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LETTER TO THE EDITOR

Transforming a thin silica layer into nanowires

Zhengjun Zhang, Ye Zhao and Jingguo Liu

Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: zjzhang@tsinghua.edu.cn

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Abstract

In this paper, we report a very simple approach to transform a thin silica cap layer, formed by thermal oxidation on Si(001) substrates, into SiO_2 nanowires, i.e. treating the silica cap layer with ferrocene molecules, heating it up in argon flow and then exposing it to methane at ∼1000 °C. During the heating process ferrocene molecules reacted with the silica surface through some chemical procedures and formed circular templates on the silica surface from which silica nanowires started to develop when exposed to methane. The nanowires so produced are amorphous, ∼15 nm in diameter and several hundred micrometres in length. Prolonged exposure to methane at this temperature transformed completely the silica cap layer into nanowires. This study provides a new method to fabricate silica nanowires on planar substrates.

Materials of reduced dimensions can possess diverse outstanding properties that are very attractive to nanotechnologies and have stimulated great research interest in the last decade [1–4]. For example, amorphous silica nanowires can emit stable blue light over a hundred times brighter than that emitted by porous silicon and are considered as a candidate material for applications in nanodevices, such as high-intensity light sources, hosts to lasing materials and low-dimensional wave guides, etc, [5]. Most research interest recently has thus been directed to develop ways to synthesize these materials, to understand their growth mechanism and to realize their controlled growth on planar substrates.

For the synthesis of amorphous silica nanowires, several approaches have already been developed, for instance, the bio-mimetic strategies [6, 7], laser ablation [8], and high-temperature solid-state reactions [9]. These techniques, however, are not capable of growing silica nanowires on planar substrates, which is necessary in order to fabricate silica nanowire-based devices. New methodologies are, therefore, in demand for the synthesis of silica nanowires on planar substrates.

We report here a simple way to synthesize silica nanowires on silicon substrates. By ferrocene treatment and methane exposure at a temperature of ∼1000 °C, a thermally grown,

thin silica cap layer on Si(001) substrates can be transformed into amorphous silica nanowires. The influence of the ferrocene treatment and the methane exposure on the growth of silica nanowires is also reported.

In our experiments a silicon wafer of (001) orientation was thermally oxidized to form a thin silica cap layer (∼125 nm thick). The wafer was supersonically cleaned in acetone, alcohol and deionized water baths subsequently, and treated with a solution of ferrocene ($FeC_{10}H_{10}$) in toluene. After the toluene was gently blown away with a helium flow, the wafer was mounted into a quartz tube that was pumped down to ∼3 Pa, backfilled with flowing argon to $\sim 10^4$ Pa and heated up gradually to a temperature of ∼1000 °C. When the temperature of the tube was stabilized at ∼1000 °C, methane was also introduced into the gas stream at a flow rate of ∼1000 sccm. The reason why we selected ∼1000 °C for the methane exposure is that exposure at temperatures higher than 1000 °C led to growth of large silica fibres, reinforced by glassy carbon at the core [10]. After methane exposure, the tube was slowly cooled to room temperature in the argon flow. The growth morphology of the silica nanowires on the substrate was examined with a scanning electron microscope (SEM). The structure and the composition of the silica nanowires was characterized with a transmission electron microscope (TEM), the selected area diffraction (SAD) and the energy dispersive x-ray (EDX) spectrometer attached to the TEM.

After methane exposure at ∼1000 °C for ∼60 min, the ferrocene-modified thin silica layer was transformed completely into nanowires. Figure 1(a) is a typical SEM micrograph of the large-scale silica nanowires transformed from the silica layer after the methane exposure. The inset of figure 1(a) is an enlarged image of the silica nanowires, showing the diameter of the nanowires. These images were taken with a JSM-6301F field emission SEM working at 20 kV. Figure 1(b) shows a bright field image of individual nanowires taken with a JEOL-200CX TEM working at 200 kV. The inset of the figure is a typical SAD pattern of the nanowires, showing the amorphous nature of the nanowires. The diameter of these nanowires, as shown by the above images, is ∼15 nm. The composition of these nanowires was examined by EDX analysis. Figure 1(c) shows a typical EDX spectrum of individual nanowires. It is seen that the amorphous nanowires consist of mainly oxygen and silicon. The composition of the nanowires was estimated from the spectrum to be $\sim Si_{32.9}O_{67.1}$, which is very close to SiO_2. These suggest that the nanowires transformed from the silica layer by this approach are amorphous SiO_2 nanowires.

In transforming the silica layer into SiO_2 nanowires, both the ferrocene treatment and the methane exposure are necessary. It was found that during the heating process in flowing argon, the ferrocene molecules reacted with the silica layer through some unknown complicated chemical procedures (involving the ferrocene decomposition and the reaction with silica), and created templates on the silica surface [10]. The templates are typically circular in shape, see figures 2(a) and (b), and of diameters closely related to the heating temperature. For example, they are about several micrometres in diameter after heating at 800 °C, and over 100 μm after heating at a temperature of 1000 °C [10]. As revealed by EDX analysis (not shown), there are small iron particles inside these templates. The iron particles are probably formed from the decomposition of ferrocene during the heating process, which might serve as the catalyst for growing SiO_2 nanowires. Therefore these templates should be the first growth sites of the SiO_2 nanowires when methane was introduced into the argon stream. Figures 2(c) and (d) are SEM micrographs of the silica surface after methane exposure at ∼1000 °C for ∼10 min, showing the development of SiO_2 nanowires inside and from these templates. It is seen that at this stage SiO_2 nanowires grew mainly from and inside the templates, outside which there is no observable growth (note the 'A' area marked in figure 2(d).) Figures 2(e) and (f) are enlarged SEM images of the 'B' and 'C' areas marked in figure 2(d), showing the growth of nanowires

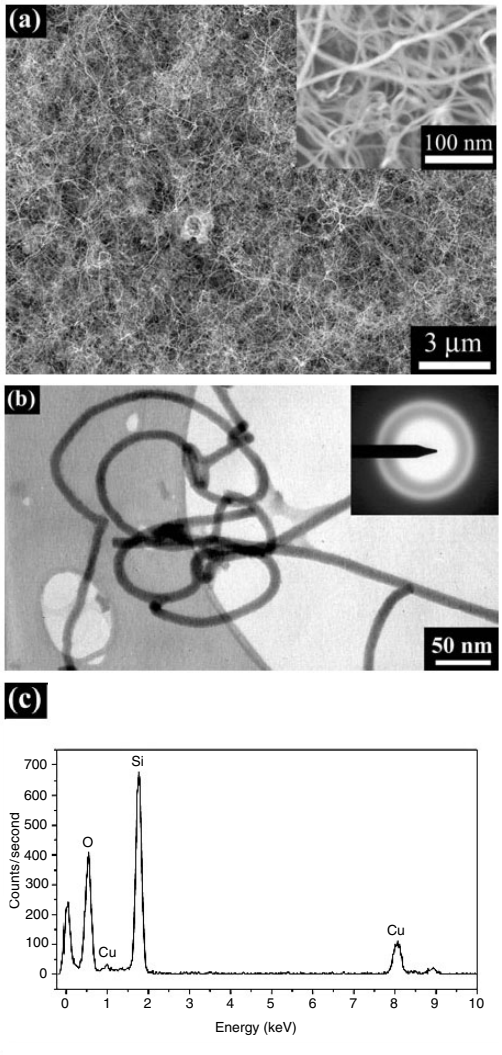

Figure 1. (a) SEM and (b) TEM images of SiO_2 nanowires formed from a thermally grown thin silica cap layer on Si(001) via pre-treatment with ferrocene molecules and post-exposure to methane at ∼1000 °C for ∼60 min. Inset of (a) and (b) is a high-magnification SEM image and a SAD pattern of the nanowires, respectively; (c) is a typical EDX spectrum of individual nanowires.

inside and from the templates, respectively. At this stage one can observe the similarity in shape of the template and the nanowire growth areas, shown by figures 2(a), (b) and (c), (d), respectively. Long-time exposure to methane at this temperature, e.g. ∼60 min, completely transformed the silica layer into nanowires as shown by figure 1(a). Therefore, the ferrocene treatment played two roles in transforming the silica layer into SiO_2 nanowires, i.e. creating the templates as the first growth sites and providing iron particles as the catalyst, through the decomposition of ferrocene and the reaction with the silica layer.

To clarify the effect of methane exposure on transforming the silica layer into SiO_2 nanowires, we have conducted experiments at ∼1000 °C without methane exposure.

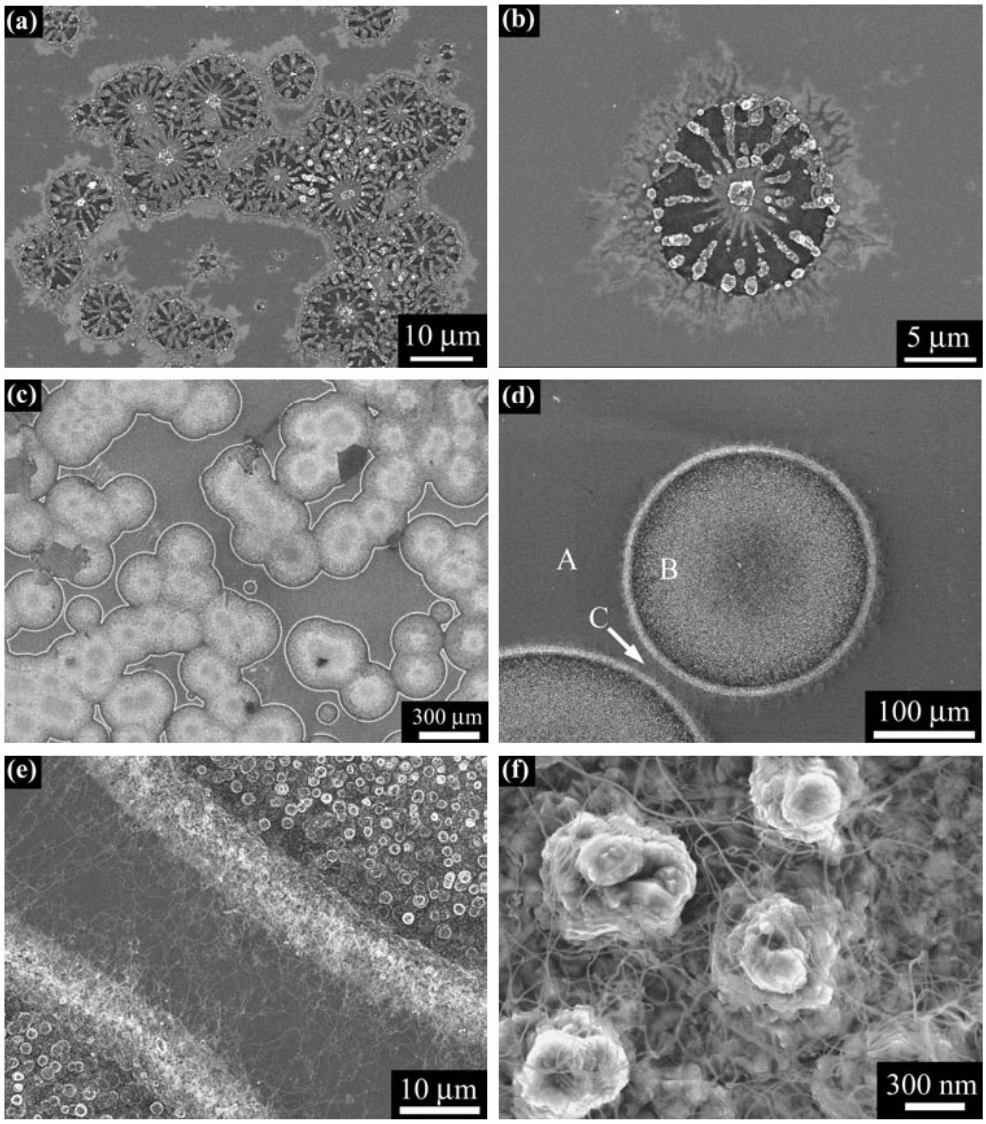

Figure 2. SEM images showing the surface morphology of the ferrocene-treated silica layer at various stages. (a), (b) after heating to ∼800 °C in flowing argon; (c), (d) after heating in flowing argon to ∼1000 °C and exposure to methane for ∼10 min. 'A' marked in (d) indicates areas not yet developed into SiO_2 nanowires. (e) and (f) are high-magnification SEM images of areas 'B'and 'C' marked in (d), showing the growth of SiO_2 nanowires.

Figures 3(a) and (b) show SEM micrographs of the ferrocene-modified silica surface after heating at ∼1000 °C for ∼10 min, in flowing argon only. Comparing with figures 2(c) and (d), we note that the shapes of the developed templates with and without methane exposure are very similar. However, the big difference is that in case of methane exposure, nanowires have grown inside and from the templates, while there is no observable growth of nanowires without methane exposure. Figures 3(c) and (d) are enlarged SEM images of areas 'B' and 'C' marked in figure 3(b). From these images we see clearly that without methane exposure there is no

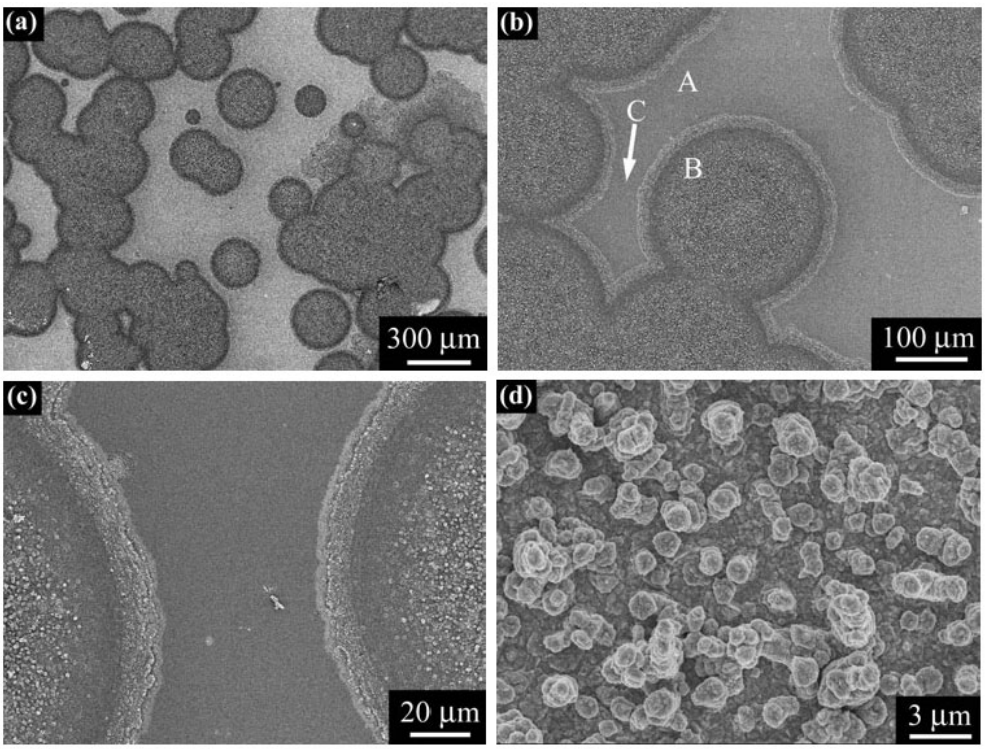

Figure 3. (a), (b) SEM images of the ferrocene-treated silica surface after heating in flowing argon to ∼1000 °C for ∼10 min, without methane exposure. (c) and (d) are high-magnification SEM images of the areas marked 'B' and 'C' in figure 2(b).

growth of nanowires inside or outside the templates. Therefore the methane exposure played a key role in triggering the growth of SiO_2 nanowires by this approach. The mechanism of transforming the silica layer into SiO_2 nanowires by methane exposure is unclear and is under investigation.

In summary, we have proposed a simple way to transform a thin silica cap layer on Si(001) substrates into SiO_2 nanowires, via pre-treatment with ferrocene molecules and post-exposure to methane at ∼1000 °C. The ferrocene molecules decomposed and reacted with the silica surface during the heating process. They then created templates as the first growth sites and formed iron particles as the catalyst, while the methane exposure at ∼1000 °C triggered the growth of SiO_2 nanowires. This study provides a simple way to fabricate silica nanowires on planar substrates on a large-scale.

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