

Synthesis and Photoluminescence of Silica Nanowires Grown on Si Substrate

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Abstract A new simple method was developed to synthesize silica nanowires by physical thermal evaporation of a mixture of silica particles and iron trichloride. The silica nanowires have diameters from 30 to 50 nm, and lengths of $\sim 10 \mu\text{m}$, with iron particles at their tips. The growth mechanism of the amorphous silica nanowires follows vapor–liquid–solid model. A broad blue–green photoluminescence band with defined maximum peak energy of $\sim 2.45 \text{ eV}$ is observed at room temperature revealing that the silica nanowires could have potential applications in optoelectronic devices.

Keywords Silica · Nanowires · Photoluminescence

1 Introduction

Silicon-based nanoscale materials have attracted much attention in recent years for their valuable semiconducting,

mechanical, and optical properties, as well as their potential applications in mesoscopic research and nanodevices. For instance, the brightness of blue light emitted by amorphous silica nanowires is a hundred-times greater than that produced by porous silicon [1], making silica nanowires attractive for use as high-intensity light sources [2–4], near-field optical microscopy probes and hosts to lasing materials and low-loss optical wave guides [5]. To realize such high-efficiency nano-scale devices, it is essential to devise simple and effective methods to synthesize silica nanowires on planar substrates such as Si.

Thus far, various methods including excimer laser ablation [1], carbothermal reduction [6], catalyzed thermal decomposition [7], and sublimation of SiC in an O_2 flow [8] have been employed for the synthesis of silica nanowires. In this paper, a new simple but effective method is reported to synthesize silica nanowires. The method is based on the physical thermal evaporation of the mixture of silica particles and iron trichloride. The growth mechanism and optical properties of the silica nanowires have been carefully investigated.

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2 Experimental

2.1 Materials

Materials used for silica nanowires synthesis: Si substrate was purchased from Branch crystal technology Co. Ltd. SiO_2 (spherical nanoparticles, size $\sim 200 \text{ nm}$) and $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ were supplied by Wangwu nano technology and Shengshi environmental protection technology Co. Ltd, respectively. Hydrogen (purity 99.999%) and argon (purity 99.99%) were produced by Changguang gas plant and used without further treatment.

2.2 Sample Preparation

The growth of silica nanowires was carried out in a horizontal tube furnace system. The system contained an alumina tube inside a furnace. The gas flow was controlled with a mass flow controller. SiO_2 (1 g) and $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ powder (0.5 g) were mixed with deionized water (5 mL). The solution (10 μL) was spread uniformly with a pipette over the surface of the Si (100) substrate, which had been cleaned with trichloroethylene, acetone, and ethanol for 10 min by ultrasonic agitation. The substrate was dried in a vacuum oven at 120 °C for 2 h to form a thin film of the mixed powders on the Si substrate. The substrate, supported by an alumina boat, was placed in the constant temperature zone of the alumina tube.

The growth process of the silica nanowires can be described as follows: First, the system was purged with 300 sccm of argon, while the constant temperature zone was heated to 800 °C. Second, the constant temperature zone was heated to 1300 °C in a hydrogen atmosphere with a flow rate of 300 sccm to eliminate the remaining chloride ions and enhance the activation of the formed iron particles. Then, hydrogen gas flow (100 sccm) was used to fabricate silica nanowires at growth temperature of 1300 °C. During growth, the horizontal tube furnace system was kept at atmospheric pressure. After 15 min of growth, the furnace was cooled to room temperature in an argon atmosphere. A white product was found on the surface of the Si substrate. To study the origin of the PL, the product was scraped off and annealed in an alumina tube at 1200 °C using an oxygen and argon mixture with a flow rate of 10 and 100 sccm, respectively.

2.3 Measurements

The products were characterized by scanning electron microscopy (SEM, Hitachi S-4800), energy-dispersive X-ray spectroscopy (EDX) (attached to the SEM), X-ray diffraction (XRD, Ricoh), transmission electron microscopy (TEM, JEM-2010), and photoluminescence spectroscopy (PL, Jobin–Yvon). The PL spectra were measured using a He–Cd laser with a wavelength of 325 nm as the excitation source.

3 Results and Discussion

3.1 Structural Characteristic of the Amorphous Silica Nanowires

A large quantity of white product was formed on the silicon substrate after growth. This product is characterized by SEM (Fig. 1). Low-magnification and high-magnification

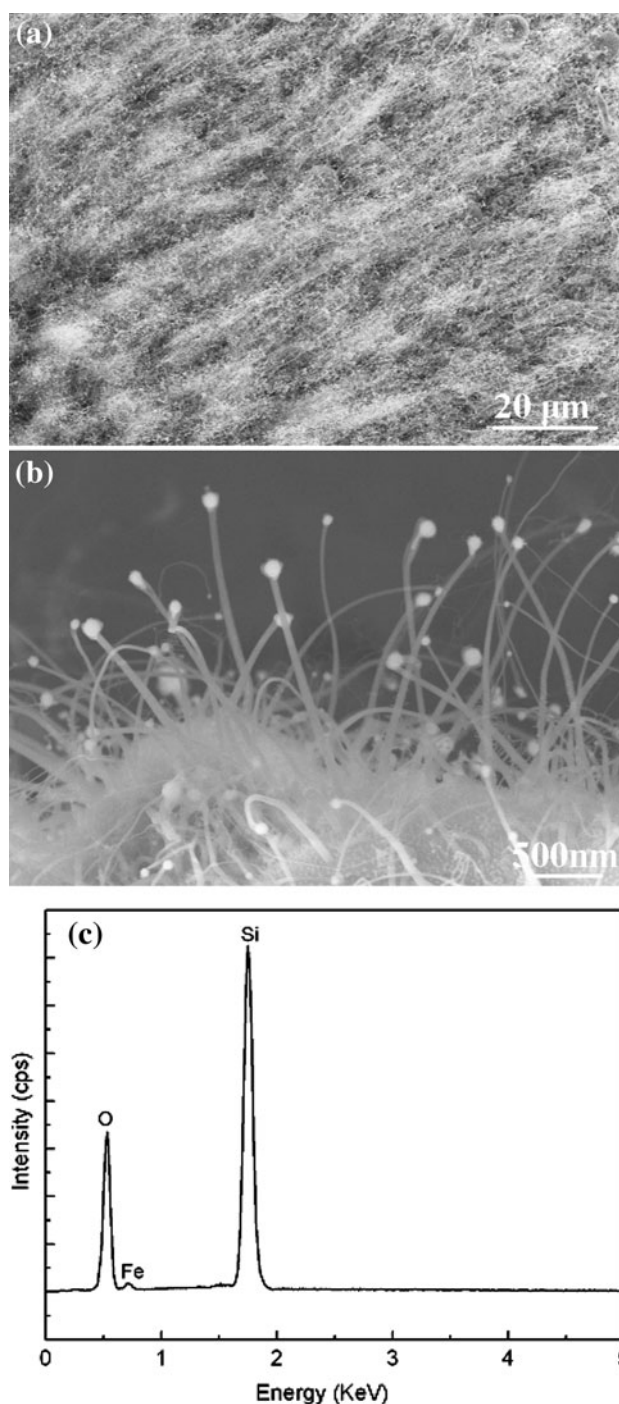


Fig. 1 **a** Low-magnification SEM image of the silica nanowires directly grown on Si substrate. **b** High-magnification SEM image of the silica nanowires. **c** EDX spectrum of the synthesized silica nanowires

SEM images of the sample are depicted in Fig. 1a and b, respectively. The size and top morphology of the nanowires are clearly seen in Fig. 1b. The nanowires have diameters of ~ 30 and ~ 50 nm and lengths of ~ 10 μm . Each nanowire has a catalyst particle at the tip (Fig. 1b).

The EDX spectrum of the sample (Fig. 1c) reveals that the product is composed of silicon and oxygen. Quantitative analysis shows that the atom ratio of Si:O is $\sim 1:2$, indicating that the product contains nano-scale silica wires. Little iron is detected by EDX.

Typical TEM and high resolution TEM (HRTEM) images of the nanowires are shown in Fig. 2. Figure. 2a shows the representative TEM image of a nanowire. Clearly, the nanowire has a smooth morphology. Furthermore, the HRTEM image (Fig. 2b) (white pane area in Fig. 2a) reveals that no fringes exist in the wire. Moreover, the XRD pattern (Fig. 3), taken of the product on the Si substrate, shows a broad diffraction band around 22° , which reveals the amorphous characteristic of the nanowires [9]. These results are supportive of an amorphous silica nanowire product.

3.2 Growth Mechanism of Silica Nanowires

In the past few years, many groups have reported silica nanostructures and studied the growth mechanism of amorphous silica nanowires. In most cases, the dominant growth mechanism follows vapor–liquid–solid (VLS) [10–12] model. The key factor in the VLS model is the formation of liquid droplets by adding a liquid forming agent, such as the Fe salt used in our experiment. The spherical droplet at the tip of the nanowires is commonly considered to be evidence for the operation of the VLS mechanism, which is in agreement with our experimental conditions and observed results.

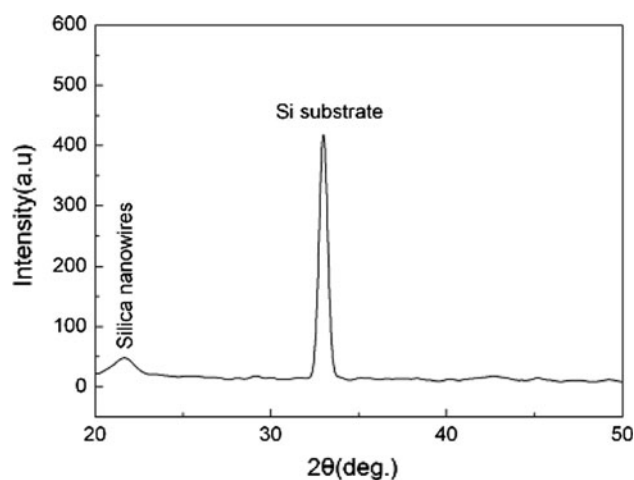


Fig. 3 XRD pattern of the silica nanowires on Si substrate

Regarding the growth process of the silica nanowires, in the previous reports the Si source of silica nanowires was mainly from Si/SiO₂ mixtures [13] or directly from Si wafers [14–16]. In this study, the Si source of silica nanowires comes from both the silica nanoparticles and Si substrate; It is postulated that the following two reactions take place at growth temperature of 1300 °C [9]:



After heat treatment, iron trichloride can be decomposed or reduced to Fe in hydrogen atmosphere. The melted Fe reacts with the Si substrate surface (eutectic point of Fe and Si is $\sim 1207^\circ\text{C}$); i.e. reaction (1) takes place and SiO

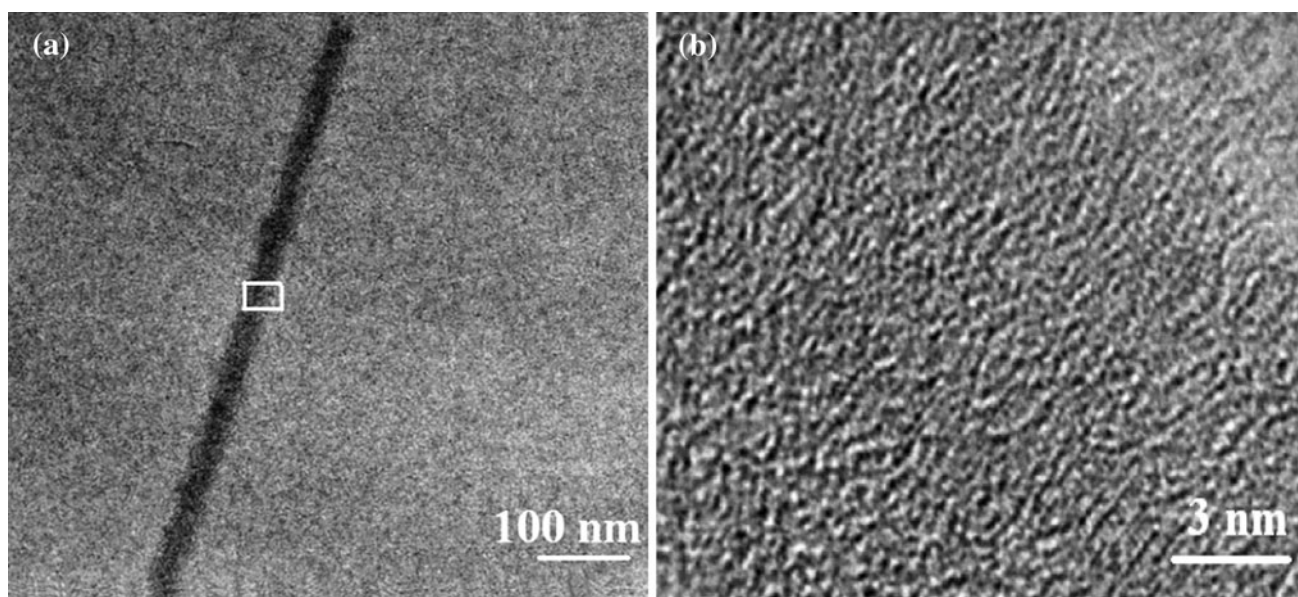


Fig. 2 **a** TEM image of a silica nanowire. **b** HRTEM image of the white pane area marked in a

vapor is generated. The molten Fe flows to the surface of the Si substrate and combines with the Si and SiO species in the vapor to form a nano-liquid droplet alloy of Fe, Si, and O. Since the SiO vapor is continuously supplied during the growth process, there will be a dense vapor of Si, O, and Fe and the nano-liquid droplet may become supersaturated in Si and O. As a result, the coexisting Si and O precipitate as nanowires.

3.3 Photoluminescence of the Silica Nanowires

An attractive property of silica nanowires is that they can emit stable and high-brightness blue–green light. A single broad blue–green photoluminescence band with defined maximum peak energy ~ 2.45 eV (about 506 nm) is observed at room temperature (Fig. 4a). It was reported previously that the luminescence bands of various silica nanowires and glasses have different energy peaks from 1.9–4.3 eV [1]. The luminescence band at ~ 2.45 eV may be a result of oxygen deficiency [17]. Oxygen deficiency may occur during the nanowire synthetic process.

To clarify the origin of the PL, the product is annealed in an oxygen and argon mixture gas mixture at 1200 °C for different time periods. Figure 4b–d shows the PL spectra of the silica nanowires with annealing time of 10, 20, and 30 min, respectively. It can be seen that the intensity of the PL bands decreases by annealing; however, the position of bands does not shift. During annealing process, the oxygen supplied to silica nanowires diminish the oxygen deficiency. With the decrease of oxygen deficiency, the intensity of the blue–green emissions decreases. This is consistent with the results. Furthermore, the trend of decreasing emission intensity lessens with increasing annealing time.

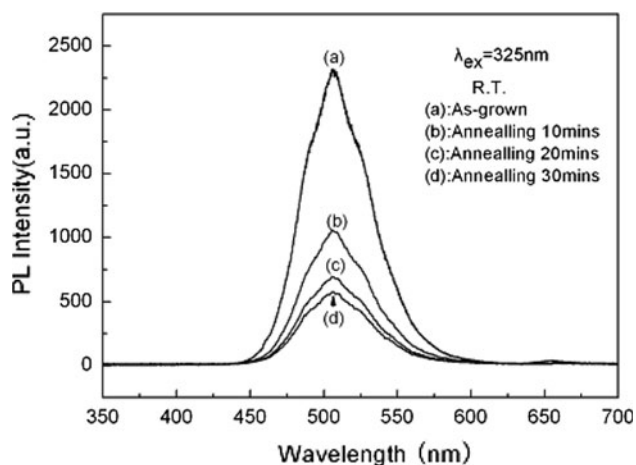


Fig. 4 a Room temperature PL spectra of the silica nanowires. b–d PL spectra of the silica nanowires with annealing time 10, 20, and 30 min, respectively

4 Conclusion

Silica nanowires were synthesized by physical thermal evaporation of a mixture of silica and iron trichloride on Si substrate. The growth mechanism of the amorphous silica nanowires follows VLS model. A high intensive blue–green light emission is observed, which may be attributed to oxygen deficiency in the nanowires. The PL intensity of the bands decrease by annealing in an oxygen and argon mixture gas atmosphere. These results not only clarify the origin of luminescence in silica nanowires but also point to the possibility of the use of this material for a high intensity blue–green luminescent source.

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References

1. D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiang, S.Q. Feng, *Appl. Phys. Lett.* **73**, 3076 (1998)
2. Y.F. Hao, G.W. Meng, C.H. Ye, L.D. Zhang, *Appl. Phys. Lett.* **87**, 33106 (2005)
3. Y.Q. Zhu, W.B. Hu, W.K. Hsu, M. Terrones, N. Grobert, T. Karali, H. Terrones, J.P. Hare, P.D. Townsend, H.K. Kroto, D.R.W. Walton, *Adv. Mater.* **11**, 844 (1999)
4. A.P. Alivisatos, *Science*. **271**, 933 (1996)
5. L.M. Tong, R.R. Gattass, J.B. Ashcom, S.L. He, J.Y. Lou, M.Y. Shen, I. Maxwell, E. Mazur, *Nature*. **426**, 816 (2003)
6. X.C. Wu, W.H. Song, K.Y. Wang, T. Hu, B. Zhao, Y.P. Sun, J.J. Du, *Chem. Phys. Lett.* **336**, 53 (2001)
7. 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, G. Wang, *J. Mater. Res.* **16**, 683 (2001)
8. H. Takikawa, M. Yatsuki, T. Sakakibara, *Jpn. J. Appl. Phys.* **38**, L401 (1999)
9. X.S. Fang, C.H. Ye, T. Xie, G. He, Y.H. Wang, L.D. Zhang, *Appl. Phys. A*. **80**, 423 (2005)
10. C.H. Liang, L.D. Zhang, G.W. Meng, Y.W. Wang, Z.Q. Chu, *J. Non-Cryst. Solids*. **277**, 63 (2000)
11. B. Zheng, Y.Y. Wu, P.D. Yang, J. Liu, *Adv. Mater.* **14**, 122 (2002)
12. Y.W. Wang, C.H. Liang, G.W. Meng, X.S. Peng, L.D. Zhang, *J. Mater.Chem.* **12**, 651 (2002)
13. Z.L. Wang, R.P. Gao, J.L. Gole, J.D. Stout, *Adv. Mater.* **12**, 1938 (2000)
14. K.H. Lee, H.S. Yang, K.H. Baik, J. Bang, R.R. Vanfleet, W. Sigmund, *Chem. Phys. Lett.* **383**, 380 (2004)
15. J.Q. Hu, Y. Jiang, X.M. Meng, C.S. Lee, S.T. Lee, *Chem. Phys. Lett.* **367**, 339 (2003)
16. L. Dai, X.L. Chen, T. Zhou, B.Q. Hu, *J. Phys. Condens. Matter*. **14**, L473 (2002)
17. Q. Wei, G.W. Meng, X.H. An, Y.F. Hao, L.D. Zhang, *Solid. State. Commun.* **138**, 325 (2006)