

Effect of oxygen working pressure on morphology and luminescence properties of SnO₂ micro/nanocrystals formed by thermal evaporation method

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The effect of oxygen pressure in the synthesis of SnO₂ micro/nanocrystals through thermal evaporation of Sn powder was investigated. The thermal evaporation process was performed at 1000 °C for 1 hr under various oxygen pressures. The pressure of oxygen changed from 10 to 500 Torr. The morphology of SnO₂ crystals changed drastically with oxygen pressure. SnO₂ nanoparticles with an average diameter of 120 nm were formed at oxygen pressure lower than 10 Torr. SnO₂ nanowires were grown under an oxygen pressure of 100 Torr. The nanowires have diameters in the range of 100 ~ 500 nm and lengths of several tens of micrometers. As increasing the oxygen pressure to 500 Torr, the sizes of wires increased. A strong visible emission peak centered at about 500 ~ 600 nm was observed in the room temperature cathodoluminescence spectra of all the products.

Key words: Tin powder, Thermal evaporation, Tin oxide, Micro/nanocrystals, Morphological change, Oxygen pressure.

Introduction

SnO₂ is a n-type semiconductor with a wide band gap of 3.6 eV, which makes it useful for a wide variety of applications including solar cells, light emitting diodes, transparent electrodes, transistors, photovoltaic cells, lithium ion battery electrodes and gas sensors. On the other hand, metal-oxide micro/nanocrystals have recently attracted attention due to their novel properties and potential applications in nanoscale electronic and optoelectronic devices. SnO₂ micro/nanocrystals have also exhibited significant improved performance of electronic devices including lithium ion batteries, gas sensors and solar cells. Accordingly, considerable effort has been devoted to the synthesis of SnO₂ micro/nanocrystals. In particular, one-dimensional (1D) SnO₂ micro/nanocrystals have received increasing attention in recent years due to superior gas-sensing and photodetection properties attributed to their high surface area to volume ratio.

So far, one-dimensional SnO₂ micro/nanocrystals with diverse morphologies including wires and rods have been synthesized by various synthesis methods, such as thermal evaporation [1], chemical vapor deposition [2], the hydrothermal method [3], sol-gel method [4], and laser ablation [5]. Among them, the thermal evaporation method is the most promising technique because it allows to synthesize one-dimensional SnO₂ crystals with high specific surface

area and excellent gas sensing properties [6]. In the thermal evaporation process, the morphology and properties of oxide micro/nanocrystals can be generally determined by the process parameters such as temperature, working pressure and ambient gas. Furthermore, the thermal evaporation process is sensitive to the concentration of oxygen because oxygen has an effect on the volatility of the source material. However, there has been very little research reported on the synthesis of SnO₂ micro/nanocrystals only in an oxygen atmosphere. Thus, it is worthwhile to study the effect of oxygen gas pressure on the morphology and optical properties of SnO₂ micro/nanocrystals synthesized by thermal evaporation technique.

In this paper, the effect on the morphology and optical properties of SnO₂ crystals formed via thermal evaporation of Sn powder is reported.

Experimental Procedure

Sn powder with a purity of 99.99% was used as the source material. Sn powders were loaded into alumina crucibles. The crucibles were placed at the center of a horizontal quartz tube furnace. The quartz tube was evacuated by mechanical pump to pressure of 1×10^{-1} Torr and then oxygen was introduced into the quartz tube until it reached the working pressure. Then, the temperature was raised with a heating rate of 10 °C/min up to 1000 °C and kept for 1 hr. In order to investigate the effect of oxygen pressure on the morphology of as-synthesized product, the oxygen working pressure changed in range of 10 ~ 500 Torr. After that, the furnace was cooled down to room temperature. The

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products in the crucibles were collected for the characterization.

The morphology and crystalline structure of the as-synthesized products were investigated by field emission scanning electron microscope (FE-SEM) and X-ray diffractometry (XRD) with Cu K_{α} radiation, respectively. The components were characterized using energy dispersive X-ray (EDX) spectroscopy. Cathodoluminescence (CL) spectrum was studied at room temperature by CL spectroscopy.

Results and Discussion

Fig. 1(a-c) demonstrate the XRD patterns of the products synthesized under different oxygen pressures of 10, 100 and 500 Torr, respectively. The XRD patterns reveal similar peak patterns for all the products. The XRD peaks at $2\theta = 26.6, 33.9, 38.0, 39.0, 42.6, 51.8, 54.8$ and 57.8 can be assigned to the (110), (101), (200), (111), (210), (211), (220) and (002) reflections of the standard tetragonal rutile SnO₂ structure with lattice constants of $a = b = 0.473$ nm and $c = 0.318$ nm (JCPDS No. 41-1445), indicating that all the products are SnO₂ with rutile structure regardless of the oxygen working pressure. No other crystalline phase or peaks of impurities such as unreacted Sn are observed, implying that the Sn powders were completely oxidized.

Fig. 2 shows the EDX spectra of the products synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of 10, 100 and 500 Torr, respectively. The EDX analysis reveals that all the products are composed of only Sn and O, suggesting high purity of SnO₂.

Fig. 3 shows the SEM images of the SnO₂ crystals synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of 10, 100 and 500 Torr, respectively. As shown in Fig. 1(a), the SnO₂ nanoparticles with spherical shape are observed, when the oxygen pressure is 10 Torr. The SnO₂ nanoparticles have an average diameter of 120 nm. As the oxygen pressure increases to 100 Torr, the structural morphology of the product changes from spherical particles to 1D nanowires. 1D structures become the dominant morphology. The nanowires have diameters in the range of 100 ~ 500 nm and lengths of several tens of micrometers. The SEM image exhibits that 1D SnO₂ nanowires have a very smooth surface. Further increase of oxygen pressure to 500 Torr increased the diameter of the 1D structures. Fig. 3(c) reveals that for the 1D SnO₂ structures synthesized under an oxygen pressure of 500 Torr, the diameter distribution is in the range of 0.7 ~ 2.4 μ m.

During the thermal evaporation of Sn powder, SnO is generally known to be formed at the initial stage. Because SnO is metastable, SnO generates solid SnO₂ according to the reaction $2\text{SnO} \rightarrow \text{SnO}_2 + \text{Sn}$ [7]. The

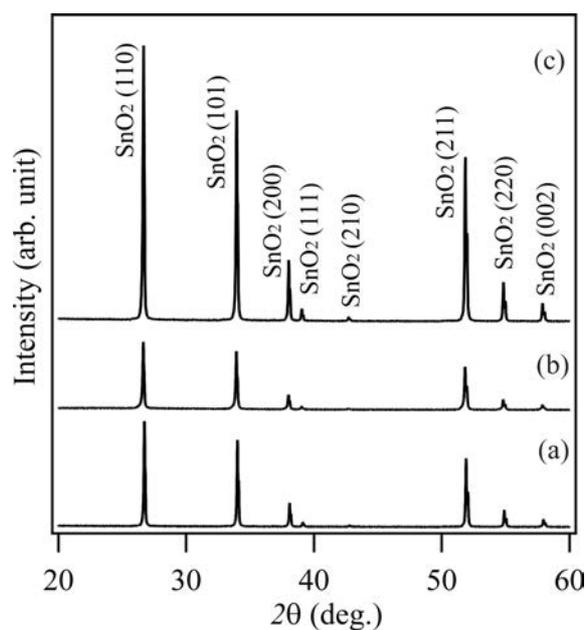


Fig. 1. XRD spectra of the products synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of (a) 10, (b) 100 and (c) 500 Torr, respectively.

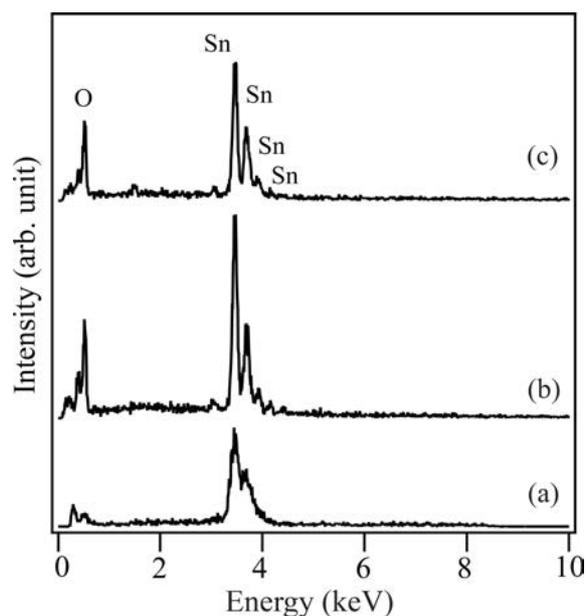


Fig. 2. EDX spectra of the products synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of (a) 10, (b) 100 and (c) 500 Torr, respectively.

SnO₂ acts as a nucleus. At the oxygen pressure as low as 10 Torr, the growth of 1D SnO₂ nanowires may be restrained due to lack of SnO and O₂ vapor, while at the oxygen pressures higher than 100 Torr, SnO and O₂ vaporized species would be sufficient for the growth of 1D SnO₂ nanowires. The oxygen working pressure during the synthesis process had a significant important role to change the morphology of SnO₂ micro/nanocrystals. The higher oxygen pressure during the

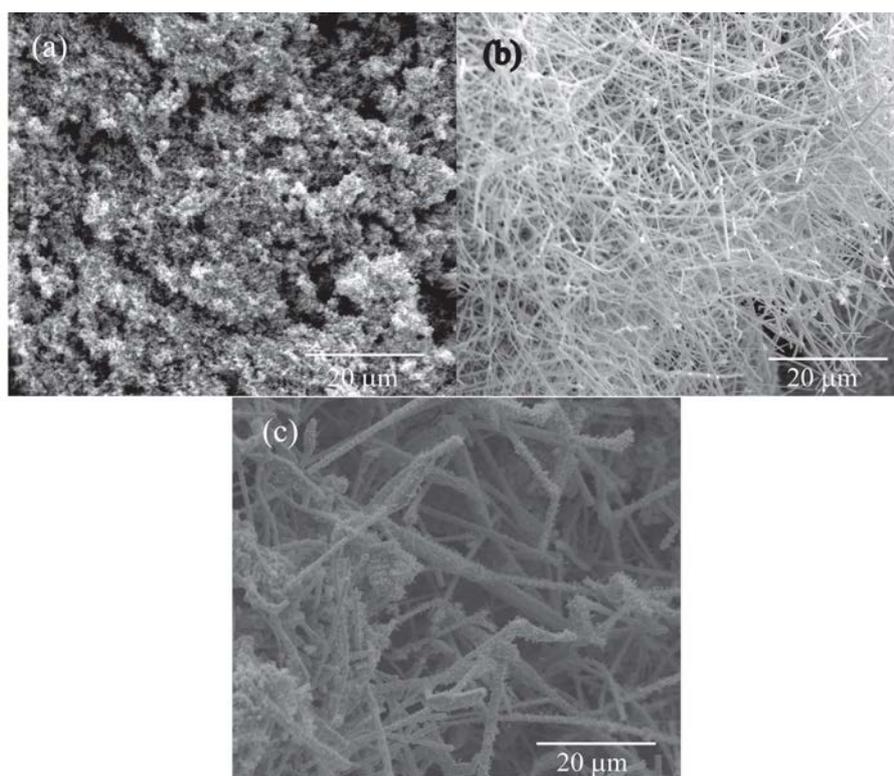


Fig. 3. SEM images of the products synthesized by thermal evaporation of Sn powder at 1000 °C for 1 h under different oxygen pressures of (a) 10, (b) 100 and (c) 500 Torr, respectively.

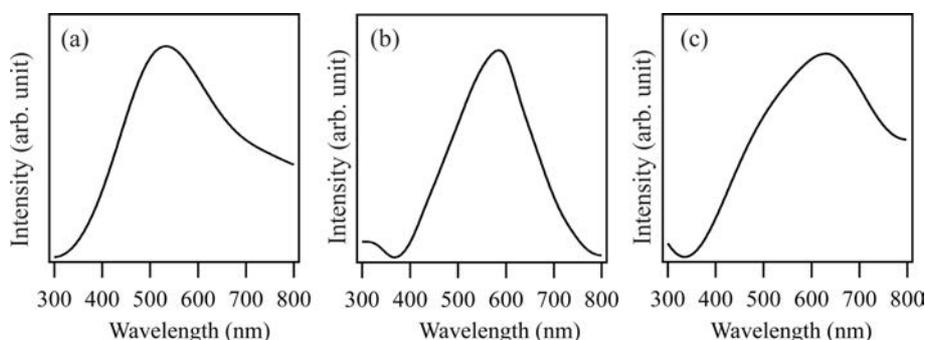


Fig. 4. Room temperature CL spectra of the products synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of (a) 10, (b) 100 and (c) 500 Torr, respectively.

thermal evaporation brought the morphological change of SnO₂ crystals from particles to 1D nanowires and microrods. When the oxygen pressure was 10 Torr, the evaporated Sn vapor would form SnO nuclei due to a low concentration of oxygen. SnO nuclei was grown to SnO nanoparticles with spherical shape. Then the SnO nanoparticles transformed into rutile structured SnO₂ [8]. When the oxygen pressure was above 100 Torr, the Sn vapor reacted with the oxygen under high oxygen concentration to form SnO₂ nuclei. The SnO₂ nuclei grew along the preferential direction, leading to the formation of SnO₂ nanowires and microrods [9].

On the other hand, in the present work, the growth of nanowires and microrods is considered to proceed via vapor-solid mechanism because no catalysts were not used and no droplets were found at the tips of the

nanowires.

Fig. 4(a-c) show the CL spectra of the SnO₂ crystals synthesized by thermal evaporation of Sn powder at 1000 °C for 1 hr under different oxygen pressures of 10, 100 and 500 Torr, respectively. The CL spectra exhibit a broad visible emission centered at 500~600 nm. All the products show similar luminescence characteristics, but the position of the luminescence peak is a little different. The emission peaks in the CL spectra of the SnO₂ nanoparticles, nanowires and microrods are centered at 530, 580 and 620 nm, respectively. These differences would be ascribed to the different morphologies and sizes. The broad visible emission has been reported from SnO₂ micro/nanocrystals [10, 11]. It is suggested that the visible luminescence originates from oxygen vacancies. Luo et al reported that the

visible emission also originated from surface oxygen vacancies [12]. SnO₂ is a n-type semiconductor. The n-type semiconducting property is attributed to the presence of oxygen vacancies. Accordingly, the visible emission observed in the present study is considered to be attributed to oxygen-related defects.

Conclusions

Crystalline SnO₂ micro/nanocrystals with spherical and wire shapes were fabricated through thermal evaporation of Sn powders in oxygen atmosphere. The oxygen pressure during the synthetic process have a significant effect on the morphology of the SnO₂ crystals. An increase in growth time caused the change in the morphology of SnO₂ micro/nanocrystals. The nanoparticles with spherical shape were formed under lower oxygen pressure. As the oxygen pressure increased, the 1D structures such as nanowires and microrods were dominant morphology. It is suggested that the growth of SnO₂ nanowires and microrods proceeded through vapor-solid (VS) mechanism. The XRD analysis showed that the SnO₂ micro/nanocrystals had tetragonal rutile structure. In the room temperature CL spectra of all the products, a strong visible emission with the wavelength range of 400 to 700 nm was observed, which might be attributed to oxygen vacancies.

Acknowledgements

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