

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7885254>

# Single Crystal SnO<sub>2</sub> Zigzag Nanobelts

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 2005

Impact Factor: 12.11 · DOI: 10.1021/ja042748d · Source: PubMed

---

CITATIONS

138

---

READS

33

8 AUTHORS, INCLUDING:



Junhong Duan

Nanchang Hangkong University

21 PUBLICATIONS 461 CITATIONS

SEE PROFILE



Hongwei Liu

University of Sydney

124 PUBLICATIONS 2,303 CITATIONS

SEE PROFILE



Youwei Du

Dalian Maritime University

317 PUBLICATIONS 4,086 CITATIONS

SEE PROFILE

Single Crystal SnO<sub>2</sub> Zigzag Nanobelts

Junhong Duan, Shaoguang Yang,\* Hongwei Liu, Jiangfeng Gong, Hongbo Huang, Xiaoning Zhao, Rong Zhang, and Youwei Du

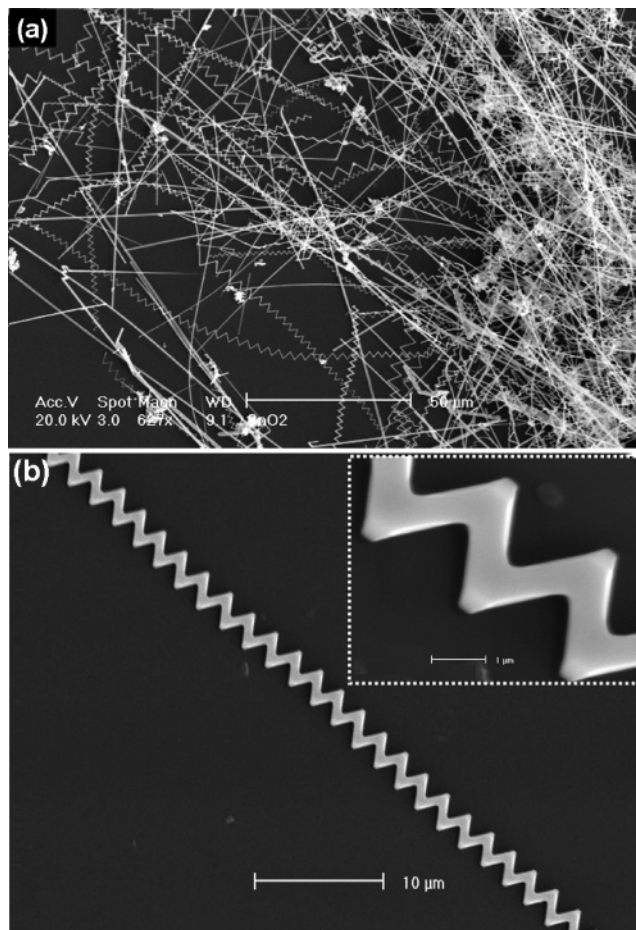
National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Received December 2, 2004; E-mail: sgyang@nju.edu.cn

Research on the growth and properties of nanobelt-based materials has increased steadily since their discovery,<sup>1</sup> largely due to their potential applications in nanoscale devices as interconnects or functional components.<sup>2</sup> A variety of nanobelts have been fabricated for a wide range of materials, such as semiconductors<sup>3</sup> and oxides.<sup>4</sup> Very recently, it has been shown that several new geometric configurations, such as nanohelices<sup>5</sup> and nanorings,<sup>6</sup> can be grown from nanobelts. SnO<sub>2</sub> is an environmentally friendly semiconductor with the band gap of 3.6 eV at room temperature. It has attracted a lot of interest as an excellent candidate for photoluminescence material and gas sensor.<sup>7</sup> Many efforts have been made on the preparation<sup>8</sup> and application<sup>9</sup> of SnO<sub>2</sub> nanobelt-based materials. In this study, we present a peculiar microstructure of nanobelt-based SnO<sub>2</sub>, zigzag structure, which was prepared by oxidizing Sn at high temperature.

The zigzag SnO<sub>2</sub> sample was synthesized by oxidizing Sn in the ambient atmosphere at the temperature ranging from 820 to 950 °C. To prepare the sample, 1 g of Sn (SCRC, 99.9%) grains was wrapped by an iron network (500 mesh, SCRC) and put into a quartz tube of 1 cm in diameter. A tube furnace was used in the sample preparation, which was kept at a constant temperature during the whole process. After 3 h reaction, a white fluffy sample was observed between the layers of the iron network. The network not only worked as a substrate to collect the zigzag nanobelts, but also provided a microenvironment in the reaction, confining the Sn vapor and the oxygen gas within it. Without the iron network or outside of it, no zigzag SnO<sub>2</sub> was observed. Zigzag SnO<sub>2</sub> is contained in the white fluffy samples as shown below. By using an asbestos network, zigzag SnO<sub>2</sub> nanobelts were also observed in our experiments. All the samples presented in this communication were prepared at 900 °C. The prepared sample was characterized by scanning electron microscopy (SEM, Philips XL30), X-ray diffraction (XRD), and transmission electron microscopy (TEM, Philips Tecnai F20).

Figure 1a is a typical SEM image of the prepared sample. Large amounts of zigzag structured materials can be observed. The longest zigzag observed in the sample is more than 0.5 mm (see Supporting Information Figure S1). In the sample, more than half is zigzag. The typical width and thickness of the zigzags are in the range of 0.1–1 μm and 30–80 nm, respectively, and the repeating length is in the range of 2–8 μm. It should be a common nature for nanobelts to form zigzag microstructures by growing along the different equivalent directions alternately. For clarifying the microstructure, a high magnification image is obtained and shown in Figure 1b with an inset of focus on part of the same zigzag. It is obvious that the zigzag is a well periodical microstructured nanobelt with a period of 2.5 μm. For this zigzag, the width and the angle are almost invariable throughout, and no evident difference was found in the thickness of the nanobelt. In a few of the zigzag microstructures, the periods changed gradually from small to large; however, the thickness and the angles of the nanobelts are invariable

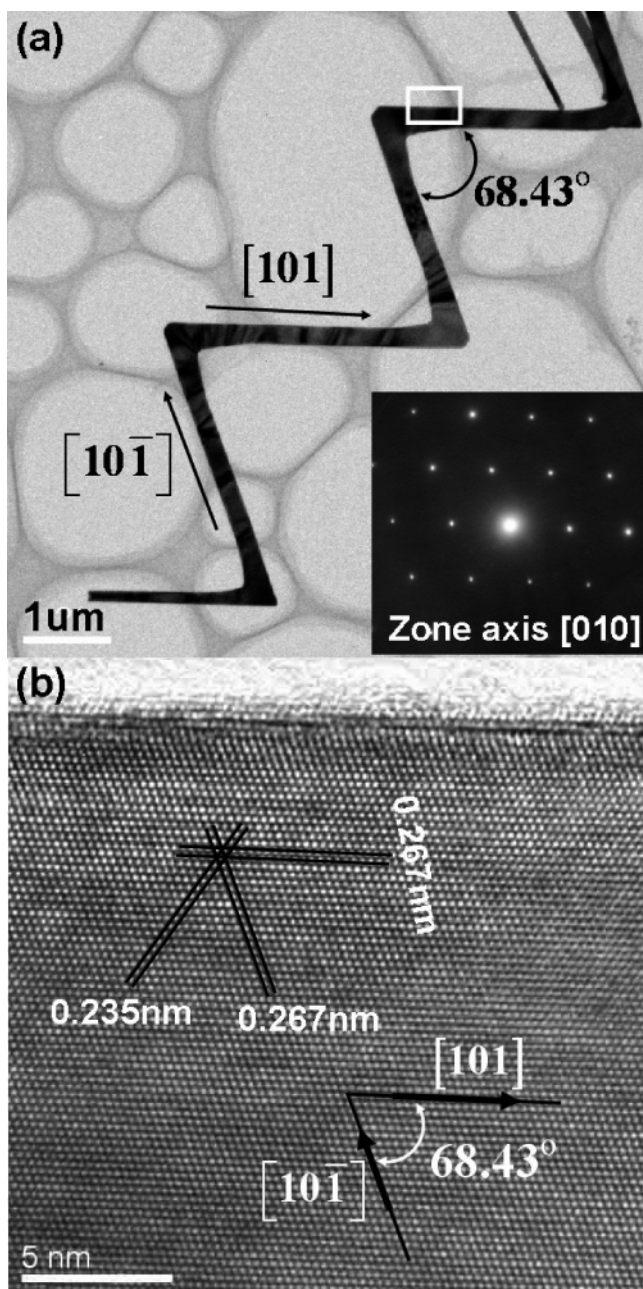


**Figure 1.** SEM images of SnO<sub>2</sub> zigzag. (a) Low magnification image of the sample with zigzag more than half of the total. (b) High magnification image of one well periodic zigzag structure with the angle of about 68°; the inset is a focused image on part of the zigzag.

(see Supporting Information Figure S1). From the SEM images, some nanobelts and wire-like materials can be observed.

XRD was employed in determination of the sample phase. Figure S3 in Supporting Information is the XRD pattern that can be indexed as tetragonal SnO<sub>2</sub> (space group: *P4<sub>2</sub>/mmm*) with crystal constant *a* = *b* = 0.4738 nm and *c* = 0.3187 nm. No any other phases can be detected by XRD, which reveals that the pure SnO<sub>2</sub> with tetragonal structure is obtained. As more than half of the obtained sample is zigzag and the others are wires/nanobelts, we can conclude that both zigzags and wires/nanobelts are pure SnO<sub>2</sub> with tetragonal structure.

TEM is employed for further crystal structure study of the sample. Figure 2a is a typical TEM image of the zigzag structure that has changed its growth direction of a measured angle 68.43°. In this image, the ripple-like contrast reveals that the thickness of



**Figure 2.** (a) TEM image of a  $\text{SnO}_2$  zigzag with inset showing the SAED pattern correspondingly. SAED patterns are the same on the whole zigzag. (b) HRTEM of the marked part in Figure 2a.

the zigzag is smaller than 100 nm. No evident difference in thickness can be observed on the whole zigzag. High resolution TEM (HRTEM) was performed on the zigzag. Figure 2b is an HRTEM image of the marked part in Figure 2a. Every HRTEM image shows a perfect single crystal structure except the sample boundary. In very recently published work,<sup>10</sup> V-shaped  $\text{SnO}_2$  has just been synthesized with twin structure at the corners. In our present work, HRTEM has been operated carefully at the corners of the zigzag, which presented almost perfect crystallographic image (see Supporting Information Figure S2). Selected area electron diffraction (SAED) patterns on the corners of the zigzag also revealed its single crystal characteristic.

Combining the HRTEM image and SAED pattern, it can be measured that the  $d$  spacings are 0.267 and 0.235 nm, which agree

well with the  $d$  spacings of (101) and (200) of tetragonal  $\text{SnO}_2$ . The angle between  $[101]$  and  $[10\bar{1}]$  is measured as  $68.43^\circ$  from the HRTEM image. The SAED pattern reveals the zigzag nanobelt as a single crystal with its top and bottom surfaces represented by the (010) and  $(0\bar{1}0)$  surfaces. It can be concluded that the zigzag structure is formed by changing the growth directions from  $[101]$  to  $[10\bar{1}]$  or vice versa.

In the crystallography,  $\langle 101 \rangle$  directions in tetragonal  $\text{SnO}_2$  are equivalent. Because of small differences in surface energy between (101) and  $(10\bar{1})$ , a slight fluctuation of the reaction conditions (partial pressures of the reactants, temperature, etc.) can cause the crystal to grow from (101) to  $(10\bar{1})$  or vice versa. This small change in growth kinetics may be the reason for the zigzag microstructure formation in the present case. When the nanobelt growth direction alternates between  $[101]$  and  $[10\bar{1}]$ , it is calculated that the angle between (101) and  $(10\bar{1})$  is about  $67.86^\circ$ , which is very consistent with the experimental result ( $68.43^\circ$ ). This will lead to the zigzag structures as shown in our experiment. According to the above analysis, there should be another possibility to form an obtuse angle zigzag structure by changing the growth direction from  $[101]$  to  $[10\bar{1}]$  and vice versa. The second kind of zigzag structure has been observed in the sample.

In conclusion, zigzag  $\text{SnO}_2$  microstructures were synthesized. This provides a new candidate for nanodevices. Growing nanobelts along different equivalent directions opens a new avenue for the preparation of unique nanostructured materials. Our experimental results also suggest the need for further extensive studies on the promising structures.

**Acknowledgment.** We thank Dr. Patrick Jasinski and Dr. Hao Zhu for help in the manuscript preparation. This work was supported by the Natural Science Foundation of China (No. 60390072) and The National Key Project for Basic Research (No. G1999064508).

**Supporting Information Available:** SEM image of long zigzag  $\text{SnO}_2$  nanobelts, HRTEM image at the corner of the zigzag, and XRD result of the sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947–1949.
- (2) (a) Melosh, N. A.; Boukai, A.; Diana, F.; Gerardot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112–115. (b) Duan, X. F.; Huang, Y.; Charles, R. A.; Lieber, M. *Nature* **2003**, *421*, 241–245. (c) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. D. *Science* **2001**, *292*, 1897–1899. (d) Law, M.; Sirbully, D. J.; Johnson, J. C.; Goldberger, J.; Saykally, R. J.; Yang, P. D. *Science* **2004**, *305*, 1269–1273.
- (3) (a) Gong, J. F.; Yang, S. G.; Duan, J. H.; Zhang, R.; Du, Y. W. *Chem. Commun.* **2005**, 351–353. (b) Jiang, Y.; Meng, X. M.; Liu, J.; Hong, Z. R.; Lee, C. S.; Lee, S. T. *Adv. Mater.* **2003**, *15*, 1195–1198.
- (4) Hu, J. Q.; Ma, X. L.; Shang, N. G.; Xie, Z. Y.; Wong, N. B.; Lee, C. S.; Lee, S. T. *J. Phys. Chem. B* **2002**, *106*, 3823–3826.
- (5) Hughes, W. L.; Wang, Z. L. *J. Am. Chem. Soc.* **2004**, *126*, 6703–6709.
- (6) (a) Kong, X. Y.; Ding, Y.; Yang, R.; Wang, Z. L. *Science* **2004**, *303*, 1348–1351. (b) Kong, X. Y.; Wang, Z. L. *Nano. Lett.* **2003**, *3*, 1625–1631.
- (7) (a) Comini, E.; Faglia, G.; Sberveglieri, G.; Pan, Z. W.; Wang, Z. L. *Appl. Phys. Lett.* **2002**, *81*, 1869–1871. (b) Kolmakov, A.; Zhang, Y. X.; Chen, G. S.; Moskovits, M. *Adv. Mater.* **2003**, *15*, 997–1000.
- (8) Comini, E.; Guidi, V.; Malagu, C.; Martinelli, G.; Pan, Z.; Sberveglieri, G.; Wang, Z. L. *J. Phys. Chem. B* **2004**, *108*, 1882–1887.
- (9) (a) Mao, S. X.; Zhao, M. H.; Wang, Z. L. *Appl. Phys. Lett.* **2003**, *83*, 993–995. (b) Shi, L.; Hao, Q.; Yu, C.; Mingo, N.; Kong, X. Y.; Wang, Z. L. *Appl. Phys. Lett.* **2004**, *84*, 2638–2640. (c) Arnold, M. S.; Avouris, D.; Pan, Z. W.; Wang, Z. L. *J. Phys. Chem. B* **2003**, *107*, 659–663.
- (10) Wang, Y.; Lee, J. Y.; Deivaraj, T. C. *J. Phys. Chem. B* **2004**, *108*, 13589–13593.

JA042748D