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2003 J. Phys.: Condens. Matter 15 L661

(http://iopscience.iop.org/0953-8984/15/44/L02)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) L661–L665 PII: S0953-8984(03)68800-4

LETTER TO THE EDITOR

Single-crystalline SnS_2 nano-belts fabricated by a novel hydrothermal method

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Received 5 September 2003
Published 24 October 2003
Online at stacks.iop.org/JPhysCM/15/L661

Abstract

SnS_2 nano-belts have been prepared by a novel thioglycolic acid (TGA) assisted hydrothermal method. X-ray diffraction reveals that the SnS_2 nano-belts are of hexagonal structure and well crystallized. Transmission electron microscopy observation shows that the SnS_2 nano-belts have a width of 80–160 nm and a length of up to several micrometres, and high-resolution transmission electron microscopy further identifies that the SnS_2 nano-belts are single-crystalline in nature. A preliminary mechanism for the TGA-assisted hydrothermal synthesis of SnS_2 nano-belts is presented.

1. Introduction

SnS_2 belongs to the interesting class of isomorphic materials that are in many ways between two-dimensional (layer type) systems and three-dimensional crystals, and exhibits a strong anisotropy of optical properties [1]. SnS_2 is a lamellar structure semiconductor with a band gap of about 2.35 eV [2] and therefore has the potential to act as an efficient solar cell material [3]. It is also of interest in holographic recording systems and electrical switching [4, 5].

Traditional methods for the preparation of tin sulfides include chemical vapour deposition [6, 7], electrochemical deposition [8], molecular beam epitaxy (MBE) [9] and spray pyrolysis [10]. However, all these reported methods require either a relatively high reaction temperature (more than 300 °C) or expensive instruments. Furthermore, over the past decade, the synthesis and functionalization of one-dimensional nano-structure materials has become one of the most highly active research areas [11–13]. Qian's groups have developed a mild solvothermal route to synthesize both SnS_2 nanocrystals [14] and belt-like SnS_2 crystals [15], but this method uses toxic, dangerous and expensive solvents. Here, we report the synthesis of SnS_2 nano-belts by a novel thioglycolic acid (TGA) assisted hydrothermal method which

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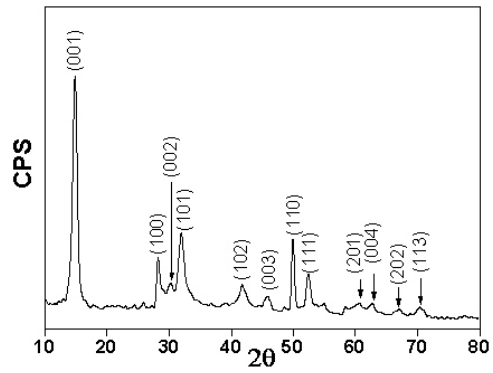

Figure 1. XRD pattern of the SnS_2 nano-belts prepared by the TGA-assisted hydrothermal method.

is milder, simpler, more practical and less harmful to the environment than the solvothermal method.

2. Experiment

All chemicals are analytical grade without further purification. First, 0.001 mol $SnCl_2{\cdot}2H_2O$ powder, 50 μL TGA, and 100 ml of Na_2S with a concentration of 0.04 M were placed into a beaker. After stirring, the reactants were put into a Teflon-lined autoclave of 150 ml capacity, which was filled with deionized water up to 80% of the total volume. Next, the autoclave was maintained at 200 °C for 20 h, then cooled to room temperature naturally. The mixture turned black due to the formation of SnS_2 precipitates. The products were filtered out, washed with alcohol and deionized water several times and then dried at 60 °C for 30 min.

An x-ray diffraction (XRD) pattern was obtained on a Rigaku D/max-ga x-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.541\,78$ Å). Transmission electron microscopy (TEM) observation was performed on a Philips CM200 high-resolution transmission electron microscope with an accelerating voltage of 200 kV.

3. Results and discussion

All the peaks in the XRD pattern (figure 1) can be indexed to the hexagonal structure of SnS_2 with lattice constants $a = 3.648$, $c = 5.899$ Å, in good agreement with JCPDS No 23-0677. XRD analysis detected no impurities such as SnO_2. The strong and sharp diffraction peaks suggest that the products are well crystallized.

Typical TEM images of as-prepared samples are shown in figure 2. This figure clearly reveals the belt-like morphology of the SnS_2 nanocrystals with a width of 80–160 nm and a length of up to several micrometres. The selected area electron diffraction (SAED) pattern confirms that the as-synthesized nano-belts consist of SnS_2, and reveals their single-crystal nature. Additional structural characterization of the SnS_2 nano-belts was carried out using a high-resolution transmission electron microscope (HRTEM). Figure 3 shows a typical HRTEM image of a SnS_2 nano-belt. The image clearly shows that fringes with a lattice spacing of about 0.315 nm can be found, which corresponds to $\{100\}$ planes of SnS_2.

The energy dispersive x-ray (EDX) spectrum of the individual SnS_2 nano-belt shown in figure 2 is given in figure 4. The very strong peaks related to Sn and S are found in the spectrum.

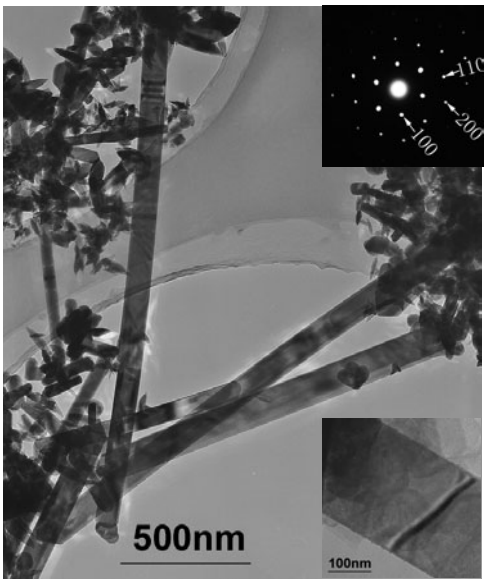

Figure 2. TEM images of multi SnS_2 nano-belts. The upper right inset corresponds to the SAED pattern of the SnS_2 nano-belts; the lower right inset corresponds to the TEM image of an individual SnS_2 nano-belt.

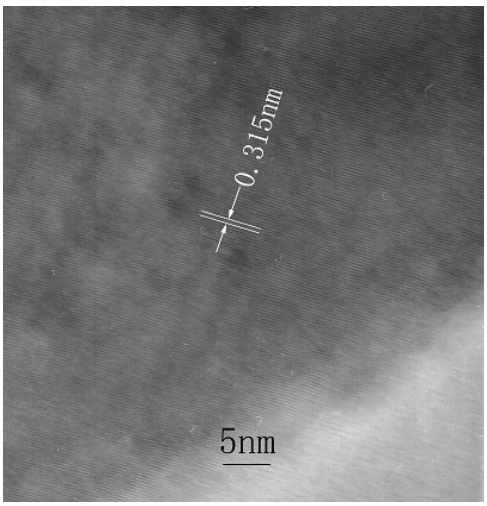

Figure 3. HRTEM image of a SnS_2 nano-belt.

The very weak O peak may originate from the oxidation of SnS_2 nano-belts exposed to the air. The C and Cu peaks come from the copper grid used to support the samples.

Previously, TGA was widely used as a stability agent preventing nano-crystals from aggregating [16, 17]. In our synthetic route, TGA is critical for the formation of the belt-like structure. The detailed mechanism can be expressed as follows:

$$SnCl_2 + H_2O \Leftrightarrow Sn(OH)Cl\downarrow + HCl \quad (1)$$

$$Sn(OH)CI\downarrow + Na_2S \Leftrightarrow SnS\downarrow + NaCl + NaOH \quad (2)$$

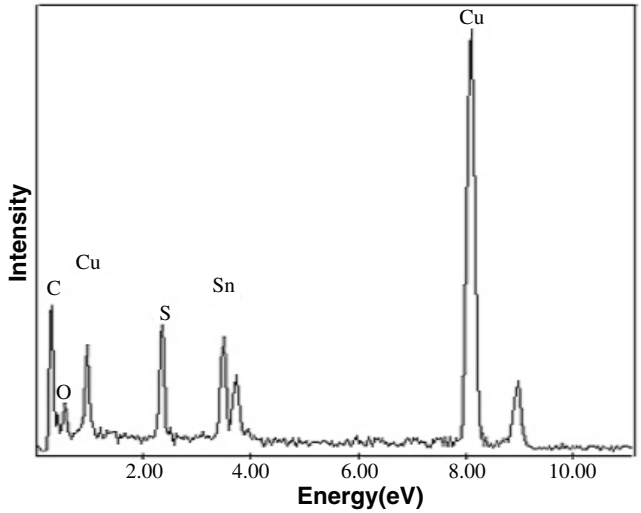

Figure 4. EDX spectrum of the individual SnS_2 nano-belt shown in figure 2.

$$SnS \Leftrightarrow Sn^{2+} + S^{2-} \tag{3}$$

$$Sn^{2+} + 2H^{+} + O_2 \Leftrightarrow Sn^{4+} + 2H_2O \tag{4}$$

$$Sn^{4+} + 2S^{2-} \Leftrightarrow SnS_2\downarrow \tag{5}$$

$$mSnS_2 + kHSCH_2COOH + kSn^{4+} \Leftrightarrow (SnS_2)_m(SnSCH_2COOH)_k^{3k+} + kH^{+} \tag{6}$$

$$(SnS_2)_m(SnSCH_2COOH)_k^{3k+} \rightarrow (SnS_2)_m(Sn^{4+})_k + kSCH2COOH^{-} \tag{7}$$

$$(SnS_2)_m(Sn^{4+})_k + 2kS^{2-} \rightarrow (m+k)SnS_2. \tag{8}$$

Prior to the hydrothermal process, the hydrolysis of $SnCl_2$ and the formation of SnS nuclei were carried out via reactions (1) and (2). Due to the instability of SnS and the excess of S^{2-}, SnS_2 nuclei were formed in the hydrothermal process according to reactions (3)–(5). Compared with the conventional hydrothermal process, in the TGA-assisted hydrothermal process the marked difference is the formation of $(SnS_2)_m(SnSCH_2COOH)_k^{3k+}$ complex clusters in the solution via reaction (6). Reaction (7) represents the dissociation of SCH_2COOH^{-} from the SnS_2 complex clusters. We believe that the dissociation of SCH_2COOH^{-} occurs in a local region of the complexed SnS_2 cluster, where there are Sn^{4+} exposed to the S^{2-} existing in the solution. Therefore, during the hydrothermal process, the formation of SnS_2 proceeds along specific directions. However, the exact mechanism for the formation of SnS_2 nano-belts in the TGA-assisted hydrothermal process is still under investigation by our group. Other quasi one-dimensional chalcogenides, such as CdS, Bi_2S_3 and PbS, have been prepared following the basic idea behind the hydrothermal process introduced in this paper has been reported [18, 19].

4. Conclusion

Single-crystalline SnS_2 nano-belts have been successfully prepared by a TGA-assisted hydrothermal method, with the advantages of simplicity, cost-effectiveness and reduced environmental impact. The growth mechanism of SnS_2 nano-belts has been discussed and the effect of TGA proposed. Furthermore, it is reasonable to believe that the TGA-assisted hydrothermal process offers great opportunity for scale-up preparation of quasi one-dimensional materials of other chalcogenides.

The authors would like to acknowledge the financial supports of 863 Project (No 2001AA513023), the Natural Science Foundation of China (No 60225010) and the Zhejiang Provincial Natural Science Foundation of China (No 601092).

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