Controlled growth of silicon nanowires synthesized via solid–liquid–solid mechanism

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Abstract

The growth of silicon nanowires using solid–liquid–solid method is described. In this method, silicon substrates coated with a thin layer of gold were heat treated in nitrogen ambient. Gold particles started to diffuse into the silicon substrate and Au–Si alloy formed at the interface. The alloy would have molten to form liquid droplets on the substrate when temperature increases above their eutectic point, and more Si atoms diffused into these alloy droplets when heating continues. Rapid cooling of the droplet surface due to nitrogen flow into the chamber would eventually lead to the phase separation of silicon atoms from the surface of the alloy, created the nucleation and thus the growth of silicon nanowires. Controlled growth of the nanowire could be achieved by annealing the sample at 1000°C with nitrogen flow rate set to around 1.5 l/min. The synthesized nanowires with diameter varied from 30 to 70 nm, were straight and grew along the N2 flow. Larger amount and longer nanowires were grown when longer period of heating was applied. Nanowires with lengths more than several hundreds of micrometers were achieved by annealing the sample for 4 h.

Keywords: Silicon nanowire; Solid–liquid–solid; Gold; Thermal anneal; N2

1. Introduction

Successful synthesis of carbon nanotubes (CNTs) by Iijima in 1991 [1] and the growth of some wire-like nanowhiskers [2,3] around that time have stimulated new momentum in the study of nanoscience. Much interest has been drawn towards these nanomaterials because of their special characteristics in one-dimensionality [4]. Meanwhile, fabrication of these one-dimensional nanomaterials can be achieved by using either ‘Top-down’ or ‘Bottom-up’ approaches [5]. Whilst top-down approach usually requires precision engineering and lithography for patterning and removing of bulk material, bottom-up approach on the other hand involves the building of nanostructure by self-arrangement of atoms or molecules through the natural interaction amount themselves. However, the later process receives more research interest as it provides a feasible and inexpensive alternative for nanomaterials fabrication.

In this paper, the synthesis of silicon nanowires using the approach of bottom-up fabrication is described. Silicon nanowires have been grown in a furnace under the flow of nitrogen gas. The growth mechanism can be explained by solid–liquid–solid method. In general, silicon from the substrate which was in solid phase would first be transferred into liquid phase upon heating with the helped of gold as catalyst. The silicon atoms were then self-assembled into wire shape (solid rod) when rapid cooling occurred at the liquid surface which was induced by the nitrogen gas flow. The effect of the nitrogen flow rate, the heating temperature and its duration onto the growth of silicon nanowires were also discussed.

2. Experimental details

The p-type silicon substrates with (100) orientation were cleaned with acetone and diluted hydrofluoric acid followed by rinsing under running deionized water. The cleaned samples were dried and transferred into a metal sputter coater, where a thin layer (10 nm) of gold was deposited. The samples were then ready to be annealed. A quartz tube
4 cm in diameter and 60 cm in length was used to place the samples and was inserted into a furnace. Purified nitrogen gas (99.999%) was flowed into the quartz tube throughout the annealing process. Typical synthetic conditions for the nanowires were 2 l/m of N\(_2\) flow rate and 1000 °C of heating temperature for 2 h duration.

The as-growth nanowires were observed by the scanning electron microscope (SEM, XL 30 Philips) as well as the tunneling electron microscope (TEM, JEM2010 JEOL). Meanwhile, chemical compounds presented in the nanowires were investigated using the energy dispersive X-ray spectroscopy (EDS, Oxford Instrument, model 7353).

3. Results and discussions

3.1. Characterization of silicon nanowires

The grown of silicon nanowires can be indicated by observing a thin layer in gray (or whitely) formed on the silicon substrate which was initially covered with gold. At the typical condition of growth, some fiber-like wires can be seen (with SEM) to have covered the treated silicon substrate (Fig. 1). Diameters of wires varied from 50 to 150 nm and their lengths were usually longer than several tens of micrometers though they were hard to be determined due to the highly compact and entangle growth.

To examine the chemical components of the nanowires, the EDS scans (Fig. 2) had been conducted by focusing onto the nanowires located at the edge of the silicon substrate. In the experiment, growth directions of the nanowires were rather irregular and some of them were grown extended out from the substrate (and suspend in air). This had provided an idea location to obtain related information from nanowires under the EDS scans without interference signals from silicon substrate underneath. As suggested by the experimental setup, Si peak was originated from the body of the wires, and not from the silicon substrate. O peak came from the silicon oxide layer. Although nitrogen was flowed throughout the experiment, small amounts of oxygen were believed still presented in the chamber and caused the formation of silicon oxide. Growth of a native oxide layer on the silicon nanowires surface after the experiment was also contributing to this signal. This argument is supported by further testing using the TEM. Fig. 3 has clearly shown a thin layer of oxide covering the surface of the silicon core wire. The strong Al signal came from beneath the nanowires, i.e. aluminum holder for the sample meanwhile the weak C peak is caused by the used of carbon tape to attach the sample.

3.2. Growth mechanism of silicon nanowires

The growth of the silicon nanowires in the experiments can be understood from the concept of eutectic. In our works, silicon and gold were the main elements in concern. By referring to the phase diagram for Au–Si eutectic alloy Fig. 4, lowest melting temperature (363 °C) can be achieved for the formation of alloy with about 20% of silicon atoms.
When the gold-coated sample being heated in the furnace, gold may diffuse into the silicon substrate to form alloy at their interface. This layer started to melt when temperature in the furnace increased above eutectic point and the process continue until all the gold would have mixed with some silicon and molten. Inter-atomic interaction and strong surface tension caused the formation of round Au–Si liquid droplets on the silicon substrate. Temperature dependent mixing as indicated by the phase diagram suggested that more silicon would diffuse in the alloy droplets when temperature continues to increase. (It is therefore super saturation of silicon in the droplets may have occurred when temperature reached 1000 °C as in the experiment).

The nitrogen flow had played the critical role for silicon nanowires growth. The cooler nitrogen molecules that flowed into the quartz tube caused cooling at the surface of the hot liquid droplets. Rapid cooling at these Au–Si droplets surface tended to separate the elements in the mixture. The nucleation of silicon may have occurred at the droplet surface where more silicon atoms could be precipitated from the alloy droplet to grow into nanowires. The growth can therefore be regarded as solid–liquid–solid (SLS) method as suggested by Yu and coworkers [6,7]. In this mechanism, the silicon source for nanowires growth originated from the substrate, which was a solid. Forming and melting of the alloy would transform the silicon into liquid. These silicon atoms then self-assembled into nanowire which was in solid again upon cooling. It has to be noted that the nanowires grown using the SLS method are differed from those grown using vapor–liquid–solid (VLS) method [8–10] which is a more popular growth mechanism for nanowires. In this later mechanism, source materials for the nanowire introduced as vaporized form, before it is transformed into liquid and finally into solid nanowire. The main difference in nanowires produced is the presence of gold cluster on the tip of nanowires grown by the later process. No Au had been found on our nanowires as indicated by EDS result. Au had played a role as catalyst for the growth, not forming any part on the nanowire except at the growth location and would stay on the silicon substrate.

In order to achieve better control on the silicon nanowires synthesized using SLS method, further studies have also been carried out to investigate the effect of annealing parameters to the growth. The synthetic conditions as well as their effects on nanowires growth were summarized in Table 1.

### Table 1

| Annealing condition | Nanowires growth                                                                 |
|---------------------|----------------------------------------------------------------------------------|
| **Temperature (°C)** | **N₂ flow rate (l/min)** | **Duration (min)** | **Note**                                                                 |
| 800                 | 2.0                           | 120               | None, only small clusters formed.                                           |
| 900                 | 2.0                           | 120               | Very few, lot of small clusters remain.                                     |
| 950                 | 2.0                           | 120               | Few, but can easily be found.                                              |
| 1000                | 2.0                           | 120               | Dense, entangled growth.                                                   |
| 1050                | 2.0                           | 120               | Very dense at certain area, but the diameters usually large (> 200 nm). Lot of big clusters with various shapes and sizes but no nanowire formed. |
| 1100                | 2.0                           | 120               | None, only big clusters formed (~ 1 μm).                                   |
| 1000                | 0.6                           | 30                | None, only small clusters seen.                                            |
| 1000                | 0.8                           | 30                | Started to form, but not straight, much entangled.                         |
| 1000                | 1.2                           | 30                | More directional than at 0.8 l/min N₂, diameter 100–150 nm.                |
| 1000                | 1.5                           | 30                | Straight and follow the N₂ flow, diameter 30–70 nm.                        |
| 1000                | 2.0                           | 30                | Quite straight and follow the N₂ flow, diameter: 50–100 nm.                |
| 1000                | 2.5                           | 30                | Started to become more entangle again.                                      |
| 1000                | ≥3.0                          | 30                | Direction become irregular again, diameter: 40–70 nm.                      |
| 1000                | 1.5                           | 15–240            | Nanowire can be formed by annealed the sample for 15 min under N₂ ambient. The growth was less compact and their direction can be controlled by the N₂ flow. The longer the heating duration, the longer the nanowires can be grown (few hundreds μm for 4 h), but too compact and entangled. |
3.3. Temperature effect to the growth of nanowires

The heating of the eutectic alloy had supplied the source for growth of the nanowires in SLS method. While a too low temperature may not create saturation of silicon atoms in the alloy to be nucleated and grown into nanowires upon cooling; a too high temperature may consume excessive energy and will not favor the cost for fabrication. In our works, the growth of nanowires could only be achieved when temperature increased above 900 °C. Below this critical point, the percentage of silicon atoms present in the alloy may not be sufficient to form the nucleation and precipitation for the nanowires growth. Only small cluster of the Au–Si alloy were found on the substrate (Fig. 5) in these cases.

Significant growth of nanowires had been achieved by setting the temperature to 1000 °C. The growth was relatively dense as shown in Fig. 1. When the temperature increased above this point (1050 and 1100 °C), the wires formed were generally larger in diameter (~200 nm). This may be due to too much of silicon in the alloy creating larger nucleation seeds for the growth of the wires. It is also noted that only small amounts of nanowires were able to form at certain areas on the substrate. Most of the areas remain covered with a thick layer of alloy clusters (Fig. 6). Almost none of the fiber-like feature could be found on the sample heat treated at 1100 °C. The reason why only relatively big alloy clusters with irregular sharps and sizes formed on the substrate as compared to those seen in Fig. 5 has yet to be understood.

3.4. Nitrogen flow rate effect to the growth of nanowires

Nitrogen flowed into the chamber was not only to mitigate the present of unwanted gases, but also to induce rapid cooling at the surface of the hot droplets. Again, a too low the flow rate may not be sufficient to cool down the surface effectively, and a too high flow will increase the production cost. In the experiments, there were no nanowires formed for the flow rates below 0.8 l/m. This may be because of too few N₂ molecules to bring away the thermal energy from the droplet surface, thus no nucleation occurred. At 0.8 l/m flow, the nanowires started to form but entangled with each other, their orientations also irregular. The growth of nanowires became more directional (along the flow of N₂) as the flow rate increased to 1.5 l/m (Fig. 7). The nanowires were relatively straight at this flow rate and their diameters were also the smallest (30–70 nm) among others. The growth direction became irregular again as the flow rate increased above 2 l/m. Supply of N₂ into the quartz at this rate may have led to the formation of turbulence flow which disturbed the directional growth of nanowires.

3.5. Heating duration effect to the growth of nanowires

The amount of silicon nanowires grown can be controlled by the annealing duration. Generally, if heating time had been kept short the growth of nanowires was less compact and their direction could be controlled by N₂ flow. Good example is shown in Fig. 7 in which the sample had
been annealed for about 30 min. Annealing time of 15 min had also been used, where much less compact of nanowires growth had been achieved. Experiment had also been carried for a duration of 4 h. The growth was highly compact and entangled. However, the length of nanowires grew more than several hundreds of micrometers in this case.

4. Conclusion

The synthesis of nanowires using solid–liquid–solid mechanism has been demonstrated in this paper. The as-growth nanowires were composed of Si and its oxide at the surface. SLS provides a relatively simple and straightforward method to grow large amount of nanowires.

Major factors that affect the growth including the heating temperature, the N₂ flow rate and the duration of annealing have been investigated. In our experiment, relatively straight and directional growth of nanowires along the gas flow could be achieved by choosing heating temperature of 1000 °C and N₂ flow at 1.5 l/min. The as-growth nanowires have diameters varied from 30 to 70 nm. It is also believed that a laminar flow of nitrogen gas with sufficient number of molecules to cool the droplet surface is essential to produce straight and directional nanowires. Heating duration on the other hand was used to control the amount of the nanowires formed. Less compact growth of nanowires was a result of short annealing duration, nanowires. In contrast, nanowires with lengths as long as several hundreds of micrometers were grown by heating the substrate for about 4 h.

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References

[1] S. Iijima, Nature 354 (1991) 56.
[2] M. Yazawa, M. Koguchi, K. Hiruta, Appl. Phys. Lett. 58 (1991) 1080.
[3] K. Haraguchi, K. Haraguchi, T. Katsuyama, K. Hiruma, K. Ogawa, Appl. Phys. Lett. 60 (1992) 745.
[4] M.S. Dresselhaus, Y.M. Lin, O. Rabin, A.G. Souza Filho, M.A. Pimenta, R. Saito, G.G. Samsonidze, A.G. Dresselhaus, Mater. Sci. Eng. C 23 (2003) 129.
[5] M.J. Madou, Fundamentals of Microfabrication, The Science of Miniaturization, 2nd ed., CRC Press, 2002.
[6] Y.J. Xing, D.P. Yu, Z.H. Xi, Z.Q. Xue, Appl. Phys. A 76 (2003) 551.
[7] H.F. Yang, Y.J. Xing, Q.L. Hang, D.P. Yu, Y.P. Wang, J. Xu, Z.H. Xi, S.Q. Feng, Chem. Phys. Lett. 323 (2000) 224.
[8] Y. Wu, P. Yang, J. Am. Chem. Soc. 123 (2001) 3165.
[9] C.Y. Lee, T.Y. Tseng, S.L. Li, P. Lin, Tamkang, J. Sci. Tech. E 6 (2003) 127.
[10] T. Märtensson, M. Borgström, W. Seifert, B.J. Ohlsson, L. Samuelson, Nanotechnology 14 (2003) 1255.