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Synthesis and photoluminescence properties of amorphous SiO_x nanowires

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Silicon oxide nanowires (SiONWs) have been synthesized on a Si substrate by the vapor transport reaction using pure silicon (99.99%) powder as the Si source with the help of a Au catalyst synthesized by chemical methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations show that the amorphous SiONWs have lengths up to several tens of micrometers and diameters of *ca.* 20 nm. Energy dispersive X-ray spectrometry (EDX) analysis reveals that the SiONWs consist of Si and O elements in an atomic ratio of approximately 1 : 1.2. The formation process of these nanowires is closely related to the vapor–liquid–solid (VLS) growth mechanism. A blue light emission was observed which could be attributed to neutral oxygen vacancies formed in the nanowires.

1 Introduction

Recent progress in the synthesis and characterization of nanowires has been driven not only by the need to understand the novel physical properties of one-dimensional nanomaterials that are different from those of the bulk materials, but also by the potential applications in constructing electronic and optoelectronic nanodevices.[1] Nanowires with different compositions have been synthesized using various methods including catalytic chemical vapor deposition (CVD),[2] solution–liquid–solid (SLS) growth at lower temperature,[3] arc discharge,[4] laser ablation[5] and a template-based method.[6,7] Most of these methods, which focused on semiconductor systems such as Si,[1] GaN,[8] and GaAs,[2] have been investigated in detail. However, as far as we know, only a few studies on oxide systems exist in the literature. Among them, SiO_2 nanowires have been synthesized by laser ablation, and show intensive blue light emission, which may have potential application in high-resolution optical heads of scanning near-field optical microscopes or nanointerconnection integrated optical devices.[9] More recently, large scale synthesis of SiO_x nanowires has been achieved by physical evaporation of the mixture of mesoporous silica containing iron nanoparticles and silicon powder.[10] Here, we report the large scale synthesis of SiO_x nanowires through a vapor phase transport process *via* the vapor–liquid–solid (VLS) mechanism. The Si vapor generated at high temperature is transported to, and reacted with, the Au catalyst on silicon substrates located downstream from the Si vapor source. Photoluminescence (PL) measurements of the SiO_x nanowires show a blue light emission, which could be attributed to neutral oxygen vacancies formed in the nanowires.

2 Experimental

A silicon wafer (10 × 20 mm) was used as the substrate for the growth of SiO_x nanowires. The substrate was cleaned by a standard treatment in piranha solution (30% H_2O_2/20% H_2SO_4) and rinsed with de-ionized water. Subsequently, monodispersed Au colloids were deposited on the substrate as the catalyst. Au colloids were prepared by the reaction of a gold salt and sodium citrate. Sodium citrate (60 mg) in 100 ml water was boiled and 9.5 mg $HAuCl_4$ dissolved in 1 ml water was added. Boiling was then continued for 15 min.[11] Pure Si (99.99%) powder used as the silicon vapor source was placed in an alumina boat, and the Si substrate coated with Au colloids was placed next to the Si powder and along the downstream side of the following argon. Then the alumina boat, which was covered with a quartz plate in order to maintain a higher silicon vapor pressure over the silicon substrate, was placed in the center of a quartz tube that was inserted into a horizontal tube furnace. Substantially, under a constant flow of Ar (90%)/O_2 (10%) gas (40 sccm), the furnace was heated to 1100 °C and held at this temperature for 20 min, and then cooled to room temperature. The Si substrate surface appeared white after the reaction, indicating the deposition of materials. The synthesized products were scraped from the substrate and weighed, their weight measuring up to 60 mg.

The synthesized products were characterized by scanning electron microscopy [(SEM) JEOL JSM-6300], transmission electron microscopy [(TEM) JEM-200CX], energy-dispersed X-ray spectrometry (EDX), and Raman scattering spectroscopy with 514.5 nm incident wavelength radiation. The specimens for TEM were prepared by placing the as-synthesized products in ethanol and immersing them in an ultrasonic bath for 15 min, then placing a few drops of the resulting suspension containing the synthesized materials onto a TEM grid. Photoluminescence (PL) measurements were carried out on a HITACHI 850-type visible-ultraviolet spectrophotometer with a Xe lamp as the excitation light source at room temperature.

3 Results and discussion

SEM observation shows that the products on the Si substrate consist of a large quantity of nanowires with typical lengths up to several tens of micrometers (Fig. 1). Representative TEM images (Fig. 2) reveal the general morphology of the nanowires. It can be seen that the diameters of the as-produced nanowires are *ca.* 20 nm, and the lengths are up to several tens of micrometers. It should be noted that a few nanoparticles do exist in the nanowires [Fig. 2(a)], as is indicated with arrowheads. Some nanoparticles are also found in the middle part of the nanowires, and the diameters of these nanoparticles are equal to those of the nanowires. However, in Fig. 2(b) we can see that the nanowires terminate at one end in nanoparticles with diameters *ca.* 1.2 times those of the connected nanowires. EDX analysis shows that the nanoparticles contain only Au

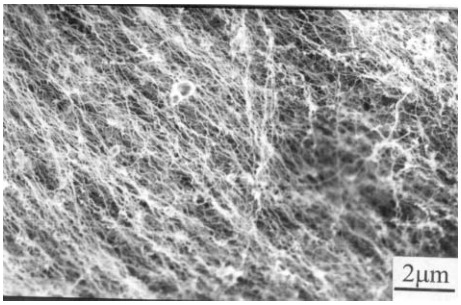

Fig. 1 SEM image of SiONWs grown on the surface of a silicon substrate coated with Au colloids.

and Si. The highly dispersed selected area electron diffraction (SAED) patterns [Fig. 2(c)] taken from each type of nanowire indicates that the nanowires are amorphous. The EDX spectrum shown in Fig. 3(a) reveals that the nanowires consist of Si and O, and further quantitative analysis shows that the atomic ratio for Si : O is *ca.* 1 : 1.2, indicating that amorphous $SiO_{1.2}$ nanowires have been synthesized. The Raman scattering spectrum on a bulk quantity of $SiO_{1.2}$ nanowires [Fig. 3(b)] demonstrates a sharp peak around 505 cm^{-1} with a broadened linewidth of *ca.* 50 cm^{-1}. Previously, Yu *et al.*[9] reported that the Raman spectrum of amorphous silica nanowires was the same as that of bulk non-crystalline SiO_2 solids, whereas some other approaches showed that there was no scattering peak in the stoichiometric SiO_2 nanowires.[12] Moreover, it has been reported that there is a peak at 480 cm^{-1} for bulk amorphous

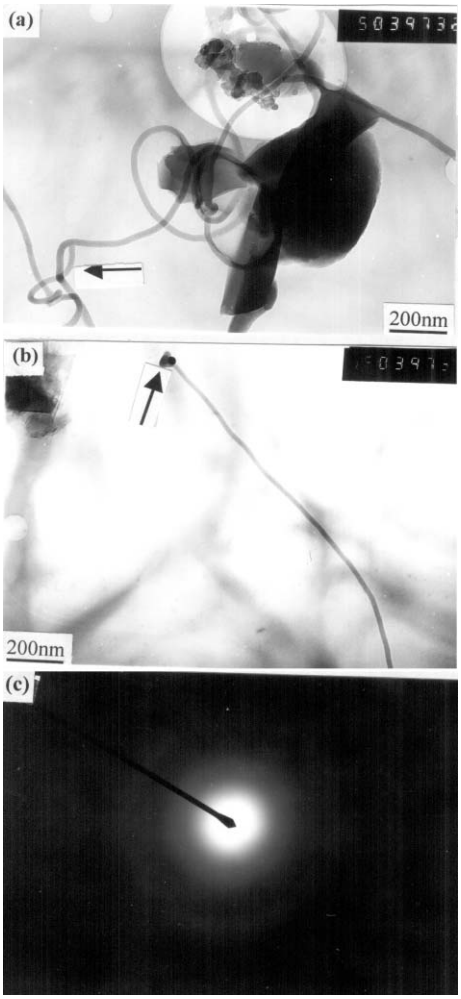

Fig. 2 Typical TEM images showing the general morphology of SiNWs, (a) and (b); (c) the corresponding highly diffusive ring pattern of electron diffraction from the nanowires.

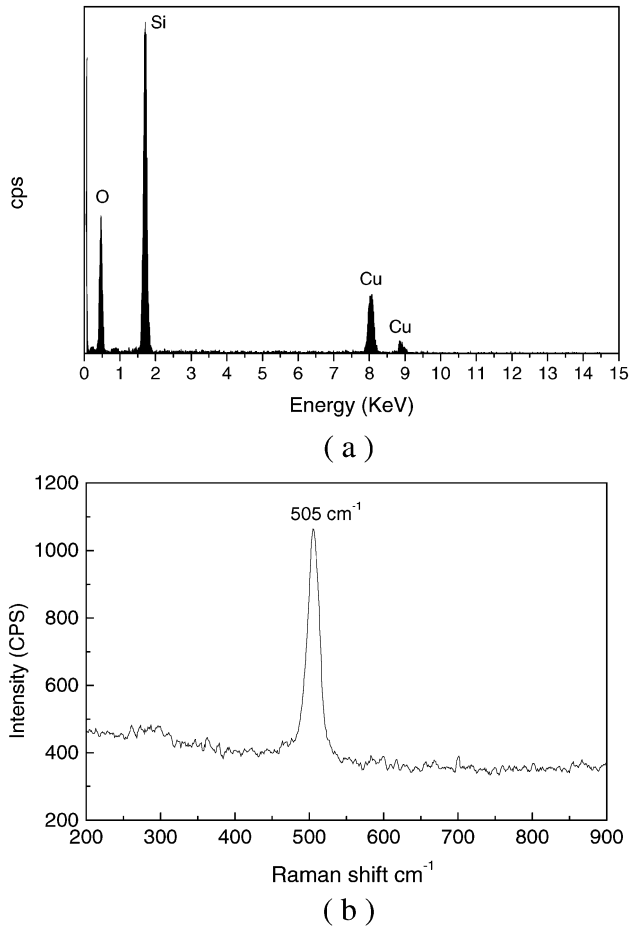

Fig. 3 (a) Energy dispersive analysis by X-ray spectrum of the SiONWs reveals the chemical composition of the nanowires. (b) Raman spectrum of the SiONWs.

silicon,[13] and a peak at 520 cm^{-1} for crystalline silicon.[14] The above investigations verified that there was no trace of a crystalline phase in our SiONWs. Furthermore, the EDX analysis indicates the oxygen non-stoichiometry, so the shift and the broadened linewidth can be attributed to the effect of the oxygen deficiency such as the formation of neutral oxygen vacancies (≡Si–Si≡),[15] which may play a similar role to the non-crystalline silicon.

A key question here is why the amorphous material is formed into nanowires, similar to the semiconductor nanowires of Si.[1] There are two possible mechanisms for the growth of conventional crystal whiskers: the screw dislocation and the vapor–liquid–solid (VLS) mechanisms. The screw dislocation mechanism loses its meaning in our work because the nanowires are amorphous. It is well known that the presence of a liquid drop is essential for the effective operation of the VLS mechanism. The solidified spherical droplets at the tips or in the middle of the nanowires are commonly considered to be the evidence for the operation of the VLS mechanism; these are in agreement with our experimental conditions and the observed results. The EDX analysis shows that these nanoparticles contain only Si and Au. In this study, the Si vapor is generated at high temperature by the vaporization of silicon powder, before being transported to and reacted with the Au catalyst on the silicon substrates located downstream to form the alloy droplets. As the droplets become supersaturated, amorphous SiONWs are formed, possibly by the reaction between Si and O_2. The presence of a small amount of O_2 is not expected to change the Au–Si phase diagram significantly, but in the meanwhile it acts as the oxygen source during the silicon oxide growth.

The photoluminescence (PL) spectrum of bulk quantities of

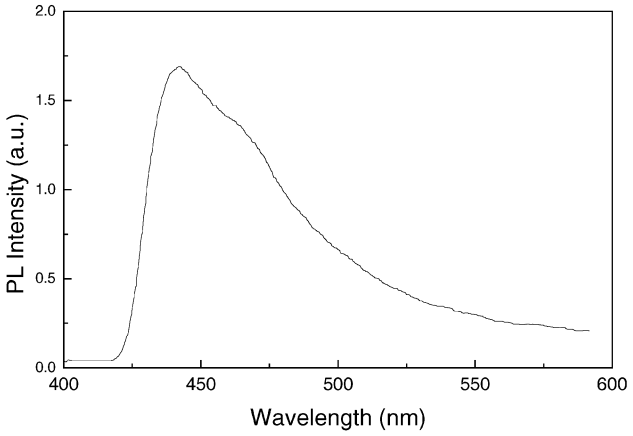

Fig. 4 PL spectrum of the SiONWs.

$SiO_{1.2}$ nanowires was measured using a Xe laser (371 nm) as an excitation source. Fig. 4 indicates that the PL peak of $SiO_{1.2}$ is at *ca.* 446 nm. Previously, Wang *et al.*[12] reported that the fully oxidized SiO_2 nanowires have a weak PL peak at about 600 nm, whereas the results of Yu *et al.*[9] showed that two broad PL peaks of SiO_2 were clearly distinguishable at *ca.* 470 and 420 nm. In addition, Zhu *et al.* reported that two broad PL peaks of SiO_x were at around 430 and 570 nm.[16] As amorphous silicon oxide films are widely used as passivation or insulation layers in integrated circuits, the PL properties of various silica glasses have been studied extensively.[14,17] Nishikawa *et al.*[15] 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 2.7 eV (*ca.* 460 nm in wavelength) band was ascribed to the neutral oxygen vacancy (≡Si–Si≡). Blue luminescence peaks were also observed in Si^+-implanted SiO_2 films at around 2.7 eV, which were attributed to the oxygen vacancy.[18] It is therefore reasonable to believe that the blue light emission from the SiONWs could be attributed to the above-mentioned neutral oxygen vacancies.

4 Conclusions

In conclusion, large scale amorphous silicon oxide nanowires have been synthesized by using silicon powder as the Si source and Au colloids as the catalyst. The amorphous silicon oxide nanowires have a uniform diameter of *ca.* 20 nm and length up to several tens of micrometers. The growth of SiONWs is controlled by the vapor–liquid–solid (VLS) mechanism. A blue light emission was observed which could be attributed to neutral oxygen vacancies formed in the nanowires.

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