

Control of Surface Migration of Gold Particles on Si Nanowires

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Received September 14, 2007; Revised Manuscript Received November 24, 2007

ABSTRACT

On the surface of silicon nanowires (SiNWs) synthesized by gold (Au)-catalyzed chemical vapor deposition (CVD), Au particles 5–20 nm in diameter are formed if the growth conditions are within a specific range. We studied the mechanism of Au particle formation by growing SiNWs under different conditions, specifically by dynamically changing the growth parameters during the growth process. We show that insufficient supply of Si source to the Au–Si eutectic on top of the SiNWs enhances the migration of Au atoms on the surface of SiNWs in the form of Au–Si eutectic, which is precipitated on the surface as Au particles during cooling. We also show that using Au–Si eutectic on the surface of SiNWs as a catalyst enables one-step growth of branched SiNWs.

Semiconductor nanowires (NWs) have recently attracted considerable research attention due to their unique physical properties^{1,2} and potential for device application as transistors,^{3,4} chemical sensors,^{5,6} and light-emitting devices.^{7,8} In particular, Si NWs (SiNWs) have been studied extensively because of their high compatibility with standard CMOS technology and possible integration in future electronic devices. To realize SiNW-based electronic devices, it is important to gain precise control of their length, diameter, conductivity, and contamination and to ensure they are kink-free. Of these, one of the most crucial but least-studied problems is contamination by catalysts. In general, SiNWs are grown using a vapor–liquid–solid (VLS) process^{9–11} employing heavy metals such as Au, Ag, Co, Cu, Ni, and Ti as catalysts.^{12,15} Gold is the most widely used catalyst for SiNW growth because of its simple eutectic-type phase diagram and low eutectic temperature ($\sim 360^\circ\text{C}$). However, Au is known to diffuse very rapidly into Si and make deep centers that increase p–n junction leakage and decrease dielectric strength. Therefore, understanding the behavior of Au in SiNWs during VLS growth is crucial for application of SiNWs in electronic devices. Recently, several groups have reported the behavior of Au in SiNWs. Yu et al. found

that Au is doped into SiNWs due to thermal diffusion of Au atoms from Au catalysts.¹³ Furthermore, Bauer et al. showed that Au particles are precipitated on the interface between native SiO_2 and SiNWs.¹⁴ Gold particles on the surface of SiNWs may affect the electric transport properties of SiNWs and thus the mechanism of their formation, so their relation to growth parameters needs to be fully clarified.

The purpose of this study is to gain an understanding of the behavior of Au atoms in SiNWs during VLS growth and to reveal the mechanism of Au particle formation. To achieve this, we grew SiNWs under a wide range of growth parameters. Furthermore, growth conditions were changed dynamically during SiNW growth and the effects were studied in detail by transmission electron microscopy (TEM). We showed that there are strong correlations between growth rate, crystallinity, and Au particle formation, all of which are controlled by the amount of Si supplied to the Au catalyst. We also compiled guidelines on minimizing the diffusion of Au atoms and preventing the formation of Au particles.

SiNWs were synthesized via VLS growth using a cold-wall infrared (IR) lamp-heated chemical vapor deposition (CVD) apparatus. Thermally oxidized Si (100) wafers were first treated with oxygen plasma and then dipped into a 1 wt % solution of 3,5-diaminopentyltrimethoxysilane. The wafers were then dipped into a gold colloid solution (Tanaka Kikinzoku Co.) for 5–30 min for attachment of Au particles. After drying, the wafers were loaded into the CVD chamber. The flow rates of Si_2H_6 precursor and H_2 were 100 and 0–1800 sccm (cubic centimeters per minute at STP), respectively. The partial pressure of the Si_2H_6 precursor was

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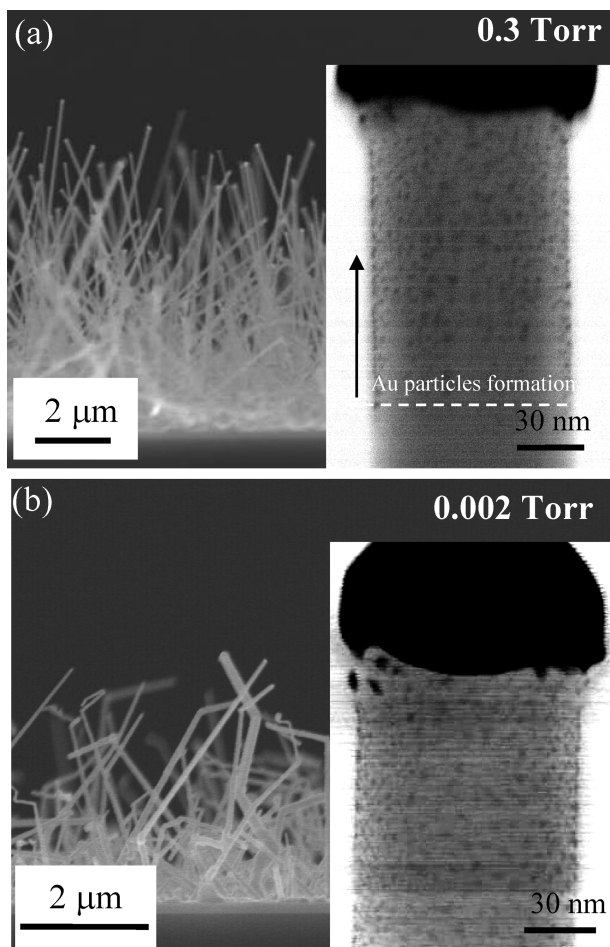


Figure 1. Cross-sectional SEM images of SiNWs grown at a total pressure of (a) 0.3 Torr and (b) 0.002 Torr. Insets are corresponding TEM images.

about 0.002 Torr. The total pressure was changed from 0.002 to 2 Torr by changing the flow rate of H_2 . The growth temperature was fixed at 450 °C. The growth duration was varied between 5 and 30 min. To study the mechanism of formation of Au particles, samples were annealed in different atmospheres, i.e., ultrahigh vacuum ($\sim 10^{-9}$ Torr) and in H_2 gas (~ 0.3 Torr), in the CVD chamber by lamp heating at 450 °C without air exposure after growth. The annealing duration was 10 min. Furthermore, to examine the influence of native oxide on the formation of Au particles, some samples were exposed to air prior to the annealing (N_2 gas ~ 1 atm, 450 °C, 10 min).

SiNWs were characterized by scanning electron microscope (SEM) (Hitachi, S-4000) and transmission electron microscope (TEM) (JEOL JEM-4000DX). For plan-view TEM observations, SiNWs were separated from the growth substrates by ultrasonication in ethanol, and the solvent containing SiNWs was dropped onto a microgrid. For cross-sectional TEM observations, SiNWs were cut by focused ion beam (FIB). Elementary analyses of SiNWs, especially the Au distributions within SiNWs, were performed by energy-dispersive X-ray spectroscopy (EDS) in TEM (TEM-EDS).

Figure 1 shows SEM and TEM images of SiNWs prepared at different total pressures. The samples shown in Figure 1a are prepared at a relatively high total pressure (0.3 Torr) and

those shown in Figure 1b at a relatively low total pressure (0.002 Torr). The growth duration for the sample in Figure 1a is 10 min, whereas that in Figure 1b is 30 min. Note that the partial pressure of the Si_2H_6 precursor is the same (0.002 Torr), and the total pressures are controlled by the flow rate of H_2 carrier gas. A comparison of panels a and b in Figure 1 clearly shows a difference in the shape of SiNWs; SiNWs grown at higher pressure (Figure 1a) are straight, whereas those at lower pressure (Figure 1b) have kinks. We believe that the kinks appear where the growth direction changes.¹² In general, the more defective the SiNWs, the more kinks appear.

In VLS growth of SiNWs, the amount of Si source gas supplied to Au catalysts depends both on the partial pressure of Si_2H_6 precursor (the flow rate of Si_2H_6) and the total pressure, since the mean free path of the Si source gas correlates with the total pressure; that is, a higher total pressure results in a larger supply of Si source to Au catalysts. Since, under our growth conditions, the growth rate is limited by the supply of the Si source, a larger supply of Si source due to a higher total pressure results in a higher growth rate. In fact, the growth rate in Figure 1a (total pressure: 0.3 Torr; $0.7 \mu m/min$) is more than four times greater than that in Figure 1b (total pressure: 0.002 Torr; $0.15 \mu m/min$), although the partial pressure of the Si_2H_6 precursor is the same (see the Supporting Information, Figure S4a, where the growth rate is plotted as a function of the total pressure at a fixed Si_2H_6 partial pressure). Figure 1 thus indicates that SiNWs grown at higher rates in an environment containing sufficient Si have higher crystallinity than those grown at lower rates under deficient Si supply conditions.

The insets in panels a and b of Figure 1 show TEM images of SiNWs. The black hemispheres at the top of the SiNWs are Au catalysts. Their diameters are usually 80–100 nm and are almost the same as those of the SiNWs grown from them. In addition to the black hemispheres, for the SiNW grown at a lower total pressure, small particles are observed to cover the surface. TEM-EDS analyses reveal that these particles are chiefly composed of Au atoms with diameters of 5–20 nm (see the Supporting Information, Figure S1). Note that one cannot distinguish whether these particles are pure Au or Au–Si alloy in the TEM-EDS analyses because of the background signal from the SiNWs. In contrast to SiNWs grown at lower total pressure, those grown at higher total pressure have Au particles in only a limited region near the Au catalyst (Figure 1b). We carried out SEM and TEM observations by systematically changing the total and Si_2H_6 partial pressures during the growth. We found that the formation of Au particles has a strong correlation with the growth rate of SiNWs. In the present SiNW growth system, Au particles are grown when the growth rate of SiNWs is smaller than $0.7 \mu m/min$ (see the Supporting Information, Figure S4).

We also studied the effects of growth temperature on the formation of Au particles by SEM and TEM. In the present growth conditions with Si_2H_6 as the Si source gas, high-quality single-crystal SiNWs can be grown within the temperature range of 350 and 500 °C. We therefore

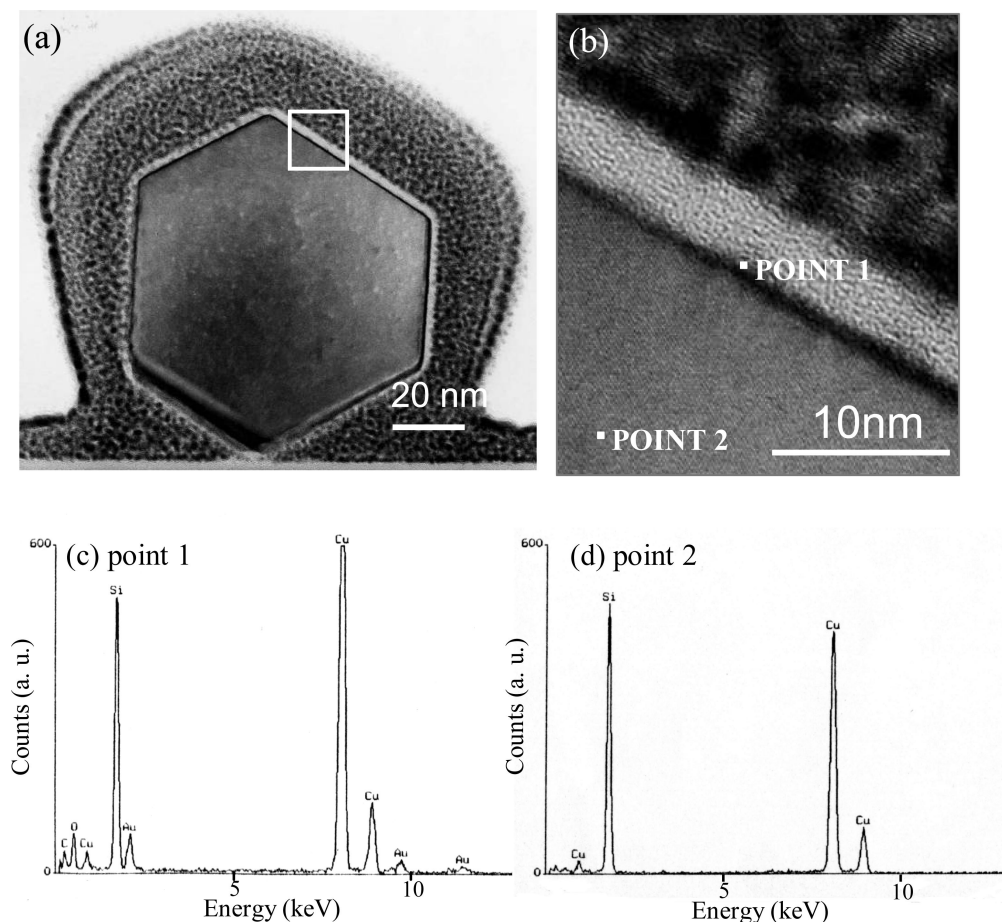


Figure 2. (a) Cross-sectional TEM image of a SiNW. Magnification of the region marked by the framed rectangle is shown in panel b. EDS spectra of points 1 and 2 in panel b are shown in panels c and d, respectively. The copper (Cu) signals in EDS spectra come from the microgrid and the sample holder.

performed experiments similar to those shown in Figure 1, panels a and b, i.e., growth at different total pressures at a fixed Si_2H_6 partial pressure, at growth temperatures of 350 and 500 °C. We found that the results are very similar to those shown in Figure 1, panels a and b, irrespective of the growth temperature; that is, defective and kinked SiNWs with Au nanoparticles in a wide range are grown only when the total pressure is low (0.002 Torr) and straight SiNWs with Au nanoparticles in a limited range near catalysts are grown at the high total pressure condition (0.3 Torr; see the Supporting Information, Figure S3).

A similar total pressure dependence of the formation of Au particles is observed when different kinds of carrier gases, helium (He) and argon (Ar) instead of H_2 , are used for CVD growth. Furthermore, even when SiNWs are grown only with a Si source gas (without any carrier gas), the pressure dependence is similar (see the Supporting Information, Figure S2).

Figure 2a shows a cross-sectional TEM image of a SiNW grown under the same conditions as those in Figure 1b. We can see that the cross-section of the SiNW is hexagonal.¹⁹ Figure 2b shows expansion of the region shown by the square in Figure 2a. Formation of native SiO_2 about 2 nm in thickness can be seen on the surface of the SiNW. Panels c and d in Figure 2 show EDS spectra at point 1 (SiNW/ SiO_2

interface) and point 2 (within SiNWs) in Figure 2b. The diameter of the electron beam for TEM-EDS is about 1–2 nm. We see that signals from Au atoms are detected at point 1, whereas they are below the detection limit at point 2. This means that Au particles are formed on the surface of SiNWs and are not incorporated into the bulk region.

The pressure-dependence of the formation of Au particles can be demonstrated by changing the pressure dynamically during the growth of SiNWs. We first grew SiNWs at a total pressure of about 0.3 Torr for 5 min. The pressure was then decreased to 0.002 Torr, and the SiNWs were continuously grown for 20 min. To change the total pressure, only the H_2 gas flow rate was changed while the partial pressure of the Si_2H_6 precursor (the Si_2H_6 gas flow rate) was fixed at 0.002 Torr (100 sccm). TEM images of a SiNW grown using this procedure are shown in Figure 3. A SiNW with a kink is seen in the low-magnification image in Figure 3a. In VLS growth of SiNWs, kinks are believed to occur due to instability at the liquid/solid interface.¹² In the SiNW shown in Figure 3a, formation of the kink is considered to be due to instability at the liquid/solid interface induced by the sudden change in pressure during the growth. Figure 3b–d shows high-magnification dark-field TEM images of the top, middle, and bottom parts of the SiNW in Figure 3a. In the top part (Figure 3b), bright areas corresponding to Au

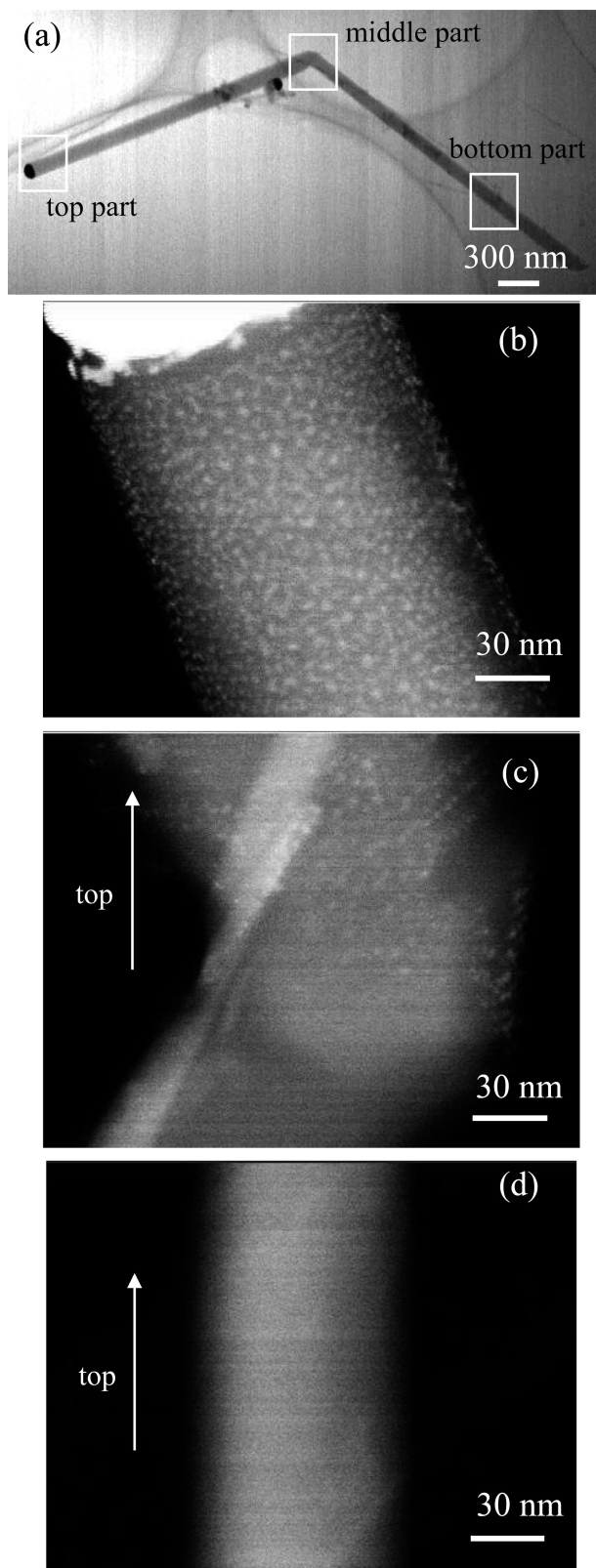


Figure 3. TEM images of a SiNW grown using a two-step process, i.e., first grown at 0.3 Torr for 10 min, and then at 0.002 Torr for 20 min (a) low-magnification image. Dark-field TEM images of the region marked by a framed rectangle in (a) are shown in panels b–d. Panels b–d correspond to the top, middle, and bottom of the SiNW, respectively.

particles are seen over the whole region. On the other hand, Au particles are not found in the bottom part (Figure 3d). In

the middle part (Figure 3c), Au particles are observed above the kink, but not below. Figure 3 thus clearly demonstrates the correlation between the formation of Au particles and total pressure.

The results of Figure 3 suggest that, by sudden change of the total pressure, formation of Au particles on desired region of SiNWs is possible. This position-controlled Au particle formation may allow us to grow branched SiNWs with branches at desired regions.

In the above experiments, total pressure was changed while the partial pressure of the Si_2H_6 precursor was maintained. Next, we changed the partial pressure of the Si_2H_6 precursor (the flow rate of Si_2H_6) while maintaining total pressure. The procedure was as follows. First, we grew SiNWs under the conditions illustrated in Figure 1a for 10 min. Under these growth conditions, Au particles are formed only in the region very close to the catalysts. We then stopped the supply of Si_2H_6 but held the total pressure for 10 min by regulating the flow rate of H_2 . The SiNWs were thus kept in an H_2 atmosphere at 450 °C for 10 min. TEM images of a SiNW grown using this procedure are shown in Figure 4, panels a and b; Figure 4a corresponds to a TEM image at the top of the SiNW, and Figure 4b to that at the middle (about 6 μm from the top). We can see Au particles on the surface of the SiNW in both panels a and b of Figure 4. This means that Au atoms migrate a significant distance along the surface of the SiNW after the Si_2H_6 flow is stopped. In Figure 4b, we notice that the density of Au particles is high on the upper half of the SiNW, whereas Au particles are only rarely observed on the lower half. Detailed observation of the whole region of the SiNW reveals that the migration distance of Au particles in this SiNW is about 6 μm . It is worth noting here that the migration distance is not always 6 μm but is distributed over a rather wide range. However, the important fact is that the migration distance always increases significantly by heating SiNWs in H_2 gas after growth.

The distance of Au migration is enhanced much further when the flow of both Si_2H_6 and H_2 is stopped and the growth chamber is pumped out to create an ultrahigh vacuum. The temperature is maintained at the growth temperature. Panels c and d of Figure 4 show TEM images of the top and bottom, respectively, of a SiNW kept in ultrahigh vacuum ($\sim 10^{-9}$ Torr) at 450 °C for 10 min after growth. We can see that Au particles are formed over the whole surface of the SiNW and the catalyst metal disappears. Under these conditions ($\sim 10^{-9}$ Torr, 450 °C, 10 min), Au particles do not evaporate. Therefore, the disappearance of the Au catalyst suggests that in ultrahigh vacuum at 450 °C, formation of thin Au–Si eutectic over the large area of SiNW surfaces is energetically lower than keeping Au–Si eutectic on top of SiNWs.

At present, the mechanism of longer diffusion length of Au atoms in ultrahigh vacuum than in H_2 gas is not clear. One possible explanation is that the melting point of the Au–Si alloy is lower in a vacuum than in an H_2 gas atmosphere.

In the light of the results in Figures 1–4, the mechanism of Au particle formation can be explained as follows. SiNWs

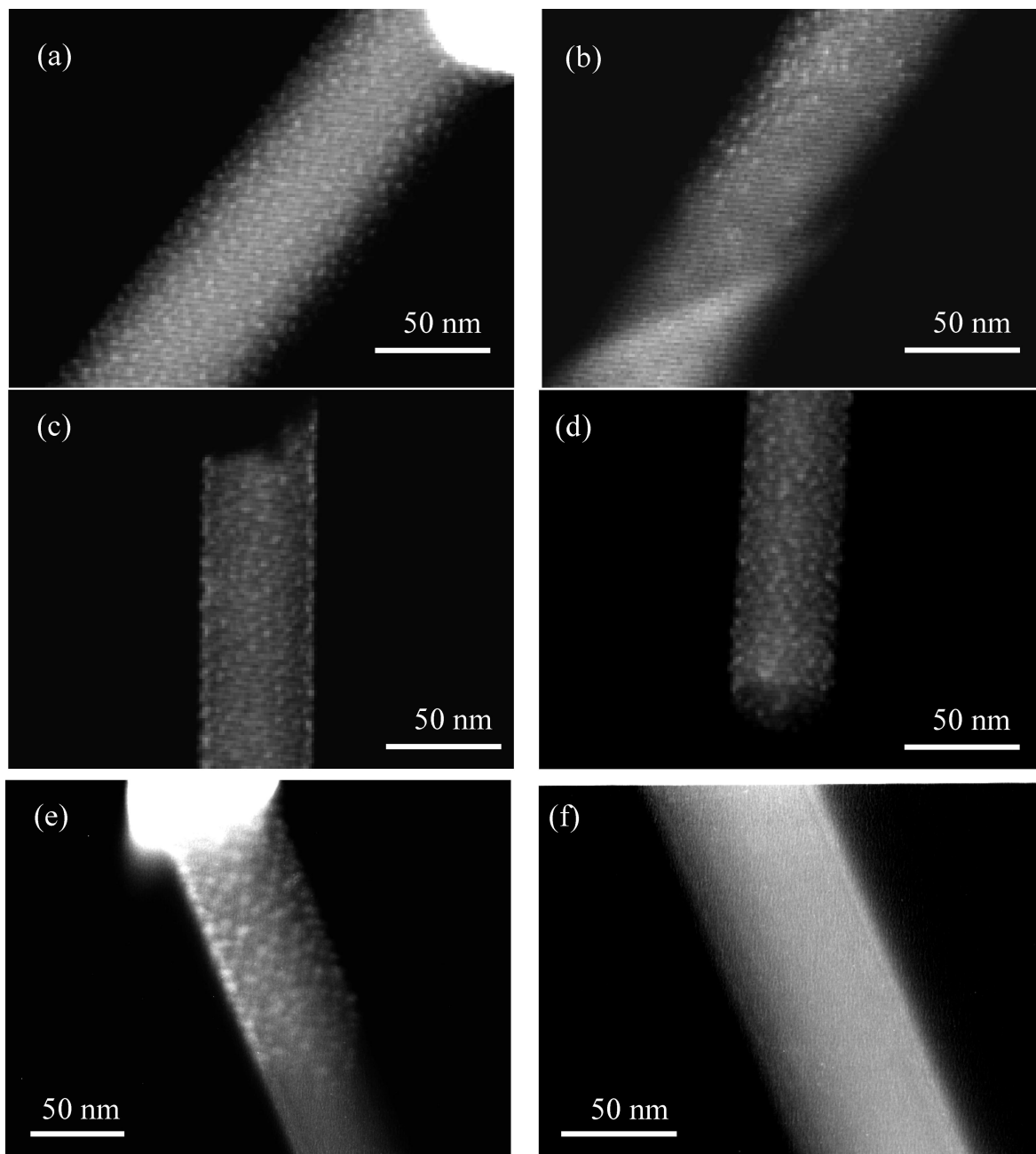


Figure 4. (a and b) Dark-field TEM images of the top and the middle (about $6\ \mu\text{m}$ from the top) of a SiNW, respectively, annealed in H_2 gas (0.3 Torr) without air exposure after growth. (c and d) Dark-field TEM images of the top and bottom of a SiNW, respectively, annealed under an ultrahigh-vacuum ($\sim 10^{-9}$ Torr) without air exposure after growth. (e and f) Dark-field TEM images of the top and the middle (about $6\ \mu\text{m}$ from the top) of a SiNW, respectively, annealed in nitrogen gas atmosphere (1 atm) after air exposure.

are known to be grown in the mixed phase of a eutectic Au–Si droplet (liquid) and Si solid due to precipitation of Si atoms at liquid/solid interfaces.¹⁸ When sufficient Si source is supplied to Au catalysts and the growth rate is high, the Si concentration in a Au–Si eutectic droplet is likely to be close to uniform, resulting in stable growth of straight SiNWs, as can be seen in Figure 1a. On the other hand, when the supply of Si source is not sufficient, the phase diagram shifts to an Au-rich position and excess Au atoms are present in the droplet. In this situation, the Au and Si concentration in the droplets is not uniform and is thus unstable. This instability in the concentration at liquid/solid interfaces results in the formation of defective SiNWs with kinks as shown in

Figure 1b. Furthermore, the existence of excess Au atoms results in the migration of Au atoms along the SiNW surface by forming Au–Si eutectic on the surface of the SiNWs. The migration of Au atoms results in the shrinkage of Au catalysts and formation of Au particles on the surface of SiNWs during cooling. An extreme case of this is seen in panels c and d of Figure 4, where Au catalysts disappear completely and Au particles precipitate over the whole surface.

For long-distance migration of Au atoms on the surface of SiNWs, formation of Au–Si eutectic is considered to be crucial.²⁰ To confirm this, we annealed SiNWs after exposure to air and compared the results with those obtained from in

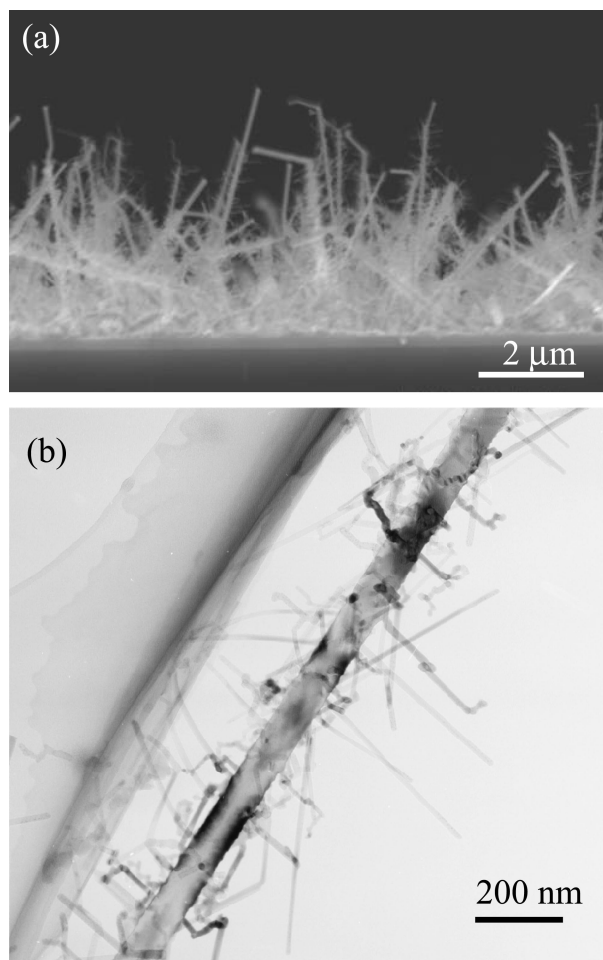


Figure 5. (a) Cross-sectional SEM and (b) TEM images of SiNWs grown at intermediate pressure (about 0.1 Torr). A SiNW with thin branches can be seen.

situ annealing (Figure 4a–d). Air exposure results in a thin native oxide to be formed on the surface of the SiNWs. Panels e and f of Figure 4 show TEM images of the top and middle (about 3 μm from the top) of a SiNW annealed in nitrogen atmosphere (~ 1 atm) at 450 $^{\circ}\text{C}$ for 10 min after air exposure. Au particles are formed only up to about 200 nm from the top. Au migration is thus prevented by the thin native oxide layer. Suppression of Au migration after air exposure is also observed even when SiNWs are annealed at higher temperatures and lower pressures. Similarly, for growth of SiNWs in the presence of oxygen, suppression of surface migration of Au is reported.^{17,20}

Under the growth conditions in Figure 1b, Au particles are formed over the whole surface. This means that Au–Si eutectics cover the surface of the SiNWs during growth. It is very plausible that these Au–Si eutectics can also catalyze SiNW growth if they are super-saturated with Si. To experimentally demonstrate this, we grew SiNWs at the boundary pressure (about 0.1 Torr) below which Au particles are formed over a large area of the SiNW surface. The total pressure is again controlled by changing the H_2 flow rate. The other growth parameters are the same as those of the samples in Figure 1. The growth duration is 10 min. Panels a and b in Figure 5 show cross-sectional SEM and TEM

images, respectively, of the SiNWs. SiNWs with multiple branches are observed. The diameter of the backbone SiNW is about 60–100 nm, and those of the branched SiNWs are about 5–20 nm. The growth rate of the branches is estimated to be about 0.3 $\mu\text{m}/\text{min}$. The growth of branched SiNWs can be explained as follows. With an insufficient supply of Si source, Au atoms migrate to the sidewalls of SiNWs in the form of Au–Si eutectic, which then acts as a catalyst, and SiNW branches grow on the sidewalls of SiNWs. Because of insufficient Si supply and the resultant low growth rate, branched SiNWs are highly defective, and many kinks can be seen (Figure 5b). It should be stressed here that the branched SiNWs are grown in one step under fixed growth conditions, i.e., both SiNW backbones and SiNW branches extend simultaneously during growth. The growth of branched SiNWs in one step excludes the possibility that Au atoms are incorporated into the interior of SiNWs during growth and are precipitated to the surface during cooling.

Finally, we discuss the mechanism of Au particle formation near Au catalysts (~ 100 nm from the top) even when total pressure is high (Figure 1a), i.e., sufficient Si is supplied. This is just due to the different response time of pressure and temperature in our CVD apparatus. To stop SiNW growth, gas flow is stopped and the growth chamber is pumped out to be ultrahigh vacuum; simultaneously, the substrate heating lamp is switched off. However, the temperature response is rather slow, and it takes about 1 min for it to fall below 300 $^{\circ}\text{C}$. During the drop in temperature, the situation is similar to that illustrated in Figure 4, panels c and d, i.e., annealing in an ultrahigh vacuum. Therefore, migration of Au atoms is possible during this time, and Au particles are formed in regions very close to the catalysts. Since the cooling speed is not controlled and not uniform, the migration distance varies slightly from wafer to wafer and also within each wafer, e.g., the migration distance in Figure 4e is greater than that in Figure 1a, despite the same growth conditions. To minimize the migration of Au atoms and prevent the formation of Au particles, samples should be cooled very fast after growth, or Si source gases should be continuously supplied until the samples have cooled.

In this study, we grew SiNWs under different conditions, specifically by dynamically changing the growth conditions during growth, and studied them using TEM and TEM-EDS. We found that migration of Au particles on the surface of SiNWs and the resulting formation of Au particles is due to insufficient supply of Si source to Au–Si eutectic. An insufficient Si supply results in a low growth rate of SiNWs and also induces instability in the Au–Si eutectic, which in turn causes the growth of defective SiNWs with kinks. Furthermore, the presence of excess Au in catalysts enhances the migration of Au atoms along the SiNW surface by forming Au–Si eutectic on the surface of the SiNWs. The migration of Au atoms results in the shrinkage of Au catalysts and the formation of Au particles on the surfaces of the SiNWs during cooling. We also show that one-step growth of branched SiNWs is possible by choosing proper growth conditions.

Acknowledgment. The authors thank Mr. Hiroyuki Masuda, Mr. Kenji Harada, Mr. Takayuki Takeuchi, and Mr. Norishige Nanai for experimental support and discussions on this work. The authors thank Mr. Sadayoshi Hotta and Mr. Goh Imamura for their suggestions and discussion on this work. This research was supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: TEM and SEM images of SiNW. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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NL072366G