Nucleation and growth of Si nanowires from silicon oxide

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Nucleation and growth of Si nanowires by laser ablation and thermal evaporation of Si powder sources mixed with SiO₂ have been investigated by means of transmission electron microscopy. At the initial nucleation stage, Si oxide vapor condensed on the substrate and formed Si nanoparticles (the nuclei of nanowires). Each Si nanowire nucleus consisted of a polycrystalline Si core containing a high density of defects and a Si oxide shell. A growth mechanism was proposed based on the microstructure and different morphologies of the Si nanowires observed. [S0163-1829(98)51348-3]

The synthesis of one-dimensional nanostructures is a challenge in materials science. Since the successful growth of Si whiskers by the vapor-liquid-solid (VLS) reaction,^{1,2} many efforts have been made to synthesize Si nanowires by employing different methods, such as photolithography technique combined with etching³⁻⁵ and scanning tunneling microscopy.^{6,7} Recently, Si nanowires have been successfully synthesized by a different method, namely, the laser ablation of metal-containing Si targets.⁸⁻¹¹ Previous investigations^{8,9} showed that metal or metal-silicide nanoparticles acted as the critical catalyst during the synthesis assisted by laser ablation. Therefore, a growth mechanism of Si nanowires has been extrapolated from the VLS reaction.^{8,9} However, a different model has been proposed which is supported by the fact that metal catalysts are not necessary during synthesis by laser ablation.¹² SiO₂ was discovered to be the special and effective catalyst which largely enhances Si nanowire growth (see Table I). Moreover, structural investigations show that high-density defects and silicon oxide outer layers may play an important role for Si nanowire growth.¹² In this paper, we report the synthesis of Si nanowires by laser ablation and thermal evaporation of highly pure Si powder mixed with SiO₂. Included are observations of the microstructure and growth morphology of Si nanowire nuclei by transmission electron microscopy (TEM) and a discussion of the growth mechanisms.

The Si nanowires investigated in this work have been synthesized by laser ablation^{10,11} and thermal evaporation in an evacuated quartz tube containing Ar gas (500 Torr). The growth rate of Si nanowires was higher with the assistance of laser ablation than with thermal evaporation alone. Si nanowires synthesized by both methods had the same morphology. The solid source was highly pure Si powder mixed with approximately 70 wt % SiO₂ (all materials from Goodfellow, purity 99.99%). The temperatures around the source and the area of the quartz tube where the nanowires grew were about 1200 °C and 930 °C, respectively. After 12 h of thermal evaporation, a Si nanowire product (spongelike, dark red in color) formed on the inside wall of the quartz tube. To collect the Si nanowire nuclei, a Mo grid was placed in the region of the quartz tube where the nanowires grew. Some Si nanowires nucleated and grew on the grid. Structural inves-

tigation was carried out using a Philips CM200FEG transmission electron microscope working under 200 kV.

As demonstrated from the data in Table I the presence of SiO₂ in the powder targets significantly enhances Si nanowire growth. The Si nanowire product obtained by using a powder target composed of 50% SiO₂ and 50% Si is 30 times greater than the amount generated by using a metal containing target. In addition, very few Si nanowires form if Si single-crystal wafers or pure Si powder are used as targets. Since SiO₂ is the dominant impurity in the two kinds of targets mentioned, it is believed that in this case, the limited amount of Si nanowire formation that does occur is also due to the presence of SiO₂. Pure SiO₂ powder can not produce Si nanowires.

A typical morphology of the as-grown Si nanowires is shown in the TEM image in Fig. 1, where two major forms can be seen. Si nanowires with uniform diameters and smooth surfaces are one major component, while the other kind, Si nanoparticles coexist with the nanowires. Most Si nanowires are extremely long (>10 μm) and randomly oriented. It is interesting to note that most Si nanoparticles appear in the form of chain (as marked by the arrow). Short bars of amorphous silicon oxide connect these nanoparticles.

Figure 2(a) shows the initial nucleation stage of the Si nanowires on the Mo grid. Si nanoparticles formed first, as

TABLE I. Yields of Si nanowires for different experimental conditions.

Target (wt. %)	Furnace temperature (°C)	Yield (mg)
Si+1-3% Fe	1200	~0.1
Si water	1200	Very few <0.01
Si powder	1200	Very few <0.01
Si+5% SiO ₂	1200	~0.3
Si+10% SiO ₂	1200	~0.5
Si+30% SiO ₂	1200	~2.5
Si+50% SiO ₂	1200	~3.0
Si+70% SiO ₂	1200	~2.5
Si+90% SiO ₂	1200	~0.5
SiO ₂	800-1200	0

FIG. 1. TEM image showing two major morphologies of Si nanowires.

identified by electron diffraction and most piled up on the substrate. However, some particles (as marked by the arrow) stood alone from the others and grew fast since their preferable growth directions were normal to the surface of the substrate [see also Fig. 2(b)]. These preferable particles were indeed the nuclei of the nanowires. As revealed in Fig. 2(b), no obvious metal catalysts or impurities formed on the tip of the nucleus. The nucleus simply consisted of a Si crystalline core with a high density of defects and an amorphous outer layer. Since only silicon and oxygen were detected by electron energy dispersive spectrometer (EDS) *in situ* the microscope, the amorphous outer layer should be silicon oxide.

Because tip areas determine the one-dimensional growth phenomenon of Si nanowires, high-resolution transmission electron microscopy (HRTEM) was employed to investigate the microstructure of the tips. A typical Si nanowire tip is shown in the HRTEM image in Fig. 3(a). The tip is generally round and covered by a relatively thick amorphous layer. Because of this feature, under low magnification, a tip looked thicker than the nanowire itself. The contrast of the amorphous layer was quite uniform and only Si crystalline structure was observed within the tip. This is contrary to the nanowires grown by the VLS where metal drops were always formed on the tips. Similar to the microstructure of the nuclei, the Si crystal core in the nanowire tip contained a high density of stacking faults and micro-twins, which were along the axis of the nanowire in the $[\bar{1}12]$ direction. These kinds of defects have been observed in most Si nanowires in our previous work.¹⁰

We believe that the amorphous silicon oxide was the key factor which significantly enhanced the nucleation and one-

FIG. 2. (a) Si nanowire nuclei formed on the Mo grid and (b) initial growth stage of Si nanowire.

dimensional growth of the Si nanowires. The growth mechanism was different from that of the classic VLS growth of Si whiskers where Si vapor diffused into metal drops (e.g., Au) and accumulated causing one-dimensional growth of Si. In the present case, however, little Si vapor was generated under 1200 °C. This was evidenced by the fact that the material deposited on the water-cooled Cu finger surface was Si_xO_y ($x=0.51$, $y=0.49$) as determined by EDS. Since the vapor phase was quenched on the cooled finger, the chemical composition of the material did not change. This indicated that the vapor phase generated by thermal evaporation of the solid source ($\text{Si}+\text{SiO}_2$) mainly consisted of SiO. The formation of SiO was due to the reaction of Si and SiO_2 since SiO is known to be an amorphous semiconductor of high resistivity that is easily generated from powder mixtures (especially in equimolar amounts of mixtures) of Si and SiO_2 by heating.^{13,14} The nucleation of nanoparticles may involve different decompositions of the Si oxide vapor phase at a relatively low temperature of 930 °C as shown below:

These decompositions resulted in the precipitation of silicon nanoparticles (the nuclei of Si nanowires) surrounded by shells of silicon oxide as observed in Fig. 2(a). Such precipitation of Si nanoparticles from SiO by annealing has been quite well known since the 1950s.¹⁵

FIG. 3. HRTEM images of (a) Si nanowire tip and (b) Si nanoparticle chain.

The growth mechanism of Si nanowires is suggested to be determined by the following factors: (1) the catalytic effect of the relatively thick Si_xO layer on nanowire tips; (2) the SiO_2 (much more stable than SiO) component in the shell, which is formed from the SiO decomposition and retards the

lateral growth of nanowire; (3) the main defects in the Si nanowires, which are stacking faults (along the nanowire growth direction of $\langle 112 \rangle$) and microtwins. The presence of these kinds of defects at the tip areas should result in the fast growth of Si nanowires; (4) the $\{111\}$ surface, which has the lowest surface energy among the Si surfaces, plays an important role during nanowire growth. Since surface energy is more important when the crystal size is reduced to nanometer scale, the presence of the $\{111\}$ surfaces parallel to the axes of the nanowires reduces the system energy. These important factors determine the growth direction of Si nanowires to be $\langle 112 \rangle$.

According to the mechanism discussed above, nucleation and growth occurred at all times during evaporation since the SiO vapor phase was continually generated. Nuclei formed on nanowire tips with different crystalline orientations during growth. These unfavorable nuclei could not grow fast along the nanowire and would cause a change of growth direction or renucleation. Such renucleations resulted in the formation of nanoparticle chains (see Fig. 1) which coexisted with the nanowires. A HRTEM image taken from a Si nanoparticle chain supports this growth mechanism. As shown in Fig. 3(b), the Si particles in the chain have different orientations and most are not aligned with their $\langle 112 \rangle$ directions parallel to the growth direction.

In summary, TEM study of Si nanowire nucleation and growth indicated that thermal evaporation of Si powder mixed with SiO_2 generated a Si oxide vapor phase. At the initial nucleation stage, Si oxide vapor condensed on the substrate and formed Si nanoprecipitates. Si nanowire nuclei consisted of a polycrystalline Si core with a high density of defects. The Si oxide vapor phase and defect structure acted as key factors which greatly enhanced the nucleation and one-dimensional growth of Si nanowires.

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¹R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).

²E. I. Givargizov, *J. Cryst. Growth* **32**, 20 (1975).

³H. I. Liu, N. I. Maluf, and R. F. W. Pease, *J. Vac. Sci. Technol. B* **10**, 2846 (1992).

⁴H. Namatsu, S. Horiguchi, M. Nagase, and K. Kurihara, *J. Vac. Sci. Technol. B* **15**, 1688 (1997).

⁵Y. Wada, T. Kure, T. Yoshimura, Y. Sudou, T. Kobayashi, Y. Gotou, and S. Kondo, *J. Vac. Sci. Technol. B* **12**, 48 (1994).

⁶T. Ono, H. Saitoh, and M. Esashi, *Appl. Phys. Lett.* **70**, 1852 (1997).

⁷R. Hasunuma, T. Komeda, H. Mukaida, and H. Tokumoto, *J.*

Vac. Sci. Technol. B **15**, 1437 (1997).

⁸A. M. Morales and C. M. Lieber (unpublished).

⁹A. M. Morales and C. M. Lieber, *Science* **279**, 208 (1998).

¹⁰N. Wang, Y. H. Tang, Y. F. Zhang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, *Chem. Phys. Lett.* **283**, 368 (1998).

¹¹Y. F. Zhang, Y. H. Zhang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, *Appl. Phys. Lett.* **72**, 1835 (1998).

¹²N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, and S. T. Lee (unpublished).

¹³S. W. Roberts, G. J. Parker, and M. Hempstead, *Opt. Mater.* **6**, 99 (1996).

¹⁴U. Setiowati and S. Kimura, *J. Am. Ceram. Soc.* **80**, 757 (1997).

¹⁵G. Hass and C. D. Salzberg, *J. Opt. Soc. Am.* **44**, 181 (1954).