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LETTER TO THE EDITOR

Ferrocene-activated growth of carbon-reinforced silica nanowires from a planar silica layer by chemical vapour deposition

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Abstract
In this letter, we report a simple procedure to synthesize carbon-reinforced silica fibres on planar silicon substrates covered with a thin silica cap layer. The procedure contains two steps, which are first activating the substrate with ferrocene and then exposing it to methane at ∼1100 °C, which transforms the silica cap layer into nanowires of ∼200 nm in diameter. The silica nanowires are reinforced by glassy carbon in the core, and have an optical band gap of ∼3.1 eV. During growth the nanowires are grown randomly inside circular areas surrounded by circular walls of large fibres, thus forming wreath-like patterns randomly distributed on the substrate surface. The growth of the nanowires and the formation mechanism of the wreath-like patterns are also discussed.

Since the first observation of carbon nanotubes in 1991, materials of reduced dimensions, e.g. nanotubes, nanorods and nanowires, etc, have stimulated a lot of research interest due to their unique properties attractive for modern nanotechnology [1–4]. For example, silica nanowires can emit stable blue light over a hundred times brighter than that emitted by porous silicon, and is thus considered as a candidate material for diverse applications in nanodevices, such as high-intensity light sources, near-field optical microscopy probes, low-dimensional waveguides and hosts to lasing materials [5]. Much attention has thus been paid to developing fabrication technologies to grow silica nanowires on planar substrates for applications in real devices, and on investigating the growth mechanisms of nanowires.

Silica nanowires/fibres can be synthesized by different approaches, for instance, they can be obtained by bio-mimetic surface-chemical strategies through induced condensation of silica precursors [6–8], laser ablation [5] or by high-temperature solid reaction [9]. However, these approaches are not capable of bringing about the alignment of silica nanowires/fibres on planar substrates, which is essential for the post-deposition in fabricating silica nanowires-based devices. Therefore new synthetic technologies are demanded for the application of silica nanowires in real devices. Here, we report a very simple two-step procedure, i.e. first activating the substrate surface with ferrocene molecules and then exposing it to methane at $\sim$1100 °C, to synthesize silica nanowires on planar silicon substrates. The nanowires so produced are reinforced by glassy carbon at the core, and have an optical band gap of $\sim$3.1 eV. We show that by this approach the nanowires can be produced in large scale on the substrate and form interesting growth patterns by self-organization during growth.

In this letter, we report on the synthesis of carbon-reinforced silica nanowires on planar silicon substrates by the two-step approach, the investigation of their structure and properties, their self-assembly behaviour and growth mechanism of the nanowires on the substrates.

The substrates used in this study were Si(001) wafers covered with a 125 nm thick silica cap layer grown by thermal oxidation. These were ultrasonically successively cleaned in acetone, alcohol and deionized water baths prior to processing. The activation of the substrate was carried out by simply dropping a solution of ferrocene dissolved in toluene onto the surface and drying away toluene with a gentle flow of helium/nitrogen. The activated substrates were loaded into a high-temperature alumina tube furnace, pumped down to 10^{-3} Torr and back-filled with flowing argon to a pressure of about 100 Torr. The furnace was then heated to 1100 °C for 30 min, after which methane was introduced into the gas stream and allowed to flow for about 1 h. The growth morphology, structure and properties of the silica nanowires grown were investigated and characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), optical and micro-Raman spectroscopy and energy dispersive x-ray spectrometer (EDX), respectively.

Figure 1 shows SEM micrographs of the morphology and diameters of silica nanowires produced by the two-step approach. Figure 1(a) shows that, by activation of the substrate surface with ferrocene molecules and exposure to methane at $\sim$1100 °C, the thin silica layer capping the silicon substrate transformed into nanowires and formed interesting growth patterns randomly distributed on the substrate surface. A typical growth pattern of the nanowires is shown in figure 1(b). One sees that the nanowires are grown along random orientations inside a circular area that is isolated by a circular wall of bigger fibres, thus forming a wreath-like closed circular pattern. The diameter and morphology of the nanowires and fibres forming the wreath-like pattern are shown in figures 1(c) and (d). We see that the nanowires are long and flexible and of diameters of $\sim$200 nm, while the fibres forming the circular wall are of larger diameters, short and straight. Another feature of the growth one may also notice is that, outside the wreath-like pattern, there is little growth of nanowires.

The structure and optical band gap of the nanowires were examined by high-resolution transmission electron microscopy (HRTEM) and determined with an optical microscope by measuring the optical absorption in the visible and ultraviolet range, respectively. Figure 2(a) shows the data near the absorption edge of an individual nanowire placed on a silica glass substrate, from which the optical band gap of the nanowires was estimated to be $\sim$3.1 eV using the Tauc relationship [10], and is $\sim$16% smaller than that of the reference silica glass substrate [11]. This narrowing in the optical band gap is attributed to the nanosized graphite particles embedded in the amorphous silica nanowires during growth. The inset of figure 2(a) is a typical HRTEM image of the nanowires, which shows clearly that nanosized graphite particles are embedded in the amorphous silica matrix. The reinforcement of the nanowires with glassy carbon was also observed by micro-Raman analysis. Figure 2(b) is a Raman spectrum taken from an individual nanowire. The large D peak at $\sim$1350 cm^{-1}, due to the disordered nature of graphite [12], confirms the existence of glassy carbon in the nanowires [11]. We were

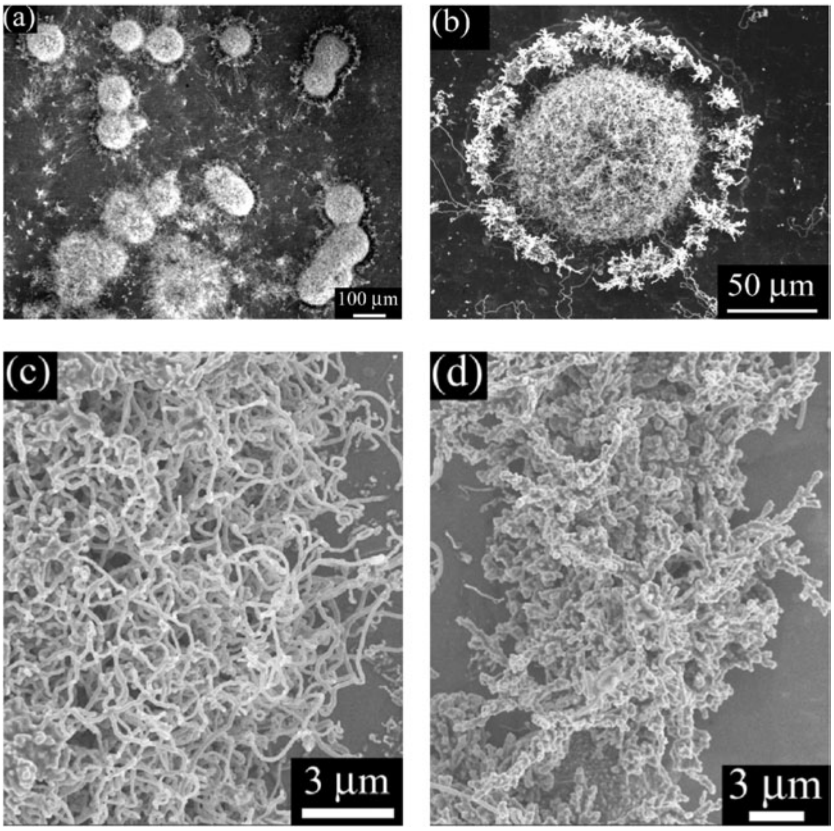

Figure 1. SEM images of silica nanowires synthesized by the two-step approach on planar silicon substrates. (a) A low-magnification image of the nanowires; (b) a typical growth pattern of the nanowires; (c) a high magnification image of the silica nanowires; and (d) a high magnification of the fibres forming the circular wall of the wreath-like patterns.

not successful in placing an individual fibre of the circular wall of the wreath-like pattern on a TEM grid or a silica glass substrate to determine its structure and optical properties. We therefore performed Raman analysis of the circular nanowires' area and the wall of the fibres for comparison. Figure 2(c) shows the Raman spectra from both areas. The apparent difference between the two spectra suggests that the short and straight fibres of the circular wall isolating the circular area of the nanowires in the wreath-like pattern are probably beta-SiC fibres.

The formation of the wreath-like of the nanowires by self-organization on the substrate surface is intriguing. To understand the growth and formation mechanism of the patterns of the nanowires, we have conducted experiments of

(1) heating the substrate activated with ferrocene and the un-activated substrate in flowing argon without methane exposure, and
(2) heating the un-activated substrate in argon and with methane exposure.

In all cases we did not observe the growth of nanowires by SEM. This suggests that both the ferrocene activation of the substrate surface and the methane exposure are needed to transform the thin silica cap layer into nanowires. On the substrate activated with ferrocene molecules, however, some circular templates have been created after heating in flowing argon,

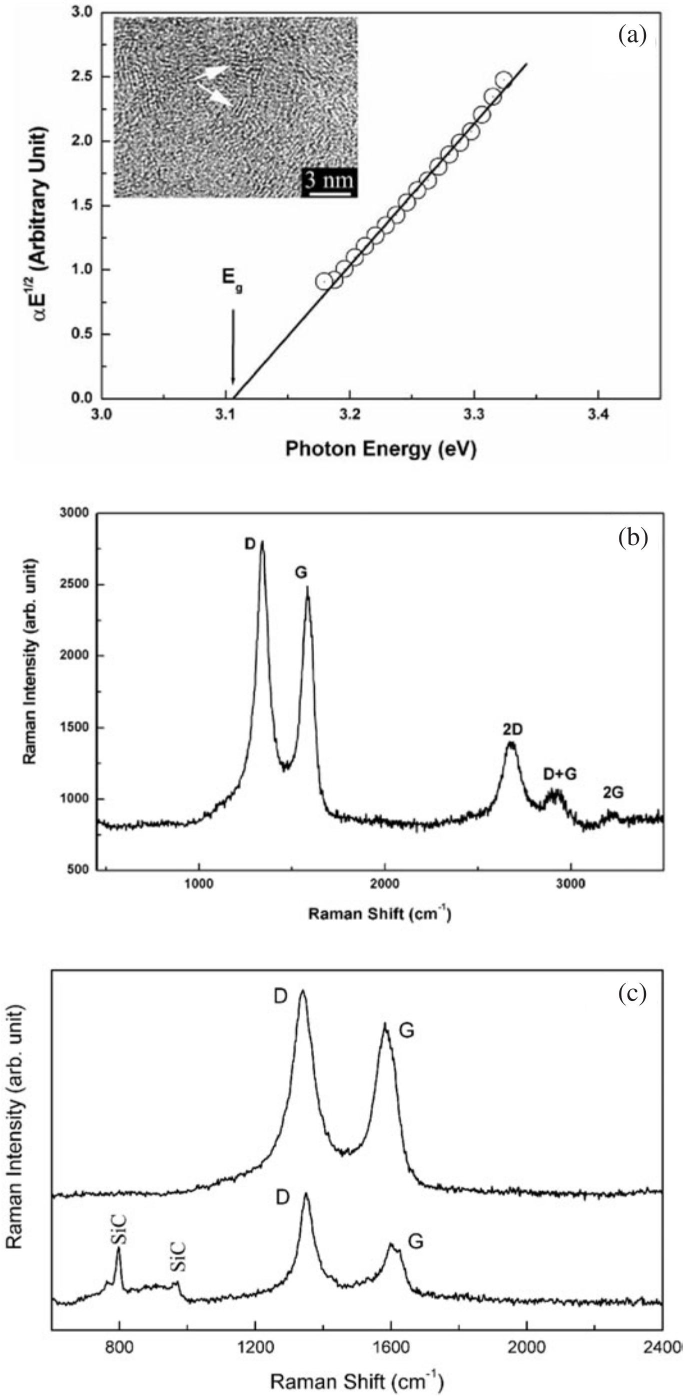

Figure 2. (a) The optical absorption spectrum and (b) the Raman spectrum of a single nanowire placed on a silica glass substrate; (c) Raman spectra obtained from the circular nanowires area (upper) and the circular wall of fibres (lower) of the wreath-like pattern shown by figures 1(b)–(d). Inset of figure 2(a) is a HRTEM image of an individual nanowire.

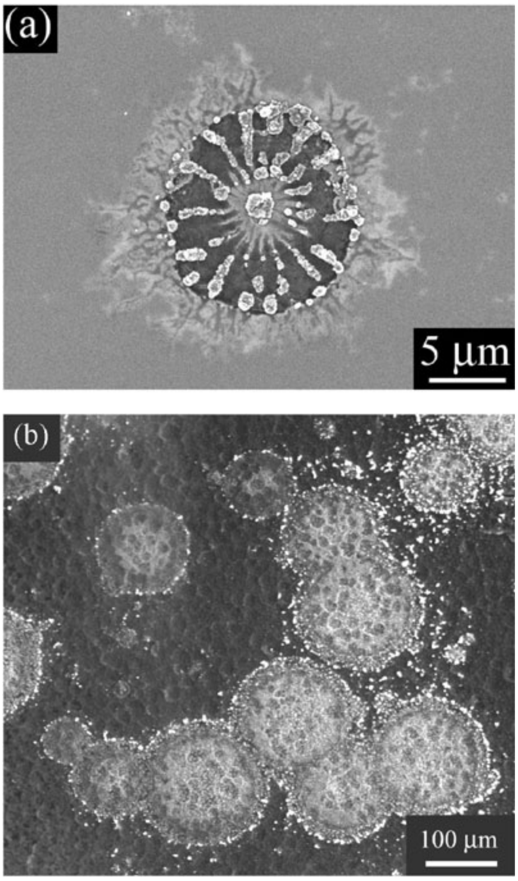

Figure 3. A typical circular template created on the surface of the ferrocene-activated substrate after heating in flowing argon at (a) 800 °C and (b) the development of these templates after heating to ∼1100 °C.

randomly distributed on the surface. Figure 3(a) shows a SEM micrograph of a typical template formed after heating in argon to 800 °C. The formation of the circular template is probably due to reactions of the silica surface with ferrocene molecules at elevated temperatures, through some complicated procedures. The templates became larger in diameter when the substrate was heated to ∼1100 °C in argon, yet no nanowires or fibre growth was observed. Figure 3(b) shows the templates after the substrate was heated at ∼1100 °C. We see that the diameter of the templates was related to that of the wreath-like patterns shown in figure 1. These results suggest that the ferrocene activation played a key role in creating the wreath-like patterns of the nanowires, and that both the ferrocene activation and the methane exposure are needed for the nanowire and fibre growth to form the wreath-like patterns. EDX analysis of these templates suggests the existence of iron particles inside, rather than outside, the templates. This could be the reason the nanowires are mainly nucleated and grown inside the circular areas shown by figure 1. The detailed growth procedure and mechanism of the carbon reinforced silica nanowires and SiC fibres forming the circular walls of the wreath-like patterns are still unclear and are under investigation.

Based on the circular templates created on the substrate surface at elevated temperatures, silica nanowires and beta-SiC fibres can form interesting patterns. Figure 4 shows repre-

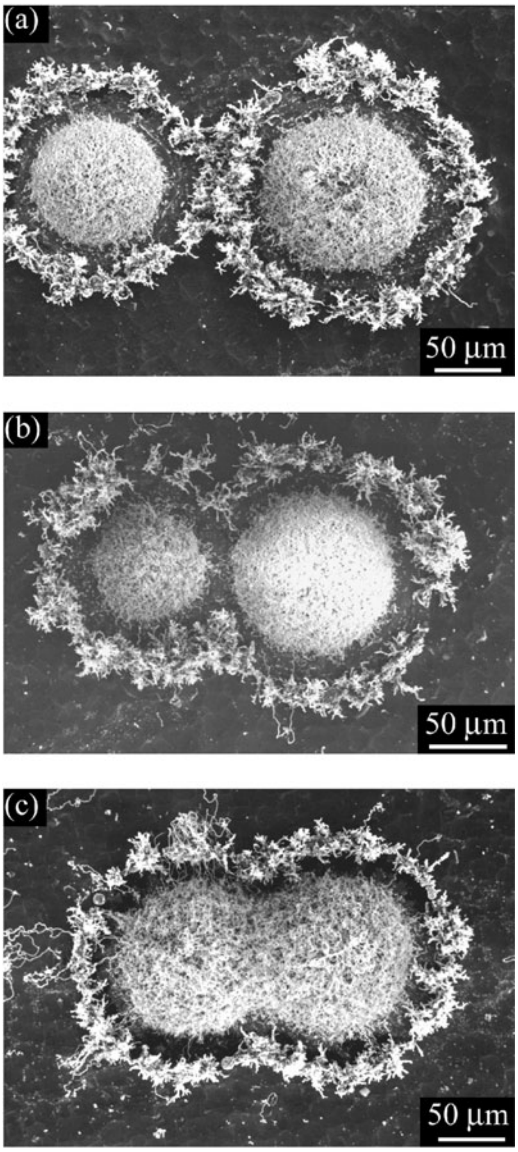

Figure 4. Growth patterns of the nanowires based on two circular templates shown by figure 3(a).

sentative patterns formed on the basis of two circular templates. We see that, at reduced distances between neighbouring templates, the two independently self-closed circular patterns (figure 4(a)) started to interact with their circular walls of larger fibres (Figure 4(b)), and then with the circular areas of randomly orientated silica nanowires (figure 4(c)), thus forming respectively, a pattern of two separated circular areas of silica nanowires surrounded by a peanut-like wall of larger fibres (see figure 4(b)), and a peanut-like pattern, i.e. a peanut-like area of nanowires closed by a peanut-like wall (figure 4(c)) Comparing figures 1 and 4, we see that, although the shape of the patterns can be different, the growth feature of silica nanowires is identical: they grow randomly inside an area surrounded by a wall of larger fibres, outside which there is little growth of nanowires.

We have demonstrated a simple two-step procedure to synthesize carbon-reinforced silica nanowires on planar silicon substrates. The influence of ferrocene activation and methane exposure on the growth of the carbon-reinforced silica nanowires and the formation of the wreath-like patterns are also discussed.

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