Research Paper

Fabrication of Nanostructured SnO by Chemical Vapor Transport Process

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Abstract

In this paper, we report the growth of nanostructured SnO by chemical vapor transport without the carbothermal reduction of the SnO source at 800 °C for 1h. After synthesis, light yellow to-yellow to-black to-gray-colored tin oxides were formed on the glass substrates at the downstream of the tube when the synthesis temperature ranged from 200 to 530 °C. The crystalline structure and surface morphologies of the materials were characterized via X-ray diffraction and field emission scanning electron microscopy. The results showed that the materials grown at the temperature of 330 and 430 °C were composed of SnO nanoplates (15-130 nm in thickness, 0.15-1.70 µm in plate diameter, and 0.30-1.80 µm in layer thickness) in the tetragonal phase of SnO. In addition, the effect of the growth temperature on the size of the SnO nanoplates was also investigated.

Keywords: SnO, Nanoplates, Chemical vapor transport

I. Introduction

In the past decades, metal oxide nanomaterials with distinct morphologies have attracted significant attention because their size and morphologies a strong effect on their properties, which are different from those of their bulk counterparts [1]. Among these oxides, stannous oxide (SnO), an important p-type semiconductor with a direct optical band gap of 2.5-3.4 eV [2], has attracted considerable attention owing to its potential application in various fields, such as a catalyst [3], coating substance [4], thin film transistor (TFT) [5], precursor for the fabrication of SnO₂ [6], and gas sensor [7,8] and an anode material for lithium-ion batteries [9]. However, SnO nanocrystals are very difficult to synthesize owing to their easy transformation into SnO₂ by oxidization.

Up to now, various morphologies of SnO have been synthesized such as diskettes [10,11], nanoplates [12], nanobranches [13], nanowhiskers [14], nanosheets [15,16], nanoflowers [17], meshes [9], nanobelts [11], and nanospheres [11] through a few synthetic routes such as the sol-gel method [18], thermal decomposition [13,19], chemical vapor deposition (CVD) [20], the hydrothermal method [12], radio frequency (RF) reactive sputtering

[21,22]. Among them, the ones based on thermal evaporation appear to be interesting owing to the simplicity of the method as well as its low cost and the good quality of the material obtained. In this method, the material typically grows following a vapor-solid (VS) or a vapor-liquid-solid (VLS) mechanism.

II. Experimental details

The tetragonal SnO nanostructures were synthesized by the vapor transport process in a horizontal quartz tube with a diameter of 40 mm and length of 800 mm. First, the glass substrates were cleaned several times with acetone, deionized (DI) water, and ethanol in an ultrasonic bath, and then dried with nitrogen gas. Commercial SnO powders with a purity of 99.5 % were used as the source material. The source material was loaded at the center of a quartz tube in an alumina boat. The glass substrates were placed downstream inside the quartz tube at the side of the quartz tube, as shown in Fig. 1. The quartz tube was evacuated to 2×10^{-2} Torr and purged several times with high-purity N₂ gas. A small amount of N₂ gas was introduced into the quartz tube and used throughout the process. The electric furnace was then heated to 800 °C at a ramp rate 5 °C/min and maintained at 800 °C for 60 min for the evaporation of the source powders. During this, the temperature of the growth region was varied from 200 to 530 °C.

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Figure 1. Schematic of the experimental set-up for the growth of tin oxide nanomaterials by the vapor phase transport method and photograph of the material on the glass substrate (top-right corner).

The surface morphologies of the samples were characterized via field-emission scanning electron microscopy (FE-SEM), which was operated at an acceleration voltage of 5.0 kV. The crystallography structures of the samples were investigated via X-ray diffraction (XRD, X'PERT-PRO) at room temperature using CuK α radiation ($\lambda = 1.54178 \text{ \AA}$) with a working voltage and current of 40 kV and 30 mA, respectively.

III. Results and discussion

Figure 2 shows the XRD patterns of the materials on the glass substrates grown at different temperatures, namely, (a) 530, (b) 430, (c) 330, and (d) 200 °C. Generally, the phase constituents of the products are remarkably affected by the temperature. Figure 2(a) displays the XRD pattern of the sample grown at 530 °C, which indicates that the phase components are complex. Specifically, SnO₂ (JCPDS No: 01-070-4177) and metallic tin (JCPDS No: 01-086-2265) are the main phases, and SnO (JCPDS No: 01-078-1913) and the intermediate tin oxides of Sn₃O₄ (JCPDS No: 16-0737) are also present in the products. However, the diffraction peaks of SnO₂, metallic tin, and the intermediate tin oxide of Sn₃O₄ disappear as the temperature decrease to below 430 °C. As shown in Figs. 2(b-d), the SnO phase (JCPDS No: 01-078-1913) is only observed in the samples when the growth is at the temperature of 430, 330, and 200 °C, respectively. No diffraction peaks corresponding to any other impurities are detected, which strongly indicates the high purity of these final samples. A previous study also confirmed that Sn₃O₄ was found to be formed by the decomposition of SnO in nitrogen gas [23]. Based on these evidences, it is inferred that the disproportionation reaction of SnO is promoted by high temperatures above 450 °C and that only the Sn₃O₄ phase can be formed as an intermediate tin oxide. The following reaction is the disproportionation reaction of

Figure 2. XRD pattern of the chemical vapor transport products obtained under different growth temperatures: (a) 530, (b) 430, (c) 330, and (d) 200 °C.

Figure 3. Morphologies of the SnO nanostructures of the chemical vapor transport products obtained under different growth temperature: (a) 200, (b) 330, (c) 430, and (d) 530 °C.

gaseous SnO occurring as the temperature is decreased:

Figure 3 presents a typical FE-SEM image showing the general view of the morphology of the as-prepared product at different growth temperatures. The FE-SEM image of SnO obtained at 200 °C is shown in Fig. 3(a). The result confirms that a uniform SnO thin film is formed. Figures 3(b)-(c) are displaying the FE-SEM images of the SnO prepared at 330 and 430 °C, respectively. These results show that the thickness and diameter of the SnO nanoplates increase with increasing synthesis temperature. Figure 3(b) presents the FE-SEM images of SnO nanoplates whose thickness ranges from 15 to 23 nm and diameter varies from 0.10 to 0.20 μm. The FE-SEM image of a sample at a higher synthesis temperature, as shown in Fig. 3(c), exhibit that the surfaces of the SnO nanoplates are smooth with diameter ranging from 0.86 to 2.15 μm,

Figure 4. Effect of the growth temperature on the size of the SnO nanoplates: (a) 280, (b) 360, (c) 400, and (d) 430 °C.

Figure 5. Effect of the growth temperature on the size of the SnO nanoplates: (a) nanoplate thickness, (b) nanoplate diameter and layer thickness.

with a thickness in the range of 75-150 nm. The morphology of the sample grown at 530 °C is shown in Fig. 3(d). The results indicate that various structures, such as ball-shaped nano- and microparticles, nanowires with length in the range from several hundreds to several tens microns, micro-rods with a large ball on the tip, and nanoplates, are formed randomly on the glass substrate. These results show that there are two types of plates: plates with a smooth surface and plates with a rough surface.

Here, based on the conditions described in the experimental section, we investigate the effect of the synthesis temperature on the size of the SnO nanoplates. Figure 4 show the typical FE-SEM images (top view and cross-section images) of the SnO nanoplates obtained at different synthesis temperatures after 1 h of fabrication. The results exhibit that the SnO nanoplates are collected in the synthesis temperature range from 280 to 450 °C and that the size of the nanoplates increase with increasing synthesis temperature. Figure 4(a) displays that SnO nanoplates with thickness ranging from 15 to 23 nm and diameter from 0.1 to 0.2 μm are formed at a low synthesis temperature of 280 °C. The sizes of the SnO nanoplates increase with the increase in the synthesis temperature Figs. 4(b-d), which is described in Fig. 5(a). When the synthesis temperature increases up to 450 °C, the average

Figure 6. XRD spectra of the SnO source (a) before the evaporation and (b) remaining after the evaporation process at 800 °C.

nanoplate thickness and plate diameter are 140 nm and 1.7 μm, respectively Fig. 4(d). In addition, the cross-section images in Figs. 4(a-d) indicate that the layer thickness of the SnO nanoplate also increased as the synthesis temperature increases. The similar behavior of the size versus the layer thickness and diameter of the SnO nanoplates, as shown in Fig. 5(b), indicate that only a single SnO layer is grown on the vertical glass substrate faces during the growth process. This result suggests that the diameter and thickness of the SnO plates can be easily controlled by adjusting the temperature distribution inside the quartz tube.

The morphology and phase structure of the product depends on not only the adopted processing parameters but also the source material employed. It is, therefore, very important to understand the characteristics of the source material on vaporization to achieve controlled growth of desired nanostructures.

The two reactions occurring during the disproportion of stannous oxide are as follows [10,23]:

Figure 6 presents the XRD spectra of the SnO source powder before- and after - evaporation at 800 °C for 1 h. It is also evident that after the thermal evaporation at 800 °C as shown in Fig. 6(b), the SnO phase completely transforms to the SnO₂ phase and metallic Sn. Some reactions may occur on the vaporization of oxides during the thermal evaporation at a high temperature:

A previous study reported that Sn(l) was formed from the decomposition reaction of SnO₂ at high temperatures (1300 °C) and low pressures ($P_{O_2} = 101,325 \times 10^{-9}$ KPa) [25-27]. Thus, the decomposition of SnO₂ is impossible as reaction (4) under the conditions of this work. Gaseous SnO is, however, relatively stable, particularly at a high temperature (> 1300 °C). If the temperature is lower than 1300 °C, the gaseous SnO will spontaneously decompose into liquid Sn and solid SnO₂ during the process of lowering the temperature [25]. However, previous our study confirmed that when the source temperature was above 700 °C, SnO(g) and O₂(g) were formed during the decomposition of SnO₂(s) [28]. Based on these results, reactions (2, 3, 5, and 6) are considered to be probably responsible for the formation of Sn(g), SnO(g), and O₂(g). Thus, after Sn(g) and O₂(g) are formed from reactions 4 and 6, the vapors flow from high-pressure (high temperature at the center of the tube) areas to low-pressure (low temperature at downstream) areas. During the flow process, SnO nanoplates and a SnO thin film form in the low-temperature region (< 430 °C) (reaction 7). SnO decomposes to form Sn₃O₄, SnO₂, and metallic Sn in the high-temperature region (> 530 °C) (reactions 2 and 3). During evaporation, Sn(l) is also easy to evaporate and collect on the plates at the growth temperature of 530 °C. These tin spheres with different sizes will act as a catalyst for the formation of SnO₂ nanowires. The catalyst droplets were found at the tips of the nanowire in Fig. 3(d), implying that the growth of the SnO₂ nanowires may follow the VLS mechanism. However, the FE-SEM result of the sample at 530 °C shows that the SnO₂ nanowires are low density whereas the Sn particles have a high density.

IV. Conclusions

In summary, we investigated the synthesis and characterization of high-purity SnO nanoplates and thin film on a glass substrate via the chemical vapor transport process at 800 °C without the carbothermal reduction. The SnO thin film was formed around 200 °C. The SnO nanoplates (15-130 nm in thickness, 0.15-1.70 μm in plate diameter, and 0.30-1.80 μm in layer thickness) were formed for the synthesis temperature range from 280 to 430 °C. The X-ray diffraction analysis indicated that the as-synthesized SnO nanostructures had a tetragonal SnO structure. The effect of the growth temperature on the size of SnO nanoplate was investigated. This result showed that SnO nanoplate sizes (plate diameter and layer thickness) remained quite similar with the synthesis temperature increase, indicated that only a single SnO nanoplate layer was grown on the vertical glass substrate faces during the

growth process. The formation of SnO(g) and O₂(g) vapors proposed to result from the decomposition of SnO₂:2SnO₂(s) = 2SnO(g) + O₂(g) at low temperature (800 °C) was found to be interesting and important for the fabrication and investigation of new SnO nanostructure without other phases.

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