

Synthesis and properties of SnO₂ one-dimensional nanomaterials on Pt-coated substrates

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Abstract. We have synthesized the belt-like structures of tin oxide (SnO₂) by carrying out the thermal evaporation of solid Sn powders. We have analyzed the samples with scanning electron microscopy, X-ray diffraction, transmission electron microscopy and photoluminescence (PL). The obtained nanobelts were single crystalline with a tetragonal rutile structure. PL spectrum exhibited the visible light emission. We have discussed the possible growth mechanisms.

Introduction

Tin dioxide (SnO₂) is an n-type semiconductor with a wide band gap ($E_g=3.62$ eV, at 300 K) and is well known for its potential applications in gas sensors, dye-based solar cells, transparent conducting electrodes, and catalyst supports. Because nanoscale one-dimensional (1D) structures have attracted great deal of interest owing to their unique electronic, optical, and mechanical properties as a result of their low dimensionality and the quantum confinement effect [1,2], various structural and morphological forms of SnO₂ 1D nanomaterials have been fabricated over the past several years, including nanowires [3], nanoribbons or nanobelts [4,5], and nanorods [6].

Although carbon nanotubes have been synthesized using platinum (Pt) catalyst [7], to our knowledge, synthesis of any inorganic nanomaterials including SnO₂, on the Pt substrate has not been reported to date. In this paper, we report an approach, in which we have produced the SnO₂ nanobelts on Pt-coated Si substrates. We have employed a thermal evaporation of Sn powders in the presence of air flow at a temperature of 900 °C. We have investigated the structural and photoluminescence (PL) properties of the as-prepared SnO₂ nanobelts.

Experiments

The synthesis process was carried out in a quartz tube (diameter 55 mm). The source material was pure Sn powders. We have employed Pt-coated Si substrates. In order to fabricate the Pt-coated Si substrates, we used Si as starting materials onto which a layer of Pt (about 150 nm) was deposited by the radio frequency magnetron sputtering. On top of the alumina boat with the source material, a piece of the substrate was placed with the Pt-coated side downwards. The vertical distance between the boat and the substrate, which were at the middle of quartz tube, was approximately 10 mm. The quartz tube was inserted into a horizontal tube furnace. During the experiment, a constant pressure with an air flow was maintained at 150 mTorr. When the system was cooled down to room temperature after 2h of typical deposition, white wool-like products were found on the substrate surface.

The as-grown samples were characterized and analyzed by glancing angle X-ray diffraction (XRD, Philips X'pert MRD) with an incidence angle of 0.5°, scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200). For TEM observation, the products were ultrasonically dispersed in acetone and a drop of the solution was placed on a Cu grid coated with a porous carbon film. PL measurements were performed by using a He-Cd laser line (325 nm, 55 mW) as the excitation source at room temperature.

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). The strong and sharp reflection peaks suggest that the as-synthesized products are well crystallized. No obvious 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 SnO_2 products were successfully obtained through the present synthetic route.

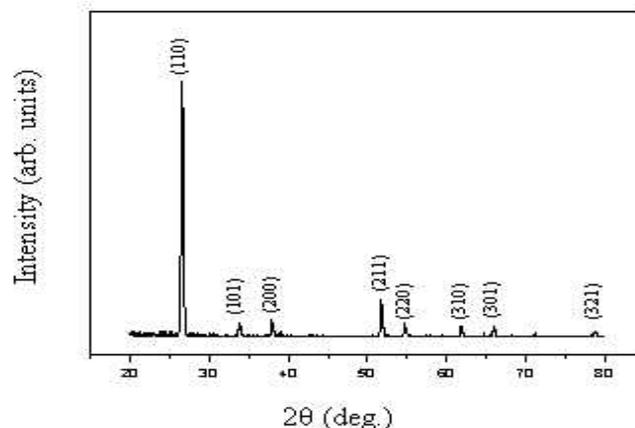


Fig. 1 XRD pattern of the products.

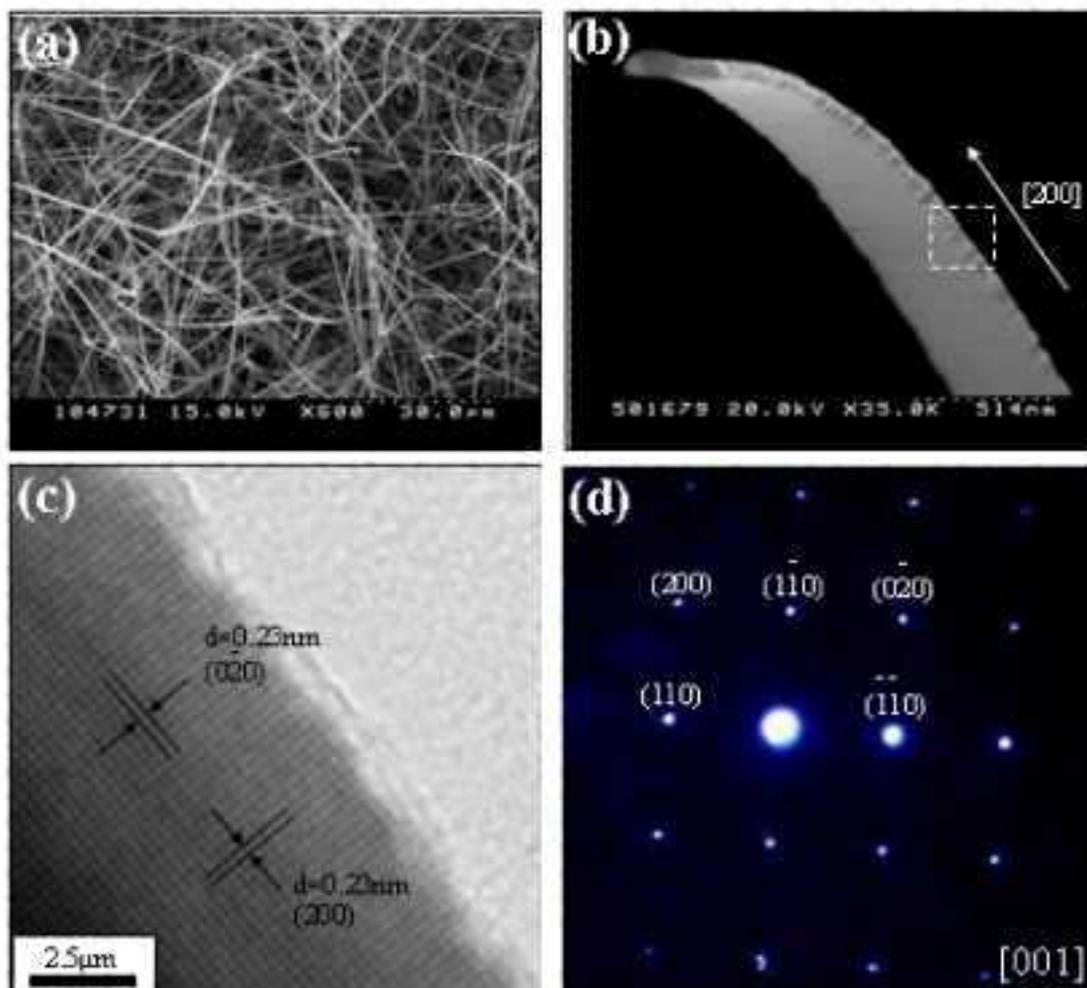


Fig. 2 (a) Top-view SEM image of the products. (b) High magnification SEM image of a nanobelt. (c) High resolution TEM image enlarging the boxed region of the nanobelt shown in Fig. 2b. (d) Corresponding SAED pattern.

Fig. 2a shows typical top-view SEM images of the samples, revealing that the products mainly consist of 1D materials. Statistical analysis of many SEM images indicates that the width of produced SnO₂ belt-like structures are in the range of 150 nm-1.8 μm. Fig. 2b reveals that no catalyst particle can be seen at tip of the nanobelt. Fig. 2c is a high resolution TEM (HRTEM) image enlarging the boxed area of a nanobelt in Fig. 2b, revealing a good crystallinity. The interplanar spacings is about 0.23 nm, corresponding to {200} planes of tetragonal rutile SnO₂. The [200] direction was parallel to the long axis of the nanobelt, as shown in Fig. 2b. Fig. 2d shows an associated selected area electron diffraction (SAED) pattern with a [001] zone axis, which indicates that the as-prepared SnO₂ nanobelts are single crystalline.

PL spectrum carried out at room temperature is shown in Fig. 3. Visible emissions with a peak wavelength position of around 560-600 nm (corresponding to 2.07-2.22 eV) is dominantly observed. The visible light emission is known to be related to defect levels within the band gap of SnO₂, associated with O vacancies or Sn interstitials that have formed during the synthesis process [8-10]. Several researchers have previously reported similar emissions from SnO₂ nanoribbons synthesized by laser ablation [8] and SnO₂ nanorods synthesized by solution phase growth [9].

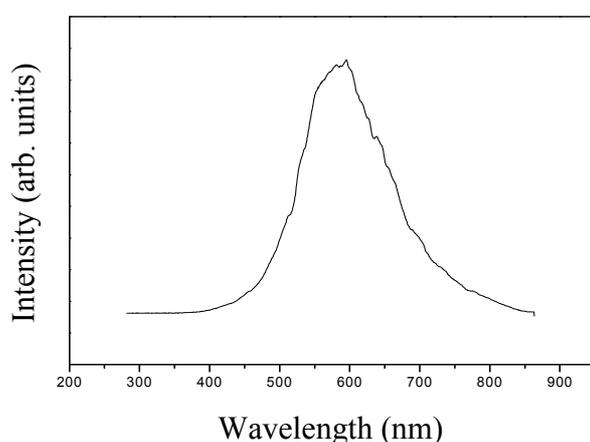


Fig. 3 Room temperature PL spectrum of the products with an excitation wavelength at 325 nm.

In the present work, although the Pt-coated substrate was employed, there were no evidence of Pt-catalyst present at tips of the structures. Therefore, the growth of the SnO₂ structure in the present route cannot be dominated by a vapor-liquid-solid mechanism. This type of growth, which is close to vapor-solid process, might be attributed to the diffusion-limited process in a supersaturated environment [11]. When the synthesis was carried out under the same conditions on SiO₂ substrates in the absence of Pt layers, we obtained the cluster-like structures without any nanobelt (Fig. 4a). When the synthesis was performed on Pt-coated substrates, with an oxygen pressure of 1000 mTorr, we obtained the thick rod- or cluster-like structures (Fig. 4b). We surmise that Pt is not easy to be oxidized and thus provides less amount of additional oxygen to the growing SnO₂ nanostructures. Also, it is evident that there exists less amount of available oxygen under the synthesis condition with the air pressure of 150 mTorr, if compared with the synthesis condition with the oxygen pressure of 1000 mTorr. The variation of SnO₂ structural morphology with O₂ content indicates that O₂ gas plays an important role in controlling nucleation and growth of SnO₂ nanobelts. It is generally agreed that the SnO(g), which forms at the initial stage of oxidation of Sn ($\text{Sn(s)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{SnO(g)}$), is metastable and decompose according to the reaction [12]: $2\text{SnO(g)} \rightarrow \text{SnO}_2\text{(s)} + \text{Sn(l)}$. The additional oxygen may facilitate large supersaturation of O₂ gas and thus SnO gas in the gaseous state, resulting in fast condensation. Under low supersaturation, narrow 1D structures are easy to grow. Under high supersaturation, however, it may activate the secondary growth sites and heterogeneous nucleation on the side of the 1D structures, tending to produce the wider or thicker structures. Efforts are now in progress to pursue these routes in more detail to reveal the synthesis mechanism.

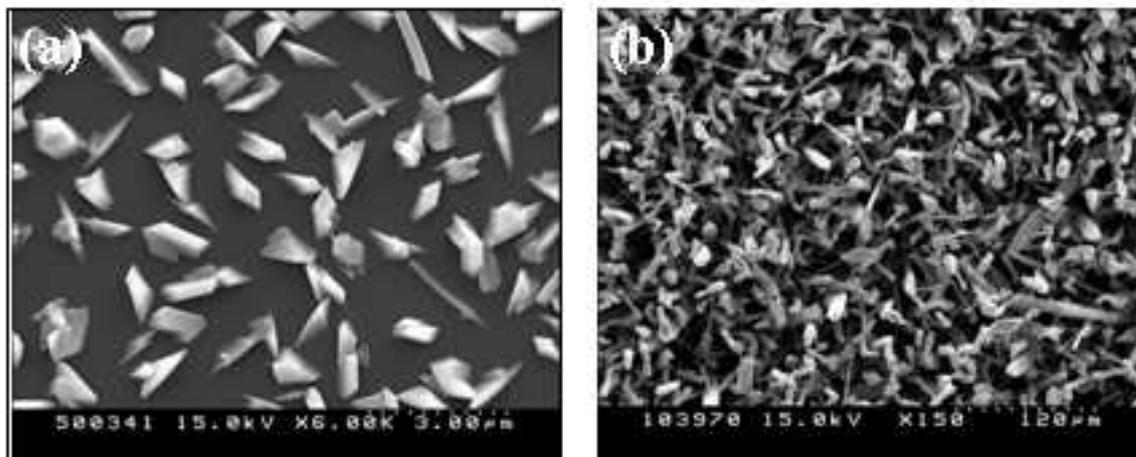


Fig. 4 SEM images of the products (a) on SiO₂ substrates in air pressure of 150 mTorr and (b) on Pt-coated substrates in oxygen pressure of 1000 mTorr.

Summary

We report the preparation of SnO₂ nanobelts on Pt substrates by performing a thermal evaporation of heating Sn powders at 900°C. TEM images and XRD spectra indicate that the resulting SnO₂ nanobelts are single crystalline. We speculate about the mechanism by which O₂ content affects the morphology. Room temperature PL spectrum shows an apparent visible light emission band centered at around 560-600 nm.

Acknowledgements

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