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Amorphous silica nanowires: Intensive blue light emitters

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We report large-scale synthesis of silica nanowires (SiONWs) using an excimer laser ablation method. Silica was produced in the form of amorphous nanowires at a diameter of ~15 nm and a length up to hundreds micrometers. The SiONWs emit stable and high brightness blue light at energies of 2.65 and 3.0 eV. The intensity of the emission is two orders of magnitude higher than that of porous silicon. The SiONWs may have potential applications in high-resolution optical heads of scanning near-field optical microscope or nanointerconnections in future integrated optical devices. © *1998 American Institute of Physics.* [S0003-6951(98)04247-8]

The discover of novel materials can usually stimulate new scientific runners-up and technological breakthrough. One-dimensional quantum wires have been a focused research field due to their great interest both in mesoscopic physics and in nanodevices. For example, GaAs, InAs nanowires have found application in developing one-dimensional high speed field effect transistor, or laser working at low-threshold current density and high gain.[1] Different approaches, such as a catalytic chemical vapor deposition (CVD),[1] solution–liquid–solid (SLS) growth at lower temperature,[2] or CVD method via carbon nanotube confined reaction,[3] were used for synthesis of semiconductor nanowires. Recently, a new approach has been developed for large-scale synthesis of silicon quantum wires[4,5] based on oven-laser evaporation combining the vapor–liquid–solid (VLS) growth.[6,7] Nano-scale optical wires are of scientific and technological interest in the fields of localization of light, lower dimensional waveguide, and scanning near-field optical microsocpy (SNOM). With the development of science towards mesoscopic scale and of technological advances in the integrated optics, it is important to synthesize nano-scale optical wires that can meet the demands of further applications. Unfortunately, such synthesis technique, to the best of our knowledge, may not exist. Based on our previous work of synthesizing quasi one-dimensional semiconduction nanostructures (single-walled BN nanotubes and silicon nanowires)[4] using excimer laser ablation, a technique is presented in this letter for large-scale synthesis of silica nanowires (SiONWs). The remarkable blue light emission property of the SiONWs is presented.

The system of ablation was the same as that used for synthesis of silicon nanowires, which was described in detail elsewhere.[4] A disk-like target was formed by pressing a mixture of silicon powder (99% in purity) and 20 wt% of silica powder (optical purity), together with 8 wt% of Fe powder being added as a catalyst. The target was placed inside a quartz tube of about 800 mm in length, pumped to 20 mTorr and heated at 850 °C for 4 h. After 20 h further heating at 1200 °C, the target was ablated using an excimer laser of 246 nm in wavelength (Sigma Physik) under flowing argon (99.999% in purity) at an ambient pressure of about 100 Torr. The laser beam was focused to a spot 1×3 mm^2 on the surface of the target, and the average energy was ~350 mJ per pulse. An opaque-colored product was found to deposit as a web-like structure onto the interior wall of the quartz tube in the front of the water-cooled copper collector mounted downstream near the rear of the quartz tube. The production of bulk quantity of SiONWs was reproducible.

A Hitachi H-9000NAR high-resolution transmission electron microscope (HREM), equipped with energy dispersive x-ray spectroscopy (EDX), was used for morphological and chemical composition analysis. Photoluminescence (PL) measurements were carried out at room temperature using a 5 mW (average power), 325 nm excitation light from the second harmonic generation of a femtosecond dye laser. Laser beam was focused into a spot diameter of about one square millimeter on the specimen.

Figure 1 shows a representative transmission electron microscopic (TEM) image revealing the general morphology of the SiONWs. It can be seen that the as-produced SiONWs have uniform distribution in diameter around 15 nm, and a length up to hundreds micrometers. Most of the SiONWs have a smooth morphology, each wire having a longitude uniformity in diameter along the wire axis. The highly diffusive ring pattern in the corresponding selected-area electron diffraction shown in the inset reveals that SiONWs are of a completely amorphous state. In contrast to the morphol-

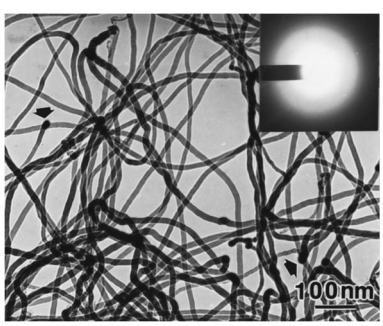

FIG. 1. TEM image revealing the general morphology of the SiONWs. Inset shows the corresponding highly diffusive ring pattern of electron diffraction.

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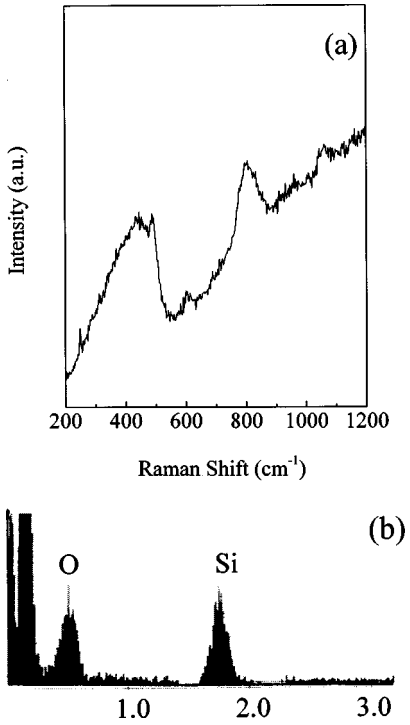

FIG. 2. (a) Raman spectrum of the SiONWs. It was identified to be of amorphous silica. (b) Energy dispersive analysis by x ray (EDAX) spectrum of the SiONWs revealing that the chemical composition of the SiONWs approximates to silica.

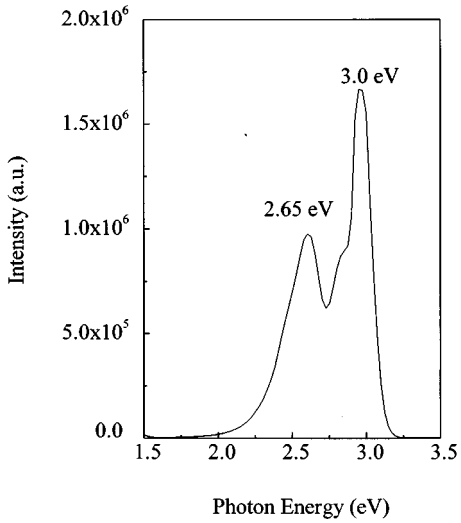

FIG. 3. PL of the SiONWs. Extremely intensive blue light emission was revealed peaking at 2.65 and 3.0 eV.

ogy of the silicon nanowires produced by Morales *et al.*,[5] our products are extremely pure, and about 99% of the product is estimated to be SiONWs. Another obvious dissimilarity between the present work and that by Morales is that their silicon nanowires are virtually terminated at one end with larger nanoparticles 1.5–2 times the diameter of the silicon nanowires. Nanoparticles do exist in the SiONWs, as is indicated with arrowheads, but instead of being attached to the end of the SiONWs, they are usually visible in the middle part of the SiONWs, and the amount of the nanoparticle is very little. Raman spectra on a bulk quantity of SiONWs [Fig. 2(a)] show that it has the characteristic Raman shifts analogous to that of pure amorphous silica. The EDX spectrum shown in Fig. 2(b) reveals that the SiONWs are composed of silicon and oxygen, and quantitative analysis shows that the atomic ratio of Si:O is about 1:2, indicating that the SiONWs are nano-scale silica wires. Because the refractive index is only dependent on the chemical composition of a substance, the SiONWs must have a similar refractive index with that of silica optical fiber.

A key question here is why the amorphous material is formed in a form of nano-scale wire, just similar to the one-dimensional crystalline semiconductor wires of Si and Ge.[4,5] There are two possible models, the screw dislocation model and the VLS model, that might account for the growth of conventional crystal whiskers, with the later being the most likely one for explaining the growth of crystal whiskers.[6,7] The dislocation model loses its meaning for our case because the nanowires are amorphous. The most likely mechanism to explain the growth of the SiONWs seems to be analogous to the VLS for the growth of silicon nanowires.[4,5] The key factor in VLS is the formation of liquid droplets due to adding a liquid forming agent, such as the Fe element used in our experiment. Due to the existence of a temperature gradient downstream the quartz tube, liquid droplets were formed from vapor phase, which was ablated off the target by the laser beam. The characteristic of the growth of whiskers controlled by the VLS mechanism is that all nanowires should be connected to nano-size particles. All of the Si nanowires are expected to be terminated at one end by a nanoparticle. As observed in Fig. 1, however, the product consists of nearly pure long SiONWs, with a few nanoparticles (marked with arrowheads) being found in the middle of the wires. EDX analysis shows that these nanoparticles contain Si, Fe, and O. Due to the high viscosity in the Si–Fe–O liquid droplets, however, the temperature was not high enough (~1200 °C) to allow recrystallization of the atomic Si–O species, resulting in the formation of the amorphous silica nanowires instead of crystalline nanowires. This makes it different from the growth of crystalline Si nanowires,[4,5] in which the eutectic point of the $FeSi_2$ compound is about 1207 °C, and absorption of Si atoms into the liquid droplet make it supersaturated, and crystalline Si nanowires precipitate continuously from the droplets. The Fe catalyst was important in the formation of high quality SiONWs and silicon nanowires, and the product could be very little with many larger nanoparticles, if there was no Fe catalyst being added in the target materials.

The most striking property of the SiONWs is that they emit stable and high brightness blue light. As is shown in Fig. 3, two broad PL peaks were clearly distinguishable at energies of 2.65 eV (about 470 nm in wavelength) and 3.0 eV (about 420 nm), respectively. The intensity of the more intensive peak (at 3.0 eV) was found more than two orders of magnitude higher than that of the porous silicon.

The question is where do the electron-hole pairs recombine to give such an intensive light emission in the SiONWs? It will be helpful to recall some PL results of silica glasses. For the reason that amorphous SiO_2 films are widely used as passivation or insulation layers in integrated circuits, the PL of various silica glass have been studied extensively.[8–10] Nishikawa *et al.* 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 band was ascribed to the neutral oxygen vacancy ($\equiv$Si–Si$\equiv$), while the 3.0 eV band corresponds to some intrinsic diamagnetic defect center, such as the twofold coordinated silicon lone pair centers (O–Si–O). These defects are clearly due to high oxygen deficiency in sample preparation. These structural defects are radiative recombination centers. Blue luminescence was also observed in Si^+-implanted SiO_2 films peaked at around 2.7 eV, which was believed to be due to oxygen vacancy.[11] Ultraviolet light emission was observed in oxidized porous silicon as well as in annealed SiO_2.[12] It is therefore reasonable for us to believe that the very intensive blue light emission from the SiONWs can be attributed to the above-mentioned defect centers arising from oxygen deficiency. It is worth noting that the completely oxidized silicon nanowires also emit blue light, but its PL peak intensity is much lower than that of the SiONWs, possibly due to the difference in structures of the two cases. The blue light emission materials have long been of great interest for semiconductor full-color display, but they are difficult to synthesize in practice. GaN (Ref. 13) has been found as a candidate material for blue light emitting diodes. The blue light emitting SiONWs may be of interest in fundamental research and technological applications. In the field of recently developed SNOM,[14] the spatial resolution depends both on the diameter of the tip and the tip-sample separation. The use of the SiONWs as the optical head in the new generation SNOM may provide an opportunity to improve the resolution. It was discovered recently that unusually high transmittivity of visible light was obtained through regular arrays of holes (about 150 nm in diameter, which are much smaller than the wavelength of the incident light).[15] This extraordinary phenomenon cannot be explained using existing optical theory. The SiONWs are probably helpful for studying the optical phenomenon beyond the diffraction limit, e.g., the behavior when visible light propagates through nano-optical wires whose diameter is far smaller than the wavelength of the propagation light.

In conclusion, nanowires of amorphous silica were synthesized in large scale using the laser ablation approach. The SiONWs have a uniform diameter and long length. The growth of SiONWs is most likely controlled by the vapor–liquid–solid (VLS) mechanism similar to that in Si nanowire growth. An extraordinarily intensive blue light emission was observed which could be attributed to defect centers of oxygen deficiency in the wires. The SiONWs are probably of interest in SNOM and integrated optics.

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