Synthesis and Photoluminescence of Amorphous Silicon Oxycarbide Nanowires

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Synthesis of amorphous SiCO nanowires was carried out by means of direct current arc discharge. Free-standing SiCO nanowires were deposited on the surface of a graphite crucible without any catalyst and template. The SiCO nanowires were analyzed by XRD, SEM, TEM, XPS, and FTIR. The SiCO nanowires were typically 20–100 μm in length and 10–100 nm in diameter as measured by SEM and TEM. The XPS and FTIR spectroscopy analysis confirmed that the Si atoms share bonds with O and C atoms in mixed SiCO units. The PL spectrum of the SiCO nanowires showed strong and stable white emissions at 454 and 540 nm. A plasma-assisted vapor-solid growth mechanism is proposed to be responsible for the formation of the SiCO nanowires.

Key words: Amorphous materials, Plasma deposition, Nanowires, Photoluminescence

I. INTRODUCTION

One-dimensional (1D) nanoscale inorganic structures, such as nanotubes and nanowires, have great potentials for testing and understanding fundamental concepts about the effects of dimensionality and size on mechanical, optical, and electrical properties [1–3]. Among these materials, silicon and carbon based ceramic nanowires have recently attracted considerable research attention due to their specific chemical and physical properties [4–7]. So far, many different methods have been employed to fabricate these ceramic nanowires, such as chemical vapor deposition (CVD) [8], carbothermal reduction [9], sol-gel [10], catalytic growth on metal particles [11], as well as infiltration of silicon containing polymers in template [12, 13].

The structure of silicon oxycarbide (SiCO) glasses has been the focus of many studies [14]. The local chemistry about Si, C, and O atoms is intensively investigated. SiCO is formed by the partial replacement of O atoms in silica network with C atoms, so that Si atoms share bonds with both O and C atoms without O–C bonds. This structure is based on the formation of a random network of Si–O and Si–C bonds with a free carbon phase [15]. The SiCO has a wide range of applications such as structural materials [16], reinforcement materials [17], catalyst support [18], and anodes for lithium batteries [19]. At present, the SiCO nanowires and nanotubes have been fabricated only by template assisted methods [12, 13]. It is indispensable to search an alternative method for synthesis of SiCO nanowires without the addition of any catalyst or template.

In this work, we describe a large-scale synthesis of SiCO nanowires by a simple method, which is based on the conventional direct current arc discharge process commonly used in the growth of silicon-based ceramic nanowires [20]. This method has also the advantages of fast yield and low cost. Hence, by utilizing this new method, we demonstrate that large-scale SiCO nanowires can be prepared by a plasma-assisted vapor-solid growing process without designed addition of catalyst or template. The formation mechanism and photoluminescence (PL) properties of the SiCO nanowires are thoroughly discussed.

II. EXPERIMENTS

The synthesis was carried out in an improved direct current (DC) arc discharge plasma setup [21]. A tungsten rod with the purity higher than 99.99%, 8 mm in diameter and 30 cm in length, was used as the cathode. Si (99.95%), SiO2 (99.99%), and graphite (99.99%) powders were mixed with molar ratio of 1:1:2 in a ball mill and pressed into columns as the reactants. A column, 18 mm in diameter and 4 mm in height, was placed into the water-cooled graphite crucible which acted as the anode. The reaction chamber was first evacuated to less than 1 Pa and then filled with argon for several times to remove the residual air completely. Then, working gas (Ar, 99.99%) was introduced into the chamber until the inner pressure reached 10 kPa. As the DC arc discharge was ignited, the input current was maintained at 100 A and the voltage was a...
little higher than 20 V. The power supply was turned off 5 min later. After passivation in Ar for 6 h, the sample, which was white powder, was collected in the graphite crucible.

The characterizations of the samples were carried out via X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy in parallel. The XRD patterns were recorded via a Bruker D8 DISCOVER GADDS diffractometer working with a Cu target. The SEM images of the sample were taken on a HITACHI S-4800 microscope equipped with an energy dispersive spectrometer (EDS). The morphology of a group of nanowires, as well as the selected area electron diffraction (SAED) pattern, was obtained via a JEM-2100F TEM using an accelerating voltage of 200 kV. The bonding states of the elements were studied via XPS on an EASY ESCA spectrometer (VG ESCA LAB MKII). The FTIR studies were carried out on a Nicolet Avatar 360 FTIR spectrometer with the prepared powders diluted in KBr pellets. The PL spectrum was measured with a JY-T800 Raman spectrometer (excited with a He-Cd line at 325 nm). All measurements were performed at room temperature.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical SEM image of a lump of sample which displays a pure white color. A few long nanowires can be found on the surface of the lump. The rough and incontinuous surface of the lump implies that the sample is composed of a large quantity of nanowires, which are interlaced and intertwined with one another and form a carpet-like structure. Figure 1(b) shows the morphology of these nanowires with a higher magnification, which clearly shows a high density of cotton-like nanowires with the length of several tens of micrometers. It can be clearly seen that the nanowires are intertwined. Further characterization of the microstructure of the nanowires was carried out by TEM. A group of nanowires are shown in Fig.1(c), which have diameters from 10 nm to 100 nm and lengths up to several tens of micrometers. The typical SAED of the nanowires is inserted in Fig.1(d), which shows only a dispersive loop. Figure 1(e) shows the HRTEM image of a representative nanowire stem. It can be seen that the lattice fringes of the nanowire lacks long-range order, but shows some degree of short-range order instead. The range of the regular fringes may cover 1–5 nm. As shown in Fig.2(a), the EDS spectrum confirms that the nanowires are composed exclusively of C, Si, and O elements. Quantitative analyses of the EDS spectrum show that the atomic proportion ratio of C, Si, and O is about 0.7:1:1.5. Figure 2(b) shows the powder XRD pattern of the nanowires. It can be found that the nanowires show a completely amorphous structure with only presence of the silica-related halo centered at about 2θ=22°. These results are in complete agreement with previously reported findings of amorphous silicon oxycarbide [22]. From HRTEM image, SAED and XRD pattern, it can be unambiguously concluded that the nanowires are in an amorphous state.

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To further confirm the composition and the bonding nature of the nanowires, the samples were characterized by XPS and FTIR. Figure 3(a) shows the full-range XPS survey spectrum, demonstrating that the nanowires are composed of only Si, C and O elements. Figure 3(b) shows that Si2p spectrum can be deconvoluted into four Gaussian peaks, which can be assigned to SiO–C3 (100.2 eV), SiO2–C2 (101.6 eV), SiO3–C (102.6 eV) and SiO4 (104.1 eV) [23, 24]. Figure 3(c) shows the C1s core level electron spectrum for the SiCO nanowires. The C 1s spectrum can be deconvoluted into three Gaussian peaks and they are assigned as follows: CSi4 (282.9 eV), C–C (284.6 eV), and C–O–Si (287.6 eV) [24]. Figure 3(d) shows the O1s core level electron high resolution scan spectrum of SiCO nanowires, which is decomposed into two components, namely, SiC2O5 (531.6 eV) and O–Si (532.7 eV) [25]. The XPS analysis of nanowires clearly shows the presence of silicon oxy carbide units in which Si–C bonds are present in mixed silicon oxy carbide units.

A typical FTIR spectrum of the SiCO nanowires is displayed in Fig.4. A broad peak between 900 and 1300 cm\(^{-1}\) is present in the FTIR spectrum. The broad peak at near 1092 cm\(^{-1}\) is relevant to ring or open link of Si–O–C and cage link of Si–O–C. A shoulder peak at 1060 cm\(^{-1}\) is relevant to the Si–O stretching of the Si–O–Si network [16]. A broad peak at 1580–1650 cm\(^{-1}\) can be assigned to the stretching mode of the conjugated C=C framework of graphite. The spectrum exhibits absorption peaks at 796 cm\(^{-1}\) corresponding to Si–C stretching, at 464 cm\(^{-1}\) corresponding to Si–O–Si rocking mode. The broad but intense absorption at 3150–3650 cm\(^{-1}\) with the maximal absorption at 3421 cm\(^{-1}\) can be attributed to an O–H stretch. These results are completely in agreement with previously reported findings of amorphous silicon oxy carbide thin films and nanotubes [12, 26–28].

The formation mechanism of the SiCO nanowires might be similar to the carbon-assisted method for syn-
the synthesis of SiO$_x$ nanowires [29, 30]. As soon as the direct current arc was ignited, the tungsten rod (cathode) and the source materials (anode) in the graphite crucible were heated to temperatures at the order of $10^3$–$10^4$ °C. The solid mixture of silicon, graphite and silicon dioxide was evaporated drastically both thermally by the high temperature and by the bombardment of radicals in the arc zone. The vapor phases of SiO and CO generated by the thermal effect (thermal evaporation) were the key factors:

$$\text{SiO}_2(s) + \text{Si}(s) \rightarrow 2\text{SiO}(g)$$
$$\text{SiO}_2(s) + \text{C}(s) \rightarrow \text{SiO}(g) + \text{CO}(g)$$

When the power was turned off, the crucible (anode) was cooled down rapidly (from $10^3$–$10^4$ °C to room temperature within several seconds) by water stream. The shape of the amorphous nanowires was thus preserved in this quenching process. By adopting carbon-assisted method, the synthesis of SiO$_x$ nanowires requires adequate source of oxygen. But in our experiments, the source of oxygen was only SiO$_2$ powder, which could not supply enough oxygen to react with C to produce CO$_2$, thus the C element was preserved in the final nanowires. Since no catalyst was added in the experiment and no nanoparticle could be found at the tips of the nanowires, these SiCO nanowires are believed to be formed via a vapor-solid model.

The PL spectrum of the synthesized SiCO nanowires measured at room temperature is shown in Fig.5. The PL properties of SiCO have been reported by several groups, because it is an intense and efficient white light source [31–33]. A broad PL emission band can be clearly observed in the 400–700 nm spectrum range with two maxima at about 454 and 531 nm. Oxygen defect centers (ODCs) can be formed in oxides due to deviation from perfect stoichiometry. These ODCs exhibit characteristic optical properties associated with their atomic/molecular transitions. For SiO$_2$, nonbridging oxygen hole centers (NBOHCs), O$_3$≡Si–O$^-$, and neutral oxygen vacancy (NOV), O$_3$≡Si−Si$^-$O$_3$, are two commonly observed ODCs, giving rise to strong luminescence in the green-red range (510–610 nm) and blue (450 nm) range [31, 34]. In comparison, defect related luminescence was seen to fall in the SiCO nanowires spectral range, implying that NBOHCs and NOVs could play a role in luminescence. This result is also the same as the luminescence source in C-doped silicon oxides [35]. The present PL curve in the green-red range (510–710 nm) exhibits many shoulder peaks. This behavior could be attributed to the existence of SiC$_x$O$_y$ nanoclusters in SiCO nanowires [34]. The exact nature of the PL of synthesized SiCO nanowires remains unclear and requires more detailed systematic investigation.

**FIG. 5** Room temperature PL spectrum of SiCO nanowires.

**IV. CONCLUSION**

Direct current arc discharge method was developed for the synthesis of amorphous SiCO nanowires. The size of the amorphous SiCO nanowires was 20–100 μm in length and 10–100 nm in diameter. The nanowires were composed exclusively of C, Si and O elements. The proposed growth process of the amorphous SiCO nanowires is based on a VS growth mechanism. A broad PL emission peak with its maximum located at about 454 and 531 nm was observed and attributed to oxygen deficient-associated defect.

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