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Synthesis and Photoluminescence of SiO_x NanotubesHai-feng Jiang^a, Yi-qing Chen^{a*}, Qing-tao Zhou^a, Yong Su^a, Shu-yuan Zhang^b, Hai-hua Xiao^a

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Amorphous SiO_x nanotubes with homogeneous diameters were fabricated in large-scale on silicon substrate by thermal evaporation method, with liquid gallium as medium. The average diameter of tubes is about 80 nm and the length is more than 10 μm, with small ratio between the inner and outer diameter of the tube. The silicon element in the substrate and the residual oxygen element in reaction chamber were first dissolved into liquid Ga. Then the SiO_x precipitated from the surface of gallium droplet, forming the nanotube structure with Ga droplet being the center. The room temperature photoluminescence measurements under excitation at 260 nm show that the SiO_x nanotubes has a strong blue emission at 453 nm with two shoulders at 410 and 480 nm respectively, which may be related to oxygen defects. The preparation method improved the traditional complicated method and also provided a new way to fabricate SiO_x nanotubes in large quantity.

Key words: Amorphous, Nanotubes, Photoluminescence

I. INTRODUCTION

Much attention has been paid to carbon nanotubes (CNTs) in the fields of nanotechnology due to their unique structures and electronic properties as well as potential applications in nanoelectronics and optic devices since the discovery of CNTs in 1991 [1]. Up to now, quasi-one-dimensional structures have been achieved in a wide range of materials, such as Si nanowires [2], amorphous SiO₂ nanotubes [3], GaN nanowires [4], ZnO nanowires [5] and nanobelts [6], etc. Among them, as a promising fluorescent material, amorphous SiO_x nanotubes have attracted much attention, which might be applied extensively in biometry, medicine, chemistry and other fields, and have great potential value in nanodevices such as nano-interconnection integrated optical devices [7,8]. Since Harda and Adachi [9] first developed a surfactant-mediated technique for the synthesis of silica nanotubes, several methods have been developed to prepare such tubular materials. Under high-temperature conditions, Wang *et al.* used silicon particle as seeds and synthesized silica nanotubes with different morphologies [10]. Chen *et al.* first prepared ZnO/SiO₂ nanocables through thermal evaporation of zinc power, and then silica nanotubes were obtained after removal of the ZnO core in a diluted HCl solution [11]. Recently, silica nanotubes have been synthesized using alumina membrane templates. Zhang *et al.* used a template-assisted sol-gel method to form pure SiO₂ nanotubes in a porous alumina membrane [7]. Such template synthesis can produce tubular structures with monodisperse diam-

eters and lengths. However, this templates-directed technique is not suitable for fabricating silica nanotubes in large quantities for potential applications, because the entire procedure is complicated. In addition, it is possible that the as-synthesis would be polluted by the elements of the template.

In this work, we successfully synthesized bulk quantities of SiO_x nanotubes with homogeneous diameters by direct thermal evaporation method, with the pure gallium as medium. Furthermore, it was discovered that the ratio between inner and outer diameter is far less than that of ordinary nanotubes. Meanwhile, the photoluminescence properties of amorphous SiO_x nanotubes have also been discussed in this paper.

II. EXPERIMENTAL SECTION

The SiO_x nanotubes in our experiment were synthesized in an alumina tube of a horizontal tube resistance furnace equipped with a gas supply and control system. First, a silicon wafer was ultrasonically cleaned for 15 min in an alcohol bath, and then dried in the air. A few metallic gallium (about 0.5 g, purity: 99.9999%) was placed in the bottom of a ceramic boat, and the boat was covered by the cleaned silicon wafer in order to increase the gallium vapor pressure and also in favor of the collection of synthesized products. Then, the ceramic boat containing the raw materials were transferred into the center of an alumina tube mounted in the horizontal tube furnace. Before heating, the alumina tube had been sealed and degassed to a background pressure of approximately 1.33 Pa by a rotary pump. Afterwards the tube was heated to 400 °C with a flow of NH₃ at a rate of 50 sccm (standard cubic centimeter per minute). After 30 min, the furnace was heated to

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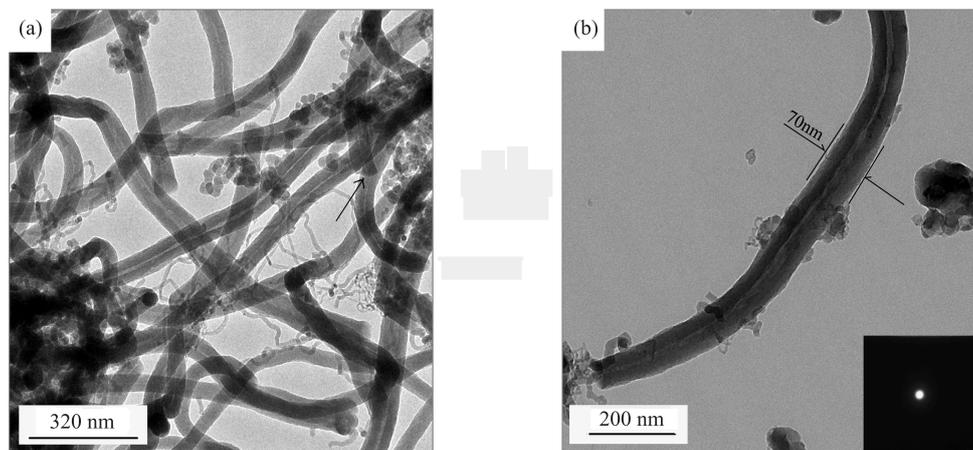


FIG. 1 (a) A TEM image of multistrand SiO_x nanotubes and nanowires; (b) A TEM image of a single SiO_x nanotube, the inset is the SEAD image.

1000 °C and then kept at this temperature for 60 min. After the tube furnace was cooled down to the room temperature in an Ar (mixed with 5% H_2) atmosphere, a layer of white silica nanotubes were collected from the surface of silicon wafer.

The component and structure of the as-synthesized products was analyzed by high-resolution transmission electron microscope (HRTEM) (JEOL-2010) with an energy-dispersive spectroscopy (EDS). The photoluminescence (PL) spectrum of the SiO_x nanotubes was measured at room temperature using a steady-state spectrofluorometer (FULOROLOG-3-TAU) with Xe lamp as the excitation light source.

III. RESULTS AND DISCUSSION

The morphology and microstructure of nanotubes had been characterized by TEM. Figure 1a shows a typical image of multistrand SiO_x nanotubes, it should be noted that many nanotubes synthesized in this work have end open (indicated by arrow in Fig.1(a)). It is different from those with both ends closed, which has been reported by Chen *et al.* [11]. Apart from nanotubes, some amount of very fine nanowires can also be observed here. The image of a single nanotube is shown in Fig.1(b), with the outer diameter of 70 nm, and the inner one of 10 nm. Compared with that of other reported nanotubes, the ratio of both diameters is quite small, which is only 1:7, resulting in rather thick tube wall of nanotubes. This is also related with the formation mechanism. The selected-area electron diffraction (SEAD) pattern, which displays a diffuse ring, reveals that the silica nanotubes are amorphous (Fig.1(b), inset). Figure 2 gives the energy dispersive spectroscopy (EDS) spectrum of a nanotube. The two distinct peaks of silicon and oxygen were observed, with the atom ratio of 1:1.5, indicating that the nanotubes are composed of amorphous SiO_x . The Cu peak originates from the

copper grid used for the TEM analysis.

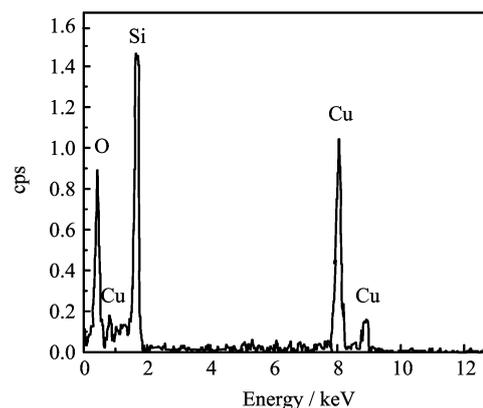


FIG. 2 The EDS spectrum of the products.

Figure 3 schematically shows a possible growth mechanism of SiO_x nanotubes. At first, volatile metal gallium deposited and gathered in the surface of Si substrate during heating process, with NH_3 serving as carrying gas. And nano-scaled Ga droplets are formed with smooth surface, as shown in Fig.3(a). According to Ga-Si phase diagram, solubility of Si in Ga-Si droplet is about 10 mol (900 °C) [12]. Therefore, with temperature elevating, Ga-Si alloy is obtained with Si atoms in substrate gradually dissolving into Ga droplet. It is obvious that there exists concentration gradient in Ga droplet, under which dissolved Si atoms in the interface of liquid Ga and Si substrate would diffuse to the free surface of liquid Ga and then the whole surface of liquid Ga sphere. As a source of silicon, the interface of liquid Ga and Si substrate is the part where most silicon gathered. Moreover, small quantity of oxygen originates from the oxide film on the surface of Ga drop and leakage in tube reactor would dissolve into liquid Ga through its free surface. Since the binding energy

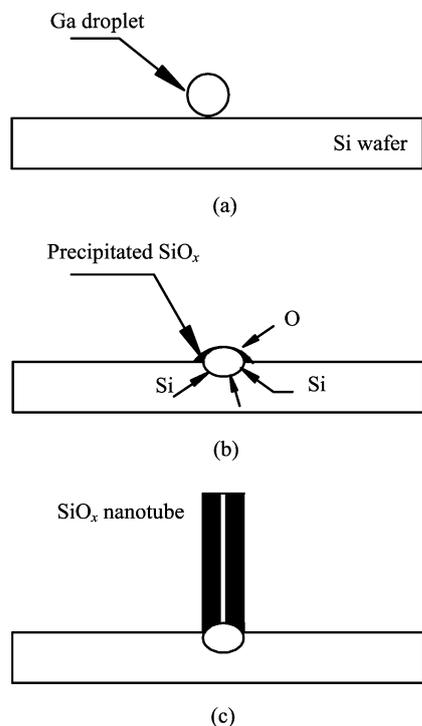
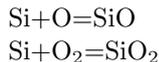


FIG. 3 The sketch diagram on the growth mechanism of SiO_x nanotubes.

of Si–O bond (185 kJ/mol) is far more than that of Ga–O bond (59 kJ/mol) and Si–N bond (104 kJ/mol) [13], it is expected that the reaction in liquid Ga would be:



SiO_x from above reaction would gather continuously in the outer layer in liquid Ga sphere and then precipitate after saturation. The first part that SiO_x precipitates should be the bottom of Ga sphere, due to the highest concentration of Si in the contact part of liquid Ga sphere and Si substrate, as shown in Fig.3(b). It is possibly the non-equilibrium crystal growth which would explain why the product is an amorphous solid and not a crystalline solid. According to the interfacial force of Ga and concentration gradient of SiO_x in liquid Ga, SiO_x would grow upward from the bottom of Ga droplet, forming a tubular structure with Ga being the center. As presented in Fig.3(c), the external diameter of this tubular structure is the bottom diameter of liquid Ga, while the inner diameter is the diameter of SiO_x that is not precipitated in the top of liquid Ga droplet. With continuous dissolving of Si and O elements into Ga droplet and the precipitation of amorphous SiO_x, such nanotubes grow upward continuously until Si in the substrate could not dissolved into liquid Ga anymore with temperature decreasing. It could be seen from the growth mechanism that a concentration gradient of SiO_x exists in liquid Ga. Therefore, no SiO_x would precipitate in the top of liquid Ga, where the

concentration of SiO_x is the lowest. That is why the inner tube is relatively thin in our products and also the ratio between inner and outer diameter is far less than that of ordinary nanotubes. However, the concentration gradient of SiO_x on Ga droplet is not sharp when the Ga droplet is small enough. The concentration of SiO_x on the top of the small droplet is nearly the same with that of other regions. Therefore, it is nanowire, instead of nanotube, that is precipitated from relatively small Ga droplet. Correspondingly, the diameter of those nanowires is smaller than that of nanotubes, as we can observe from TEM, which is only about 10 nm.

The optical properties of the silica nanotubes were investigated at the room temperature. Figure 4 shows the photoluminescence (PL) spectrum under excitation at 260 nm. The PL spectrum consists of a main, intense peak at 453 nm (2.74 eV) with two shoulders at 410 nm (3.03 eV) and 480 nm (2.58 eV) respectively. Nishikawa *et al.* [14] observed several luminescence bands in various types of high purity silica glasses, with different peak energies ranging from 1.9 to 4.3 eV under 7.9 eV excitation. It was revealed that the 2.74 eV band was ascribed to the neutral oxygen vacancy ($\equiv\text{Si}-\text{Si}\equiv$); while the 3.03 eV band corresponded to two-fold-coordinated silicon lone-pair centers (O–Si–O) [15]. As radioactive recombination centers, these structure defects were due to the oxygen deficiency of the SiO_x sample. Therefore, it is reasonable to believe that the blue emission from the SiO_x nanotubes can be attributed to the above mentioned defect centers.

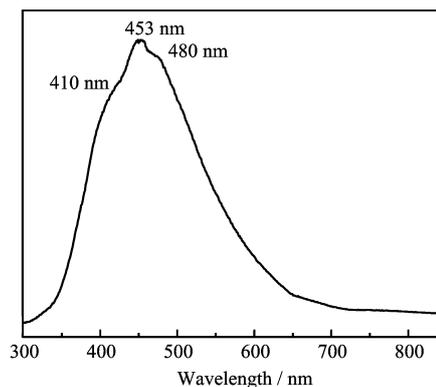


FIG. 4 The PL spectrum of SiO_x nanotubes.

IV. CONCLUSION

In summary, amorphous SiO_x nanotubes are successfully fabricated by thermal evaporation method, with liquid Ga as medium. The average diameter of nanotubes is 70–80 nm and the length is about 10–20 μm. In particular, the wall thickness of silica nanotubes is thicker than those reported previously. The room temperature PL spectrum is carried out to study the light emitting properties of the synthesized products.

A strong and stable blue light emission with two shoulders was observed at 453, 480 and 410 nm respectively, which may be related to various oxygen defects. The growth mechanism mentioned in this work provides a new way in fabricating SiO_x nanotubes.

V. ACKNOWLEDGMENTS

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- [1] S. Iijima, *Nature* **56**, 354 (1991).
- [2] D. P. Yu, C. S. Lee, I. Bello, *et al.* *Solid State Commun.* **403**, 105 (1998).
- [3] M. Zhang, Y. Bando and K. Kurashima, *J. Mater. Sci Lett.* **18**, 1911 (1999).
- [4] C. C. Chen, C. C. Yeh, C. H. Chen, *et al.* *J. Am. Chem. Soc.* **123**, 2791 (2001).
- [5] M. H. Huang, Y. Wu, H. Feick, *et al.* *Adv. Mater.* **13**, 113 (2001).
- [6] Z. L. Wang, *Materialstoday* **6**, 26 (2004).
- [7] M. Zhang, E. Ciocan, Y. Bando, K. Wada, L. L. Cheng and P. Pirouz, *Appl. Phys. Lett.* **80**, 491 (2002).
- [8] K. Okamoto, C. J. Shook, L. Bivona, C. S. Lee and S. T. Lee, *Nano. Lett.* **4**, 233 (2004).
- [9] M. Harada and M. Adachi, *Adv. Mater.* **12**, 839 (2000).
- [10] Z. L. Wang, R. P. Gao, J. L. Gole and J. D. Stout, *Adv. Mater.* **12**, 1938 (2000).
- [11] Y. J. Chen, X. Y. Xue and T. H. Wang, *Nanotechnology* **16**, 1978 (2005).
- [12] Y. U. Jueqi, *et al.* *Constitution of Binary Alloy*, Shanghai: Shanghai Science and Technology Press, (1984).
- [13] I. A. Dean, *et al.* *Lange's Handbook of Chemistry*, 14th Ed., New York: McGraw-Hill, (1992).
- [14] H. Nishikawa, T. shiroyama, R. Nakamura and Y. Ohki, *Phys. Rev. B* **45**, 586 (1992).
- [15] A. Pisch and R. Schmid-Fetzer, *J. Crystal Growth* **187**, 329 (1998).