Change in the morphology of SnO$_2$ crystals synthesized by thermal evaporation of SnO$_2$ powder mixed with graphite in ambient air

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The morphology of tin oxide (SnO$_2$) crystals, which were formed by thermal evaporation of SnO$_2$/graphite powder mixture, was changed with the ratio of graphite to SnO$_2$ powder in the source material. The synthesis process was performed in air at atmospheric pressure and no catalysts and substrates were used, which makes the process very simple and low cost. At the low ratios of graphite to SnO$_2$ powder in the source material, the SnO$_2$ crystals had a spherical shape with nanometer dimensions. With increasing the ratio of graphite to SnO$_2$ powder, the morphology of SnO$_2$ crystals changed from particle to belt. The belt-shaped SnO$_2$ crystals had the widths in the range of 1.2–3.1 μm and the lengths of several tens of micrometers. X-ray diffraction analysis showed that all the SnO$_2$ crystals had a rutile tetragonal crystal structure. Visible emission band with the wavelength in the range of 400–600 nm was observed in the cathodoluminescence spectra of the SnO$_2$ crystals.

Key-words : Tin oxide, Morphology variation, Thermal evaporation, Graphite, Mixing ratio, Air

1. Introduction

Tin oxide (SnO$_2$) is an important n-type semiconducting oxide with a wide band gap of 3.62 eV at room temperature. This characteristic enables a number of potential applications in transistors, transparent conducting electrodes, gas sensors and solar cells. In recent years, SnO$_2$ micro/nanostructures have attracted significant attention due to their superior performance and functionality compared to the bulk and/or thin film. At present, the SnO$_2$ micro/nanostructures have been successfully applied in many fields including gas sensors,$^{1,3}$ field emitters,$^{2,3}$ solar cells,$^{3}$ and lithium-ion batteries.$^{4}$ Thus, much effort has been devoted to synthesize SnO$_2$ micro/nanostructures. So far, SnO$_2$ micro/nanostructures have been synthesized using different synthetic methods, including thermal evaporation,$^{5,7}$ chemical vapor deposition,$^{6,9}$ laser ablation,$^{7}$ hydrothermal method$^{8}$ and sol–gel method.$^9$ Among these methods, the thermal evaporation is the most widely used method because it has the advantage of low cost and simplicity.$^{10–12}$ However, the thermal evaporation process is typically conducted under vacuum and/or inert gas environments. Hence, it is a little difficult to conduct efficiently the thermal evaporation process.

In this paper, a simpler thermal evaporation method is introduced to synthesize SnO$_2$ micro/nanostructures in air at atmospheric pressure without any catalysts. In particular, the morphology of the SnO$_2$ micro/nanostructures could simply change with varying the ratio of SnO$_2$/graphite in source material. The effect of the ratio of SnO$_2$/graphite in source material on the morphology of SnO$_2$ micro/nanostructures is discussed.

2. Experimental procedure

SnO$_2$ micro/nanostructure were synthesized by thermal evaporation method. Pure SnO$_2$ powder and SnO$_2$/graphite powder mixture were used as the source materials. The synthesis process was carried out at 1200°C in air at atmospheric pressure. No catalysts and substrates were utilized in the process. The source materials with different ratios of SnO$_2$/graphite were used to examine the effect of the ratio of SnO$_2$/graphite on the morphology of as-synthesized SnO$_2$ crystals. The weight ratio of SnO$_2$/graphite was changed in the range of 0.5/0, 0.5/0.25, 0.5/0.5 and 0.5/1.0. The source materials were put in alumina crucibles. Then the alumina crucibles were placed at the center of the furnace. The furnace was heated to 1200°C and maintained for 1 hr. After the process, the furnace was turned off and cooled down to room temperature. The as-synthesized products were collected from the crucibles for the analysis and characterization.

The crystallographic structures of the products were investigated by X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.154$ nm) operated at a power of 40 kV and 30 mA. The morphologies of the products were observed by field emission scanning electron microscope (FESEM) operated at a voltage of 15 kV. The components of the products were examined by energy dispersive X-ray...
(EDX) spectroscopy. The cathodoluminescence (CL) was measured by CL spectroscopy at room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the products prepared using the source materials with the SnO$_2$/graphite ratios of 0.5/0, 0.5/0.25, 0.5/0.5 and 0.5/1.0. All the products exhibit very similar diffraction patterns. The diffraction peaks are in accordance with a tetragonal rutile structure of SnO$_2$ having the lattice constants of $a = b = 0.473$ nm and $c = 0.318$ nm. The XRD patterns show that the products are SnO$_2$ crystals with the rutile crystal structure. No other peaks related to impurities or other tin oxide were detected, which implies the high purity of the SnO$_2$ products.

Figure 2 represents the EDX spectra of the products prepared using the source materials with the SnO$_2$/graphite ratios of 0.5/0, 0.5/0.25, 0.5/0.5 and 0.5/1.0, respectively. Only Sn and O elements are detected in the EDX spectra, indicating that no other elements except Sn and O were present in the SnO$_2$ products.

Figure 3 shows the SEM images of the SnO$_2$ products prepared using the source materials with the SnO$_2$/graphite ratios of 0.5/0, 0.5/0.25, 0.5/0.5 and 0.5/1.0, respectively. When the source materials with the SnO$_2$/graphite ratios of 0.5/0 and 0.5/0.25 are employed, the

![XRD patterns](image1)

![EDX spectra](image2)

![SEM images](image3)
Similar CL spectra were observed from all the SnO$_2$ belt-shaped SnO$_2$ crystals also have extremely shaped SnO$_2$ crystals starts to be formed only when the belt-thickness is 470 nm and the length of the belts extends up to several tens of micrometers. It is noted that the belt-shaped SnO$_2$ crystals could be synthesized only when the SnO$_2$/graphite ratio reaches a value above 0.5/0.5. The belt-shaped SnO$_2$ crystals also have extremely flat and smooth surface.

When the ratio of graphite to SnO$_2$ vapor is low, the concentration of SnO$_2$ vapor will be high, resulting in the formation of a large number of nuclei. For a given concentration of growth species, a large number of nuclei mean small sized nuclei. Furthermore, high concentration of growth species favors three-dimensional growth on the surface of the nuclei, inducing the spherical growth of crystals. On the contrary, a high ratio of graphite to SnO$_2$ vapor is likely to lead to the low concentration of SnO$_2$ vapor. The low concentration of growth species results in a low growth rate of crystals. The low growth rate makes the surfaces with low surface energy stable, which may result in the formation of belt-shaped crystals. The low growth rate is also favorable for enhanced surface smoothness.

**Figure 4** represents the typical CL spectra of the SnO$_2$ product prepared using the source materials with the SnO$_2$/graphite ratio of 0.5/0, 0.5/0.25, 0.5/0.5 and 0.5/1.0, respectively.

The visible emission band observed in the spectra. It is generally suggested that the visible emission originates from oxygen vacancies in the crystals, which act as electron trapping sites in the band gap. SnO$_2$ is a typical n-type semiconductor. The semiconducting characteristic of SnO$_2$ is ascribed to the presence of oxygen vacancies. The oxygen vacancies produce the defect energy levels in the band gap of SnO$_2$ crystal, leading to the emission in the visible region. The visible emission has been particularly observed in SnO$_2$ micro/nanocrystals because the large surface area to volume ratio of micro/nanocrystals results in the increasing surface defects including oxygen vacancies. The high concentration of surface oxygen defects is responsible to the high intensity visible emission. Therefore, the visible emission band observed in the present work is also suggested to be caused by the oxygen vacancies in the SnO$_2$ micro/nanocrystals.

On the other hand, there are two growth mechanisms to explain the growth of one-dimensional structures such as belts and wires. One is vapor–liquid–solid (VLS) mechanism and the other is vapor–solid (VS) mechanism. In the VLS process, a catalyst droplet is observed on the tip of one-dimensional structures. Catalyst is required for the VLS growth. The catalyst forms liquid droplets during the growth of crystals. Then the growth species in vapor form preferentially dissolves into the catalyst droplets. As the growth species continue to dissolve in the catalyst droplets, the concentration of growth species in the droplets reaches the supersaturation necessary for nucleation. The supersaturation leads to the nucleation and the one-dimensional growth of the crystals. In the present work, since no catalyst droplets were found at the tips of the belts and no catalyst was used, it is supposed that the belt-shaped SnO$_2$ crystals were grown via VS mechanism.

### 4. Conclusions

SnO$_2$ crystals with spherical shape and belt shape were synthesized by a simple catalyst-free thermal evaporation method in ambient air. SnO$_2$/graphite powder mixtures were used as the source materials. At the weight ratio of SnO$_2$/graphite below 0.5/0.25, the as-synthesized SnO$_2$ crystals exhibited spherical shape. As the ratio of SnO$_2$/graphite in the source material increased to 0.5/0.5, the morphology of the SnO$_2$ crystals changed from spherical particles to belts. The ratio of graphite to SnO$_2$ in the source material had an effect on the morphology of the SnO$_2$ crystals. From the experimental result, it is found that the belt-shaped SnO$_2$ crystals could be synthesized when a mixture with SnO$_2$/graphite ratio above 0.5/0.5 was used as a source material. XRD analysis revealed that all the SnO$_2$ crystals had tetragonal rutile structure. A broad visible emission at around 500–600 nm was detected in the CL spectra of all the products, which is supposed to originate from the high oxygen vacancy concentration in the crystals.

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