SiO$_x$ Nanowire Assemblies Grown by Floating Catalyst Method

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Silicon oxide (SiO$_x$) nanowire assemblies have been synthesized using anhydrous ferric chloride (FeCl$_3$) as a catalyst precursor and silicon wafers as both the silicon source and substrate by means of floating catalyst chemical vapor deposition (CVD) in order to produce different morphologies. It is found that the growth and morphology of SiO$_x$ is strongly temperature-dependent, as tested within the temperature range 1000–1200 $^\circ$C. The sublimation of FeCl$_3$ and its subsequent reduction in the gas phase to produce Fe nanoparticles with high catalytic activity allows for the efficient growth of SiO$_x$ nanowires via vapor–liquid–solid (VLS) mechanism. The prepared amorphous SiO$_x$ nanowires show photoluminescence and emit blue light. This floating catalyst method offers a simple and comprehensive approach for the large-scale production of SiO$_x$ nanostructures with tunable assemblies.

**Keywords:** Silicon Oxide, CVD, Ferric Chloride, Nanowires Assembly, VLS.

1. INTRODUCTION

Silicon oxide nanowires have attracted great attention in recent years because of their intense and stable blue light emission at room temperature which allows for promising potential applications in integrated optical devices, including high-resolution optical heads for scanning near-field optical microscopes and catalysis.$^{1-3}$ In the past few years, various methods have been developed for synthesizing silicon oxide nanowires including chemical vapor deposition (CVD),$^6$ laser ablation,$^7$ thermal growth,$^8$ etc. Silicon oxide nanowires are usually grown using catalytic methods, with Ga, Ge, Sn, Pd, Au, Ni, Co, Fe, and their alloys or mixtures as the catalysts.$^{9-20}$ For example, Pan et al.$^9$ and Zheng et al.$^{10}$ reported the growth of highly aligned silicon oxide nanowires by using molten Ga as the catalyst and a silicon wafer as the silicon source via an expanded vapor–liquid solid (VLS) process and, consequently, obtained different SiO$_x$ nanowire assemblies including fishbone-like, gourd-like, and octopus-like structures. Hu et al.$^{11}$ demonstrated a temperature-dependent growth of a series of silicon oxide based composite nanostructures by using the combination of laser ablation of a germanium target and thermal evaporation of silicon monoxide powders. Silicon oxide nanowire assemblies with lantern-like morphology were synthesized by thermal evaporation of the mixed powder of SnO$_2$ and activated carbon at 1000 $^\circ$C. It has been reported that carbon reduces SnO$_2$ and produces Sn vapor that catalyzes the growth of silicon oxide.$^{12}$ Noble metals, such as Pt and Au, are also effective catalysts for the growth of silicon-based one-dimensional nanostructures. For instance, with the use of Pt as a catalyst, SiO$_x$ nanowires were successfully prepared by rapid thermal annealing at 900 $^\circ$C, and the growth of the nanowires was found to occur via a catalytic VLS mechanism.$^8$ Because of the high price of
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noble metals, attempts have been made to use common metals, such as iron, to replace them for catalyzing the growth of SiOx nanowires. Wu et al. reported that silicon oxide nanowires assembled into elegant heliotrope-shapes have been synthesized by the evaporation of Fe and Si mixture sources at 1300 °C for 1 h then at 1500 °C for 3 h.15 A Fe-based nano-catalyst is required for the synthesis of SiOx nanowires, making this process tedious and time-consuming. Though much work on the growth and assembly of silicon oxide has been completed, most of the methods require the passage of a gas phase silicon source over fixed catalysts, and many methods use rare noble metal catalysts. More facile approaches and less expensive catalysts are needed for decreasing the price and increasing availability of nanowires on a commercial scale.

Volatiles organometallic complexes (typically ferrocene and iron pentacarbonyl (Fe(CO)5)) have been widely used in the synthesis of carbon nanotubes (CNTs).21-25 These volatile Fe-containing compounds decompose at high temperatures into metal ions/ radicals/ neutrals and coalesce to form clusters in the gas phase that catalyze the condensation of carbon to produce CNTs. The process where the catalyst and carbon source are both in the gas phase is called “floating catalyst” CVD. Being less toxic and less expensive compared to ferrocene and iron carbonyl, covalently bonded anhydrous FeCl3 can be sublimated at elevated temperatures and can act as a floating catalyst in the synthesis of nanostructures. Inspired by the synthesis of CNTs, we developed a method for producing silicon oxide nanowire assemblies using floating catalyst CVD with anhydrous FeCl3 as the catalyst precursor and a silicon wafer as both the silicon source and the substrate. The formation mechanism proposed is based on the combination of VLS and the features of floating catalysts in the CVD process.

2. EXPERIMENTAL DETAILS

The growth of silicon oxide was conducted in a two-stage horizontal quartz tube furnace. Anhydrous ferric chloride (FeCl3, 0.1 g), which was used as the catalyst precursor, was placed inside a quartz boat in the middle of the first-stage furnace. A clean Si(100) substrate (5 mm × 5 mm), which was used as the silicon source and the substrate for nanowire deposition, was placed in the middle of the second-stage furnace. To avoid undesired vaporization of FeCl3 during the ramping step, the quartz tube was pulled out to keep FeCl3 outside the furnace before the furnaces were heated. During the heating process, N2 was introduced into the furnace to remove air from the reaction system. The first-stage furnace temperature was set at about 300 °C while the second-stage furnace temperature was set at 1000–1200 °C. After both furnaces reached the preset temperatures, the tube reactor was pushed back to place FeCl3 and the Si substrate at the centers of the first and second furnace, respectively. A mixture of pure N2 (100 mL min⁻¹) and H2 (100 mL min⁻¹) was used as a carrier gas. Each run lasted for 1 h. The sample was then cooled to room temperature in N2. The obtained products on the silicon were examined using scanning electron microscopy (SEM, Hitachi-600) and transmission electron microscopy (TEM, Hitachi-600). The composition of the products was analyzed by energy-dispersive X-ray spectroscopy (EDS) in SEM. The photoluminescence (PL) spectra were recorded at room temperature on Perkin Elmer LS-55 instrument, using a xenon laser as the excitation source.

3. RESULTS AND DISCUSSION

Since reaction temperature is known to be a critical factor for controlling the growth and self-assembly of silicon oxide using the floating catalyst CVD.9 The effect of temperature on the growth of SiOx, was investigated in the present work. It was found that the amounts of the product obtained on the substrate are negligible either at low temperature (<1000 °C) or at high temperature (>1200 °C). Therefore, we studied the morphology of the products generated in the temperature range of 1000–1200 °C.

After the reaction at 1000 °C for 1 h, a large quantity of nanowire assemblies formed on the silicon wafer, as shown in Figure 1(a). There are bundles of nanowires that resemble jellyfish, so we will call them “jellyfish-like” assemblies. Most of them are randomly distributed on the substrate with small bright spheres located on their tops. Interestingly, these jellyfish-like assemblies look like they are swimming. SEM observations show that these bundles are about 2.5 μm in diameter and up to 15 μm in length with nanowires as their building blocks. EDS analysis indicates that the bundles of nanowires are composed of Si and O with Si/O atomic ratios of about 1.5~1.8. It can be seen that a spherical particle with a diameter of about 0.6~1.3 μm is attached to the top of each nanowire bundle. EDS suggests that the spheres consist of Fe and Si with the atomic percentages of 95% and 5%, respectively, indicating that metallic Fe serves as the catalyst for the growth of silicon oxide nanowires (Fig. 1(c)). A weak Si peak in EDS may come from the surface of the silicon substrate. The low magnification TEM image (Fig. 1(b)) confirms the jellyfish-like morphology observed with SEM. The arrow in Figure 1(b) indicates a 0.7 μm catalyst particle from which the bundle of nanowires originates. The fact that the nanowires and Fe nanoparticles are above the silicon wafer substrate (Fig. 1(a)) suggests the silicon oxide comes from the vapor phase. This corresponds to the morphology of VLS-grown nanowires, implying that the growth of the jellyfish-like bundles is likely governed by the VLS mechanism. Every catalyst particle with the size of about 1 μm initiates and catalyzes the growth of a bundle of SiOx nanowires. This growth phenomenon...
was observed by Pan et al.,\textsuperscript{9,26} when highly aligned silica nanowires were grown batch by batch from the same catalytic droplet. It is manifested by one catalytic site directing the batch-wise growth of many nanowires repeatedly until the reaction terminates.

Figure 2 shows the as-grown nanowires covering the substrate after deposition at about 1100 °C. It can be observed that many bundles (Fig. 2(a)) with diameters of about 5 \( \mu \text{m} \) and lengths of up to 10 \( \mu \text{m} \) grow in groups with a high yield. For each bundle, tens of secondary bundles radially grow sideward, forming a feather duster-like structure.\textsuperscript{27} One end of the feather duster-like bundle stands on the silicon wafer and the other end terminates with a cavity on top (Fig. 2(b)). By comparison to the products obtained at 1000 °C (Fig. 1), it was concluded that the cavity was probably occupied by the catalyst particle previously.

Figure 2(b) shows a high magnification SEM image of the feather duster-like bundles containing dense bundles. Obviously, the nanowire density in these structures is much higher than that in the jellyfish-like SiO\textsubscript{x} nanowire assemblies. Within the feather duster-like bundles, sub-branches derived from branch-splitting can be found (marked by arrow in Fig. 2(c)), suggesting that secondary nucleation may occur on the surface of the initially grown nanowires. Figure 2(c) shows a magnified TEM image of the nanowires in a feather duster-like assembly, showing that the nanowires are very uniform, with a diameter in the range of 30–50 nm. Their aligned structures did not break after a long time of ultrasonic treatment (15–20 min), indicating a strong interconnectivity between the nanowires. A magnified TEM image (Fig. 2(d)) and a high resolution TEM image (inset in Fig. 2(d)) of an individual nanowire in the duster-like morphology reveal that the silica nanowire is amorphous, which is in agreement with the results reported in literature.\textsuperscript{8,11,12,17,26,28}

When the temperature in the furnace was increased to 1200 °C, tadpole-like bundles with a large head and a long tail made of nanowires appeared on the Si substrate, as shown in Figure 3. EDX measurements show that the tails were composed of SiO\textsubscript{x} with \( x \sim 0.9 \). The heads of the formed SiO\textsubscript{x} assemblies tend to be densely surrounded by
the SiO$_x$ wires with the increase of the temperature from 1000 °C to 1200 °C. We also note that there are no catalyst nanoparticles in the head of the tadpole, unlike those found in the product produced at a low temperature, 1000 °C (Fig. 1). Also no holes were left by the catalyst particles. It is reasonable to assume that the contact angle between the substrate and the catalyst (Fe or Fe with some Si dissolved) decreases with the increase of temperature, which leads to a larger interface and surrounding growth of SiO$_x$ at higher temperatures.$^{29}$ The fact that catalyst particles can only be observed at the low temperature indicates the occurrence of catalyst evaporation via form low boiling point Fe-containing substance at elevated temperature during the growth of silica nanowire assemblies. TEM examination

![Fig. 2](image1.png)

**Fig. 2.** SEM and TEM images of silicon oxide nanowires synthesized at 1100 °C on a silicon wafer: (a) low magnification SEM image of the as-grown products, showing the grouped feather duster-like bundles; (b) high magnification SEM image of feather duster-like bundles; (c) magnified TEM image of nanowires in the feather duster-like bundles; (d) high magnification TEM and high resolution TEM images (inset) of nanowires in the feather duster-like bundles.

![Fig. 3](image2.png)

**Fig. 3.** Silicon oxide nanowires synthesized on a silicon wafer at 1200 °C (a) low magnification SEM image and (b) high magnification SEM image with TEM image insets, showing tadpole-like bundles composed of a large head and a long tail made of nanowires.
shows that tadpole-like assemblies are composed of sparse nanowires with diameters of about 40~60 nm (upper inset in Fig. 3(b)) in the head part and rope-like nanowire bundles (lower inset in Fig. 3(b)) in the tail part. In contrast to the head part of the tadpole structure, the nanowire ropes remain intact in the tail part after ultrasonic treatment, which can be explained by tighter entanglement in the long tail in the tadpole-like assemblies.

The above results indicate that FeCl₃ can serve as catalyst precursor for the growth and assembly of amorphous SiOₓ via the floating catalyst VLS process. A growth model proposed for the SiOₓ is shown in Figure 4 and presents the following steps:

1. Fe catalyst formation from FeCl₃: Anhydrous FeCl₃, with a low boiling point (315 °C), sublimes in the first-stage furnace and is transferred to the second-stage furnace by the carrier gas. In the reaction chamber, FeCl₃ vapor, H₂ and N₂ species are mixed in the vapor phase and FeCl₃ is reduced by H₂ to form metallic Fe atoms in the gas phase according to reaction:

\[ 2\text{FeCl}_3(g) + 3\text{H}_2(g) \rightarrow 2\text{Fe}(g) + 6\text{HCl}(g) \]  

2. The Fe atoms cluster to form nanoparticles in the gas phase, which subsequently deposit on the silicon substrate and coalesce to micrometer scale particles with a high catalytic activity for the growth of silicon oxide nanowires.

3. Formation of gaseous Si species: It is apparent that traces of oxygen are present in the system, which may come from the carried gas with insufficient purity. Moreover, it should be noted that HCl produced by reaction (1) can etch the silicon wafer to produce gaseous SiClₓ \((x < 4)\) vide the reaction:

\[ \text{Si}(s) + x\text{HCl}(g) \rightarrow \text{SiCl}_x(x < 4)(g) + x/2\text{H}_2(g) \]  

4. The presence of SiO and/or SiClₓ vapor around the silicon wafer will provide a source of silicon in the gas phase which enables the formation of SiOₓ nanowires by the VLS mechanism. The silicon surface can be readily oxidized by oxygen in the system at elevated temperatures due to the high bond energy of Si–O (185 kJ/mol), which is much larger than that of the Fe–O (95 kJ/mol). It is reasonable to assume that the vaporization and migration of SiO will take place from the dissociation of silicon oxide from the wafer surface in the temperature range of 1000~1200 °C as follows:

\[ 2\text{Si}(s) + \text{O}_2(g) \rightarrow 2\text{SiO}(g) \]  

5. Furthermore, it should be noted that HCl produced by reaction (1) can etch the silicon wafer to produce gaseous SiClₓ \((x < 4)\) vide the reaction:

\[ \text{Si}(s) + x\text{HCl}(g) \rightarrow \text{SiCl}_x(x < 4)(g) + x/2\text{H}_2(g) \]  

6. Dissolution of oxygen and other species in the iron-based particles might further decrease its melting point below 1000 °C. The catalyst absorbs the Si-containing species (such as SiO, SiClₓ) in the gas phase and the precipitation of SiOₓ from liquid catalyst takes place due to the supersaturation of silicon oxide in the Fe-Si droplets. Obviously, there are multiple nucleation sites around the Fe-Si alloy droplet, which result in multiple amorphous nanowires growing from the same catalyst particle. As a result, the catalyst particles are lifted up from the silicon wafer surface by the growing SiOₓ nanowires. The obtained SiOₓ assemblies grown on the silicon wafer with a larger size and higher density in the head (close to the catalyst particle) compared to the
tail (Figs. 1–3) may originate from the change in catalytic activity of the droplet during the reaction. The hierarchical bird nest-like structures of the SiO$_x$ assemblies suggest the possible slippage of the Si species along the surface of catalyst particles to the lower hemisphere instead of diffusion through the metal particle. Furthermore, it should be noted that the atomic Si:O ratio in silicon oxide varies (SiO$_x$, 1 < x < 2) to some degree during the growth process in a oxygen-lean environment.\(^{17,33,34}\)

Photoluminescence (PL) spectra (Fig. 5) of the silica nanostructures obtained at different temperatures have been measured at room temperature as shown in Figure 5. The amorphous SiO$_x$ nanowires exhibit a broad PL emission centered at 453 nm (2.7 eV). It has been suggested that the 2.7 eV band originates from the neutral oxygen vacancy (≡Si–Si≡),\(^{35}\) which can be expected when the high oxygen deficiency resulting from the reducing environment during sample preparation in the present experiment is taken into consideration. These structural defects have been demonstrated to act as the radiative recombination centers.\(^{36}\) It should be noted that the PL emissions of SiO$_x$ grown under different conditions vary due to differences in the structure and stoichiometry.\(^{37}\) The silica bundles obtained by the proposed method can be potentially become an abundant and safe luminescent material for the visible light region.

4. CONCLUSION

SiO$_x$ nanowires have been synthesized by using anhydrous ferric chloride as a catalyst precursor and a silicon wafer as both silicon source and substrate by floating catalyst CVD. It is found that the temperature change leads to the formation of various kinds of SiO$_x$ nanowire bundles in the temperature range between 1000 °C and 1200 °C. The synthesis of silicon oxide nanostructures show blue emission and their synthesis on Si wafers may find potential applications in photoelectronic devices. The use of FeCl$_3$ as a floating catalyst precursor provides a simple and versatile method for the controlled synthesis of silica nanowires.

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