Synthesis and Characterization of Tin Disulfide (SnS₂) Nanowires

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Abstract The ordered tin disulfide (SnS₂) nanowire arrays were first fabricated by sulfurizing the Sn nanowires, which are embedded in the nanochannels of anodic aluminum oxide (AAO) template. SnS₂ nanowire arrays are highly ordered and highly dense. X-ray diffraction (XRD) and corresponding selected area electron diffraction (SAED) patterns demonstrate the SnS₂ nanowire is hexagonal polycrystalline. The study of UV/Visible/NIR absorption shows the SnS₂ nanowire is a wide-band semiconductor with three band gap energies (3.3, 4.4, and 5.8 eV).

Keywords Nanomaterials · SnS₂ · Nanowire · AAO · Template

Introduction

In recent years, one-dimensional (1-D) nanostructural materials have been attractive due to their physical and chemical properties. These nanostructures in particular show results in electronics [1], magnetic [2], optics, etc., that have great potential applications in the next generation of nanodevices [3]. Anodic aluminum oxide (AAO) template-based assembling has been widely applied in recent years to produce nanowires with extremely long length and high aspect ratio, and it also provides a simple, rapid, and cheap way for fabricating nanowires as aligned arrays [4].

Tin disulfide (SnS₂) is an n-type semiconductor with hexagonal cadmium iodide (Cdl₂) structure. It is composed of sheets of tin atoms sandwiched between two close-packed sheets of sulfur atoms [5]. Single crystal and polycrystalline films of SnS₂ have shown optical band gaps in the range of 2.12–2.44 eV [6]. As an important member of the IV–VI group semiconductors, SnS₂ is a possible choice in solar cells and optoelectronic devices [7]. A variety of methods have been developed into synthesized SnS₂ nanoparticles, films, and crystals. SnS₂ nanoparticles were synthesized through the microwave plasma process either by the reaction between chloride or carbonyl of tin and H₂S [8]. The films of SnS₂ were prepared by chemical deposition from an acidic medium solution containing Sn⁴⁺ ions [9]. Single crystals of SnS₂ have been grown by the vapor phase [10]. In addition, SnS₂ nanocrystallites with hexagon flake shape were synthesized by a hydrothermal reaction between SnCl₄ · 5H₂O and (NH₂)₂CS [11]. SnS₂ nanobelts were produced from SnCl₂ · 2H₂O and Na₂S by a thioglycollic acid (TGA) assisted hydrothermal method [12]. However, SnS₂ nanowires are fabricated within AAO template synthesis, using the electrodeposition and sulfurizing methods that are not yet reported.

For this purpose, we report a new synthesis method for semiconductor SnS₂ nanowires. Pure metal Sn is electrodeposited in the nanochannels of the AAO template. Sn nanowires are sulfurized in the S atmosphere to form SnS₂ nanowires. According to past research, our first successful fabrication attempt was sulfurizing the Sn nanowires that were electrodeposited in the AAO template and studying its properties.
**Experimental Details**

**Preparation of AAO Template**

The AAO template used in our experiment was prepared by a two-step anodization process as described previously [13]. Briefly, high purity aluminum sheet (99.9995%) was first anodized at constant voltage in the sulfuric acid solution for 3 h. After anodization, the anodized Al sheet was put into an acid to completely remove the porous layer. Then, the AAO template can be fabricated by repeating the anodization process under the same conditions of the first step anodization. The AAO template was obtained by etching away the underlying aluminum substrates with a mercuric chloride solution. The transparent AAO template was immersed in a phosphoric acid solution to widen the nanochannels. After this process, the diameter of the nanochannel was about 40 nm.

**Preparation of SnS2 Nanowires**

In order to prepare Sn nanowires, a platinum (Pt) film was deposited by vacuum evaporation onto one surface of the AAO template to provide a conductive contact. The Sn nanowires were electrodeposited in the pore of the nanochannels of AAO template under constant voltage, using an electrolyte containing SnSO₄ and distilled water. After washing with distilled water and air drying, the AAO template with Sn nanowires was put into a glass tube with the pure S powder together. The glass tube was evacuated by using a pump, and it was placed into the furnace. The samples were then heated from room temperature (heating rate: 5 °C/min) to 500 °C and kept at this temperature for 10 h to completely sulfurize the Sn nanowires. It is expected that S atoms would react with the metal Sn to form SnS₂. After the reaction was terminated, the furnace was naturally cooled down to room temperature and SnS₂ nanowires were completely formed after sulfurization.

**Characterization of SnS2 Nanowires**

The morphology and microstructure of the as-prepared SnS₂ nanowires were characterized by field emission scanning electron microscopy/energy dispersive spectrometer (FE-SEM/EDS, HITACHI S-4800). The identification of the crystallization and phase structure were analyzed by X-ray diffraction (XRD, SHIMADZU XRD-6000) utilizing Cu Kα radiation. More details about the microstructure of the SnS₂ nanowires were investigated by the high-resolution transmission electron microscopy/corresponding selected area electron diffraction (HR-TEM/SAED, JEOL JEM-2010). For HR-TEM and SAED analysis, the SnS₂ nanowires were dispersed in ethanol and vibrated for few minutes. Then, a few drops of the resulting suspension were dripped onto a copper grid. For optical analysis, the AAO template was dissolved by NaOH solution at room temperature and was washed with distilled water to expose freely nanowires of SnS₂. After the SnS₂ nanowires are absolutely dispersed in distilled water using a supersonic disperser, the absorption spectra of the SnS₂ nanowires were measured on an UV/Visible/NIR spectrophotometer (HITACHI U-3501).

**Results and Discussion**

**Morphology of AAO Template and SnS2 Nanowires**

The morphology of the as-synthesized product was examined by FE-SEM. Typical FE-SEM morphology (Fig. 1a) shows the pores on the AAO template had a uniform size and were arranged in a honeycomb hexagonal structure. Figure 1b shows the pure Sn nanowire arrays in the pore of nanochannels of AAO template. It shows the length of Sn nanowires is about 5 μm. Figure 1c shows the SnS₂ nanowires embedded in an AAO template. It reveals the aspect ratio (length/diameter) of SnS₂ nanowires around 125. When the sulfurization temperature was fixed at 500 °C, the formation of SnS₂ nanowires was confirmed by sulfurization up to 10 h. From the high-magnification FE-SEM micrograph (Fig. 1d), SnS₂ nanowires with the diameter of about 40 nm can be clearly observed. The chemical composition of the SnS₂ nanowires was investigated by EDS. Figure 1e reveals EDS spectra of SnS₂ nanowires arrays, indicating only aluminum, oxygen, tin, and sulfur were present, and that there was no contamination by other elements. Quantitative analysis reveals the atomic ratio of Sn to S with 33.92:66.08 is close to 1:2, indicating the SnS₂ nanowires are well-crystallized, and they are in good agreement with the XRD results. In order to investigate the morphology of the SnS₂ nanowires, the AAO template was completely removed in NaOH for 15 min to expose them, followed by thoroughly rinsing with distilled water. Figure 1f reveals the SnS₂ nanowires with diameter of about 40 nm detached from the AAO template. The individual SnS₂ nanowires were almost the same diameter of the AAO template. The geometrical characteristics of the SnS₂ nanowires could be controlled by choosing the proper type of AAO template.

**Crystal Structures of SnS2 Nanowires**

Figure 2 shows the X-ray diffraction (XRD) spectra of the as-prepared SnS₂ nanowires without AAO template, which makes the crystal structure of the SnS₂ nanowires convenient for characterization. It can be seen that there are no
peaks of Sn and S after the metal Sn nanowires are sulfurated at 500 °C for 10 h. Furthermore, the Sn peaks totally disappear after sulfuration and the SnS₂ peaks appear. The indicated formation of SnS₂ in hexagonal crystal phase has a preferred orientation (011), which is in good agreement with the reported values (JCPDS Card no.83-1705). Metal oxides such as SnO₂ nanowires have been prepared by oxidation of metal Sn nanowires, and it is generally accepted that the chemical properties of oxygen and sulfur are similar to each other. Hence, the technique used here for formation of SnS₂ is understandable. The formation mechanism of SnS₂ nanowires with the reaction equation can be expressed as follows:

\[
\text{Sn}^{4+} + 2 \text{S}^- \rightarrow \text{SnS}_2
\]

in which the S atoms would react with metal Sn atoms at high temperatures to form SnS₂ nanowires. Since the reaction rates of S and Sn atoms are mainly dominated by time and temperature, long periods and high temperatures of the sulfuration process were needed to prepare the fine crystalline SnS₂ nanowires. When the sulfuration time was fixed for 10 h, the formation of SnS₂ nanowires were confirmed by sulfuration at a temperature of 500 °C.

Detailed information on the microstructure of as-prepared SnS₂ nanowires was obtained by HR-TEM. Low-magnification HR-TEM image (Fig. 3a) illustrates the numerous SnS₂ nanowires. Figure 3b reveals the HR-TEM image of an individual SnS₂ nanowire. The diameter of the nanowire is about 40 nm. Nevertheless, the grain size of the SnS₂ nanowire cannot be clearly observed. In Fig. 3c, the corresponding SAED pattern of an individual nanowire exhibits a polycrystalline. Moreover, the concentric diffraction rings could be indexed outward as (011), (001), (012), and (110) lattice planes of hexagonal SnS₂. The HR-TEM image (Fig. 3d) shows a single nanowire with the lattice spacing of about 0.2777 nm, which corresponds to (011) plane of SnS₂.

Optical Properties of SnS₂ Nanowires

Figure 4 shows the UV/Visible/NIR absorbance spectra of the as-grown sample recorded in the spectral range 200–900 nm for SnS₂ nanowires. Our absorption spectra results of SnS₂ nanowires have a very strong absorption peak at
260 nm, no other peaks can be observed. We infer the absorption peak at 260 nm in ultraviolet region is due to the phase of the tin disulfide (SnS$_2$). SnS was not observed because it has a strong absorption onset around 980 nm of direct band gap and a weaker absorption edge near 1100 nm of the indirect band gap [14]. This result proves our sulfured nanowires are SnS$_2$ phase, and it is in accordance with our XRD results. To determine the band gap energy ($E_g$) of the SnS$_2$ nanowires, the dependence of absorption coefficient ($\alpha$) on the photon energy equation is given as follows [15]:

$$\alpha h\nu = A (h\nu - E_g)^m$$

where $h\nu$ is the photon energy, $E_g$ the band gap energy, and $A$ is the constant having separate values for different transitions. The values of $m$ for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transition are 1/2, 2, 3/2, and 3, respectively. This equation gives band gap ($E_g$) when straight portion of $(zh\nu)^{1/m}$ versus $h\nu$ plots are extrapolated to the point $z = 0$. However, $m = 3/2$, 2, and 3, the band gap energies were found to be a negative number which is not reasonable in physics. Relationship fitting to the absorption spectra of SnS$_2$ as $m = 1/2$, which means these nanowires are allowed direct transition. As $m = 1/2$, the $(zh\nu)^2$ versus $h\nu$ plot is shown in the inset in Fig. 4, exhibiting a linear relationship at 3.9–4.75, 5.4–6.1, and 6.2–6.35 eV, respectively. The band gap
energies of 40 nm SnS2 nanowires are estimated to be 3.3, 4.4, and 5.8 eV by the extrapolation of relation. According to the most recent study about the optical characteristics of the SnS2 films, absorbance spectra were recorded in the spectral range 350–800 nm. Deshpande et al. [16] recently reported the band gap energy of the allowed direct transitions at 2.2 eV in the SnS2 films with average grain sizes of: 180–220 nm. The band gap energies of SnS2 nanowires were higher than that of SnS2 films. Panda et al. [17] observed the direct optical transition and the band gap energy was 3.5 eV with crystalline nanoparticles of 15 nm annealed at 150 °C for 1 h. In this study, the band gap energy of the allowed direct transitions at 3.3 eV of SnS2 nanowires with 40 nm diameter is agreeable to those obtained of Panda et al. Our band gap energy (3.3 eV) of SnS2 nanowires is reasonable when compared with the band gap energy (2.2-3.5 eV) of SnS2 films. Wang et al. [18] reported the absorption spectra were recorded in the spectral range under 350 nm. They observed the emission or excitation bands of SnS2 nanocrystallites, which are associated with the transition between those sub-bands. Those bands of SnS2 nanocrystallites may be associated with the presence of defect either interface or interior. Our band gap energies (4.4 and 5.8 eV) of SnS2 nanowires are probably a result of sub-band in the electronic structure. Chang et al. reported SnS2 nanotubes could be a one-dimensional sensor material for NH3 detection, indicating that SnS2 nanowires may be suitable for NH3 sensor applications [19]. This can be explained by the calculated binding energies for a NH3 molecule on the SnS2, which are very close to those obtained previously in calculations of NH3 adsorption onto a carbon nanotube [20]. In the future, we will study the energy jump of physical phenomenon, development and applications in gas sensor and solar cell.

Conclusions

SnS2 nanowires arrays have been successfully fabricated within template synthesis by using the electrodeposition and sulfurizing methods. The results show SnS2 nanowires have high wire packing densities with uniform wire diameters and lengths of about 40 nm and 3–5 μm, respectively. In XRD results, after sulfuring the Sn nanowire at 500 °C for 10 h, the sulfured nanowires have SnS2 phase and a preferred orientation (011). The analysis of the HR-TEM/SAED reveals the SnS2 nanowire is polycrystalline. The SnS2 nanowires show three band gap energies (3.3, 4.4, and 5.8 eV) and exhibit a linear relationship at 3.9–4.75, 5.4–6.1, and 6.2–6.35 eV, respectively as m = 1/2. The absorption spectra of nanowires contain three spectral intervals with the shapes typical for direct allowed interband transitions with the effective bandgaps.

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