Research Article

Synthesis of Core-Shell SiO_x /Carbon Nanofibers on Silicon Substrates by Ultrasonic Spray Pyrolysis

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We synthesized the core-shell SiO_x /carbon nanofibers with diameters of 200–300 nm using ultrasonic spray pyrolysis with a phosphorus/ethanol mixture. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive spectroscopy (EDS) investigations confirmed the core-shell structure, which consisted of a core of SiO_x and a shell of amorphous carbon. The phosphorus atoms corroded the entire silicon substrate surface, and the Si-P liquid-catalyzed the solid-liquid-solid mechanism is proposed to explain the growth of the core-shell SiO_x /carbon nanofibers.

1. Introduction

In recent years, the SiO_x -based nanofibers have attracted interest worldwide because of their small sizes, which enable higher levels of functionality within a given space, and because of their peculiar and fascinating properties. The nanodevices and large-surface-area structures [1], which are a type of one-dimensional nanostructures, have many potential applications and have been used as versatile building blocks in the miniaturization of electronic and optoelectronic devices [2]. These devices also have a high strength-to-weight ratio and superior stiffness, as well as other excellent engineering properties such as good wear resistance, low expansion coefficients, and low relative flexibility. These properties allow them to be used as one-dimensional quantum transistors, composites, light-emitting diodes [3], and optical sensors [4]. For the realization of these excellent properties, the surface of the SiO_x core needs to be passivated with highly thermally and chemically stable protective shells, for which carbon is an ideal candidate [5]. Several methods have been used to synthesize these SiO_x -based nanofibers, including laser ablation [6], thermal stress [7], physical evaporation [8], and chemical vapor deposition (CVD) [9]. The growth of such SiO_x -based nanofibers is attributed to the solid-liquid-solid (SLS) growth mechanism

[10], and different metal catalysts such as Ni [11], Co [12], and Au [13] are used.

In the present study, we report a simple method for the synthesis of core-shell SiO_x /carbon nanofibers using ultrasonic spray pyrolysis. The silicon oxide shows stable and bright blue light emission [14] and is widely used for fabricating insulation layers in integrated circuits. The carbon is one of the most popular materials for the formation of protective shells because of its superior physical and chemical properties [15]. In particular, amorphous-carbon-coated nanofibers have been found to exhibit significantly enhanced field-emission properties [16]. A possible growth mechanism of such core-shell nanofibers is also discussed in the present study.

2. Experimental

Figure 1 shows a schematic diagram of the CVD apparatus. An ultrasonic nebulizer was connected to a quartz tube and N_2 gas cylinder. Si (100) substrates of size 10×10 mm were cleaned with acetone and methanol in an ultrasonicator, washed with deionized water, and finally dried using a nitrogen blower. The substrates were kept in a quartz boat, which was placed at the center of the quartz tube. One end of the quartz tube was attached to the ultrasonic

FIGURE 1: Schematic image of the apparatus of the ultrasonic spray pyrolysis CVD.

FIGURE 2: Typical SEM image of nanofibers synthesized at 950°C.

nebulizer, and the other to the gas bubbler. Phosphorus (phosphorus powder, Kojundo Chemical Laboratory, 99.5%) was mixed in the ethanol and placed inside the atomization chamber. A flow of N_2 gas was introduced into the mixture of ethanol and phosphorus (100 mL, 10 wt%) to enter the quartz tube at a rate of 0.1 L/min. When the temperature of the electric furnace reached 950°C, the ultrasonic nebulizer was switched on, and the ethanol/phosphorus mixture was converted into a thin mist. The flow of N_2 was maintained to pass this mist inside the electric furnace. The deposition was performed for one hour. After deposition, the furnace was switched off and allowed to cool down to below 100°C. In the ultrasonic spray pyrolysis, electric vibrators (1.65 MHz, Atom Medical Corp., Model 303) produced a mist of ethanol and phosphorus. Finally, the deposited samples were analyzed using scanning electron microscopy (SEM, Hitachi, S-3000H), scanning transmission electron microscopy (STEM), energy-dispersive spectrometry (EDS) (Hitachi, JEM-z2500), Raman spectroscopy (JASCO, NRS-1500), and X-ray photoelectron spectroscopy (XPS, Ulvac, PHI-5000). In the XPS measurements, a tablet of the deposition (peeled from the Si substrate and mixed with indium powder) was used in order to prevent any signal from the silicon substrate.

3. Results and Discussion

Figure 2 shows the typical SEM image of the product synthesized at 950°C. A high density of nanofibers of 200–300 nm in diameter is observed.

Figure 3 shows typical TEM images and the corresponding EDS spectra. The TEM images in Figure 3(a) show that the diameter of the fiber is about 300 nm. TEM observation also indicated that these nanofibers have a clear core (spot (i)); we also observed the amorphous carbon structure outside the core (spot (ii)). Figures 3(b)–3(d) show the elemental mapping of the nanofiber with an energy-filtered image, from which we found that the constituent parts of the fiber are composed primarily of carbon, oxygen, and silicon atoms. The Si and O atoms are mainly grouped in the core of the nanofiber, whereas the C atoms are primarily found in the shell. In addition, we found that Si, O, and C coexisted with each other. The EDS characterization revealed proportions of 95.54% carbon, 2.11% oxygen, and 1.40% silicon and showed that the fiber does not contain phosphorus. The EDS spectrum of this nanofiber (Figure 3(f)) shows three very distinct peaks of carbon, oxygen, and silicon, with the carbon peak possibly coming partially from the carbon supporting film on the TEM grid. We did not find any phosphorus in the nanofiber within the detection limits.

Figure 4 shows the Raman spectra of the sample, which were obtained using a green laser with an excitation wavelength of 532 nm. The carbon shared two common features in the Raman spectra: a G-peak at around 1580–1620 cm^{-1} and a D-peak at around 1350 cm^{-1} . We observed that the D-peak of the nanofibers was comparatively higher than the G-peak. The D-peak is induced by the disorder of the graphite structure, whereas the G-peak is caused by the stretching of the sp^2 carbon atom in the graphite structure. The Raman spectra of the samples has strong D-peak, suggesting more disordered nanocrystalline structural defects such as distortion, vacancies, and straining of graphitic lattices; these features are all prevalent in the nanofibers [17].

Figure 5 shows the survey XPS spectra of the prepared nanofiber composite and the high-resolution XPS spectra of silicon and carbon. The survey XPS spectra (Figure 5(a)) clearly indicate that carbon, oxygen, and silicon exist in

FIGURE 3: (a) TEM images of a core-shell nanofiber. EDS elemental mappings for (b) carbon, (c) oxygen, (d) silicon, and (e) phosphorus in the core-shell nanofiber; (f) EDS spectrum of a representative nanofiber fabricated using a mixture of phosphorus and ethanol.

the prepared nanofiber composite. In Figure 5(b), the two C 1s peaks are located at 284.4 and 285.6 eV, corresponding to the sp^2 and sp^3 atoms, respectively. The silicon-carbon composite peak is located at 282–283 eV, so it does not originate from SiC. The XPS peaks at 102.25 and 103.65 eV, corresponding to the lower oxide components of Si (Si^{3+}), are clearly observed in Figure 5(c). These nanofibers show an XPS peak in the SiO_x/C composite that is related to x , as

shown in Figure 5(c) [18]. The peak suggests that the nanofibers have an SiO_x composition.

Figure 6(a) is a schematic illustration of the growth mechanism. It involved in the formation of the amorphous-carbon-coated SiO_x core are proposed as follows. Initially, the phosphorus coating on the silicon substrate forms a P film, as illustrated in Figure 6(a)-(i). When the temperature increases, the silicon substrate is oxidized by O_2 in

FIGURE 4: Raman spectrum of nanofibers synthesized at 950°C.

(a)

(b)

(c)

FIGURE 5: XPS spectra of the nanofiber film fabricated using a mixture of phosphorus and ethanol: (a) survey spectrum; (b) C 1s spectrum; (c) Si 2p spectrum. The solid curves in (b) and (c) are the best Gaussian fits for the two peaks.

the carrier N_2 and by water from the decomposition of ethanol. An eutectic reaction between the oxidized Si and P occurs to form an Si-P eutectic liquid [19], as illustrated in Figure 6(a)-(ii). Because the melting point of silicon is 1414°C, a temperature at which the Si vapor phase is

(a)

(b)

FIGURE 6: (a) Schematic illustration of the growth processes; (b) SEM image revealing that core-shell SiO_x /carbon nanofibers were grown from the surface of the silicon substrate.

negligible, and the silicon substrate itself serves as an Si source without any additional external source, the nanofibers should be formed via a solid-liquid-solid (SLS) mechanism [20]. Finally, the surface of the Si-P eutectic liquid soon becomes supersaturated, and then, SiO_x /carbon nanofibers precipitate out and continue to grow from this supersaturated surface, possibly through the oxidation reactions of $Si + O_2 \rightarrow SiO_x$. At the same time, the amorphous carbon shell is also deposited from the carbon of the ethanol dissolved on the outside of the SiO_x core, as illustrated in Figure 6(a)-(iii). These growth processes occurred in the presence of all the four elements (silicon, oxygen, carbon, and phosphorus) and affected each other to varying degrees. Figure 6(b) shows an SEM image of the core-shell SiO_x /carbon nanofibers in a low-density area, which allows us to see clearly that the core-shell SiO_x /carbon nanofibers are grown from the Si substrate at the critical temperature of 930°C [21].

4. Conclusion

In the present study, we successfully synthesized the nanofibers with a mixture of phosphorus/ethanol on a silicon

substrate using ultrasonic spray pyrolysis method. The Core-shell SiO_x /carbon nanofibers were produced on the surface of the silicon substrate, and the molten phosphorus played an important role in their synthesis. A possible mechanism for this process is the formation of the SiO_x core of the nanofibers from the surface of the Si-P liquid and the formation of the carbon shell from the ethanol. We believe that this approach to the synthesis of core-shell SiO_x /carbon nanofibers may be further used in the fabrication of building blocks for device miniaturization and optoelectronic devices.

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