PREPARATION AND PROPERTIES OF SnO_2 NANOWIRES

Nguyen Thanh Binh, Le Thi Thanh Binh, Le Duy Khanh, Nguyen Ngoc Long

Department of Physics, College of Science, VNU

Abstract: Tin oxide (SnO_2) nanowires have been synthesized in bulk quantities at 1000°C by thermal evaporation of granular metallic tin (Sn). The X ray diffraction (XRD) pattern and scanning electron microscope (SEM) images show that the nanowires have the width in the range of 30–200nm. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were investigated. The peaks of PL spectra appeared at ~ 415 nm, 437 nm, 580 nm, 652 nm and that of excitation spectra at 369 nm.

1. Introduction

Semiconductor one-dimensional nanostructures such as nanowires, nanorods and nanoribbons, have stimulated a great interest due to their importance in basic scientific research. They also have attracted a great attention for their potential applications in device and interconnect integration in nanoelectronics and molecular electronics [1]. Among them, SnO_2 is the most important metal-oxide semiconductor. It is well known for its potential applications in gas sensors, transparent conducting coating of glass and solar cells [2]. The nanostructures SnO_2 have been fabricated by different methods such as magnetron sputtering [3], precursor thermal decomposition [4], sol-gel [5] and thermal vacuum evaporation [6, 7]. In this paper the preparation and optical properties of SnO_2 nanostructures by simple thermal evaporation are reported.

2. Experiment

The experimental apparatus used for the preparation consists of a horizontal tube furnace, a quartz tube with one sealed end and some ceramic crucibles. The granular metallic tin was used as the source material that was placed in a ceramic crucible. The ceramic crucible was then located at the sealed end of the quartz tube. Several Si plates (5 mm × 5 mm) were placed horizontal on the ceramic crucible.

The temperature of the furnace was increased from room temperature to 1000°C with the rate of 10 K.min-1 and the kept at 1000°C for 4h. After the furnace was cooled to room temperature, the ceramic crucible is carefully removed out of the quartz tube. It was observed that a thick ivory-yellow cotton-wool-like product was formed in a high yield on the surface of the crucible and on the Si plates. The products can be taken off from crucible in a form of a bulk sample or powder sample. The structural properties of the deposited product was characterized by SIMENS D5005 X-Ray diffractometer. The surface morphology of the product was analyzed by means of scanning electron microscopy using JEOL 5410VL microscope. The PL and PLE spectra of the product were recorded by spectro-fluormeter FL3-22.

3. Results and discussion

The typical XRD pattern of the sample is shown in Fig. 1. The chemical composition of the nanostructures was determined to be SnO_2. It can be seen that all diffraction peaks are indexed to a tetragonal rutile structure of SnO_2 with lattice constants of a =4.7334 Å and c = 3.1845 Å, which are consistent with those of pattern 41-1445. No characteristic peaks of impurities such as elemental Sn or other tin oxides were observed. The average grain size estimated by the Sherrer's formula is 377 nm.

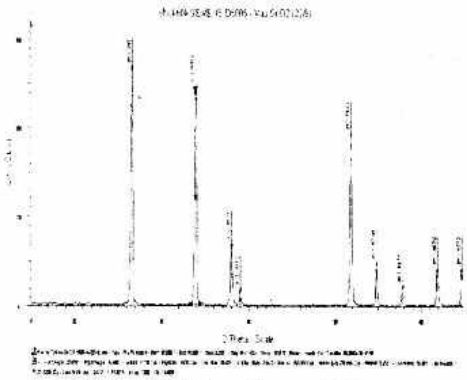


Fig.1: XRD pattern of the as-prepared SnO_2 nanoribbons.

Fig.2 shows the SEM image of SnO_2 bulk sample. A large quantity of nanowires and particles under the nanowires are clearly observed. Fig. 3 shows a typical high magnification SEM image of the as-prepared sample. The wirelike shape is further verified by the SEM image. The typical diameter of the nanowires are in the range of 30-200 nm. A lot of nanowires has a uniform width along its entire length. The lengths of the nanowires are up to one hundred micrometer.

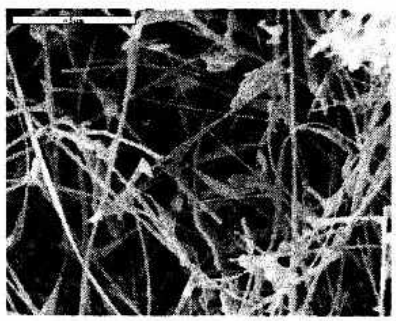


Fig. 2. SEM image of the as-prepared SnO_2 nanoribbons

In the growth of SnO_2 nanowires, the melting of metallic tin takes place at 231.9°C. The liquid tin could react with oxygen to yield tin oxides. As the temperature further increases the liquid tin is oxidized rapidly at 700-800°C. In general, SnO forms at the initial stage of the oxidation of tin. Because of absence of a carrying gas the SnO vapor can be deposited over the source material. SnO is metastable and will decompose to SnO_2 and Sn by the following reaction: $2SnO \rightarrow SnO_2 + Sn$.

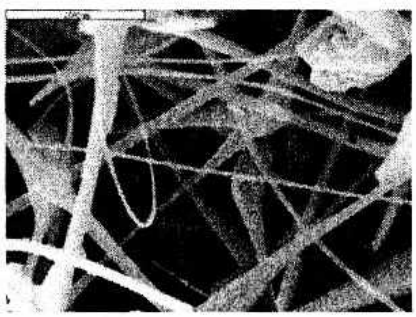
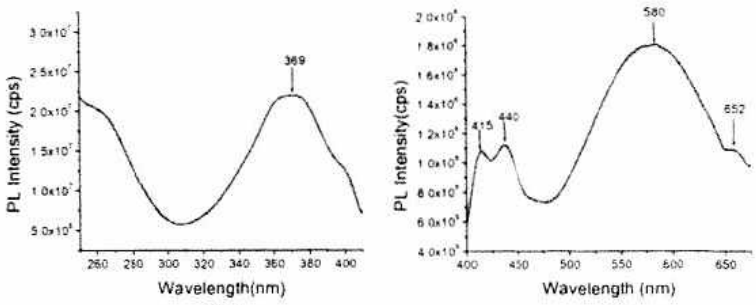


Fig. 3. High magnification SEM image of the as-prepared SnO_2

In general, there are two possible models for the growth of nanowires, namely the vapor-liquid-solid (VLS) and vapor-solid (VS). VLS mechanism often takes place in the case of nanowires grown by catalytic-assisted technique. It is well known that in VLS growth process, the droplet is located at the growth front of the nanowires and acts as the catalytic active site. From SEM image in Fig. 2, no solidified spherical droplet was observed at the end of the nanowires. So the growth mechanism of SnO_2 nanowires can be ascribed to the VS mechanism.

The room temperature excitation and emission spectra of the as-prepared bulk sample are shown in Fig. 4. The excitation spectrum shows a broad band at 369 nm (3.36 eV). The emission spectrum present four bands at 415nm (2.99 eV), 437 nm (2.84 eV), 580 nm

(2.14 eV) and 652 nm (1.90 eV), respectively. Since luminescence properties of SnO_2 strongly depend on growth method and preparation conditions, the emission peaks observed in different researches are quite different. Compared to earlier PL and PLE results [5, 8, 9, 10], we suppose that the electron transition from valent band to oxygen vacancy $V_o^{\cdot}$ state corresponds to the peak at 3.36 eV in excitation spectrum. The PL peaks at 2.99 eV and 2.84 eV might be attributed to donor-acceptor pair recombination, in which vacancy $V^{\cdot}_{o}$ plays the role of donor. The peaks at 2.14 eV and 1.90 eV might originate from the luminescence centers such as tin interstitials in the present SnO_2 nanowires or residual strains within thin nanowires, but that is not yet clear.



(a) (b)

Fig.4: Room temperature PLE (a) and PL (b) spectra of as-prepared SnO_2 bulk sample

4. Conclusion

In summary, SnO_2 nanowiress were fabricated simply through thermal evaporation using granular metallic Sn as source material. The growth mechanism of SnO_2 nanowires can be ascribed to the VS mechanism. From X-ray measurements, the chemical composition of the nanostructures was determined to be SnO_2 with lattice constants a = 4.7334 Å, c = 3.1845 Å. SEM images of as-prepared SnO_2 nanowires shows that the samples consist of a large quantity of nanowires with typical diameter in the range of 30 -200 nm. The PL peaks in the blue range are attributed to donor-acceptor recombination. The other PL peaks are related with crystal defects created during the growth of the SnO_2 nanowires.

References

1. Z. R. Dai, Z. W. Pan and Z. L. Wang, *Sol. State Commun.* **118**(2001), 351-354.
2. J. Zhang, F. Jiang and L. Zhang, J. *Phys. D:Appl. Phys.*, **36**(2003), L21-L24.
3. S. I. Rembeza, T. V. Svistova, E. S. Rembeza and O. I. Borsyakova, *Semiconductors*, V**35**. N**7**(2001), 796-800.
4. W. Wang, C. Xu, Y. Liu, and C. Zheng, *J. Appl. Phys.*, V**92**, N**5**(2002), 2740-2742.
5. F. Gu, S. Wang, C. F. Song, M. K. Lu, *Chem. Phys. Lett.*, **372**(2003), 451-454.
6. S.H. Sun, G. W. Meng, G. Zhang, T. Gao, *Chem. Phys. Lett.*, **376**(2003), 103-107.
7. Z.L. Wang and Z. Pang, *Inter. J. Nano.*, V**1**, N**1**(2002), 41-45.
8. J.Q. Hu, Y. Bemdo, D. Golberg, *Chem. Phys. Lett.*, **372**(2003), 758-762.
9. J.Q. Hu, X. L. Ma, N. G. Shoung, Z. Y. Xie, N. B. Wong, C. S. Lee, and S. T. Lee, *J. Phys. Chem.*, **106**(2002), 3823-3826.
10. T.W. Kim, D. U. Lee, D. C. Choo, J. H. Kim, H. J. Kim, J. H. Jeong, M. Jung, J. H. Bahang, H. L. Park, Y. S. Yoon, *J. Phys. Chem. Sol.*, **63**(2002), 881-885.