

Formation of silicon oxide nanowires in nanomaterial synthesis experiments based on the usage of tube furnace

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In an effort to synthesize doped ZnO nanowires, SiO_x nanowires were obtained accidentally. In the experiment, mixed powders containing chemicals such as ZnO, graphite, Ga₂O₃, and In₂O₃ were placed in the center of a tube furnace, where the temperature was set to 1200 °C and the vacuum was approximately 27 Pa. Silicon wafers were placed around the vicinity of the furnace exit to collect the expected nanomaterials. After prolonged heating, grey layers were found on top of one wafer located inside the furnace. The layer showed no adhesion to the substrate. Characterization by using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Energy Dispersive X-ray Spectroscopy (EDS) revealed that this layer consisted of SiO_x nanowires. Formation of Si-containing liquid drop and the subsequent growth of SiO_x nanowires out of it are suggested as the growth mechanism.

Keywords: *silicon; oxide; nanowires*

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1. Introduction

Nanomaterials are attractive due to the dramatic change in their properties accompanying the reduction of size. Examples of such changes include the emission of light with different wavelengths due to the effect of quantum confinement [1], and the improved efficiency of catalyst in the shapes of nanoparticles due to increased surface area [2]. Nanomaterials made of substances widely used in the bulk form are more attractive since they can be integrated to existing technology relatively easily [3, 4]. One example is the fabrication of SiO_x nanowires. In this paper, we define silicon oxide as SiO_x, with x values ranging from 1 to 2. In the form of bulk, silicon oxide is widely used as a window material in construction and as an insulator in the semiconductor industry. It has been reported that such ordinary materials show novel properties when fabricated as nanomaterials such as SiO_x nanowires displaying luminescence [5]. For these

reasons, fabrication of SiO_x nanowires draws the attention of many researchers.

There were several previous reports regarding the fabrication of SiO_x nanowires which we would like to divide into two groups, depending on their suitability for mass production [6]. Examples of approaches unsuitable for mass production include laser ablation, rapid thermal annealing, and sol-gel approaches. Laser ablation without a catalyst was reported by Yu et al. [7]. A similar experiment was performed by Aharonovich with a catalyst added [8]. Lai et al. used rapid thermal annealing to synthesize SiO_x nanowires [9]. Sood et al. obtained SiO_x nanowires by annealing Si wafers doped with Pd at 1100 °C [10]. Liang et al. yielded SiO_x nanowires based on the usage of sol-gel process [11]. Synthesis of SiO_x based on the heating of Si or SiO_x is considered to be suitable for mass production. Jiang et al. used Chemical Vapor Deposition (CVD) to obtain SiO_x, where Fe-Co-Ni alloy was used as the catalyst and Si powder as the source [12]. A similar experiment was performed

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by Yang et al. [13]. Saulig-Wengner et al. reported the direct formation of SiO_x from commercial Si powder in the presence of graphite powder [14]. The importance of graphite presence and the subsequent formation of CO and CO_2 was pointed out. In a similar experiment, Li et al. confirmed the effectiveness of graphite source in promoting the formation of SiO_x [15]. In addition to graphite, the importance of Au as catalyst was emphasized in this later report. The effectiveness of graphite in promoting the formation of SiO_x nanowires was supported by the experiment of Pukird et al., where SiO_x nanowires were synthesized from rice husks using coconut shells [16]. In the present paper, we report the formation of SiO_x nanowires in a CVD experiment. This experiment was originally designed to fabricate In or Ga doped ZnO nanowires, but SiO_x nanowires were created accidentally. The approach used here is different from any of those described above. The formation mechanism is discussed in relation with the above mentioned reports.

2. Experimental

A schematic drawing for the configuration of the synthesis experiment is shown in Fig. 1. The furnace used was 51.5 cm long with a ceramics tube of 1 m length and 52 mm inner diameter inserted inside of it. In the vacuum pump side (downstream), the ceramics tube projected 15 cm out of the furnace. Raw powders of ZnO, graphite, Ga_2O_3 , and In_2O_3 in different weight ratios were mixed thoroughly by grinding for a duration of 30 minutes. In some of the experiments, In_2O_3 powder was not used. One gram of the pre-prepared powder was packed in a relatively small ceramics boat of dimensions $2.96 \times 0.81 \times 0.69 \text{ cm}^3$. This small ceramics boat was, in turn, placed in the center of a larger boat. Two extra empty small boats were placed on both sides of powder-containing boat to hold it in position. The large boat was placed in the center of the furnace. Four or six Si wafers of 3 to 3.5 cm in length were placed in medium sized ceramics boats with dimensions $4.04 \times 3.06 \times 0.71 \text{ cm}^3$. These boats were placed in the vicinity of the down stream

furnace exit with equal numbers inside and outside of the exit. The original purpose of the Si wafer was to be used as the substrate for the synthesized doped ZnO nanomaterials. The ceramics tube was evacuated to a vacuum of 27 Pa. The temperature was raised from room temperature to 1200 °C in two hours. The furnace was held at this temperature for three hours, and then allowed to cool to room temperature naturally. While the temperature at the center of the tube furnace was maintained at 1200 °C, there was decreasing temperature gradient from the inner Si wafer to the outside one. Since melt glass layers were found occasionally on the surface of the innermost Si wafer, the temperature at this point is estimated to be around 1000 °C while the temperature at the location of wafers placed in the outmost location is estimated to be around 400 °C. Examination of the large and small ceramics boats after the experiment found leftover black graphite powder, implying that other source materials were completely exhausted. The SiO_x nanowires were found on the surface of Si wafers placed inside the furnace. Such SiO_x nanowires were examined by Scanning Electron Microscope (SEM) (JEOL JIB-4500 Multi Beam System) and Energy Dispersive X-ray Spectroscopy (EDS) (EDAX Genesis). Some of the samples were examined by Transmission Electron Microscopy (TEM) (JEOL JEM-2100).

3. Results and discussion

SiO_x nanowires were found in a synthesis experiment with mixed raw powders of $\text{ZnO}:\text{C}:\text{Ga}_2\text{O}_3:\text{In}_2\text{O}_3$ with a weight ratio of 10:2:1:2 respectively. The surface morphology of the Si wafer, on which SiO_x nanowires were found, is shown in Fig. 2. The whole wafer was covered with a layer of grey color. There is little adhesion between the SiO_x layer and the substrate such that even normal breathing could separate them. The upper right corner shows the morphology when the layer is intact while the lower left corner shows the substrate when the layer was removed. A SEM image of the SiO_x nanowire layer peeled off from the substrate is shown in Fig. 3(a). The layer showed strong charging effect, implying the insu-

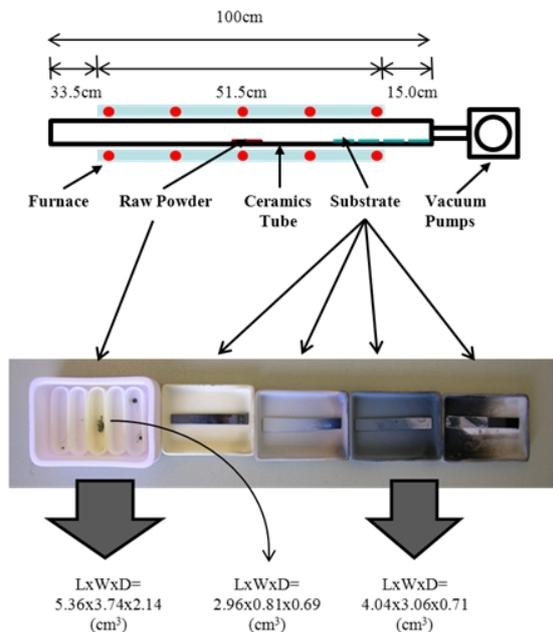


Figure 1. Schematic diagram and picture of the instrument used in the present work.

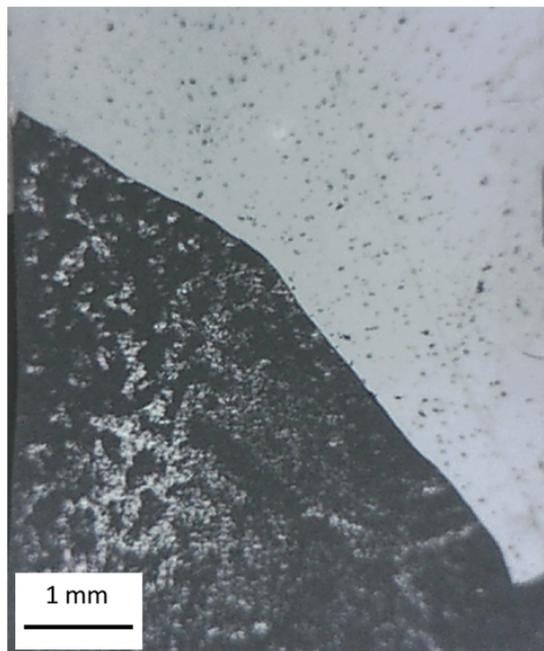


Figure 2. An optical image of the Si wafer with SiO_x nanowires formed on the surface.

lator character. Imaging had to be performed on areas close to the edge of the clump and close to the conductive carbon tape used. The diameters of the wires were in the range of 30 to 100 nm, which was confirmed by TEM observation to be described later. Though an accurate measurement was difficult, the length of most of the wires was estimated to be more than $20 \mu\text{m}$ as shown in Fig. 3(a). An EDS analysis, the result of which is shown in Fig. 3(b), revealed that the wires consist of Si and O elements.

To find out the dominant elements in the formation of SiO_x nanowires, different mixtures were used to repeat the experiment. Using the mixture of $\text{ZnO}:\text{C}:\text{Ga}_2\text{O}_3$ with a weight ratio of 10:2:1, similar results were obtained. Experiments based on the usage of mixed powder of $\text{ZnO}:\text{C}:\text{In}_2\text{O}_3$ with a 10:2:2 weight ratio failed to obtain the same results. It was observed that no deposition was formed on the surface of the Si wafers when the experiment was carried out in a vacuum of 2700 Pa. As mentioned above, it was noticed that there was no adhesion between the SiO_x layer and the Si substrate. In order to have a better understanding about the for-

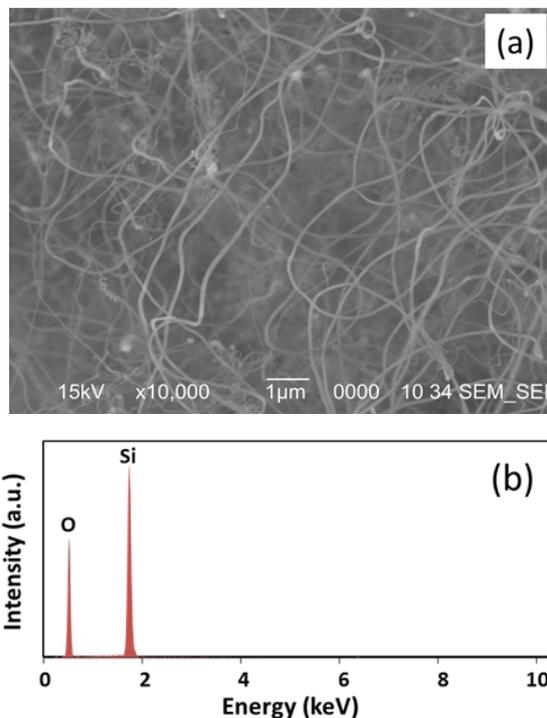


Figure 3. (a) A SEM image of SiO_x nanowires obtained with mixed raw powders of $\text{ZnO}:\text{C}:\text{Ga}_2\text{O}_3:\text{In}_2\text{O}_3 = 10:2:1:2$ in weight ratio. (b) EDS spectrum taken from the nanowires.

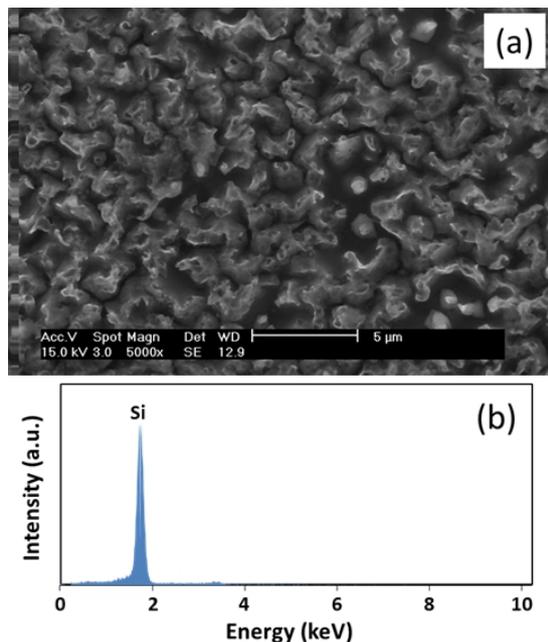


Figure 4. SEM image of the underlying Si substrate when the top SiO_x layer is peeled off (a) and the corresponding EDS spectrum (b).

mation mechanism, the Si substrate with SiO_x layer removed was examined by SEM. A SEM picture of the Si substrate is shown in Fig. 4(a). The rough surface implies reaction between the substrate and some of the vapors from the raw material. EDS spectrum shown in Fig. 4(b) was taken from the substrate, indicating that the substrate remains as pure Si after reaction.

The crystal structure of the nanowires was examined by TEM. Figs. 5(a) and (b) show the TEM image, confirming the SiO_x nanowires' diameter range described above. The high resolution image shown in Fig. 5(c) confirms the amorphous nature of the SiO_x nanowires. An electron diffraction pattern taken from a single SiO_x nanowire is shown in the inset of Fig. 5(c). The halo pattern supports the conclusion that the present SiO_x nanowires are amorphous.

In one of our experiments using the mixed powders of $\text{ZnO}:\text{C}:\text{Ga}_2\text{O}_3$ with weight ratio of 10:2:1, SiO_x nanowires with slightly different morphology were observed. As revealed by the SEM image of Fig. 6(a), SiO_x nanowires with grey contrast were

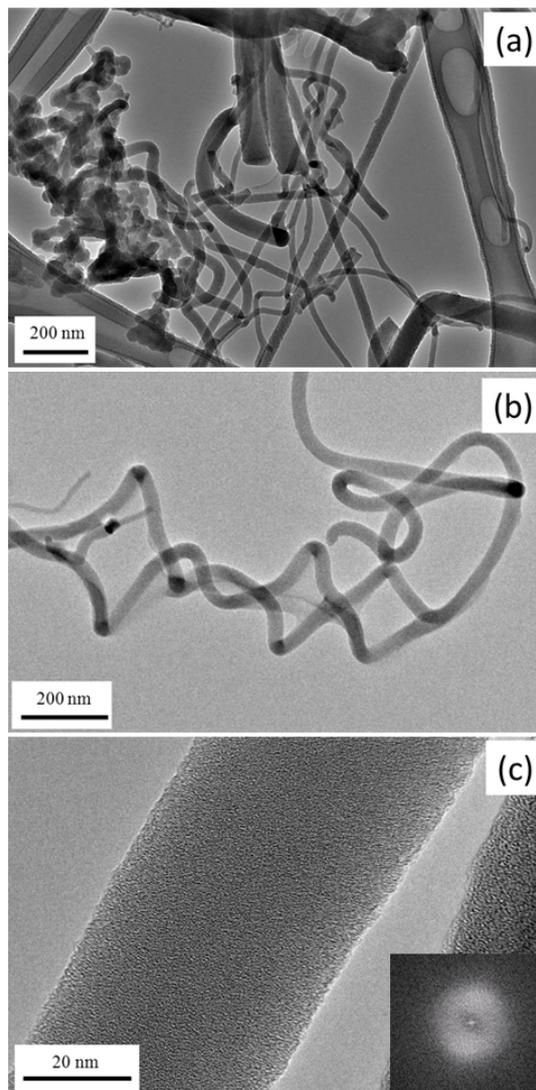


Figure 5. TEM images (a) and (b), and a high resolution TEM image (c). The high resolution TEM image (c) and the electron diffraction pattern shown in the inset of (c) confirm the amorphous nature of the nanowires.

observed clumping together on a bright sphere. As shown by the EDS spectra in Figs. 6(b) and (c), the grey part is featured by the high concentration of Ga compared to the rest.

As mentioned in the introduction section, there are previous reports regarding the formation of SiO_x nanowires. The report that is most closely related to the present work was made by Li et al. [15]. In their experiment, the mixture of $\text{ZnO}:\text{C}$ equal to 1:1 in weight ratio was used as the source and

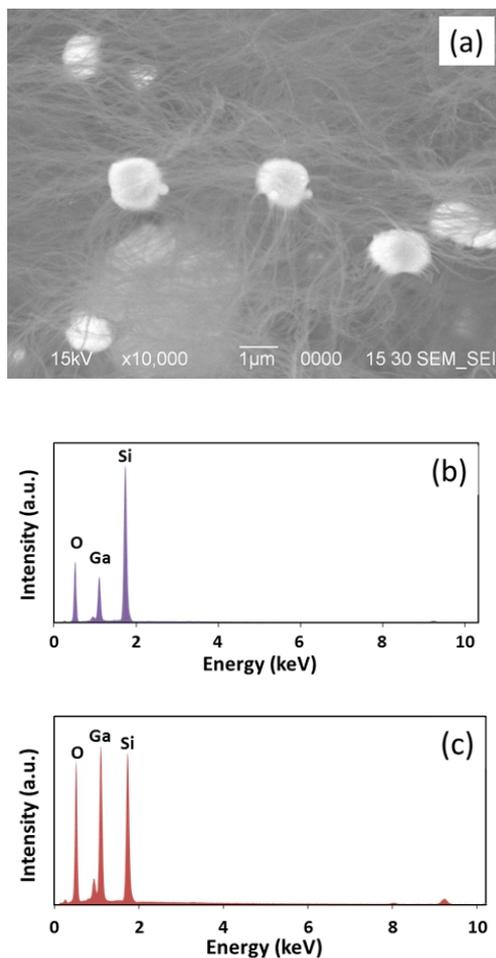


Figure 6. SEM image (a) and EDS spectra (b) and (c) of SiO_x nanowires with different morphology than those observed in Fig. 3. EDS spectrum (b) was taken from SiO_x nanowires and (c) from the grey part.

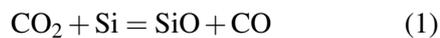
was placed in the center of a tube furnace. Three types of substrates, Si wafers coated with Au or Cu thin films and bare Si wafers, were placed downstream. It was reported that SiO_x nanowires were formed only on the wafer with Au coating, indicating the importance of Au in the experiment. It has been proven that the presence of graphite is also crucial regarding the formation of SiO_x, consistent with preceding reports [18, 19].

Based on these previous reports and the results of the present experiments, the following model for the formation mechanism of the present SiO_x nanowires is suggested. Since the experiments demonstrated that the mixture of ZnO, graphite,

and Ga₂O₃ is sufficient for the formation of SiO_x nanowires, we use the experiment of ZnO, graphite, and Ga₂O₃ as an example to explain the model. The presences of Ga₂O₃ and graphite are considered to be important for the formation of SiO_x nanowires in this model. The entire formation process of SiO_x nanowires can be divided into two phases. The first phase is the formation of a Ga–Si liquid alloy drop. Since the dissolving and subsequent precipitation of Si play important roles in the present model, some of the thermal dynamic data of Ga–Si system is provided here. Ga has melting and boiling temperatures of 303 K and 2477 K, respectively, and the melting temperature of Si is 1687 K. The heat of vaporization for Ga and Si are 254 and 359 kJ·mol⁻¹, respectively. The heat of fusion for Si is 359 kJ·mol⁻¹. The molar heat capacity for Ga and Si are 25.9 and 19.8 J·mol⁻¹·K⁻¹, respectively. Heating of the raw powders at 1200 °C causes the reduction of Ga and Zn from their corresponding oxide state to the atomic state in the presence of C. These reduced metals evaporate and drift downstream. Upon encountering the Si substrate at relatively low temperature, they condense and form a liquid drop. Due to the boiling temperature of Ga is much higher than that of Zn, Ga condenses on the inner Si wafer preferentially [17]. The Ga liquid drop dissolves the Si substrate and forms Ga–Si alloy melt drops. The maximum concentration of Si in the Ga–Si liquid drop increases with temperature.

Based on the aforementioned dynamic data, it is reasonable to consider that the initially formed liquid drop is at high temperature close to the boiling temperature of Ga and can dissolve more Si. At the melting temperature of Si, a simplified calculation estimates that the heat released by the condensation of a certain number of Ga atoms in vapor phase is enough to melt down five times the number of Si atoms, forming a GaSi₅ liquid drop. The second phase of the model is the precipitation of Si and the subsequent formation of SiO_x nanowires from the Si rich Ga–Si liquid drop. In this phase, the Ga–Si liquid temperature decreases which could be caused by the heat loss from the liquid to the substrate via conduction, and the concentration of Si in the Ga–Si liquid drop is supersat-

urated. Then, Si starts to precipitate and is oxidized in a form of nanowires. It is believed that oxidation, and hence the growth of SiO_x nanowires, happens on the interface between SiO_x nanowires and liquid Ga–Si drop with the assistance of CO or CO_2 . CO or CO_2 originates from the graphite placed in the raw powder mixture due to the relatively low vacuum (abundant of residual oxygen) and high furnace temperature. SiO could be further oxidized to SiO_x . Some of the wires grow downward and push the liquid drop upward. Eventually, this will lead to the separation of the liquid drop from the substrate, shutting down the Si source. SiO_x nanowires will continue to draw Si and grow longer until the Si source in the floating liquid drop is exhausted. There are two different opinions regarding the function of graphite in this step represented by the following two chemical reactions.



The first reaction was suggested by Carter et al. [18] while the second reaction was given by Zhu et al. [19]. If reaction 2 occurs, carbon deposit is expected. Since we did not observe such carbon around SiO_x nanowires, reaction 1 is favored. It is worth to point out that the observation of graphite leftover in the ceramics boats, where the raw powder mixture was placed, imply that these carbon containing gases last much longer than the Ga/Zn vapors.

This model is supported by previous reports and results from current experiments. First, it is supported by the occasional observation of SiO_x nanowires clumped together on Ga-rich spheres as shown in Fig. 6. The formation of such a structure is explained as follows. Once the Si in the floating Ga–Si liquid drop is exhausted, the remaining pure Ga drop has possible outcomes. If SiO_x nanowires are formed on top of a wafer closer to the center of the tube furnace and the substrate has a higher temperature, the residual Ga will be gradually evaporated further downstream and leave no trace. This corresponds to the case shown in Fig. 3. If the liquid drop is formed on the wafer placed

relatively closer to the exit of the tube furnace, and the substrate has relatively lower temperature, the residual Ga has a lower probability to evaporate completely. Instead, some of the Ga will form oxide with the residual oxygen and stay. This corresponds to the case shown in Fig. 6. Second, this model is supported by the observation that the layer made of SiO_x nanowires has little adhesion to the substrate despite the fact that Si substrate is the obvious source for the formed SiO_x nanowires. This lack of adhesion is explained as the result that the whole Ga–Si liquid drop has been lifted up from the substrate at some point. It should be pointed out that the formation of this free standing SiO_x nanowire layer is quite unique among reports regarding the formation SiO_x nanowires. Other experiments, such as those described by Li et al. [15], have to use aggressive acid such as HF to remove the formed nanowires from the Si substrate. Third, this model explains the fact that no Ga is detected in the Si substrate though reaction between Ga and Si substrate is assumed.

4. Conclusion

Upon heating the mixed powders of ZnO, graphite, and Ga_2O_3 (or ZnO, graphite, Ga_2O_3 , and In_2O_3), layers composed of SiO_x nanowires were found on the surface of Si wafers placed downstream. These layers displayed no adhesion to the substrate. Analysis of previous reports and the present experiment led to the conclusion that the presence of Ga and graphite is crucial for the formation of SiO_x nanowires. A model based on the formation of Ga–Si liquid drop and the subsequent growth of SiO_x nanowires out of such drop assisted by CO_2 was suggested. Present work provides a better understanding for the formation mechanism of SiO_x nanowire, and a new approach for the synthesis of pure SiO_x nanowires was added to the existing recipes. Further, the present result is helpful for the analysis of occasional unexpected synthesis results using similar instruments.

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