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Synthesis of CdS nanowires by sulfurization

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Abstract

Semiconductor CdS nanowires have been fabricated by sulfurizing metal Cd that was electrodeposited in the nanochannels of porous anodic alumina template. The obtained CdS nanowires have been characterized using X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray energy dispersion analysis (EDAX), respectively. Investigation results demonstrate that large-scale polycrystalline CdS nanowires with hexagonal phase structure have been produced, having uniform diameters of about 50 nm and lengths up to tens of microns.

Keywords: CdS; Nanowires; Sulfurization; Template synthesis

1. Introduction

Recently, the investigations of ordered semiconductor nanostructures have attracted considerable attention owing to their novel physical properties and the potential applications in nanodevices [1–3]. As one of the most important II–VI group semiconductors, CdS plays an important role in nonlinear optical materials [4,5] and electroluminescent devices [6,7]. Great efforts have been carried out to fabricate the CdS nanowires and/or nanorods with fine crystalline structure, such as non-aqueous synthesis [8], electrochemical deposition (ECD) [9,10], surfactant-assisted synthesis [11], and laser-assisted catalytic growth (LCG) [12].

Synthesis of semiconductor CdS nanowires by using different approaches is important, not only for the studies of that material, but also for the development of material science and engineering. Although varieties of fabrication methods have been used to synthesize CdS nanowires and/or nanorods, it is also of interest to fabricate semiconductor CdS nanowires by using techniques different from those approaches mentioned above.

For such purpose, we report herein a new synthesis method for semiconductor CdS nanowires. Briefly, pure metal Cd is electrodeposited in the nanochannels of the PAA template, and then the obtained Cd nanowires are sulfurized in the S atmosphere to form CdS nanowires.

2. Experimental procedure

The PAA template used in this work were prepared via a two-step aluminum anodic oxidation process in a

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0.3 M oxalic acid solution, which was similar to that described previously [13–16]. The channel diameters and lengths of the through-hole PAA template were about 50 nm and 30 μm, respectively. A thin gold layer was evaporated onto one side of the PAA template and served as a working electrode in the subsequent ECD process of metal Cd nanowires.

A conventional three-electrode aqueous bath containing the mixture solutions of 0.2 M $CdCl_2$ and 0.1 M H_3BO_3 was used to electrodeposit the metal Cd nanowires. The deposition potentials were controlled in the range of -0.68 to -0.7 V saturated calomel electrode (SCE) for 20–30 min at room temperature. After ECD, the sample surface was polished by using a 50-nm SiC polishing sandpaper to get rid of the Cd particles that grown excessively and stuck to the surface.

After washing with deionized water and drying in air, the PAA template with Cd nanowires was put into a quartz boat and covered with a layer of pure S powder. The quartz boat was placed into the hot zone of a recrystallized alumina tube furnace. The reaction chamber was evacuated by using a mechanical pump, and then it was backfilled with high purity Ar gas (0.1 M Pa). After that, the samples were heated up to 300 °C within 30 min from room temperature and maintained at this temperature for 30 h to sulfurize the Cd nanowires completely. It is expected that S atoms would react with the metal Cd to form CdS. After the sulfurization process, the PAA template with CdS nanowires was cleaned with CS_2 to remove the remaining S powder, then washed with ethanol and deionized water in turn, and dried in air before characterization.

The phase structures of the CdS nanowires were investigated by X-ray powder diffraction (XRD, D/MaxrA). For comparison, the as-prepared metal Cd nanowires within the nanochannels of the PAA template and the blank PAA template heated at 300 °C for 30 h were also characterized. The morphology of the prepared CdS nanowires was observed by using scanning electron microscope (SEM, JEOL JSM-6300) and transmission electron microscope (TEM, JEM-200CX). Selected area electron diffraction (SAED) and X-ray energy dispersion analysis (EDAX, Kevex Super 8000 analyzer) technique that equipped on the TEM were used to characterize the crystalline structures and stoichiometry of CdS nanowires.

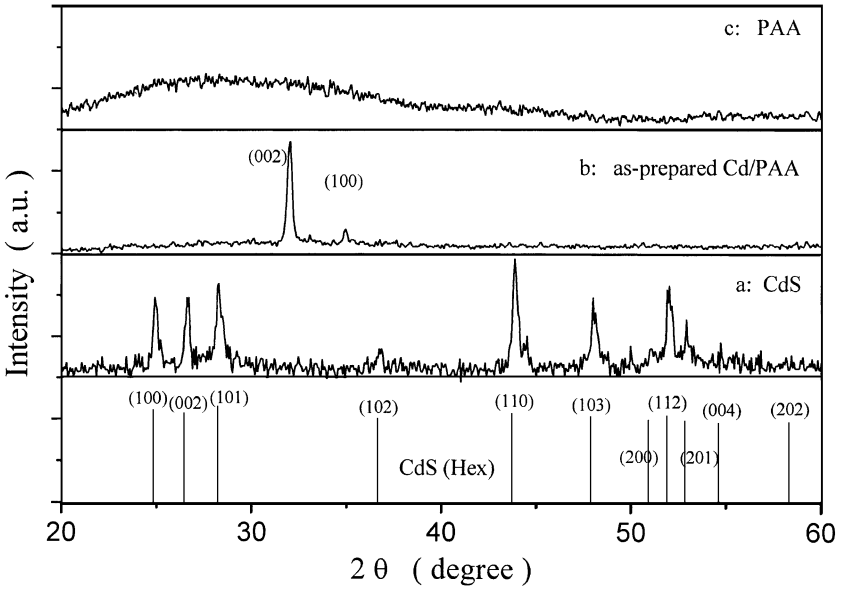

Fig. 1. XRD spectra of the CdS nanowires within PAA template (a), the as-prepared Cd nanowires within PAA template (b), and the blank PAA template after being heated at 300 °C for 30 h (c). Included are also the corresponding line spectra of the bulk hexagonal structures of CdS provided by the JCPDS (06-0314).

3. Results and discussions

Fig. 1 shows the X-ray powder diffraction spectra of the as-prepared metal Cd nanowires within PAA template, the blank PAA template heated at 300 °C for 30 h, and the CdS nanowires embedded in the PAA template after 30 h sulfurization. It can be seen that there are no peaks of CdS before the metal Cd nanowires being sulfurated. Furthermore, the Cd peaks totally disappear after sulfuration and the CdS peaks appeared. All the intense XRD peaks of the prepared CdS nanowires are consistent with the same positions as the polycrystalline hexagonal structural CdS standard, indicating that CdS nanowires with hexagonal phase structure are fabricated.

Metal oxides such as ZnO nanowires have been prepared by oxidation of metal Zn nanowires [16], and it is generally accepted that the chemical properties of oxygen and sulfur are similar with each other. Hence, the technique used here for formation of CdS is understandable. The growth of CdS nanowires could be shown as follows:

$$S + Cd(\text{nanowires}) \Rightarrow CdS(\text{nanowires}) \quad (1)$$

in which S atoms would react with metal Cd atoms at high temperatures to form CdS nanowires. Since the reaction rates of S and Cd atoms are mainly dominated by temperature, high temperatures and long periods of the sulfurization process were needed to prepare the fine crystalline CdS nanowires.

The morphology and structure of CdS nanowires were characterized by SEM and TEM techniques, in which the PAA template was partly and totally dissolved by using 5% NaOH solution, respectively. A typical SEM micrograph (Fig. 2) reveals that large scales of CdS nanowires have been synthesized. High magnification TEM image (Fig. 3) shows that single CdS nanowires are smooth and uniform with a diameter of about 50 nm. The length of CdS nanowires is up to tens of microns. The crystalline structure of CdS nanowires was characterized by electron diffraction and shown in the inset of Fig. 3. Most of CdS nanowires appear to be polycrystalline, the diffraction rings in the SAED pattern corresponding to (100), (101), (110), and (112) crystal plane of the hexagonal structural CdS are clearly seen. Additionally, the stoichiometry of the single CdS nanowire was characterized using X-ray energy dispersion analysis (EDAX) technique. The EDAX spectrum shown in Fig. 4 reveals that the nanowires are composed of S and Cd, and quantitative analysis indicates that the atomic ratio of S

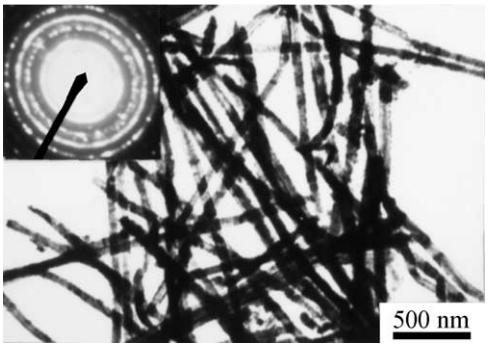

Fig. 3. TEM image of CdS nanowires. Inset shows the SAED patterns of the CdS nanowires.

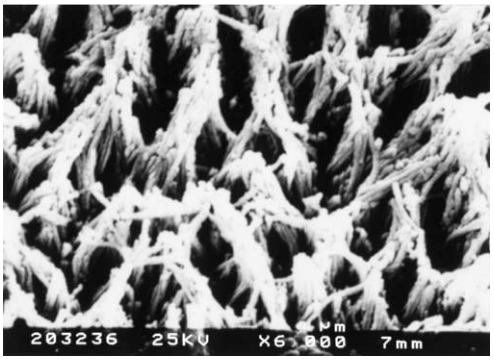

Fig. 2. SEM image of the CdS nanowires.

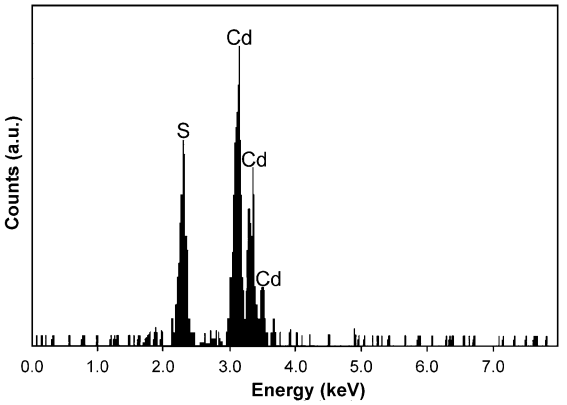

Fig. 4. EDAX spectrum of the CdS nanowires.

and Cd is 1:1, demonstrating that CdS nanowires are obtained [10].

Additionally, template synthesis has been proven to be a versatile and simple method for preparation of one-dimensional nanostructures [17,18]. Furthermore, PAA membranes, having ordered nanochannel arrays and controllable geometrical characteristics, have been widely investigated [13–16]. Hence, by choosing a suitable PAA template, CdS nanowires with different geometrical characteristics, high packing density, and high aspect ratios would be obtained by using the technique presented here. However, it should be pointed out that some complex questions remain for the synthesis approach presented in this work. For example, the obtained CdS nanowires are always polycrystalline. Further work, therefore, is necessary for the fabrication of single crystalline CdS nanowires by sulfurization process.

4. Conclusions

Polycrystalline CdS nanowires have been synthesized by electrodepositing the pure metal Cd in the nanochannels of the PAA template, and then sulfurizing the obtained Cd nanowires in S atmosphere at 300 °C for 30 h. The results show that CdS nanowires have high wire packing densities with uniform wire diameters and lengths of about 50 nm and tens of microns, respectively. This approach could be extended to form other sulfide semiconductor nanowires, such as ZnS, SnS, and PbS.

Acknowledgements

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