>2</sub>S nanowires (40 °C/5 days) is shown in Figure 1. It can be seen that Ag<sub>2</sub>S nanowires are abundantly produced with uniform diameters (40–150 nm) and high aspect ratios (~1000). The lengths of the nanowires are up to 100  $\mu$ m. The elemental analysis of the nanowires by EDX (inset of Figure 1) shows the significant presence of only Ag and S with an atomic ratio (Ag/S) of 2.1, which matches well with the chemical formula of Ag<sub>2</sub>S. The powder XRD pattern of the as-synthesized Ag<sub>2</sub>S nanowires recorded directly on the Ag (see Figure S1 in the Supporting Information). Except for the Ag peaks from the substrate, all

the diffraction peaks can be indexed to the monoclinic Ag<sub>2</sub>S: Achantite, a = 4.221 Å (4.229 Å); b = 6.928 Å (6.931 Å); c = 7.840 Å (7.862 Å);  $\beta = 99.61^{\circ}$  (99.61°) [the numbers in parentheses are taken from JCPDS 14-0072]. Control measurements on the Ag surface after the oxidation step but before the Ag<sub>2</sub>S nanowire growth showed a relatively smooth surface (see Figure S2 in the Supporting Information).

Figure 2A shows a low-magnification TEM image of an individual Ag<sub>2</sub>S nanowire, which is  $\sim$ 75 nm in diameter with the top end slightly thinner than the bottom end. Selected area electron diffraction (SAED) from the nanowire displays a spotted pattern (Figure 2B), indicating the monocrystallinity of

the nanowires. The SAED pattern tallies closely with the [010] zone axis of Ag<sub>2</sub>S and suggests the nanowire growth direction along the normal of (101). The HRTEM image in Figure 2C reveals clear lattice fringes, which are perpendicular to the nanowire and run through it without interruption. The fringe spacing measures 0.40 nm, which is very close to the interplanar spacing of (101) and therefore taken to corroborate the above inference of the Ag<sub>2</sub>S nanowire growth direction from the SEAD pattern. This growth direction is quite different from that of Cu<sub>2</sub>S nanowires,<sup>24</sup> which extend along the [001] direction instead of the normal of (101). Further studies are needed to clarify the different nanowire crystal growth kinetics of the two systems.

We have studied the effect of the extent of surface oxidization on the growth of Ag<sub>2</sub>S nanowires. The extent of surface oxidation was monitored by XPS. The energy was calibrated by fixing the binding energy of C 1s as 285.0 eV. The Ag  $3d_{5/2}$ peak of a clean Ag foil (Figure 3A(a)) is located at a binding energy of 368.3 eV, which is characteristic of elemental Ag. The Ag  $3d_{3/2}$  peak ( $3d_{3/2}$ : $3d_{5/2} \approx 2$ :3) was also monitored but not shown here. After being oxidized in air for 6 months, the Ag 3d<sub>5/2</sub> peak shifted down to 368.0 eV (Figure 3A(b)), indicating the formation of Ag<sub>2</sub>O on the silver surface.<sup>42</sup> XPS spectra of the Ag foils oxidized by the electrochemical method display similar binding energy downshifts (Figure 3A(c) and 3A(d)). More detailed chemical information can be extracted from the corresponding Ag MNN Auger spectra in Figure 3B. For the clean Ag foil, the Auger spectrum shows two distinctive kinetic energy peaks at 357.2 and 351.2 eV (Figure 3B(a)). Upon oxidization in air or in the electrochemical cell for 5 min, two new peaks started to develop at kinetic energies of 355.1 and 349.1 eV (Figure 3B(b) and 3B(c)), hinting at the formation of Ag<sub>2</sub>O. After being oxidized by the electrochemical method for a longer time (15 min), the two old peaks are almost completely replaced with the two new peaks, which indicates the nearly complete transformation of Ag to Ag<sub>2</sub>O on the substrate surface (Figure 3B(d)).<sup>43</sup>

Shown in Figure 4 are SEM images of Ag<sub>2</sub>S nanostructures grown on the Ag foils with different extents of oxidation. When the Ag foil is oxidized insufficiently, e.g., with oxidation in air for 2 months, only irregularly shaped but faceted Ag<sub>2</sub>S particles with an average size of submicron are formed on the surface (Figure 4A). Some of the Ag<sub>2</sub>S particles have a cone structure (about 1  $\mu$ m long, 300 nm thick at the root, and several nm at the tip, as seen in the dashed white cycle), which is perhaps the preferred site for the nanowire growth. For the Ag foil that has been oxidized in air for 4 months, sharp-tipped Ag<sub>2</sub>S nanorods  $2-3 \ \mu m$  in length emerge (Figure 4B). After the Ag foil is oxidized in air for an even longer time (6 months), we have produced copious Ag<sub>2</sub>S nanowires, which are uniform in diameter (50-300 nm) and several tens of micrometers in length (Figure 4C). Electrochemical oxidation at  $\sim 0.16 - 0.30$  V is a convenient method to shorten the time for the surface oxidization of the Ag foil. For example, with only  $\sim$ 5 s of electrochemical preoxidation at 0.30 V, the Ag<sub>2</sub>S nanowires already grow faster than those from the Ag foil preoxidized in air for 4 months (see Figure 4D; the nanowires are longer than those in Figure 4B). For even longer electrochemical oxidation times (Figure 4E, 0.3 V, 5 min; Figure 4F, 0.3 V, 10 min), the Ag<sub>2</sub>S nanowires grow much longer (10–20  $\mu$ m) after a similar reaction period with the only difference being that the nanowires in the latter case are much less straight. It can be concluded that the preoxidization of the silver surface is necessary for the growth of the Ag<sub>2</sub>S nanowires. However, overoxidation may somehow



**Figure 5.** SEM images of Ag<sub>2</sub>S nanowires synthesized by reactions at 25 °C for 30 days (A) and 40 °C for 5 days (B). Inset: TEM images of a single nanowire grown at the corresponding reaction conditions  $(O_2/H_2S = 1)$ .

impede the formation of the  $Ag_2S$  nanowires; the nanowires are less straight (Figure 4F). It follows that the  $Ag_2S$  nanowires are produced by the following reactions:<sup>44</sup>

$$Ag(s) + O_2(g) = Ag_2O(s) \qquad \Delta G = -11.2 \text{ kJ/mol}$$

$$Ag_2O(s) + H_2S(g) = Ag_2S(s) + H_2O(l)$$

$$\Delta G = -233.2 \text{ kJ/mol}$$

A

Clearly, the oxidation step is critical to the Ag<sub>2</sub>S nanowire growth given that the formation of Ag<sub>2</sub>O is not very thermodynamically favorable. This is in marked contrast to the reactions involved in the Cu<sub>2</sub>S nanowire growth process:<sup>44</sup>

$$Cu(s) + O_2(g) = Cu_2O(s) \qquad \Delta G = -146.0 \text{ kJ/mol}$$

$$Cu_2O(s) + H_2S(g) = Cu_2S(s) + H_2O(l)$$

$$\Delta G = -143.9 \text{ kJ/mol}$$

Here the oxidation step is much more facile simply on thermodynamic grounds. This explains why  $Cu_2S$  nanowires are more easily synthesized than the  $Ag_2S$  nanowires by the gas—solid reactions, and in fact, the  $Cu_2S$  nanowires can be grown into uniform arrays. It is believed that by varying the reaction conditions favoring the oxidation step, uniform  $Ag_2S$  nanowire



**Figure 6.** Low-magnification TEM image of a single  $Ag_2S$  nanowire before (A) and after (B) electron beam irradiation (200 kV) for 2 h. (C and D) The corresponding ED pattern and HRTEM image of the nanowire in part B (etched part enclosed by the ellipsoid).

arrays of  $Ag_2S$  can also be prepared. This work is underway in our laboratory.

The SEM images in Figure 5 show the effect of reaction temperature on the growth of Ag<sub>2</sub>S nanowires. The silver foils used for the Ag<sub>2</sub>S nanowire growth were preoxidized under the same electrochemical conditions (at 0.3 V for 5 min; the standard potential of  $Ag_2O/Ag$  is 0.342 V<sup>44</sup>). It is apparent that the Ag<sub>2</sub>S nanowire growth is more efficient (both in abundance and lengths of the nanowires) at 40 °C (Figure 5B) than at room temperature (Figure 5A). Notice that the reaction time in Figure 5A is 30 days whereas the reaction in Figure 5B has lasted for only 5 days. Moreover, the nanowire morphology is also different at the two different growth temperatures. At room temperature, the nanowires are grown slowly (only  $\sim 10 \ \mu m$ long after reaction for 30 days) with a sharp tip (inset of Figure 5A). At 40 °C, however, the nanowire growth is much faster (several tens of micrometers long after reaction for only 5 days) and the nanowires are more like a cable with uniform diameters along the growth direction (see inset of Figure 5B).

Our method for the growth of Ag<sub>2</sub>S nanowires is characterized by the gas–solid reaction at low temperatures. The nanowires synthesized by gas–solid reaction are often accompanied by a sharp tip.<sup>23,24,45,46</sup> In the nanowire growth process of gas–solid reaction, the solid metal serve sas both a feeding material and a supporting substrate. The gas phase reagent diffuses to the oxidized metal surface and reacts at appropriate conditions. After the formation of a nanoparticle seed, a preferential growth direction may develop as an entry to the formation of 1D nanostructures. The active site for the nanowire growth is likely to be at the tip. As such, the diameter and morphology of the nanowires are mainly controlled by two factors. One is the growth rate along the wire direction relative to those of other directions. The other factor is perhaps the diffusion rate of Ag atoms from the substrate to the nanowire growth site, from which the nanowire propagates. Because the atomic diffusion of Ag in the growing nanowire is expected to be slow at low temperature, the Ag atom supply becomes shorter and shorter to sustain the uniform nanowire growth as the nanowire gets longer and longer and this would result in the formation of a nanocone structure with a sharp tip as observed in Figure 4A. As the temperature is increased, however, the atomic diffusion rate of Ag increases, which provides a sufficient amount of Ag at the nanowire tip for the growth. As a result, the individual nanowire (Figure 5B) diameters are more uniform with relatively blunt tips. When the atomic diffusion of Ag is fast enough



**Figure 7.** Typical optical microscope images of  $Ag_2S$  nanowires. (A) Overview of the  $Ag_2S$  nanowires. (B and D) A single  $Ag_2S$  nanowire before the laser irradiation (782 nm, 0.10 mW). (C and E) A single  $Ag_2S$  nanowire after the laser irradiation.

compared to the nanowire growth rate, the nanowire diameters are expected to be uniform from the root to the top (Figure 1).

An interesting phenomenon we observed is that the Ag<sub>2</sub>S nanowires are more unstable than nanowires of other semiconductor materials, such as ZnO, under high energy electron beam radiation. We irradiated a single Ag<sub>2</sub>S nanowire with an electron beam in the TEM machine at relatively high magnification conditions. Figure 6B shows the TEM image from the same nanowire shown in Figure 6A after being irradiated with the electron beam (200 kV) for 2 h. Clearly, at the position irradiated by the electron beam (in the white circle), the diameter of the nanonanowire decreases from 75 to 50 nm. This suggests that the Ag<sub>2</sub>S nanowires is easily etched away by high energy electrons. Moreover, the crystal structure of the nanowire is preserved. This is shown in the corresponding ED (Figure 6C) and HRTEM (Figure 6D): the  $Ag_2S$  nanowire after electron beam induced thinning keeps the same monoclinic crystal structure and the length direction normal to the (101) plane. We also tried to cut the Ag<sub>2</sub>S nanowires using a laser beam, which is easier to operate than the high-energy electron beam because there is no need for a vacuum. For this, a diode laser (782 nm, 0.10 mW) with a beam spot of 3  $\mu$ m was used. The images were recorded by a CCD through a 50× ultra-long working distance objective. Presumably due to the light scattering effect when excited with white light, we could observe the Ag<sub>2</sub>S nanowires clearly (in a slightly red color) under an optical microscope though the nanowire is only several tens of a nanometer in diameter. Figure 7A shows a typical OM image of the Ag<sub>2</sub>S nanowires on the substrate. For the facility of observation, we select a single nanowire to process the cutting experiment. Figure 7B,C and Figure 7D,E show optical images of two single Ag<sub>2</sub>S nanowires before and after being cut by the laser. For the first nanowire, both broken parts can be seen (Figure 7C), whereas only the left part can be seen for the second after cutting (Figure 7E); the other piece may have fallen out of focus and disappeared from view. It is clear that the nanowires could be cut very easily when we focus the laser spot on the nanowires with the help of the crosshairs shown in the images. The whole laser radiation time was only about 1 s. The success rate of the cutting was 100% and  $\sim$ 15 nanowires were cut in this way in our experiment. The facile thinning and cutting of Ag<sub>2</sub>S nanowires by electron beam and laser suggest that the methods may find use in the fabrication of future nanoscale devices. Clearly, understanding the atomistic details of these processes under more controlled conditions is necessary to facilitate the applications of the radiation-sensitive nanowires.

### Conclusion

We have succeeded in synthesizing Ag<sub>2</sub>S nanowires 40-150 nm in diameter and several tens of micrometers in length by a gas-solid reaction method on silver substrates. Reaction conditions including surface oxidation of the Ag substrate and reaction temperature have been investigated. The Ag<sub>2</sub>S nanowires are found to grow along the normal of (101) instead of [001] as with Cu<sub>2</sub>S nanowires. The normal of (101) is believed to be the fastest growing crystal direction for Ag<sub>2</sub>S under our experimental conditions. The morphology and size of the nanowires grown by the gas-solid reaction method are determined mainly by the competition of the growth rate and the atomic diffusion rate. On the basis of these studies, a possible nanowire tip growth mechanism has been discussed. In addition, we have demonstrated methods for the nanoscale tailoring of individual Ag<sub>2</sub>S nanowires. Specifically, by using a high-energy electron beam and a laser beam, individual Ag<sub>2</sub>S nanowires could be thinned out and cut, respectively. In conclusion, the current work extends the gas-solid reaction method to the synthesis of Ag<sub>2</sub>S nanowires under mild conditions and demonstrates simple nanoengineering methods for the thinning and cutting of the individual nanowires. This is an important step toward the development of fabrication methods for nanoscale devices.

Acknowledgment. We are grateful to the Research Grant Council of Hong Kong and the Chemistry Department of the Hong Kong University of Science and Technology for supporting the research. S.Y. wishes to thank the Hong Kong Young Scholar Cooperation Research Foundation of NSFC.

**Supporting Information Available:** Figures showing the XRD pattern of the as-prepared Ag<sub>2</sub>S nanowires on an Ag substrate and SEM image and XRD pattern of the oxidized Ag foils before the growth of Ag<sub>2</sub>S nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.

## **References and Notes**

(1) Cui, Y.; Wei, Q. Q.; Park, H. K.; Lieber, C. M. Science 2001, 293, 1289.

(2) Ghosh, S.; Sood, A. K.; Kumar, N. Science 2003, 299, 1042.

(3) Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. Science 2001, 293, 2227.

(4) Lauhon, L. J.; Gudiksen, M. S.; Wang, D. L.; Lieber, C. M. Nature 2002, 420, 57.

- (5) Huang, Y.; Duan, X. F.; Cui, Y.; Lauhon, L. J.; Kim, K. H.; Lieber, C. M. Science 2001, 294, 1313.
- (6) Zhong, Z. H.; Qian, F.; Wang, D. L.; Lieber, C. M. Nano Lett. **2003**, *3*, 343.
- (7) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. Nature 1998, 391, 775.
- (8) Wang, J. F.; Gudiksen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. Science 2001, 293, 1455.
- (9) Tang, Z. Y.; Kotov, N. A.; Giersig, M. Science 2002, 297, 237. (10) Huang, M. H.; Mao. S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind,
- H.; Weber, E.; Russo, R.; Yang, P. D. Science 2001, 292, 1897.
- (11) Duan, X. F.; Huang, Y.; Agarwal, R.; Lieber, C. M. Nature 2003, 421, 241.
- (12) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. Science 2001, 291, 1947.
- (13) Gates, B.; Wu, Y. Y.; Yin, Y. D.; Yang, P. D.; Xia, Y. N. J. Am. Chem. Soc. 2001, 123, 11500.
  - (14) Sun, Y. G.; Xia, Y. N. Adv. Mater. 2002, 14, 833.
- (15) Shi, W. S.; Zheng, Y. F.; Wang, N.; Lee, C. S.; Lee, S. T. Adv. Mater. 2001, 13, 591.
- (16) Zhan, J. H.; Yang, X. G.; Wang, D. W.; Li, S. D.; Xie, Y.; Xia, Y. N.; Qian, Y. T. Adv. Mater. 2000, 12, 1348.
- (17) Goldberger, J.; He, R. R.; Zhang, Y. F.; Lee, S. K.; Yan, H. Q.; Choi, H. J.; Yang, P. D. Nature 2003, 422, 599.
- (18) Reches, M.; Gazit, E. Science 2003, 300, 625.
- (19) Hong, B. H.; Bae, S. C.; Lee, C. W.; Jeong, S.; Kim, K. S. Science 2001, 294, 348.
  - (20) Barsoum, M. W.; Farber, L. Science 1999, 284, 937.
- (21) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. Science 1995, 270, 1791.
  - (22) Martin, C. R. Science 1994, 266, 1961.
  - (23) Wang, S. H.; Yang, S. H. Chem. Phys. Lett. 2000, 322, 567.

  - (24) Wang, S. H.; Yang, S. H. Chem. Mater. 2001, 13, 4794.
    (25) Chen, J.; Deng, S. Z.; Xu, N. S.; Wang, S. H.; Wen, X. G.; Yang,
- S. H.; Yang, C. L.; Wang, J. N.; Ge, W. K. Appl. Phys. Lett. 2002, 80, 3620.

- (26) Wen, X. G.; Yang, S. H. Nano Lett. 2002, 2, 451.
- (27) Zhang, W. X.; Wen, X. G.; Yang, S. H. Langmuir 2003, 19, 4420. (28) Numerical Data and Functional Relationships in Science and Technology, Group 3, Crystal and Solid State Physics, 17e, Semiconduc-
- tors: Physics of Non-Tetrahedrally Bonded Elements and Binary Com-
- pounds I; Madelung, O., Ed.; Springer-Verlag: Berlin, 1983; p 157. (29) Dlala, H.; Almouk, M.; Belgacem, S.; Girard, P.; Barjon, D. Eur.
- Phys. J. A 1998, 2, 13.
- (30) Kitova, S.; Eneva, J.; Panov, A.; Haefke, H. J. Imaging Sci. Technol. 1994, 38, 484.
  - (31) Hodes, G.; Manasen, J.; Cahen, D. Nature 1976, 261, 403.
  - (32) Abass, A. K. Solar Energy Mater. 1988, 17, 375.
- (33) Terabe, K.; Hasegawa, T.; Nakayama, T.; Aono, M. Nature 2005, 433, 47.
- (34) Zhang, W. X.; Zhang, L.; Hui, Z. H.; Zhang, X. M.; Qiang, Y. T. Solid State Ionics 2000, 130, 111.
- (35) Armelao, L.; Bertoncello, R.; Cattaruzza, E.; Gialanella, S.; Gross, S.; Mattei, G.; Mazzoldi, P.; Tondello, E. J. Mater. Chem. 2002, 12, 2401.
- (36) Armelao, L.; Colombo, P.; Fabrizio, M.; Gross, S.; Tondello, E. J. Mater. Chem. 1999, 9, 2893.
  - (37) Mitchell, J. W. J. Imaging Sci. Technol. 1998, 42, 215.
  - (38) Baetzold, R. C. J. Imaging Sci. Technol. 1999, 43, 375.
- (39) Bruhwiler, D.; Leiggener, C.; Glaus, S.; Calzaferri, G. J. Phys. Chem. B 2002, 106, 3770.
- (40) Peng, X. S.; Meng, G. W.; Zhang, J.; Wang, X. F.; Zhao, L. X.; Wang, Y. W.; Zhang, L. D. *Mater. Res. Bull.* **2002**, *37*, 1369.
- (41) Lu Q. Y.; Gao, F.; Zhao, D. Y. Angew. Chem., Int. Ed. 2002, 41, 1932
- (42) Waterhouse, G. I. N.; Bowmaker, G. A.; Metson, J. B. Appl. Surf. Sci. 2001, 183, 191.
- (43) Handbook of X-ray Photoelectron Spectroscopy; Chastain, J., Ed.; Perkin-Elmer Corporation, Physical Electronics Division, USA, 1992; p 207.
- (44) Handbook of Chemistry and Physics, 77th ed.; Lide, D. R., Editorin-Chief; CRC Press: New York, 1996-1997; p 5-4.
- (45) Suzuki, H.; Fukuzawa, N.; Tanigaki, T.; Sato, T.; Kido, O.; Kimura, Y.; Kaito, C. J. Cryst. Growth 2002, 244, 168.
- (46) Jiang, X. C.; Herricks, T.; Xia, Y. N. Nano Lett. 2002, 2, 1333.