Growth of SiO_2 nanowires on different substrates using Au as a catalyst

Li Yuguo(李玉国)†, Yang Aichun(杨爱春), Zhuo Boshi(卓博世),
Peng Ruiqin(彭瑞芹), and Zheng Xuelei(郑学垒)

Semiconductor Institute, College of Physics and Electronics, Shandong Normal University, Jinan 250014, China

Abstract: SiO_2 nanowires were prepared on a SiO_2/Si(111) or Si substrate using Au as a catalyst. The products were characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM shows that large amounts of SiO_2 nanowires with a diameter of 20–150 nm and length of several nanometers were formed on the entire surface of the substrate. XPS analysis indicates that the nanowires have the composition of Si and O in an atomic ratio of about 1 : 2, and their composition approximates that of SiO_2. The formation of the SiO_2 nanowires was controlled by the vapor-liquid-solid mechanism. It is found that the annealing time affects the morphology of the products. Finally, the effect of the substrates on the growth of SiO_2 nanowires was discussed. The Si source of the SiO_2 nanowires comes from the substrate or Si powder for different substrates.

Key words: SiO_2; nanowires; substrate; mechanism
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1. Introduction

One-dimensional nanomaterials attract more and more attention due to their unique chemical and physical properties and great potential applications in nano-electronics and nano-optoelectronics[1]. Nanowires can offer the opportunity to investigate electrical and thermal transport processes in dimensionally confined systems, with the possibility of providing a deep understanding of physics at the nano-scale[2]. SiO_2 nanowires have been studied extensively over the past few years due to their potential application in realizing multi-functional nano-sized devices, such as blue light emitters and optical sensors with high sensitivity[3, 4]. In fact, several different methods have been used in the preparation of SiO_2 nanowires, such as laser ablation[5], thermal evaporation[6] and chemical-vapor-deposition (CVD)[7]. And different growth models of nanowires have been studied based on vapor–liquid–solid (VLS), vapor–solid (VS) and solid–liquid–solid (SLS) mechanisms[8].

Elechiguerra *et al*. reported that nanowires of amorphous SiO_2 were synthesized by thermal processing of a Si(100) substrate at 1100 ℃ in the presence of a nitrogen flow, and using a 15 nm thick high silicon-solubility Pd/Au film as a catalyst. The substrate itself was the only source of silicon for the nanowire growth[9]. Liang *et al*. reported that large-scale synthesis of amorphous silicon oxide nanowires was achieved by using simple physical evaporation of the mixture of silica xerogel containing Fe nanoparticles and silicon powder[10]. It was reported that tiny SiO_2 nanowires were synthesized on a p-Si (111) wafer by the chemical-vapor-deposition method. The minimum diameter of the nanowires was around 9 nm, and the length was longer than 10 μm[11]. To our knowledge, it was seldom reported that the SiO_2 nanowires were prepared on different substrates using Au as a catalyst.

In this paper, we present the preparation and characterization of SiO_2 nanowires using Au as a catalyst. In order to study different growth models of the SiO_2 nanowires, SiO_2/Si(111) and Si(111) were used as the substrate in the experiments, respectively. Specially, Au was deposited on the substrates by a radio frequency magnetron sputtering system before the annealing process. The SiO_2 nanowires were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). It is found that the annealing time affects the morphology of the products and the source of silicon for the SiO_2 nanowire growth is different from the substrates used in the experiments.

2. Experiment

SiO_2 nanowires were prepared on SiO_2/Si(111) and Si(111) substrates, respectively. For experiment A (Fig. 1(a)), SiO_2 thin film with a thickness of about 200 nm was deposited on the Si(111) by sputtering a SiO_2 target (99.99 %) in Ar in a JCK-500A RF magnetron sputtering system with 1.9×10^{-3}

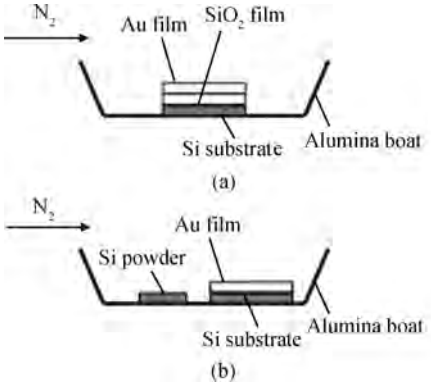

Fig. 1. Schematic diagram of the side-view of the system for synthesizing SiO_2 nanowires on substrates of (a) SiO_2/Si(111) and (b) Si(111).

† Corresponding author. Email: liyuguosd@hotmail.com
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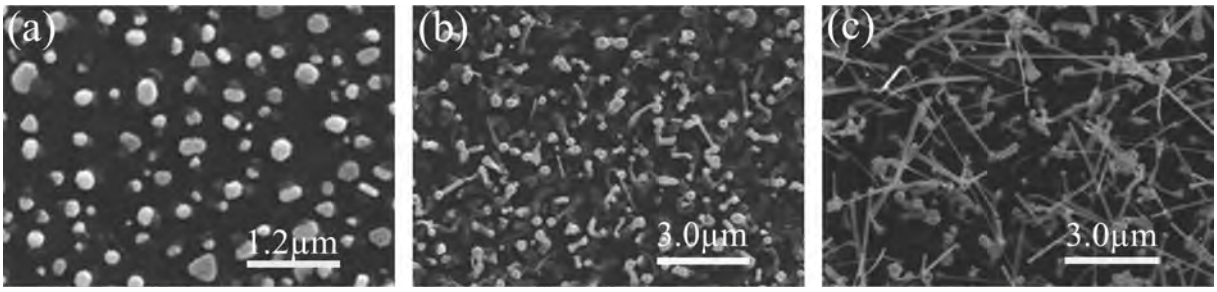

Fig. 2. SEM image of samples annealing at 1100 ℃ for different times. (a) 20 min. (b) 25 min. (c) 30 min. SiO_2/Si(111) was used as the substrate.

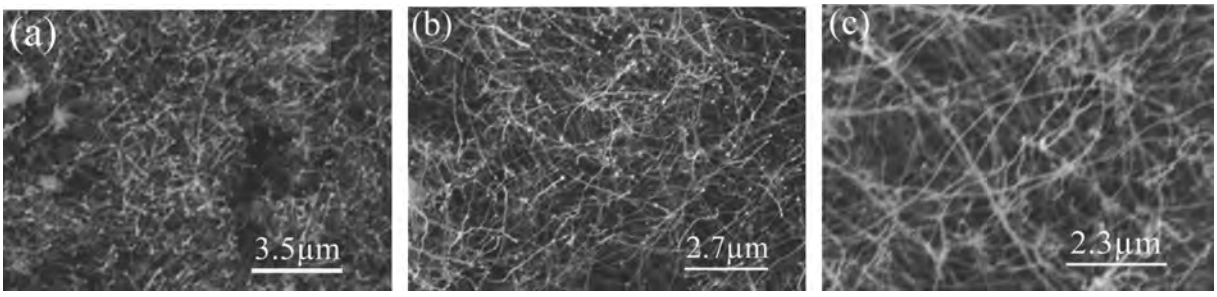

Fig. 3. SEM images of the SiO_2 nanowires annealing at 1100 ℃ for different times. (a) 20 min. (b) 25 min. (c) 30 min. The substrates were Si covered with Au films.

Pa basic pressure. Then Au thin film with a thickness of about 18 nm was deposited on the SiO_2 thin film. The distance between the target and the substrate was 80 mm. The sputtering time of SiO_2 and Au was 30 min and 6 s, respectively. The substrates were ultrasonically cleaned in alcohol for 15 min, and then dried. The RF sputtering power was 150 W. Subsequently, the as-deposited samples were annealed in tube furnace in N_2 atmosphere with a flow rate of 500 mL/min at 1100 ℃ for 20, 25 and 30 min, respectively.

3. Results and discussion

For experiment B (Fig. 1(b)), Au thin film as catalyst was deposited on the Si(111) substrates by sputtering an Au target (99.99 %) for 6 s. The thickness of the Au film was about 18 nm. The other sputtering condition was the same as experiment A. Subsequently, the as-deposited samples and Si powder (99.99% purity) were put on the same alumina boat and annealed in a tube furnace in N_2 atmosphere with a flow rate of 500 mL/min at 1100 ℃ for 20, 40 and 60 min. The samples were placed on the downside of the flowing N_2, next to the Si powder. Prior to annealing, air still existed in the system.

The products were characterized using SEM and XPS.

Figure 2 shows typical micrographs of the samples annealing at 1100 ℃ for 20, 25 and 30 min in experiment A. As can be seen in Fig. 2(a), Au nanoparticles as catalyst were distributed over the entire surface of the substrate and there was no nanowire observed after annealing for 20 min. After the annealing time was increased to 25 min, nanowires began to grow (Fig. 2(b)). The length of the nanowire was about several hundred nanometers. After the samples were annealed at 1100 ℃ for 30 min (Fig. 2(c)), large amounts of nanowires with a length of 3 μm were formed and they were very straight with a smooth surface. Particles at the tip of the nanowires imply the VLS process growth mechanism of nanowires[1]. The distribution of the nanowires was not ordered, which can be attributed to the aggregation of the nanoparticles in the growth process. That is to say, SiO_2 nanowires will grow where the Au nanoparticles aggregate.

Lai *et al*.[12] reported the growth of Pt-catalyzed SiO_x nanowires by rapid thermal annealing at 900 ℃. The growth of the nanowire was found to occur via a catalyst driven VLS mechanism. SiO_2 films with a thickness of 11 nm were grown on p-type silicon (100) substrates by thermal oxidation. A 50-nm-thick Pt layer was then deposited on SiO_2 by thermal evaporation. The Pt/SiO_2/Si structure was subjected to rapid thermal annealing (RTA) in nitrogen ambient at 700, 800, and 900 ℃ for 60, 180, and 300 s, respectively. Energy-dispersive X-ray (EDS) analysis shows that the wire is mainly composed of Si and O, whereas the seed particle is constituted of Pt and Si. Accordingly, we think SiO_2 nanowires were probably formed in experiment A.

Figure 3 shows typical SEM images of the SiO_2 nanowires annealing at 1100 ℃ for 20, 25 and 30 min in experiment B. After the samples were annealed at 1100 ℃ for 20 min, large amounts of short SiO_2 nanowires with a diameter of 20 to 150 nm were formed on the surface of the substrates (Fig. 3(a)). As shown in Fig. 3(a), particles are observed at the ends of the nanowire, which implies the conventional VLS process proposed for nanowires grown by a catalytic-assisted technique[10]. Figure 3(b) shows SiO_2 nanowires with a grass-like array distributed on the substrate and the length of the SiO_2 nanowires increased to several microns as the annealing time was increased. The nanowire grows along a certain direction, which retards the sideways growth of the nanowire and reduces the system energy[13]. After the samples were annealed at 1100 ℃ for 30 min (Fig. 3(c)), the SiO_2 nanowires became curly with the aggregation of the particles at the tip of the

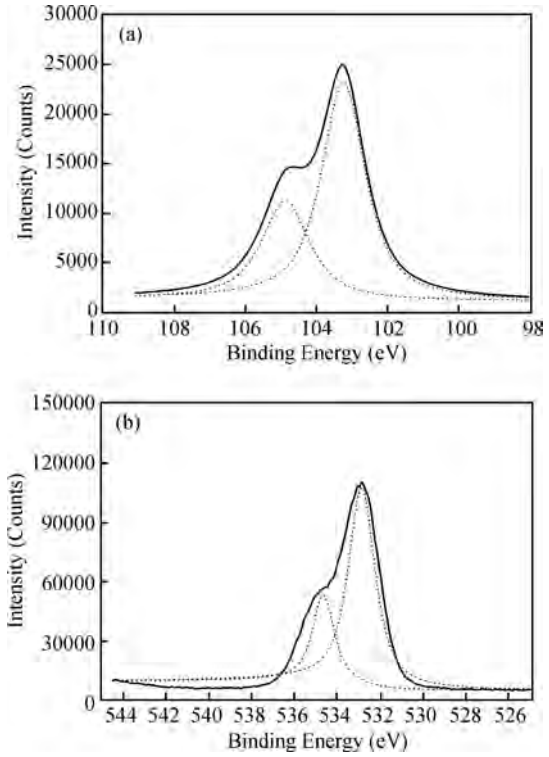

Fig. 4. XPS spectra of the samples annealing at 1100 ℃ for 40 min. (a) Si2p. (b) O1s. The substrates were Si covered with Au films.

nanowires. Compared to Fig. 3(a), no granules of metallic Au which remains unalloyed were observed in Fig. 3(c). Combined, the image of the SiO_2 nanowires is affected by the annealing time. In our experiments, the SiO_2 nanowires were long and straight when the annealing time was 25 min.

Figure 4 shows XPS spectra of the samples annealing at 1100 ℃ for 40 min. The substrates were Si covered with Au films. In Fig. 4(a), the strong peak at 103.3 eV corresponds to the binding energy of Si2p for SiO_2[14], and the shoulder around 105 eV probably comes from the surface contamination of Si. In Fig. 4(b), the strong peak at 532.8 eV corresponds to the binding energy of O1s for SiO_2[15], and the shoulder around 535 eV probably comes from adsorption oxygen of the sample[16].

In experiment B, melted droplets are formed at high temperature as a result of alloying between Si and Au. If Au particles are too large or have bad contacts with the Si substrate, they may remain unalloyed. As air was in the system, oxygen would have reacted with the Au–Si eutectic liquid alloy droplets resulting in the formation of the Au/Si/O liquid alloy droplets. Then the Si vapor was transported to the Au/Si/O liquid alloy droplets by the flowing N_2 to form a steady structure with the ratio of Si/O equaling 1 : 2[17]. With the compositional supersaturation of the Au/Si/O liquid alloy droplets, the SiO_2 would separate from the droplet, resulting in the growth of the nanowires. This analysis is supported by quantification of the peaks in XPS spectra, as shown in Fig. 4, which reveals that the atom ratio of Si to O is about 1 : 2.

Finally, we discuss the effect of substrates on SiO_2 nanowire growth. The growth mechanism of SiO_2 nanowires on different substrates is described in Fig. 5.

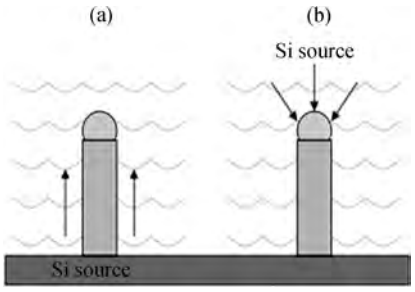

Fig. 5. Mechanism of growth of SiO_2 nanowires. The substrates were (a) SiO_2/Si(111) and (b) Si covered with Au films.

On the one hand, different substrates result in different yield and morphology in fabricating the SiO_2 nanowires. A large scale of SiO_2 nanowires was synthesized on Si, compared to that on Si(111) with the SiO_2 layer about 200 nm, which indicates that the SiO_2 layer probably blocked the growth of the nanowires. Also, the liquid alloy droplets were difficult to form for the Au catalyst and SiO_2 layer. At high temperatures, Si and SiO_2 may react with each other according to the following steps[18],

$$\mathrm{Si} + \mathrm{SiO_2} \rightarrow 2\mathrm{SiO}, \tag{1}$$

$$\mathrm{SiO} \rightarrow \mathrm{Si} + \mathrm{SiO_2}. \tag{2}$$

These reactions result in the nuclei of nanowires. On the other hand, the Si source is different in experiments A and B. In experiment A, the source comes from the substrate. In experiment B, the Si powder provides the source of the Si vapor at high annealing temperature. As in our comparative experiment of fabricating SiO_2 nanowires, we found that there is no nanowire grown on the substrate if Si powder is not used in the annealing process and the other experiment condition is identical.

4. Conclusions

SiO_2 nanowires were prepared on SiO_2/Si(111) or Si substrate using Au as a catalyst. The SEM shows that large amounts of SiO_2 nanowires with a diameter of 20–150 nm and length of several nanometers were formed on the entire surface of the substrate. The XPS analysis indicates that the nanowires have the composition of Si and O in an atomic ratio of about 1 : 2. Their composition approximates that of SiO_2. As the annealing time increased, the SiO_2 nanowires became longer. The formation of the SiO_2 nanowires was controlled by the VLS mechanism. The yield, morphology and Si source of the SiO_2 nanowires were different for the different substrates.

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