

Characteristics of SnO₂ One-dimensional Nanomaterials Synthesized on TiN-coated Substrates by the Evaporation of Sn Powders

Hyoun Woo Kim^a, Seung Hyun Shim and Ju Hyun Myung

School of materials science and engineering, college of engineering, Inha University, 253 Yong Hyun Dong, Nam Gu, Incheon 402-751, Republic of Korea

^aemail: hwkim@inha.ac.kr

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Abstract. One-dimensional structures of tin oxide (SnO₂) on TiN-coated substrates were obtained by simple heating of Sn powders. X-ray diffraction, high-resolution transmission electron microscopy, and the selected area electron diffraction showed that 1D structures are composed of SnO₂ with rutile structure. The photoluminescence of the structures in the visible region suggests possible applications in nanoscaled optoelectronic devices.

Introduction

One-dimensional (1D) nanostructures have been actively studied, responding to the need for understanding their novel physical properties and developing nanoscale electronic and optoelectronic devices [1-4]. Tin dioxide (SnO₂) is regarded as one of the most promising materials for gas sensors, dye-based solar cells, transparent conducting electrodes, and catalyst supports. Therefore, it is natural that there has been an intense interest in synthesizing SnO₂ 1D nanomaterials, such as nanowires [5], nanoribbons or nanobelts [6,7], and nanorods [8]. Although silica nanowires have been synthesized using TiN substrates [9], synthesis of SnO₂ 1D structures on the TiN substrate has not been reported to date.

Here, we report on a route for synthesis of SnO₂ 1D structures on TiN-coated Si substrates, by means of the thermal evaporation technique.

Experiments

Pure Sn powders were placed in an alumina boat, which was put in the middle of a quartz tube inserted in a horizontal tube furnace. We used Si(001) as a starting material onto which a layer of titanium nitride (TiN) was deposited. On top of the boat, a piece of the substrate was placed with the Ir-coated side downwards. The vertical distance between the alumina boat and the substrate was approximately 10 mm. During the experiment, the furnace was kept at 850°C for 2 h and a constant pressure with an air flow of 150 mTorr. After evaporation, the substrate was cooled down and then removed from the furnace for analysis. A white layer was found on the surface of the substrate.

Low angle (0.5°) X-ray diffraction (XRD: CuKα₁ radiation) patterns were obtained on a Philips X'pert MRD diffractometer with an incidence angle of 0.5°. Scanning electron microscopy (SEM) studies were carried out on a Hitachi S-4200. Further structural analysis using transmission electron microscopy (TEM) was performed on a Philips CM-200. For TEM observation, the products were ultrasonically dispersed in acetone, and then a drop of the suspension was placed on amorphous carbon films supported by copper grids and dried in air. PL spectrum was measured at room temperature by a 325 nm He-Cd laser (Kimon, 1K, Japan).

Results and discussion

Fig. 1 shows the typical XRD pattern of the as-synthesized product. Miller indices are indicated on each diffraction peak. The reflection peaks of (110), (101), (200), (211), (220), (310), (301), and (321) can be readily indexed to a tetragonal rutile structure of SnO_2 with lattice constants $a=4.734\text{\AA}$ and $c=3.185\text{\AA}$ (JCPDS Card File No. 41-1445). No reflection peaks from impurities, such as unreacted Sn or other tin oxides, can be detected. In our XRD measurements, the angle of the incident beam to the substrate surface was about 0.5° , and a detector rotated to scan the samples.

Therefore, we surmise that the peaks are mainly from the products. The XRD analysis indicates that the well-crystallized and pure SnO_2 products were successfully obtained through the present synthetic route.

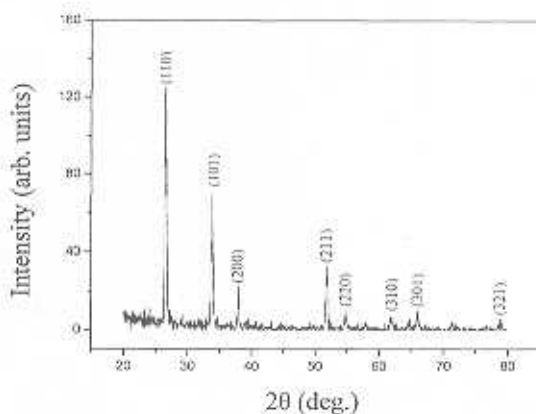


Fig. 1 XRD pattern of the products.

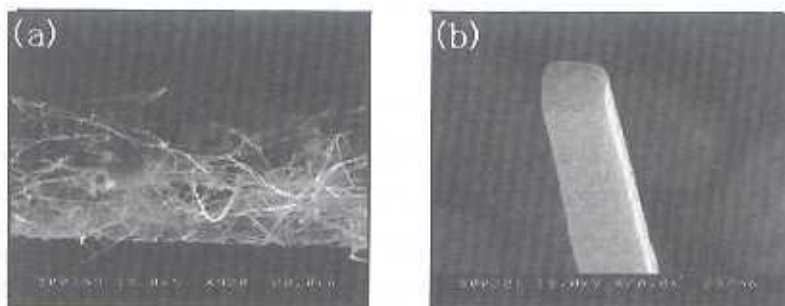


Fig. 2 (a) Side-view SEM image of the products. (b) High magnification SEM image of a 1D structure.

Fig. 2a shows typical side-view SEM images of the samples, revealing that the products mainly consist of 1D materials. Statistical analysis of many SEM images indicates that the average diameter of produced 1D structures are in the range of 60-800 nm. Fig. 2b reveals that no catalyst particle can be seen at tip of the rod. Fig. 3a shows the TEM image of a 1D structure which has a jagged surface and the corresponding selected area electron diffraction (SAED) pattern, recorded perpendicular to the rod long axis. The SAED pattern can be indexed for the [001] zone axis of crystalline SnO_2 . The length direction of the structure, indicated by an arrow, is along the [110] direction. Fig. 3b is the enlarged high resolution TEM (HRTEM) image of a rectangular box marked in Fig. 3a. Lattice fringes are clearly visible from the image, revealing its single crystalline nature. The interplanar spacings are approximately 0.33, 0.47, and 0.47 nm, respectively, corresponding to the (110), (100), and (010) planes of tetragonal rutile SnO_2 .

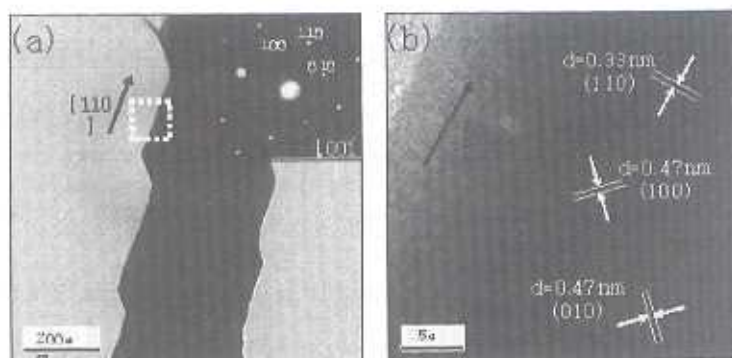


Fig. 3 (a) TEM image of a single SnO_2 structure. The inset shows the corresponding SAED pattern recorded along the $[001]$ zone axis. (b) HRTEM image of a white rectangular box marked in (a).

Fig. 4 shows the PL spectrum measured at room temperature. The products have a strong peak centered at around 560-600 nm (corresponding to 2.07-2.22 eV). The visible light emission spectrum is similar to that of SnO_2 1D nanomaterials previously synthesized by using laser ablation [10] and solution phase growth [11]. The visible-light emission of SnO_2 is known to be related to defect levels within the band gap of SnO_2 , associated with O vacancies or Sn interstitials that formed during the synthesis process [10-12].

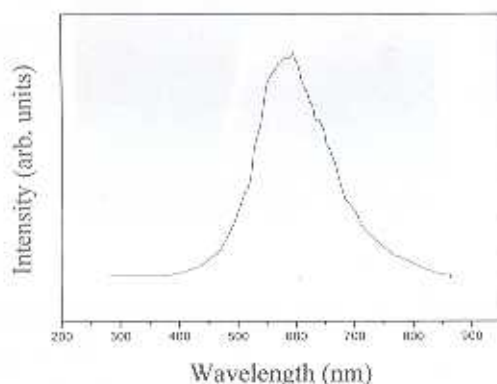


Fig. 4 Room temperature PL spectrum of the products with an excitation wavelength at 325 nm.

In the present study, although the TiN-coated substrate was employed, there is no evidence that a TiN-related catalyst presents at tips of the structures. Therefore, the growth of the SnO_2 structure in the present route cannot be dominated by a vapor-liquid-solid mechanism but it is close to a vapor-solid process, which might be attributed to a diffusion-limited process in a supersaturated environment [13]. When the synthesis was performed in the experiment under the same condition but with a higher oxygen pressure of 1000 mTorr, we obtained the thick rod- or cluster-like structures without any thin 1D structure (Fig. 5). The variation of SnO_2 structural morphology with O_2 content indicates that O_2 gas plays an important role in controlling nucleation and growth of SnO_2 . It is generally agreed that the $\text{SnO}(\text{g})$, which forms at the initial stage of oxidation of Sn ($\text{Sn}(\text{s}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{SnO}(\text{g})$), is metastable and decompose according to the reaction [14]: $2\text{SnO}(\text{g}) \rightarrow \text{SnO}_2(\text{s}) + \text{Sn}(\text{l})$. The higher oxygen partial pressure provides additional oxygen, which may facilitate a large supersaturation of O_2 gas, subsequently leading to a large supersaturation of SnO in the gaseous state and resulting in a fast condensation of solid SnO_2 on the substrate. Therefore, a large supersaturation may activate a secondary growth sites and heterogeneous nucleation on the side of the 1D structures,

tending to produce thicker structures. Under low supersaturation, however, narrow 1D structures are easy to grow. Further systematic study is underway in order to reveal the detailed synthesis mechanism.



Fig. 5 SEM image of products grown at higher oxygen pressure.

Summary

We have successfully fabricated 1D structures of SnO_2 on TiN substrates by performing a thermal evaporation of elemental Sn powders at 850°C . XRD and TEM characterizations show that the as-prepared SnO_2 1D structures are of a crystalline rutile structure. Room temperature PL spectrum shows an apparent visible light emission band centered at around 560-600 nm. We discuss the possible growth mechanism.

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