A simple route to synthesize impurity-free high-oriented SiO$_x$ nanowires

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ABSTRACT

Impurity-free silicon oxide nanowires were synthesized on a 3 cm x 3 cm alumina plate uniformly by thermal evaporation of a mixture of powder of graphite powders and SiO$_x$@Si core-shell particles under argon atmosphere with a flow rate of 50 sccm at 1100 ^{o}C for 3 hours. The as-synthesized products characterized by field-emission scanning electron microscopy, field-emission transmission electron microscopy and energy-dispersive spectroscopy show that SiO$_x$ nanowires were of diameters ranging from 50-100 nm and the height is up to several millimeters. The growth mechanism of SiO$_x$ nanowires was studied and suggested to be the vapor-solid (VS) mechanism.

Keywords: silicon oxide, nanowires, thermal evaporation, vapor-solid mechanism.

1 INTRODUCTION

Recently, one-dimensional (1-D) silicon oxide (SiO$_x$) nanostructures (nanotubes, nanorods, nanowires, nanocable and nanobelts) are drawing a significant attention due to its optical properties and exhibit potential applications in photoluminescence (PL), near-field optical microscopy, waveguides and optical devices due to the blue emission and stable properties [1-6]. In the past decade, fabrication of the SiO$_x$ nanowires was carried out by several techniques, including thermal evaporation [7], chemical vapor deposition (CVD) [8, 9], carbon-assisted method [10, 11] etc. In general, there are two fabrication methods: non-catalyst-based and catalyst-based. In the most cases, the formation mechanism of SiO$_x$ nanowires has been due to the vapor-liquid-solid (VLS) growth [12]. The VLS mechanism proposed by Wagner and Ellis in 1964 for silicon whisker growth is the fundamental model of one-dimensional formation.

Among these synthetic routes, both the CVD method and carbon-assisted method are the widely used techniques to synthesize 1-D silicon oxide nanostructures. For instance, Li et al synthesized SiO$_x$ nanowires on Au-coated Si substrate during attempts o fabricate ZnO nanowires [5]. They found that the formation of the SiO$_x$ nanowires depends on a series of experimental conditions, such as substrate coating (Au), the presence of graphite powder, the substrate temperature, the oxygen flow, and the growth time. However, synthesis of SiO$_x$ nanowires still needs utilizing complex experimental step, catalyst such as Au, Fe, Co, Ni, Ge, Pb and other metal alloys etc [6, 13]. Therefore, it is essential to develop a simple synthesis route for the fabrication of impurity-free SiO$_x$ nanowires.

In this study, a novel and simple method for the synthesis of the SiO$_x$ nanowires was developed. The SiO$_x$ nanowires synthesized on the alumina plate by thermal evaporation of the mixture powders (the core-shell SiO$_x$@Si particles and graphite powders) at 1100 ^{o}C for 3 hours. It was successful formed without the participation of catalyst. The growth mechanism of SiO$_x$ nanowires was studied and suggested to be the vapor-solid (VS) mechanism.

2 EXPERIMENTAL

2.1 Preparation of precursor for synthesis of SiO$_x$ nanowires

Si particles (325 mesh, purity 99%, Aldrich) covering with SiO$_x$ thin layers were prepared by the thermal treatment. The powders were heated in oven at 550 ^{o}C for 0.5 h. The SiO$_x$@Si core-shell particles were formed for the synthesis of SiO$_x$ nanowires.

2.2 Synthesis of SiO$_x$ nanowires

0.25 grams of the prepared SiO$_x$@Si core-shell particles and 0.25 grams of graphite powders were well mixed and loaded on an alumina cup (O.D. 2.8 cm, I.D. 2.4 cm, and height 1.2 cm) covered with alumina plate. The cup was then placed in the center of a quartz tube (O.D. 7.5 cm, I.D. 7.0 cm, and length 120 cm) in a furnace. The experiment started with purging the reactor by Ar (500 sccm) (high-purity argon, 99.99%) for 1 hour. The temperature raised to 1100 ^{o}C with a heating rate of about 20 ^{o}C/min under a flow of Ar (50 sccm) and maintained for 3 hours. Finally, the furnace cooled down to the room temperature with an Ar atmosphere. A white colored mallow-like material was found on the alumina plate. SiO$_x$ nanowires were therefore formed.

The morphologies of the materials were examined by the field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The crystalline structure and atomic arrangements of the products were observed by the high resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010) equipped with an energy dispersion spectrometer (EDS). For FE-SEM observation, a white colored mallow-like material scraped from alumina plate was put on the holder and loaded into SEM vacuum chamber. For HR-TEM analysis, as-produced material scraped alumina plate ultrasonically dispersed in ethanol

and a drop was placed onto an amorphous carbon-coating copper grid.

3 RESULTS AND DISCUSSION

Figure 1 show the as-produced material synthesized on the alumina plate by thermal evaporation of the mixture powders (the SiO_x@Si core-shell particles and graphite powders) at 1100 ^{o}C for 3 hours. The picture is an alumina plate deposited with white mallow-like product. A ruler with millimeter markings underneath the boat was for size reference. It can be seen that the height of the as-produced material is up to several millimeters, shown in Figure 1(a). A top-view picture shown in Figure 1(b) reveals that the diameter of the deposited material is about 24 millimeters the same as the inner diameter of an alumina cup.
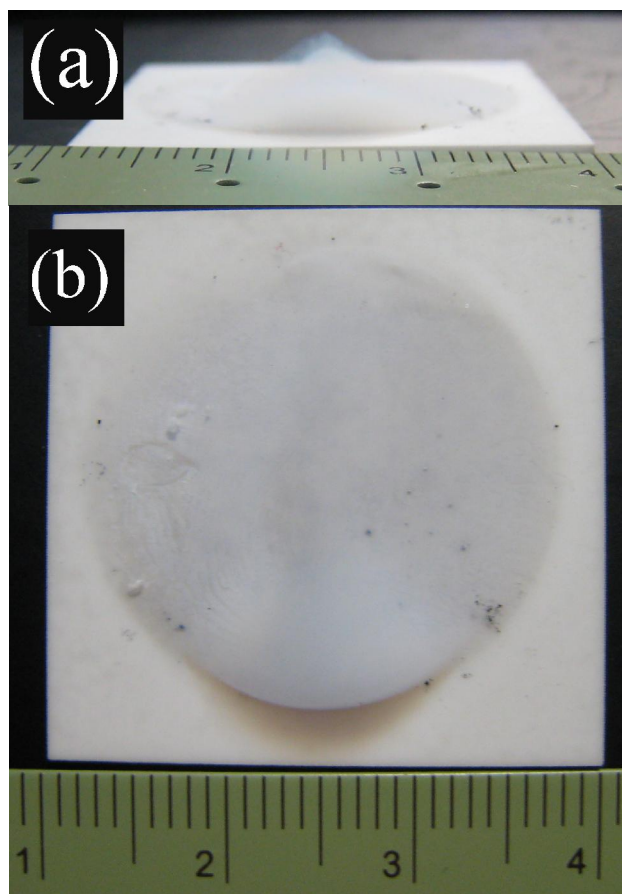

Figure 1. A image of as-produced mallow-like material on the alumina plate (a) side-view, (b) top-view.

Figure 2(a) shows a low magnification SEM image of as-produced one-dimensional nanostructures. It was found that the high purity one-dimensional nanostructures were successful formed without the participation of catalyst. A SEM image of the one-dimensional nanostructures with the diameters of 50-100 nm and the lengths of several hundreds of micrometers was shown in Figure 2(b). As can be seen,

there was no impurity observed on/in the one-dimensional nanostructures. The surface of one-dimensional nanostructures revealed smooth morphology. Besides, the end of these straight nanostructures all have a flat tip without catalyst existing.
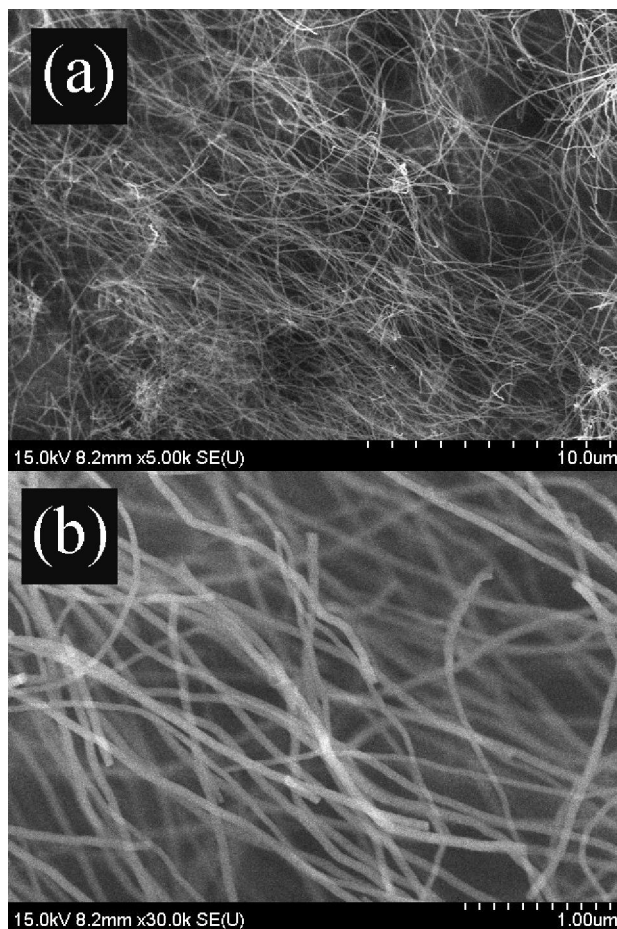

Figure 2. (a) The low-magnification image of as-produced mallow-like one-dimensional nanostructures. (b) FE-SEM image of impurity-free one-dimensional nanostructures.

In the conventional high resolution transmission electron microscopy image of the as-produced material scraped from the alumina plate surface shown in Figure 3(a), a single nanowire is the amorphous structure and has a diameter of about 50 nm. The inset in Figure 3(a) showed the selected area electron diffraction (SAED) pattern. The SAED pattern demonstrates that the nanowire does not reveal any characterization crystalline structure. EDS spectra recorded from a single nanowire demonstrate the chemical composition of Si, O, and Cu (Figure 3b). (Appearance of Cu peak in Figure 3(b) was due to the TEM grid.) A quantitative analysis shown in the inset of Figure 3(b) revealed that the atomic ratio of Si and O is nearly 1:1.1, confirming that the chemical composition of nanowire is SiO_x. Therefore, the as-produced material is

defined as SiO_x nanowires. As expected, we don't found catalyst in the SiO_x nanowires in this study.
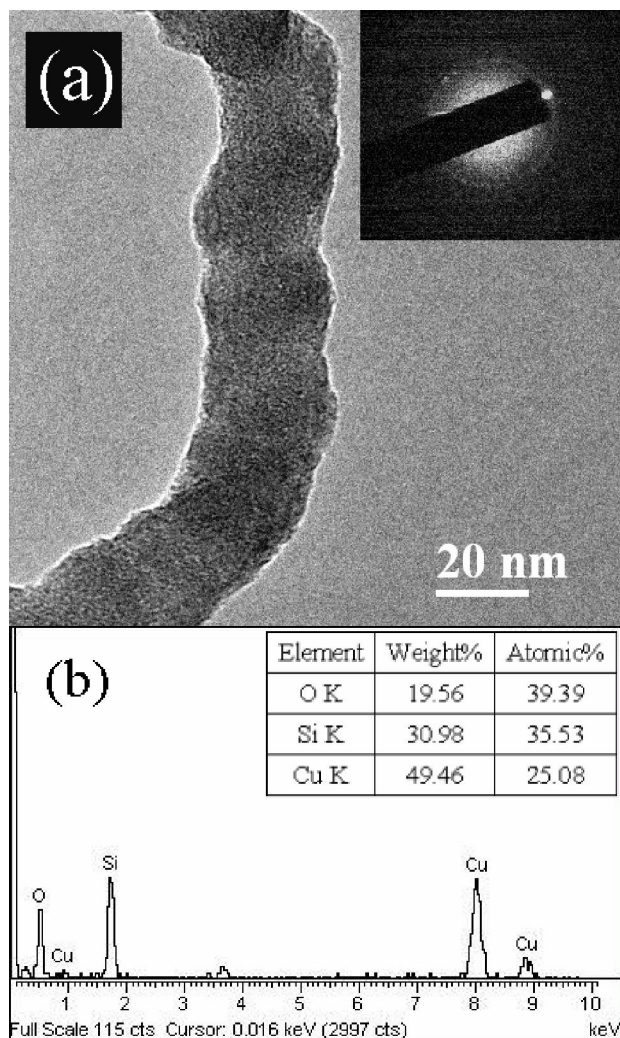

Figure 3. (a) TEM image and SAED pattern of a SiO_x nanowire and. (b) EDS spectrum of the SiO_x nanowire.

Based on the experiment results aforementioned, it is believed that the morphology of as-synthesized SiO_x nanowires via the vapour-solid (VS) mechanism. The possible growth mechanism in this study was proposed. Firstly, it was known that SiO vapor can be generated from a mixture of Si and SiO_2 powders in Ar atmosphere at high temperature. It can be explained as follows [14, 15]:

$$Si_{(s)} + SiO_{2(s)} \grave{a} \ 2SiO_{(v)} \tag{1}$$

Here s and v refer to the solid state and vapor state, respectively. Simultaneously, the high temperature caused the vaporization of both SiO_x@Si core-shell particles and graphite powders from the mixture powders. The equation known as carbothermal reaction of silica [14, 16, 17], which can be expressed as:

$$SiO_{2(s)} + C_{(s)} \grave{a} \ SiO_{(v)} + C_{(v)} \tag{2}$$
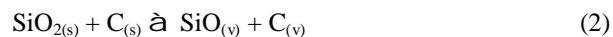
In second step, the residue O_2 gas shown in Equation (3) was then reacted with the SiO vapor and formed SiO_2 clusters in the gas phase.

$$2SiO_{(v)} + O_{2(g)} \grave{a} \ 2SiO_{2(s)} \tag{3}$$

Equation (3) is a vapor phase reaction between SiO and O_2 to form SiO_x clusters in gas phase. During the thermal evaporation process, SiO and O_2 deposit on the alumina plate surface and format of SiO_x clusters on the alumina plate, which are considered to be the seed structures for the nanowire growth. According to the research regarding the solid-phase diffusion mechanism reported by A. I. Persson et. al. [18, 19], the seed structures are the solid phase on the alumina plate surface during nanowire growth. By the vaporization onto the alumina plate surface, the SiO vapor thereby incorporated into the SiO_x seed structures and then the nanowires have the grown. Based on the results and the analysis above, it is believed that the as-produced SiO_x nanowires via the vapor-solid mechanism. The SiO_x nanowires with consistent diameter are dictated by the size of the seed particle. Therefore, the growth of SiO_x nanowire in this study is suggested to be a VS mechanism without catalyst.

4 CONCLUSION

In summary, a simple route to synthesize impurity-free high-oriented SiO_x nanowires through thermal evaporation of the mixture powders (the SiO_x@Si core-shell particles and graphite powders) without catalyst method. The height of the as-produced material is up to several millimeters and the diameter of the deposited material is about 24 millimeters. The high purity SiO_x nanowires have the diameters of 50-100 nm and lengths of about several hundreds of micrometers. The growth of SiO_x nanowire in this study is suggested to be a VS mechanism without catalyst.

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