NANO: Brief Reports and Reviews
Vol. 2, No. 2 (2007) 91–95

SIMPLE AND CATALYST-FREE SYNTHESIS OF SILICON OXIDE NANOWIRES AND NANOCOILS

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Received 22 January 2007

In this paper, a simple method for synthesizing SiO_x nanowires and nanocoils is presented. Si substrates with an oxide layer were placed in a tube furnace exposed to temperatures ranging from 900°C to 1200°C for a few hours under a mixture of flowing Ar and H_2 gas maintained at ambient pressure. Nanowires were grown from the surface when the furnace temperature was above 1000°C and a high yield could be achieved at 1100°C. SiO_x nanocoils have also been observed and the sample treated at 1000°C had the highest concentration of them. TEM images show that the nanowires and the nanocoils have an amorphous structure and analysis of EDX spectra (obtained in the TEM) shows that x varies from 1.2 to 2.0. The mechanism of growth is discussed.

Keywords: Silicon oxide; nanowire; nanocoil; amorphous; EDX; TEM.

1. Introduction

Silicon oxide nanowires may have many applications due to their electrical, mechanical and optical properties. Silicon oxide is an electrically insulating material and can emit stable blue light. Conventional glass fibers are used in the reinforcement of composites and nanowires could find similar use. Many methods have been reported for the synthesis of silicon oxide nanowires including catalytic chemical vapor deposition (CVD),[1–17] catalyst-free CVD,[18–22] laser ablation,[23] and via sol–gel templating.[24] We describe a simple method to synthesize silicon oxide nanowires and nanocoils. A piece of Si wafer with a SiO_2 layer was loaded into a thermal CVD tube furnace and heated above 1000°C for a few hours in a mix of flowing Ar and H_2 maintained at ambient pressure. Upon completion of the reaction, a gray layer was observed on the substrate. Characterization by scanning electron microscopy (SEM) showed this layer to consist of nanowires. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analysis showed the nanowires to be amorphous SiO_x. We also found that SiO_x nanocoils could be concurrently synthesized under certain conditions. No catalyst was used so the product is composed of clean SiO_x nanostructures free of any metal contamination.

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2. Experimental Procedures

A Si(100) substrate was thermally oxidized to form a 230 nm thick SiO_2 layer on Si. The wafer was cleaved into 1 cm × 1 cm square pieces and cleaned in an ultrasonic bath of acetone for 30 min. After this pretreatment, a single piece of substrate was placed on an alumina board which was heated in an alumina tube furnace (Lindberg/Blue M, Asheville, North Carolina) at temperatures ranging from 900°C to 1200°C for periods of time varying between 10 min to 5 h. The ramp up rate was 50°C/min and the ramp down was by natural cooling by turning off the power. The substrate was exposed to Ar gas during the entire process sequence including temperature ramp up and down cycles. H_2 gas was introduced only when the desired temperature was reached. The Ar gas flow rate was 180 sccm and the H_2 gas flow rate was 900 sccm. The furnace was maintained at one unit of atmospheric pressure. Depending on the growth temperature, the growth time, and the flow rate of H_2(g), nanowires and nanocoils grew from the edge and the top surface of the substrate. The product nanomaterials have been characterized with SEM (Leo 1525), TEM (Hitachi HF-2000), and EDX (attached on the same Hitachi HF-2000 TEM).

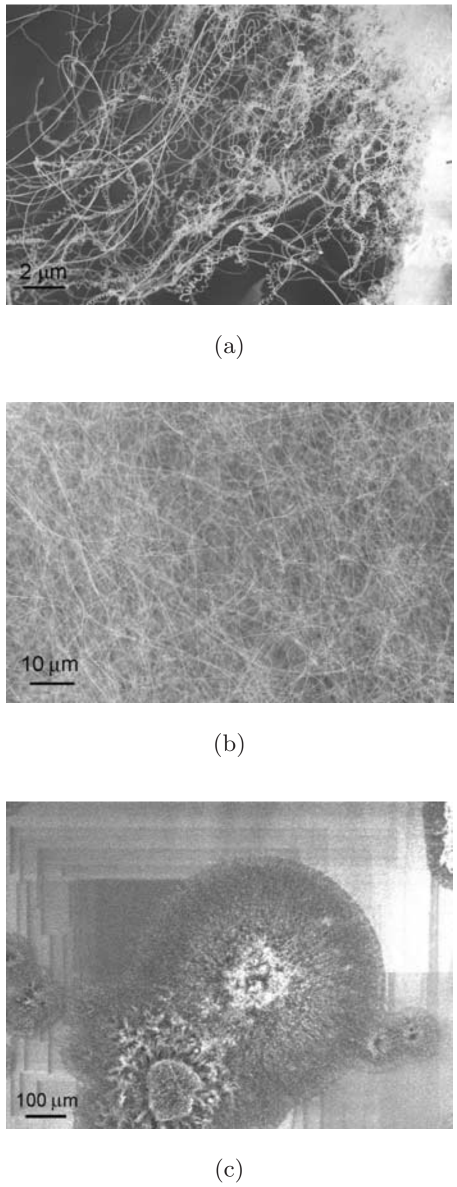


Fig. 1. SEM images of the substrate treated at (a) 1000°C, (b) 1100°C, and (c) 1200°C for 3 h with an Ar (180 sccm) and H_2 (900 sccm) gas flow.

3. Results and Discussion

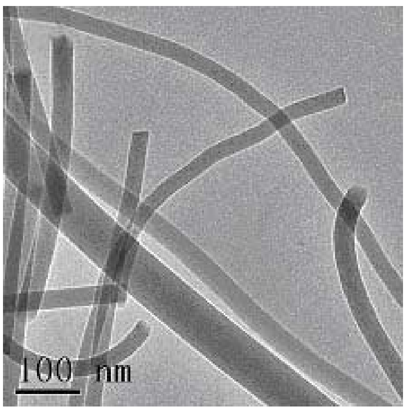
The Ar and H_2 gas flow rates used for the experiment were 180 sccm and 900 sccm, respectively. The growth time was 3 h and the substrate type was Si/SiO_2. Four different furnace temperatures were used: 900°C, 1000°C, 1100°C, and 1200°C. No nanostructures were observed on the surface of the substrate treated at 900°C. When the temperature was increased to 1000°C, nanowires were (subsequently, by SEM) readily observed on the substrate. The surface, however, was not densely covered by nanowires. They grew from isolated spots rather than uniformly covering the surface. Also, the nanowires grew much more densely at the edges of the substrate than in the central region. SEM images showed that the nanowires were aligned and had grown perpendicular to the edges. There were ∼20–30% nanocoils with the remainder being straight nanowires. The nanocoils had similar diameters and lengths as the nanowires, and had a wide range of pitches and coil diameters. SEM image is shown in Fig. 1(a).

At a furnace temperature of 1100°C, a gray layer of nanowires was formed on the surface of the same type of substrate. The nanowires had grown much more densely on both the edges and the top surface. SEM images showed that the nanowires were aligned perpendicular to the edges but were essentially randomly oriented in the central region. Nanocoils were also observed, but with a lower concentration than that on the sample treated at 1000°C. SEM image of a typical sample is shown in Fig. 1(b).

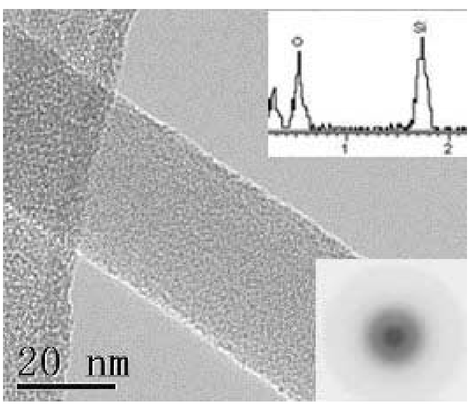
When a furnace temperature of 1200°C was used, the morphology was much different.

Figure 1(c) shows an SEM image of a typical surface after the reaction. Many "flower-like" spots of different sizes were observed on the surface. Closer observation showed that a dense field of nanowires grew radially from a central cavity that possessed a very low concentration of nanostructures. Aligned nanowires at the edges of the substrate were not observed, in contrast to those observed on the substrates treated at 1000°C and 1100°C.

The surfaces of the substrates treated at 1100°C for 3 h were scratched with holey carbon TEM grids (Structure Probe, Inc. West Chester, Pennsylvania) and analyzed using the TEM. The TEM images are shown in Fig. 2. High-resolution TEM images and electron diffraction revealed that the examined structures are amorphous. EDX analysis showed that the nanowires examined consist of O and Si. The atomic ratio based on EDX

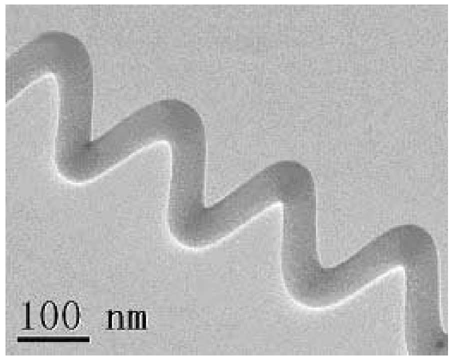


(a)

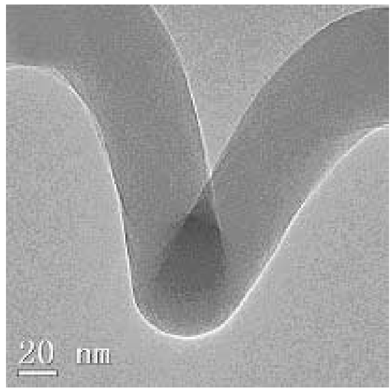


(b)

Fig. 2. TEM images of SiO_x nanowires: (a) low-mag TEM image and (b) high-mag TEM image. Upper inset: EDX of individual nanowire; lower inset: electron diffraction pattern of individual nanowire.



(a)



(b)

Fig. 3. TEM images of SiO_x nanocoil: (a) low-mag TEM image and (b) high-mag TEM image showing an amorphous structure.

data taken from individual nanowires and multi-nanowires was determined. The atomic ratio of Si and O varied from 1:1.2 to 1:2.0.

The nanocoils from the sample treated at 1000°C have similar composition and structure to the straight nanowires. The TEM images of these nanocoils are shown in Fig. 3.

We have measured the diameter of 72 nanowires based on the low-mag TEM images. The diameter range is from 20 nm to 85 nm with a mean of 40 nm. Lengths up to 100 μm were observed by SEM.

As control experiments, we heat-treated Si/SiO_2 substrates at 1200°C for 3 h with only Ar(180 sccm gas flow), only H_2 (900 sccm flow), and with neither gas introduced. No nanowires were observed on the substrates treated with only Ar gas flow, or with both Ar and H_2 absent, and the surface appeared as smooth as it was before the treatment. However, with only H_2 gas flow, nanowires and nanocoils were clearly present. This suggests that, for the experimental parameters explored,

H_2 is critical for SiO_x nanostructure growth. A Si substrate with only a natural oxide layer (thus, a few nanometers thick) was treated in the tube furnace at 1200°C for 3 h under the same environment. We found that the surface was etched and there were many pits, but only a small number of nanowires were observed.

Crowley[25] reported hydrogen–silica reactions in refractories (defined as a material that has a high melting point and is therefore able to withstand high temperatures without crumbling or softening, e.g., silica, fireclay and metal oxides, which are used to line furnaces, etc.) contained silica. The weight loss of the refractories when exposed to H_2 at atmospheric pressure was caused by the reaction of H_2 and SiO_2:

$$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)\,. \qquad (1)$$

Because there was no significant nanowire growth when the Si substrate (with only the natural oxide layer) was used, the thermally oxidized SiO_2 layer is evidently important for the synthesis of nanowires. According to Crowley's paper, the minimum reaction temperature of H_2 and SiO_2 is about 1700°F (930°C), which is in agreement with our results. Formula (1) may, therefore, represent the reaction occurring in our tube furnace. The water vapor may be carried away with the Ar and unreacted H_2 gas. The vapor phase SiO, however, might react with O_2 arising from impurities in the Ar and H_2 gases to form solid SiO_x nanowires and nanocoils.

Another interesting phenomenon is that the nanowires at the edge of the substrate were aligned perpendicular to the edges, but were randomly oriented at the center. The cause of this variation in orientation has not been determined.

4. Summary

We have presented a simple catalyst-free thermal CVD method for synthesizing amorphous SiO_x nanowires and nanocoils free of any metal. The value of x determined by EDX is in the range ~ 1.2–2.0. The diameters of the nanowires ranged from 20 nm to 85 nm, and lengths up to 100 μm were observed. We studied the possibility of growth in the temperature range from 900°C to 1200°C, in 100°C increments. No growth occurred at 900°C for the time and gas exposure we used. 1100°C was the most favorable temperature for nanowire growth and 1000°C was most favorable for nanocoil growth, of the three temperatures (1000°C, 1100°C, and 1200°C) where growth of some type occurred.

Acknowledgments

The SEM and TEM work were performed in the EPIC facility of NUANCE Center at Northwestern University. NUANCE Center is supported by NSF-NSEC, NSF-MRSEC, Keck Foundation, the State of Illinois, and Northwestern University.

References

1. S. H. Li, X. F. Zhu and Y. P. Zhao, *J. Phys. Chem. B* **108**, 17032 (2004).
2. J. L. Elechiguerra, J. A. Manriquez and M. J. Yacaman, *Appl. Phys. A: Mater. Sci. Process.* **79**, 461 (2004).
3. Y. W. Wang, C. H. Liang, G. W. Meng, X. S. Peng and L. D. Zhang, *J. Mater. Chem.* **12**, 651 (2002).
4. K. H. Lee, C. Loftona, K. Kima, W. S. Seob, Y. Leeb, M. H. Leeb and W. Sigmunda, *Solid State Commun.* **131**, 687 (2004).
5. J. Niu, J. Sha, N. Zhang, Y. Jia, X. Ma and D. Yang, *Physica E* **23**, 1 (2004).
6. J. Jian, X. Chen, Y. Ma and X. Li, *J. Phys.: Condens. Matter* **15**, 8177 (2003).
7. P. A. Hu, *Appl. Phys. A: Mater. Sci. Process.* **77**, 743 (2003).
8. Z. Pan, S. Dai, D. B. Beach and D. H. Lowndes, *Nano Lett.* **3**, 1279 (2003).
9. B. Zheng, Y. Wu, P. Yang and J. Liu, *Adv. Mater.* **14**, 122 (2002).
10. Y. J. Chen, J. B. Li, Y. S. Han, Q. M. Wei and J. H. Dai, *Appl. Phys. A: Mater. Sci. Process.* **74**, 433 (2002).
11. C. H. Liang, L. D. Zhang, G. W. Meng, Y. W. Wang and Z. Q. Chu, *J. Non-Cryst. Solids* **277**, 63 (2000).
12. K. H. Lee, S. W. Lee, R. R. Vanfleet and W. Sigmund, *Chem. Phys. Lett.* **376**, 498 (2003).
13. H. F. Zhang, C. M. Wang, E. C. Buck and L. S. Wang, *Nano Lett.* **3**, 577 (2003).
14. Z. Zhang, Y. Zhao and J. Liu, *J. Phys.: Condens. Matter* **15**, L505 (2003).
15. X. Zhang, C. Li and Z. Zhang, *Mater. Lett.* **58**, 1917 (2004).
16. S. H. Sun, G. W. Meng, M. G. Zhang, Y. T. Tian, T. Xie and L. D. Zhang, *Solid State Commun.* **128**, 287 (2003).
17. K. H. Lee, H. S. Yang, K. H. Baik, J. Bang, R. R. Vanfleet and W. Sigmund, *Chem. Phys. Lett.* **383**, 380 (2004).

18. J. Q. Hu, Y. Jiang, X. M. Meng, C. S. Lee and S. T. Lee, *Chem. Phys. Lett.* **367**, 339 (2003).
19. Y. Zhang, N. Wang, S. Gao, R. He, S. Miao, J. Liu, J. Zhu and X. Zhang, *Chem. Mater.* **14**, 3564 (2002).
20. Z. L. Wang, R. P. Gao, J. L. Gole and J. D. Stout, *Adv. Mater.* **12**, 1938 (2000).
21. G. W. Meng, *Appl. Phys. A* **76**, 119 (2003).
22. Y. Zhang, N. Wang, R. He, J. Liu, X. Zhang and J. Zhu, *J. Cryst. Growth* **233**, 803 (2001).
23. D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong and S. Q. Feng, *Appl. Phys. Lett.* **73**, 3076 (1998).
24. M. Zhang, Y. Bando, K. Wada and K. Kurashima, *J. Mater. Sci. Lett.* **18**, 1911 (1999).
25. M. S. Crowley, *Am. Ceram. Soc. Bull.* **49**, 527 (1970).