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Formation of hook-shaped and straight silica wires by a thermal vapor method

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ABSTRACT

Hook-shaped and straight silica wires have been successfully synthesized on silicon wafer through a simple thermal vapor method with or without assistance of Al, respectively. The hook-shaped silica wires have amorphous structures with nearly 100 μm long and about 4 μm in average diameters, while the straight silica wires are hundreds of micrometers long and approximately 50–300 nm in diameters. The composition analysis revealed that larger Al/SiO_x islands can form on the silicon substrate with Al catalysts, whereas tiny silica clusters form without Al catalysts. They could act as the nucleation centers for the growth of silica wires with different shapes. The formation process of hook-shaped silica microwire results from a thermal gradient on the silicon substrate. The thermal gradient may be caused by the cold gas flowing during the process or other factors that lead to uneven temperature. On the contrary, straight growth of silica submicrowire is unacted on the thermal gradient factor due to the tiny silica clusters as nucleation centers. The present simple and low-cost process of producing hook-shaped and straight silica wires in bulk may lead to potential applications in catalysts, electrode materials, biosensing, etc.

1. Introduction

In recent years, silica wire materials have attracted great attentions because of potential applications in catalysis, optoelectronics, biosensors, etc. Silica wires can be prepared using carbon-assisted growth, laser ablation, oxide-assisted growth (OAG), solid–liquid–solid (SLS), and vapor–liquid–solid (VLS) techniques [1–5]. Due to unique chemical and physical properties tailored by the material morphology, shape-controlled synthesis of microstructures has long been pursued [6]. Generally, a catalyst or template has been employed to control the morphology of silica microstructures. For example, silica wires have been prepared using gold (Au), ferrum (Fe), tin (Sn), copper (Cu), and aluminum (Al) as the catalyst [7–11]. Specially, clustered one-dimensional SiO_x amorphous nanowires [12], curved silica wires, silica bundles [13], and helical nanostructures [14] have been synthesized using various metallic catalysts and templates. Liu et al. [15] synthesized flower-like silica nanostructure through combining the thermal evaporation of silicon monoxide powders in an evacuated quartz tube with the VLS growth mechanism at 1100 °C. Jung et al. [11] adopted Al as the catalyst for the growth of Si wires based on Al-Si alloy islands formed by preannealing since it provides a selective etching solution along with reasonable melting and eutectic temperatures. Thus, it is of interest to synthesize different shapes silica wires with an Al-catalyzed process that can be explored for further applications.

Here, we report the synthesis of novel hook-shaped silica microwires by a thermal vapor method using Al as catalyst because of its low melting point. A possible interpretation for bending growth of silica wires on Si surface is estimated and discussed. We further investigate the role of aluminum on the growth of silica wires through a comparative experiment without Al catalyst, which obtains straight silica submicrowires. Such a synthesis route adds a useful and available way for the growth mechanism and morphology control of silica wires.

2. Experimental

The growth process of silica wires was carried out in a horizontal tube furnace. The requisite amount (1.5–2.0 g) of high-purity silicon monoxide powder (SiO; purity 99.99%; 200 mesh; Aladdin Reagent, Shanghai, China) was placed in an alumina boat in the center zone of a horizontal tube furnace before heating. The boat was covered with single side polished

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p-type silicon (1 0 0) wafer (boron-doped). Ultrasonically cleaned silicon wafer was immersed in 5% aqueous HF solution for 5 min at room temperature to remove the native oxide. The surface of silicon monoxide powder in an alumina boat was covered over with a thin layer of aluminum powder (purity 99.99%; 100 mesh), the schematic of which is shown in Fig. 1. After the furnace was evacuated to a base pressure of 6.0×10^{-2} kPa, the furnace was purged with argon carrier gas with a constant flow rate of 5.0 L h^{-1} for 2 h. Then, the furnace was heated to 1300 °C and kept at this temperature for 2 h under normal pressure. After cooling down the furnace at a rate of 100 °C h^{-1} to room temperature under argon flow, a thick layer of white wool-like silica material was found on the silicon substrate with a ring-like distribution (shown in Fig. 2) as well as the inside of the alumina boat.

In order to study the role of aluminum powder on the growth of silica wires, only silicon monoxide placed in the boat covered with a silicon wafer was evaporated at 1300 °C for 2 h. It is found that the white material was also deposited on the silicon substrate.

The morphology and structure of as-grown silica wires were investigated by scanning electron microscopy (SEM; TESCAN, VEGA II LMU) operating at 20 kV equipped with energy dispersive X-ray spectroscopy (EDX; Oxford Instrument, INCAx-act), high-resolution transmission electron microscopy (HRTEM; FEI, Tecnai G2 F20), and X-ray diffractometer (XRD; Shimadzu, LabX XRD-6000) with CuKα radiation. Specially, it must be pointed out that the silica wires were scraped out from the wafer for high-magnification SEM, HRTEM and XRD analysis.

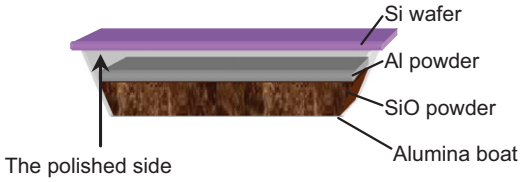

Fig. 1. Schematic diagram of alumina boat in horizontal tube furnace.

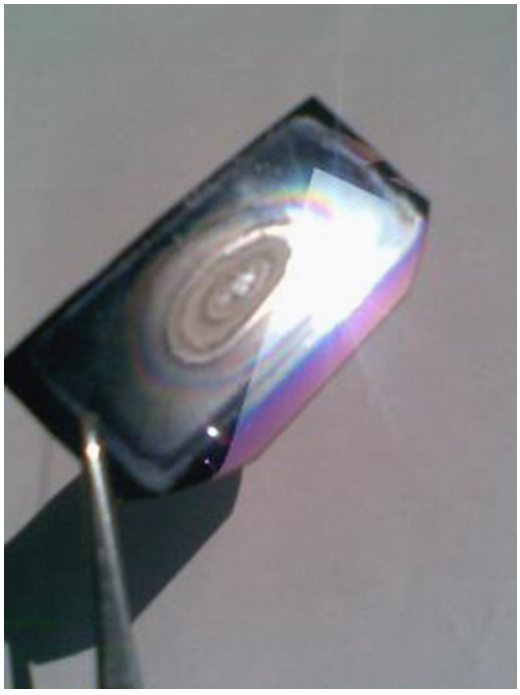

Fig. 2. Photograph of the silicon substrate with deposited silica wires.

3. Results and discussion

3.1. Microstructural analysis

The typical hook-shaped silica microwires deposited on silicon wafer are shown in Fig. 3(a). It shows that every hook-like

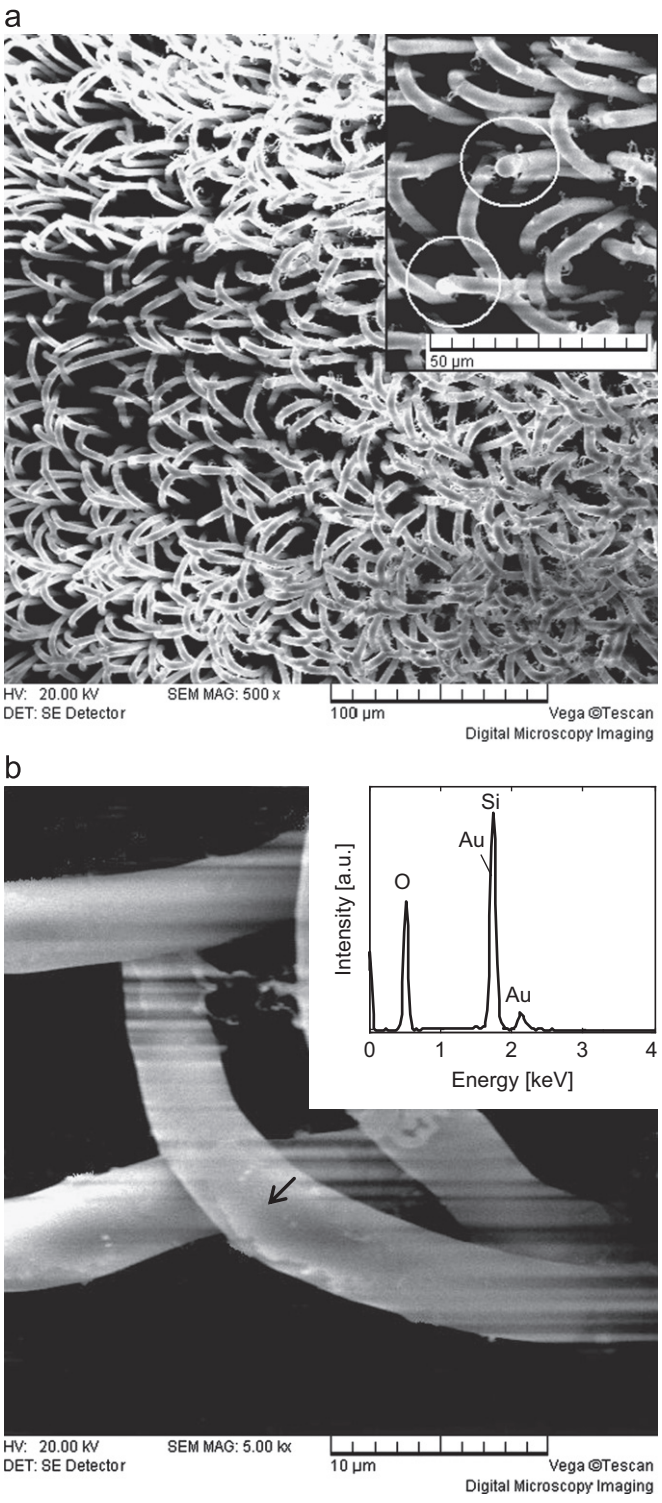

Fig. 3. (a) SEM micrographs of the hook-shaped silica microwires deposited on Si wafer,the magnified view of which is shown in the inset showing the ends with circular cross-section (shown by circles); (b) high-magnification SEM micrograph of the curved wires scraped out from Si substrate with EDX spectrum in the inset, the investigation point of which is shown by the arrow in the micrograph.

microstructure is made up of a curved microwire. The length of the silica wires reaches almost 100 μm and the average diameter is about 4 μm. It clearly seen from the magnified view of Fig. 3(a) that the microwires have circular cross-section, which reveals the cylindrical character (indicated by circles in the inset). Based on the high-magnification SEM micrograph of microwires scraped out from Si substrate demonstrated in Fig. 3(b), it is found that the diameters remain nearly constant throughout the length of the microwires, that means, the size of microwires is quite uniform. In addition, the microwires have remarkably neat and smooth surface. The inset of Fig. 3(b) is the corresponding energy dispersive X-ray spectroscopy (EDX) data of the microwires scraped out from Si substrate, which indicates that they consist of only two elements Si and O with an atomic ratio approximately 1: 2. No other elements were detected, except for Au from ion beam coating before SEM experiments.

To investigate the effect of aluminum on the growth of silica wires, we conducted comparative experiment wherein the surface of silicon monoxide powder had no aluminum powder cover. As revealed in Fig. 4(a), a mass of straight line silica wires was found lying over the silicon substrate in the absence of Al. The wires have diameter in the range 50–300 nm with center of the distribution at about 200 nm, and it can be found that these submicrowires are quite straight, uniform, smooth, and without large particles on the surface of silica wires, which have been found by Fan et al. [16] These observations confirm that the straight growth of silica wires in the present process is probably not governed by the VLS or SLS mechanism, which essentially is a catalytic process [4,5]. Furthermore, the HRTEM (Fig. 4(b)) study showed amorphous character of the straight silica wires. No Si/SiO_2 core-shell structure was observed, which reveals that the straight silica wires have uniform amorphous structure across the diameter and length.

Fig. 5(a) and (b) shows the XRD patterns of the as-grown hook-shaped and straight silica wires scraped out from silicon wafers, respectively, which reveal their amorphous character as well. No c-Si peaks have been seen from the XRD patterns [9].

3.2. Nucleation centers for the growth of silica wires

In order to understand the growth formation of hook-shaped silica microstructures as well as straight silica wires, silicon monoxide powders covered over with and without aluminum powder were evaporated at 1300 °C for 20 min using silicon wafers as substrates. Fig. 6(a) shows the SEM micrograph and EDX spectrum of as-deposited film on silicon substrate in the presence of aluminum powder. At this stage, the Al film was deposited on the silicon wafer by thermal evaporation of aluminum powder in the alumina boat, and then broke up and formed large particles (like islands) with diameters in the range 3–5 μm on the silicon surface. SiO vapor was simultaneously attracted to the Al droplet and migrated to form composite islands. These islands act as the nucleation site for the growth of hook-shaped silica wires [9]. EDX spectra (shown in Fig. 6(a)) taken from these islands revealed the presence of aluminum, silicon, and oxygen (Au signals are attributed to the Au ion beam coating before SEM experiment), indicating these islands to be aluminum/silica composite particles [17]. Fig. 6(b) shows the morphology of the silicon substrate heated without Al for 20 min, revealing the initial nucleation stage of the silica wires. At this temperature the silicon wafer and SiO vapor may have been reacted with the oxygen present in the deposition system to give numerous SiO_x tiny particles, partially covering the wafer to give the distinctive pattern shown in Fig. 6(b). EDX spectrum shown in the inset of Fig. 6(b) revealed the presence of only two elements silicon and oxygen. This phenomenon confirms that the silica clusters are the origin of the straight silica wires [18].

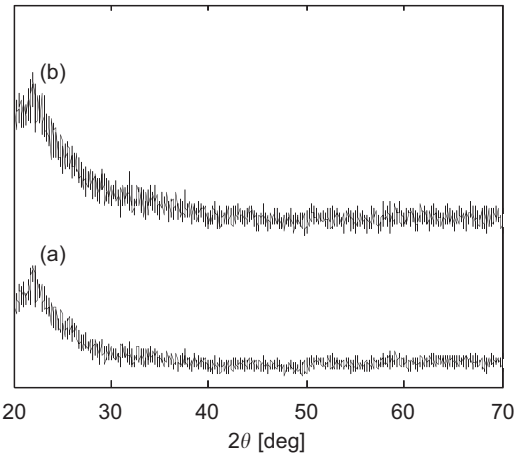

Fig. 5. XRD patterns of (a) hook-shaped and (b) straight silica wires scraped out from Si substrate.

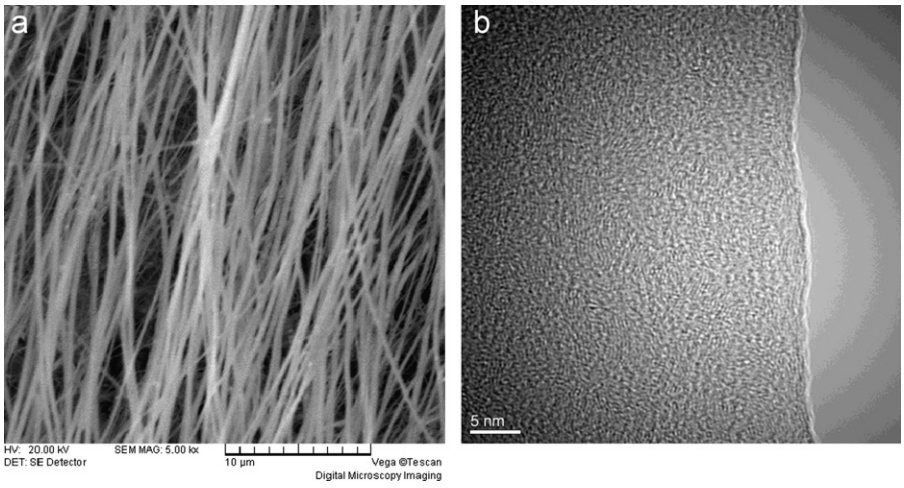

Fig. 4. (a) SEM micrograph of straight silica submicrowires deposited on Si wafer in the absence of aluminum powder; (b) HRTEM micrograph of a submicrowire showing its amorphous structure.

3.3. Growth mechanism

Obviously, a non-catalytic growth leads to straight silica wires, whereas the Al-catalyst tends to bend the silica wires growth in the present approach. What causes the differences between them? A new growth process and analysis is introduced to elucidate the curved silica wire growth mechanism. Since Al/SiO_x islands and SiO_x clusters (Fig. 6) result in different nucleation site for the growth of silica wires, two possible growth mechanisms of silica wires are proposed here, wherein the bending growth of silica wires is based on the following processes.

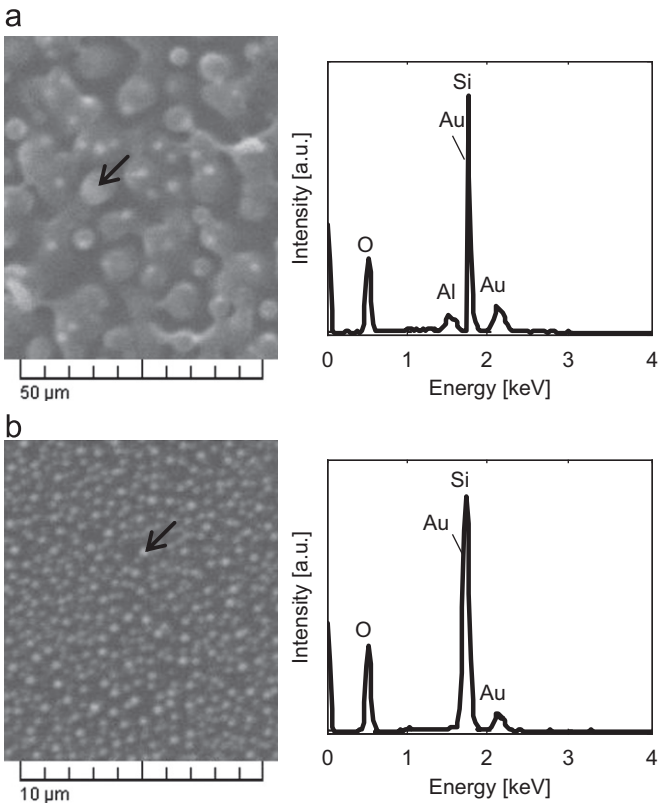

Fig. 6. SEM micrographs and EDX spectra of (a) Al/SiO_x islands and (b) SiO_x cluster. The arrows in the micrographs show the investigation point of EDX study.

In the early part of the reaction the Al film forms liquid micro-droplets, which might absorb SiO vapor and oxygen from the surrounding atmosphere at high temperature to form Al-SiO_x composite islands. When the furnace was heated to higher temperature, evaporated silicon monoxide could disproportionate into Si and SiO_2. Moreover, the role of traces of oxygen cannot be eliminated at high temperature while the carrier gas flowed into the tube in furnace system. The concentration of the residual oxygen in the chamber met the requirement on O_2 partial pressure, thus the following reactions could occur:

$$2SiO(g) \rightarrow Si(s) + SiO_2(s) \quad (1)$$

$$Si(s) + O_2(g) \rightarrow SiO_2(s) \quad (2)$$

$$SiO(g) + 1/2O_2(g) \rightarrow SiO_2(s) \quad (3)$$

The formed SiO_2 molecules condense on the islands and aggregate to induce linear SiO_2 microstructures to minimize the systemic energy [19]. The interaction of the cold argon carrier gas flow and the setup of the alumina boat covered with silicon wafer with poor obturation produced a thermal gradient on the silicon substrate [14], the center of which is the high-temperature zone whereas the edge is low-temperature zone, which may find experimental support by the deposited film with the ring-like distribution shown in Fig. 2. In addition, the thermal gradient may also cause by limited heating zone of the tube furnace and improper placement of the boat in the furnace. Due to larger diameter of silica wires, the existing thermal gradient along the lateral direction of silica wires results in bending growth, because of certainly first solidification in the low-temperature side. With time the hook-shaped silica wires formed (Fig. 7(a)). The proposed model may find similar experimental explanation by Saulig-Wenger et al. [14] who found that the formation of silica helical nanostructures from direct thermal treatment of a commercial silicon powder in the presence of graphite, which results from the self-assemblage of silica wires, may be due to the gas flowing during the process.

In the case of straight silica wires, the growth mechanism has been explained using the oxide-assisted growth process proposed by Lee et al. in the past [3]. Otherwise, Srivastava et al. [18] proposed that in-situ formation of SiO_2 vapors via reaction of SiO

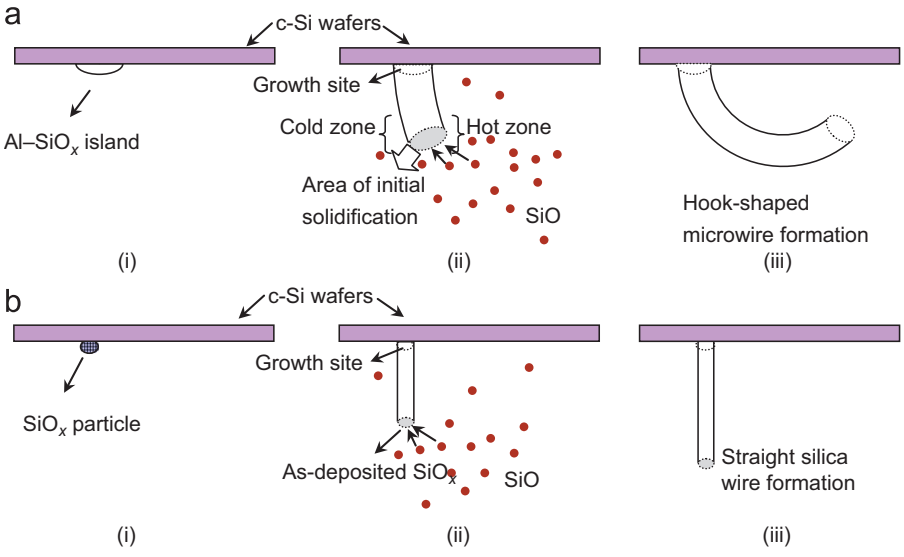

Fig. 7. Schematic of possible growth mechanisms for (a) hook-shaped and (b) straight silica wires.

vapors with O_2 leads to the formation of SiO_2 nanoclusters, which consequently results in the formation of large nanowires. The latter may be appropriate in case of amorphous silica wires to explain the present experimental observation. In the absence of Al, the formed SiO_2 molecules condense on the silicon wafer to form SiO_2 clusters that then act as nucleation center for the growth of straight silica wires, shown in Fig. 7(b). SiO_2 clusters may congregate in succession, and cause SiO_2 quasi one-dimensional structures to reduce the systemic energy [19]. Because of tiny particles nucleation center with minor diameters in the range 50–300 nm, the effect of the thermal gradient on the growth of silica wires can be neglected. As a result, the straight silica wires originate from these tiny clusters.

4. Conclusions

In summary, hook-shaped and straight silica wires have been synthesized by a thermal vapor method with or without Al, respectively. We have shown evidence of the mechanisms of bending growth and straight growth of silica wires. The thermal gradient on the silicon substrate, generated from the interaction of the cold argon carrier gas flow and the reaction setup with poor obturation, and other factors that lead to uneven temperature induce bending growth of silica wires with Al/SiO_x islands as nucleation center, while straight silica wires originated from silica clusters is unacted on the factor of thermal gradient. Though the exact mechanism behind the role played by the aluminum powder and thermal gradient in controlling the silica wires growth needs further investigation, the provided fundamental understanding of silica wires formation could be applied to guide the development of advanced microstructures with shape control and unique properties.

Acknowledgments

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