

Pt-Catalyzed Growth of Amorphous SiO_x Nanowires

Hyoun Woo KIM,* Seung Hyun SHIM and Jong Woo LEE

School of Materials Science and Engineering, Inha University, Incheon 402-751

Mi Kyoung PARK

Center for Research Facilities, Inha University, Incheon 402-751

Jae-Won SOH, Keun Hyeung LEE, Wan In LEE, Ik-Mo LEE and Sang-Eon PARK

Department of Chemistry, Inha University, Incheon 402-751

(Received 16 February 2007)

We have fabricated SiO_x nanowires on a large scale through a Pt-catalyzed process. The scanning electron microscopy (SEM) investigation revealed that the nanowires had diameters in the range of 30 ~ 130 nm. X-ray diffraction (XRD), selected area electron diffraction (SAED), and energy-dispersive X-ray (EDX) analyses indicated that the nanowires were amorphous and consisted only of Si and O elements. The growth of the SiO_x nanowires was most likely controlled by the base-growth mechanism with the assistance of the underlying Pt layer. The room-temperature PL spectrum measurement showed a broad emission band, peaking around 3.0 eV. This simple heating method, with the effectiveness of the Pt catalyst, can be applied to a wide range of substrate materials, which may contribute to producing various useful nanostructures.

PACS numbers: 61.10.Nz, 78.55.-m, 81.07.-b

Keywords: Nanowires, SiO_x

I. INTRODUCTION

Since the first pioneering work that resulted in the discovery of carbon nanotubes by Iijima [1], other one-dimensional (1D) nanomaterials in the form of tubes, wires, and belts have aroused considerable attention among scientists from a diverse range of research fields because of their interesting geometries, novel properties, and potential applications [2–8]. Silicon (Si) and silica (SiO_x) nanostructures have become the focus of intensive research due to their unique properties and promising applications in mesoscopic research, nanodevices, and opto-electronics devices [9–11]. Particularly, SiO_x is an important material for photoluminescence (PL) [12,13]. Since the majority of SiO_x nanowires fabrication methods are catalyst-based methods, different kinds of metal catalysts, including Au [14–16], Fe [17,18], Ga [19,20], Ni [21], and Sn [22], have been used.

Platinum (Pt) is a good conductor of heat and electricity (second only to silver in electrical conductivity) and has long been widely used in electronic devices. Also, Pt tends to remain pure during chemical reactions, being a good candidate as a catalyst. Although carbon nanotubes (CNTs) have been synthesized using platinum

(Pt) as a catalyst [23–25], to the best of our knowledge, the synthesis of an inorganic nanostructure by the assistance of Pt has rarely been reported. In this paper, we report the production of SiO_x nanowires by using Pt as a catalyst. We suggest a possible growth mechanism in regard to the role of the underlying Pt layers.

II. EXPERIMENTS

The synthesis of nanostructures was performed in a high-temperature tube furnace, which has been previously described [26]. A quartz tube was placed horizontally inside the tube furnace. We used Si substrates as starting materials onto which a layer of Pt with the thickness of about 5 nm was deposited by using a sputter coater (Emitech, K757X). A piece of the Pt-coated substrate was placed in the middle of the quartz tube. During the experiment, an ambient gas (~3.15 % O_2 in a balance of argon) was maintained at a constant pressure of 2 Torr. The substrate temperature was set to 1040 °C. After 2 h of typical deposition, the substrate was cooled down and then removed from the furnace for structural and optical characterizations.

The morphologies and the crystal structures of the samples were characterized using grazing angle X-ray

*E-mail: hwkim@inha.ac.kr; Fax: +82-32-862-5546

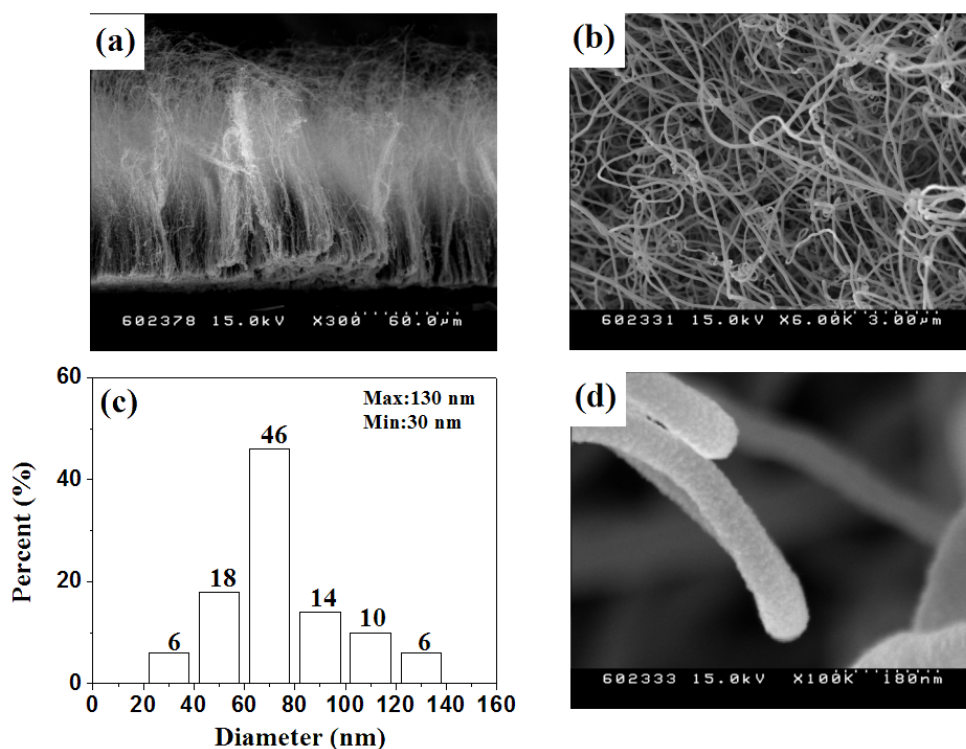


Fig. 1. (a) Side-view and (b) plan-view SEM images of the product. (c) The diameter distribution of the nanowires. (d) High-magnification SEM image of the nanowires.

diffraction (XRD: CuK_{α1} radiation) (Philips X'pert MRD) with an incidence angle of 0.5° and scanning electron microscopy (SEM, Hitachi S-4200), respectively. Further structural analysis of individual nanostructures was performed using transmission electron microscopy (TEM, Philips CM-200) with an energy-dispersive X-ray (EDX) spectroscope installed. The PL measurement was performed at room temperature by using the He-Cd laser (Kimon, 1 K, Japan) line of 325 nm as the excitation source.

III. RESULTS AND DISCUSSION

Figure 1(a) is a side-view SEM image of the deposits on the surface of the substrate, indicating that the deposits are wool-like with a thickness of approximately 130 μm. Figure 1(b) is a typical plan-view SEM image, showing that the wool-like product consists of a large quantity of nanowires. The waving and twisting shapes of the nanowires are apparent. Statistical observation of many SEM images indicated that the diameters of nanowires varied from 30 to 130 nm. The diameter distribution of the nanowires is shown in Figure 1(c), revealing that the maximum of the diameter distribution occurred in range of 60 ~ 80 nm. Figure 1(d) shows a high-magnification SEM image, revealing that the cross-section of the nanowires had a circular shape with no

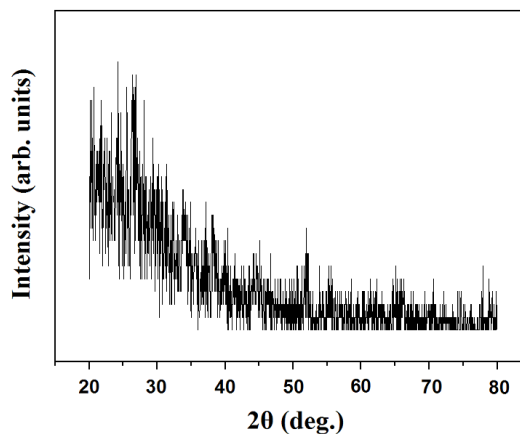


Fig. 2. X-ray diffraction pattern of the product.

nanoparticles at the tips. Figure 2 shows the XRD pattern of the product, revealing that the nanowires are fully amorphous. In the present XRD measurements, the angle of the incident beam relative to the substrate surface was approximately 0.5°, and the detector was rotated to scan the samples, minimizing the contribution from the underlayer or the substrate. In order to further investigate the composition and the crystalline structure of the nanowires, we carried out TEM with selected area electron diffraction (SAED) and EDX analyses. Before these tests, the nanowires were removed from the substrate by

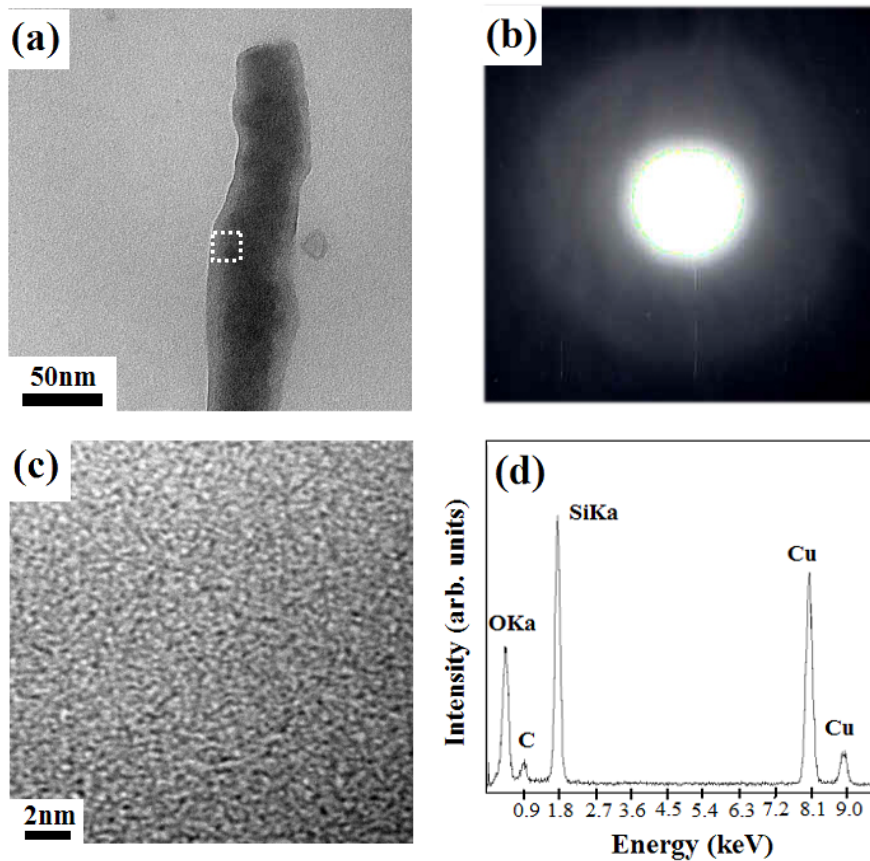


Fig. 3. (a) Low-magnification TEM image showing the general morphology of a SiO_x nanowire. (b) Corresponding highly diffusive SAED pattern of SiO_x nanowires. (c) High-resolution TEM image enlarging an area enclosed by the dotted square in (a). (d) EDX spectrum taken from the tip of a nanowire.

ultrasonic vibration in acetone; and then, the nanowires were positioned onto an amorphous carbon-coated Cu grid. Figure 3(a) shows the TEM image of a nanowire. No nanoparticles are observed at the end of the wire, agreeing with the SEM image (Figure 1(d)). The highly diffusive ring pattern in the corresponding SAED pattern shown in Figure 3(b) reveals that the nanowires are of a completely amorphous state. Also, the high-resolution TEM (HRTEM) image, an enlargement of the area enclosed by the dotted square in Figure 3(a), indicates the amorphous characteristics of the nanowires, due to the absence of lattice fringes (Figure 3(c)). The EDX measurement made on the wire tip (Figure 3(d)) indicates that the peaks correspond to Si and O. C and Cu signals are generated from the microgrid mesh supporting the nanowires. Although it is difficult to determine the ratio quantitatively due to the uncertainty of the EDX intensity detected for lighter elements, we revealed that the structure consisted of Si and O elements, regardless of their positions in the nanowire from the stem to the ends.

In our preliminary experiments, when the heating was carried out under the same growth conditions on bare-Si substrates in the absence of Pt layers, we did not

obtain any nanostructure, revealing that the Pt layer played a crucial role in the formation of the nanowires. To present, SiO_x nanowires have mainly been fabricated using the vapor-liquid-solid (VLS) method [14, 16–20, 22]. The solidified spherical droplet at the tip of the nanowires is commonly considered to be evidence for the operation of a conventional tip-growth VLS mechanism. However, although a Pt-coated substrate was employed in the present work, the SEM and the TEM analyses provided no evidence that the Pt catalyst was present at the tips of the nanowires. One possibility is that the growth mechanism of SiO_x nanowires can be mainly controlled by the base-growth mechanism, in which the metal catalyst remains situated at the bottom of the nanowires. By using the base-growth mechanisms, Fan *et al.* [27], Kim and Shim [28], and Yu *et al.* [29] reported the production of CNTs, MgO nanowires, and amorphous Si nanowires, respectively.

The growth of the SiO_x nanowires in the present study can be divided into three steps. In the first step, when the Pt-coated Si substrate was heated, Pt/Si liquid droplets form at a growth temperature of 1040 °C because of the relatively low eutectic temperature of PtSi: from the Pt-Si binary phase diagram, the eutectic point

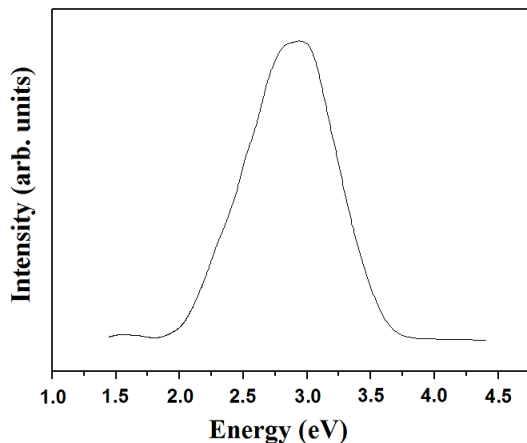


Fig. 4. Room-temperature PL spectrum of the product.

of PtSi is about 979 °C [30]. Since no extra Si source was introduced in the vapor phase of the present study, we suggest that the only possible Si source should be the Si substrate. The present synthesis process mainly involves the solid phase with respect to the Si, in addition to the Si-related vapor in the system at a high temperature of 1040 °C due to the thermal evaporation directly from the Si layer. In the second step, the droplets or nanoparticles act as the nucleation sites, initiating the growth of SiO_x nanowires. The most likely source of oxygen may come from the O₂ in the carrier gas, which can provide a constant supply of oxygen during the growth of SiO_x nanowires. Another likely source is the oxygen adsorbed on the Si wafer due to air exposure during the processing. Residual oxygen may also be a source, as the base pressure (8×10^{-2} Torr) of the vacuum system was relatively high. The liquid state particles should easily absorb oxygen, and the presence of a relatively small amount of oxygen is not expected to change the Pt-Si phase diagram significantly. As the droplets or particles become supersaturated, SiO_x nanowires are formed, resulting from the reaction between Si and O. In the third step, by continuously dissolving Si and O onto nanoparticles, the SiO_x nanowires may subsequently grow. The droplets will continuously absorb Si atoms as the droplets are abundant in the system, whereas O₂ in the carrier gas can supply a constant oxygen source during the process. In our experimental process, the temperature (1040 °C) is only slightly higher than the eutectic point of the PtSi compound (979 °C). Therefore, when liquid Pt-Si-O alloy drops become supersaturated with Si and O atoms, re-crystallization of the atomic Si-O species is prevented, resulting in the formation of amorphous SiO_x nanowires instead of the crystalline nanowires, which is different from the growth of crystalline silicon nanowires [2, 31]. Although the Pt catalyst was found to be effective in the large-scale production of SiO_x nanowires, further systematic study is underway in order to reveal the detailed growth mechanism in terms of the role of the Pt layers.

The PL spectrum of the SiO_x nanowires at room tem-

perature is shown in Figure 4. There is an apparent broad, strong blue emission PL peak centered at about 3.0 eV. Similar blue emissions with peak positions in the range of 2.64 ~ 3.00 eV have been previously observed in the PL spectrum of SiO_x nanowires [15–17, 32] and have been attributed to neutral oxygen vacancy or oxygen deficiency-related diamagnetic defect centers [17]. Particularly, the blue light emission at 2.96 eV was previously reported for SiO_x nanowires synthesized by using a carbothermal reduction reaction [33]. The PL study suggests that the blue light emission from the SiO_x nanowires in the present study can be ascribed to the above-mentioned defects arising from oxygen deficiencies that can be generated during the high temperature synthetic process.

IV. CONCLUSION

We report a large-scale synthesis of SiO_x nanowires by simple heating of Pt-coated Si substrates. The structure, morphology, and chemical composition of the SiO_x nanowires were characterized by using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy. The as-synthesized SiO_x nanowires had amorphous structures with diameters in the range of 30 ~ 130 nm. The photoluminescence spectrum of the SiO_x nanowires showed a blue emission at 3.0 eV. We discussed the possible growth mechanism of the SiO_x nanowires.

ACKNOWLEDGMENTS

This work was supported by the Inha Research Fund 2006.

REFERENCES

- [1] S. Iijima, *Nature* **354**, 56 (1991).
- [2] A. Morales and C. M. Lieber, *Science* **279**, 208 (1998).
- [3] Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science* **291**, 1947 (2001).
- [4] J. Kim, B. S. Hwang, J. H. Jeong and M. H. Kwon, *J. Korean Phys. Soc.* **47**, S204 (2005).
- [5] W. I. Park, J. Yoo and G.-C. Yi, *J. Korean Phys. Soc.* **46**, L1067 (2005).
- [6] S. S. Kim, H. J. Lim, H. Cheong, W. I. Park and G.-C. Yi, *J. Korean Phys. Soc.* **46**, S214 (2005).
- [7] H. W. Kim, S. H. Shim and C. Lee, *J. Korean Phys. Soc.* **49**, 628 (2006).
- [8] H. W. Kim, J. W. Lee and C. Lee, *J. Korean Phys. Soc.* **49**, 632 (2006).
- [9] S. Mann and G. A. Ozin, *Nature* **382**, 313 (1996).
- [10] A. Katz and M. E. Davis, *Nature* **403**, 286 (2000).

- [11] C. T. Kresge, M. W. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature* **359**, 710 (1999).
- [12] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohiki, K. Nagasawa and Y. Hama, *Phys. Rev. B* **45**, 586 (1992).
- [13] L. S. Liao, X. M. Bao, X. Q. Zheng, N. S. Li and N. B. Min, *Appl. Phys. Lett.* **68**, 850 (1996).
- [14] J. S. Wu, S. Dhara, C. T. Wu, K. H. Chen, Y. F. Chen and L. C. Chen, *Adv. Mater.* **14**, 1847 (2002).
- [15] Z. Q. Liu, S. S. Xie, L. F. Sun, D. S. Tang, W. Y. Zhou, C. Y. Wang, W. Liu, Y. B. Li, X. P. Zou and G. Wang, *J. Mater. Res.* **16**, 683 (2001).
- [16] Y. W. Wang, C. H. Liang, G. W. Meng, X. S. Peng and L. D. Zhang, *J. Mater. Chem.* **12**, 651 (2002).
- [17] 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).
- [18] H.-F. Zhang, C.-M. Wang, E. C. Buck and L.-S. Wang, *Nano Lett.* **3**, 577 (2003).
- [19] Z. Pan, S. Dai, D. B. Beach and D. H. Lowndes, *Nano Lett.* **3**, 1279 (2003).
- [20] Z. W. Pan, Z. R. Dai, C. Ma and Z. L. Wang, *J. Am. Chem. Soc.* **124**, 1817 (2002).
- [21] Z. Zhang, G. Ramanath, P. M. Ajayan, D. Golberg and Y. Bando, *Adv. Mater.* **13**, 197 (2001).
- [22] S. H. Sun, G. W. Meng, M. G. Zhang, Y. T. Tian, T. Xie and L. D. Zhang, *Solid State Commun.* **128**, 287 (2003).
- [23] M. Yudasaka, Y. Kasuya, F. Kokai, K. Takahashi, M. Takizawa, S. Bandow and S. Iijima, *Appl. Phys. A* **74**, 377 (2002).
- [24] C. J. Lee, J. Park, J. M. Kim, Y. Huh, J. Y. Lee and K. S. No, *Chem. Phys. Lett.* **327**, 277 (2000).
- [25] Y. Saito, K. Nishikubo, K. Kawabata and T. Matsumoto, *J. Appl. Phys.* **80**, 3062 (1996).
- [26] H. W. Kim, N. H. Kim, J. H. Myung and S. H. Shim, *Phys. Stat. Sol. (a)* **202**, 1758 (2005).
- [27] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Cassell and H. Dai, *Science* **283**, 512 (1999).
- [28] H. W. Kim and S. H. Shim, *Chem. Phys. Lett.* **422**, 165 (2006).
- [29] D. P. Yu, Y. J. Xing, Q. L. Hang, H. F. Yan, J. Xu, Z. H. Xi and S. Q. Feng, *Physica E* **9**, 305 (2001).
- [30] T. B. Massalski, *Binary Alloy Phase Diagrams*, 1st ed. (American Society for Metals, Metals Park, 1986), Vol. 1.
- [31] D. P. Yu, C. S. Lee, I. Bello, X. S. Sun, Y. H. Tang, G. W. Zhou, Z. G. Bai, Z. Zhang and S. Q. Feng, *Solid State Commun.* **105**, 403 (1998).
- [32] G. Z. Ran, L. P. You, L. Dai, Y. L. Liu, Y. Lv, X. S. Chen and G. G. Qin, *Chem. Phys. Lett.* **384**, 94 (2004).
- [33] X. C. Wu, W. H. Song, K. Y. Wang, T. Hu, B. Zhao, Y. P. Sun and J. J. Du, *Chem. Phys. Lett.* **336**, 53 (2001).