Synthesis of silicon nanowires using laser ablation method and their manipulation by electron beam

N. Fukata\textsuperscript{a,b,c,*}, T. Oshima\textsuperscript{a}, T. Tsuru\textsuperscript{d}, S. Ito\textsuperscript{d}, K. Murakami\textsuperscript{a,b}

\textsuperscript{a}Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan
\textsuperscript{b}Special Research Project on Nanoscience, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan
\textsuperscript{c}Nanomaterials Laboratory, National Institute for Materials Science, 1-1 Namiki, 305-0044 Tsukuba, Japan
\textsuperscript{d}Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Received 29 March 2005; revised 20 May 2005; accepted 7 June 2005
Available online 13 September 2005

Abstract

Size control of silicon nanowires (SiNWs) synthesized by laser ablation of a Si target with iron or nickel as catalysts were investigated by changing the synthesis parameters such as the content of catalyst in targets and laser power during synthesis. The diameter and length of SiNWs significantly depended on the synthesis parameters, i.e. the size of SiNWs can be controlled by the synthesis parameters. Manipulation of SiNWs was also performed during the observation of scanning electron microscope. By changing the degree of charge-up for free-standing adjacent intertwined SiNWs at an edge of Si substrate, the distance and speed of opening motion of them can be controlled. This motion is probably caused by the Coulomb repulsive interaction between them.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Silicon nanowires; Laser ablation; Scanning electron microscope

1. Introduction

Silicon nanowires (SiNWs) are of great interest in the fields of both fundamental and application research [1–4]. The growth mechanism of the nanowires is so called vapor–liquid–solid (VLS) mechanism [5,6] and there are two main methods to synthesis semiconductor nanowires. One is a laser ablation method [7,8]. The other is a chemical vapor deposition (CVD) method [9,10]. The remarkable point for the former method is that SiNWs can be synthesized in gas phase without forming and putting metal catalyst with nanometer size as seeds of SiNWs, which are necessary for the latter method. The latter method is, however, superior to the former method in terms of the size and site control. The size control of SiNWs is one of the important subjects for practical applications and also for studying the effects of quantum confinements [11–15], which are one of the unique physical properties for nanostructures. Such controls have not been investigated in the former method except our recent study about SiNWs synthesized by using Si targets with a nickel (Ni) catalyst [15].

It is also interesting to investigate the possibility about the manipulation of SiNWs. If SiNWs are freely manipulatable and intelligent functions can be added by doping or surface-modification, the further application will be expected. Especially, the investigation of the response of SiNWs to external fields and the manipulation by them are important for applying SiNWs to bio/chemical sensors and probe microscopy tips.

In the present study, in order to achieve the size control of SiNWs even in the case of a laser ablation method, we synthesized SiNWs under various conditions and investigate the dependence on the synthesis parameters such as content of iron (Fe) catalyst and the laser power during laser ablation. The response and manipulation of SiNWs were experimentally investigated during SEM observations for the first time.

2. Experimental

SiNWs were synthesized by laser ablation of a Si target with Fe or Ni catalyst. Four kinds of Si_{100-x}Fe\textsubscript{x} targets,
namely, Si$_{99}$Fe$_{1}$, Si$_{98}$Fe$_{2}$, Si$_{95}$Fe$_{5}$, Si$_{90}$Fe$_{10}$ and one kind of Si$_{100-x}$Ni$_x$ target, namely, Si$_{99}$Ni$_{1}$ were used. These targets were made by sintering Si and metal catalyst powders at 900–950 °C. Each target was placed in a quartz tube and heated at 1200 °C in a flowing argon (Ar) gas of 50 sccm. The temperatures were determined from the eutectic point of Si–Fe or Si–Ni. Ar gas pressures were set at 500 Torr. After reaching the temperature, a frequency-doubled NdYAG laser (wavelength 532 nm) was focused on to the target. In order to avoid continuing irradiating the same position, the focused point was scanned during laser ablation. The laser power was at about 200 or 100 mJ/pulse with a pulse duration of 7 ns at 10 Hz. In this experiment, SiNWs were directly collected on a Si substrate which was set on a water cooled molybdenum holder. Owing to this, SiNWs can be observed as they are deposited. The distance between the target and the substrate was set to be 7 cm. Scanning electron microscopy (SEM: JEOL, JSM-5610, 20 kV) and transmission electron microscopy (TEM: JEOL, JEM4000EX, 400 kV) were used to observe SiNWs and to investigate the structures of them. To investigate their motion and response to electron beam irradiation during SEM scanning, the electron beam current was changed from 20 to 70 µA and the scanning speed was changed from 0.4 to 900 µm/s. In this experiment, first the image of the SiNWs were taken and then the motion of them were recorded as movies. Micro-Raman scattering measurements were performed at room temperature (RT) with a 100x objective and a 532 nm excitation light at a power of 0.02 mW.

### 3. Results and discussion

#### 3.1. Size control of SiNWs

The diameter of SiNWs is controllable by changing the content of Fe catalyst. The dependence of the diameter on the content of Fe is shown in Fig. 1(a). The temperature was set at 1200 °C since, the eutectic point of Si–Fe alloy is around 1200 °C. The laser power was 200 mJ/pulse during the synthesis of SiNWs. The representative SEM images of SiNWs synthesized by laser ablation of the Si$_{100-x}$Fe$_x$ targets and the representative SEM images of SiNWs synthesized by laser ablation of (b) Si$_{90}$Fe$_{10}$ and (c) Si$_{98}$Fe$_{2}$ targets, respectively. The laser power was at about 200 mJ/pulse.

The average length of the SiNWs depended on the laser power, namely, about 3 µm in the case of 200 mJ/pulse and about 20 µm in the case of 100 mJ/pulse.

The diameter also depended on the synthesis temperature. The dependence of the diameter of SiNWs on the synthesis temperature has been investigated for recent our experiments [15], i.e. the diameter of SiNWs decreased with decreasing the synthesis temperature.

The dependence of the diameter of SiNWs on the content of metal catalyst can be explained by the following explanation. In case of the laser ablation method, Si atoms and metal catalysts are evaporated in atomic states by ablation and they form liquid nano-alloys by clustering in a high pressure of inert gas. The liquid nano-alloys act as seeds of SiNWs, i.e. the growth of SiNWs begins from the liquid nano-alloys after they become supersaturated in Si. The volume of the supersaturated liquid nano-alloys depends on the amount of Si atoms which can be dissolved into it before supersaturation and the amount of Si atoms decreases with decreasing that of metal catalyst in liquid nano-alloys.

![Fig. 1. (a) Dependence of the diameter of SiNWs on the content of Fe in Si$_{100-x}$Fe$_x$ targets and the representative SEM images of SiNWs synthesized by laser ablation of (b) Si$_{90}$Fe$_{10}$ and (c) Si$_{98}$Fe$_{2}$ targets, respectively. The laser power was at about 200 mJ/pulse.](image1)

![Fig. 2. Dependence of the diameter and length of SiNWs on the laser power. SiNWs were synthesized by laser ablation of Si$_{99}$Fe$_{10}$.](image2)
Consequently, the volume of the supersaturated liquid nano-alloy decreases with decreasing the amount of metal catalysts in liquid nano-alloy. Hence, the diameter of SiNWs decreases with decreasing the content of metal catalyst.

The diameter of SiNWs is also affected by the amount of ablation atoms. In Fig. 2, the diameter of SiNWs depended on the laser power. The amount of ablation atoms increases with increasing the laser power. This affects the size of supersaturated liquid nano-alloys and consequently the diameter of SiNWs increases with increasing the laser power. On the other hand, the explanation about the dependence of the length of SiNWs is difficult. The length of SiNWs is influenced by the duration of supersaturation and the amount of extra Si atoms dissolved into the liquid nano-alloys during supersaturation. The former probably do not strongly depend on laser power since the synthesis temperature and the content of Fe catalyst are constant. Considering the latter case, the growth of SiNWs from liquid alloys with smaller diameters is easier than that with larger diameters since SiNWs can grow even with smaller amount of extra Si atoms.

The temperature dependence of the diameter of SiNWs can be explained by the following explanation. The progress of the supersaturation decelerates at higher synthesis temperatures since Si-metal nano-alloys can keep melting states for longer time at higher temperatures. This leads to the formation of larger size of liquid nano-alloys and finally the increase in the diameter of SiNWs. Based on the results obtained in this study, thinner and longer SiNWs can be synthesized by decreasing the content of metal catalyst, laser power and synthesis temperature during laser ablation.

### 3.2. Manipulation of SiNWs

The investigation of the response of SiNWs to external fields and the manipulation by them are important for the application of SiNWs to intelligent nanoprobe [16] or nanotweezers. In this study, the response and the possibility of the manipulation of SiNWs were investigated during SEM observations as the first step. Fig. 3 shows the motion of SiNWs by electron beam irradiation during SEM observations. SiNWs were grown by ablating the Si$_{90}$Fe$_{10}$ target with a laser power of 100 mJ/pulse to synthesis longer SiNWs and to easily observe the response during the SEM observation. We used SiNWs deposited at the edge of Si wafer (Fig. 3(a)) since these kinds of SiNWs are freestanding and thereby they are very sensitive to the external fields compared to SiNWs deposited on the Si wafer surface. Here, SiNWs shown in SEM images show that one of the SiNW is not single but intertwined with another SiNW. In the case of the single SiNWs, the motion under electron beam irradiation is very big and fast. Therefore, the single SiNWs are sometimes broken by the abrupt and strong Coulomb repulsive interaction or they are detached from the Si substrate. The second case is due to that freestanding SiNWs are used for the manipulation experiments. Hence, it was difficult to investigate the motion of the single SiNWs in this study. The electron beam current was changed from 20 to 70 µA. The scan speed was set at 900 μm/s. By electron beam irradiation, the distance of adjacent SiNWs can be controlled to widen as shown in Fig. 3(b)–(e). After finishing the electron beam irradiation, the distance of the SiNWs was reverted back to the first immediately.

The motion of SiNWs showed more drastic change with increasing the electron beam current, i.e. it was controllable by changing the electron beam current as shown in Fig. 3(f). The separation width of the SiNWs increased with increasing the electron beam current. Furthermore, the speed of opening motion of SiNWs also depended on the electron beam current; i.e. it becomes faster with increasing the electron beam current. No response showed less than the electron beam current of 30 µA for SiNWs shown in Fig. 3(f). Furthermore, the motion of SiNWs depended on the scanning speed of electron beam. The scanning speed was changed from 0.4 to 900 μm/s. The separation between two SiNWs increased with decreasing the scanning speed.

The response of SiNWs like nanotweezers was repeatable many times over. This motion is probably caused by the Coulomb repulsive interaction between the adjacent SiNWs. Electrons irradiated during SEM observation
accumulate in SiNWs, resulting in the Coulomb repulsive interaction between them. The EDX spectrum obtained in this study confirmed the composition of individual SiNWs to consist of Si and oxygen. The oxygen signal resulted from a small fraction of native surface oxide. Furthermore, in order to check the existence of crystalline Si in the core of SiNWs, micro-Raman measurements and TEM measurements were performed. Fig. 4 shows optical phonon peaks observed for SiNWs synthesized by using Si$_{99}$Fe$_{10}$ target and for bulk-Si. The Raman shift observed for SiNWs is close to that for bulk-Si. This result shows that the core of SiNWs is crystalline Si. TEM images obtained for SiNWs synthesized by using Si$_{99}$Ni$_{1}$ target is shown in Fig. 5 as an example. The result clearly showed a Si lattice fringe in the core of the SiNW and a surrounding surface oxide layer. The surface oxide layer causes the charge accumulation for SiNWs because it is an insulator. The conductivity of crystalline Si core in SiNWs is much higher than that of the surface oxide layer. After intensive electron beam irradiation, accumulated electrons in the surface oxide layer diffuse away through the conductive Si core region to Si substrate, resulting the abrupt decrease in the Coulomb repulsive interaction. Finally, the distance of the SiNWs is reverted back to the first immediately.

4. Summary

Size control of SiNWs synthesized by laser ablation of Si targets with Fe catalysts was investigated. The diameter and length of SiNWs can be controlled by changing the synthesis parameters such as content of catalyst in targets and laser power during synthesis of SiNWs.

The control of the motion of SiNWs was performed during SEM observation for the first time. The motion is probably caused by the Coulomb repulsive interaction between the adjacent SiNWs and the distance and speed of opening motion of them depended on the current and the scanning speed of the electron beam.

Acknowledgements

Parts of this study were supported by the ‘Research Consortium for Synthetic Nano-Function Material Project’ of NEDO, and the 21 COE program entitled ‘Promotion of Creative Interdisciplinary Materials Science for Novel Functions.’ TEM observations were partly supported by ‘Nanotechnology Support Project’ of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

[1] Y. Cui, C.M. Lieber, Functional nanoscale electronic devices assembled using silicon nanowire building blocks, Science 291 (2001) 851–853.
[2] J.F. Wang, M.S. Gudiksen, X.F. Duan, Y. Cui, C.M. Lieber, Highly polarized photoluminescence and photodetection from single indium phosphide nanowires, Science 293 (2001) 1455–1457.
[3] X.F. Duan, Y. Huang, Y. Cui, J.F. Wang, C.M. Lieber, Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices, Nature 409 (2001) 66–69.
[4] Y. Cui, Q. Wei, H. Park, C.M. Lieber, Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species, Science 293 (2001) 1289–1292.
[5] R.S. Wagner, W.C. Ellis, Vapor–liquid–solid mechanism of single crystal growth, Appl. Phys. Lett. 4 (1964) 89–90.
[6] E.I. Givargizov, Fundamental aspects of VLS growth, J. Cryst. Growth 31 (1975) 20–30.
[7] A.M. Morales, C.M. Lieber, A laser ablation method for the synthesis of crystalline semiconductor nanowires, Science 279 (1998) 208–211.
[8] Y.F. Zhang, Y.H. Tang, N. Wang, D.P. Yu, C.S. Lee, I. Bello, S.T. Lee, Silicon nanowires prepared by laser ablation at high temperature, Appl. Phys. Lett. 72 (1998) 1835–1837.
[9] J. Westwater, D.P. Gosain, S. Usui, Control of the size and position of silicon nanowires growth via the vapor–liquid–solid technique, Jpn. J. Appl. Phys. 36 (1997) 6204–6209.
[10] Y. Cui, L.J. Lauhon, M.S. Gudiksen, J. Wang, C.M. Lieber, Diameter-controlled synthesis of single-crystal silicon nanowires, Appl. Phys. Lett. 78 (2001) 2214–2216.
[11] X. Zhao, C.M. Wei, L. Yang, M.Y. Chou, Quantum confinement and electronic properties of silicon nanowires, Phys. Rev. Lett. 92 (2004) 1–4 236805.
[12] D.P. Yu, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, J.S. Fu, H.Z. Zhang, Y. Ding, G.C. Xiong, L.P. You, J. Xu, S.Q. Feng, Direct evidence of quantum confinement from the size dependence of the photoluminescence of silicon quantum wires, Phys. Rev. 59 (1999) R2498–R2501.
[13] D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, S.T. Lee, Small-diameter silicon nanowire surfaces, Science 299 (2003) 1874–1877.
[14] S. Piscanec, M. Cantro, A.C. Ferrari, J.A. Zapien, Y. Lifshitz, S.T. Lee, S. Hofmann, J. Robertson, Raman spectroscopy of silicon nanowires, Phys. Rev. B68 (2003) 1–4 241312.
[15] N. Fukata, T. Oshima, K. Murakami, T. Kizuka, T. Tsurui, S. Ito, Phonon confinement effect of silicon nanowires synthesized by laser ablation, Appl. Phys. Lett. 86 (2005) 213112 (3p.).
[16] T.J. Vo-Dinh, Nanobiosensors: Probing the sanctuary of individual living cell, Cell. Biochem. 87 (2002) 154–161.