Si Nanowires

Size-Dependent Surface Migration of Au Alloys on Si Nanowires at Different Cooling Rates

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Abstract: Understanding metal alloy migration in metal-catalyzed nanowires growth is a prerequisite for improving its potential applications in the field of nanodevices. Here, we explored the surface migration of Au alloys in vertically aligned Si nanowires with different cooling rates. We varied the diameter of Au alloys by controlling the thickness of Au film as a catalyst for SiNW growth, and found that the behavior of Au alloys migration is dependent on size of Au alloys. In addition, the size-dependent migration mechanism of Au alloys was investigated at different cooling rates, which is related to different Au-Si eutectics.

Low-dimensional silicon nanomaterials, such as Si nanoparticles (NPs) and nanowires (NWs), are attractive as building blocks for improving the performance of novel nanodevices, including field-effect transistors,[1] sensors,[2] solar cells,[3] and biological devices.[4] To successfully apply SiNWs to such devices, it is important to accurately control the diameter,[5] length,[6] and density[7] of NWs, as these parameters directly influence the device performance. In general, SiNWs can be synthesized using various methods, such as laser ablation,[8] molecular beam epitaxy,[9] and chemical vapor deposition (CVD)[10] via a vapor-liquid-solid (VLS) mechanism assisted by a metal catalyst.[11] The VLS mechanism is crucial for the fabrication of high-quality single-crystalline one-dimensional nanostructures and it is necessary to understand the growth process to achieve control of the morphologies of the NWs, including their diameter,[12] length,[13] density,[14] growth direction,[15] and shape.[16]

SiNWs were successfully grown via a Au catalyst-assisted VLS mechanism by exploiting the availability, stability, and nontoxicity of Au.[17] The production of SiNWs incorporated into Au alloys is desirable; however, one major problem with this method is the contamination of the sidewalls of the SiNWs by the Au alloy due to the rapid diffusion and migration of Au into Si.[18] The Au contaminations caused by Au migration on the NWs can act as impurities, leading to deep levels in the bandgap and the degradation of electronic properties.[19] Therefore, it is important to understand the migration behavior of Au alloys on/in SiNWs to ensure their successful application in electronic devices. To date, the studies on Au migration behavior have focused on various aspects of Au alloy migration from the tops of the NWs during the growth step, highlighting the growth parameters, such as partial pressure of the precursor and growth temperature.[20,21] However, surface migration of Au alloys induced by different cooling conditions has not been reported yet. Considering the influence of temperature on the kinetics of Au migration, variation of the cooling conditions, such as cooling rate and duration, is expected to induce different surface migration behaviors of Au alloys, affecting the overall quality of the resulting SiNWs.

In this study, for the first time, the surface migration behavior of Au alloys is explored through variation of the cooling conditions after growth of vertically aligned SiNWs (v-SiNWs) via a Au cataly-stassisted VLS mechanism. We controlled the size of the as-produced Au alloys at the tops of the SiNWs by regulating the thickness of the Au film as a catalyst for SiNW growth and investigated the size-dependent behavior of the Au alloy at different cooling rates. The Au alloys remained on the tops of the SiNWs during fast cooling, regardless of the Au alloy diameter, because of the short duration of the high temperature. In contrast, during slow cooling, small Au alloys migrated along the sidewalls of the SiNWs, whereas large Au alloys stayed at the top of the SiNWs. This behavioral difference is related to the different Au-Si eutectics, which is dependent on the diameter of the Au alloy. Remarkably, v-SiNWs that were cooled slowly accelerated the oxidation of gold silicide in the Au alloy.

The v-SiNWs were grown by CVD via a Au catalyst-assisted VLS mechanism as shown in Figure 1 and in the Experimental Section. Figure 2 shows 20° tilt-view scanning electron microscopy (SEM) images of the v-SiNWs grown using Au films of different thicknesses as catalysts, cooled at different rates. The diameters of the SiNWs were controlled by varying the thickness of the Au film, because thicker Au films form larger Au nanoparticles (AuNPs) resulting in thick-SiNWs.[14] Under growth temperature conditions, the agglomeration of the Au film on the Si substrate occurred via coalescence and Ostwald ripening to reduce the total interfacial energy of the system, forming AuNPs on the Si substrate.[22] The average diameters of the produced SiNWs were 160 ± 24.07 and 250 ± 41.78 nm for the 5- and 10 nm-thick Au films, denoted as thin- and thick-SiNWs,
respectively, under equivalent growth conditions, as shown in Figure 2. According to the VLS growth mechanism, the diameter of the NWs was determined by the size of the Au alloy that was present at the top of the NWs during the NW growth. 

When the v-SiNWs were cooled at the fast cooling rate of $13^\circ \text{s}^{-1}$, spherical Au alloys were observed at the top of both the thin- and thick-SiNWs, because the SiNWs were maintained at the high temperatures required for migration of the Au alloys for only a short period of time (Figure 2a and b). However, the migration behavior of the Au alloys was different based on their size at the slow cooling rate of $0.271^\circ \text{s}^{-1}$ after SiNW growth. In this case, the Au had sufficient time to migrate onto the SiNW because of the longer exposure to high temperature conditions. All Au alloys migrated along the sidewalls of the thin-SiNWs, and no Au alloys were observed at the tops of these NWs, as shown in Figure 2c. Although the Au alloys can migrate from the tops of the SiNWs to their sidewalls when the NW diameter is relatively small, caused by large diameter distribution, Au alloys were observed at the tops of 66% of the thick-SiNWs grown on a 10 nm-thick Au film, and their shape was flower-like, as shown in Figure 2d.

Morphological differences in the Au alloy were investigated through X-ray diffraction (XRD) analysis of the v-SiNWs synthesized with different Au film thicknesses and cooling rates, as shown in Figure 3. The XRD patterns of the SiNWs cooled at
rates of 13 and 0.271 °C s⁻¹ showed a major Si(111) peak (PDF#00-003-0544) at 28.58°, which indicates that epitaxial growth of the SiNWs was common among all the SiNWs. However, the relative intensities of the gold silicide peaks at 34.68°, 35.66°, and 39.52°, corresponding to Au₃Si(121), Au₃Si(014) (PDF#00-024-0463), and Au₅Si₂(130) (PDF#00-036-0938), respectively, differed among the samples.

Incorporation of Si into Au during VLS growth and consequent formation of liquid-phase gold silicide in the Au alloys could proceed via one of two possible mechanisms. The first is the incorporation of Si from the vapor-phase Si precursors into the liquid-phase Au alloys at their hemispherical surface. The second is the incorporation of Si atoms in the SiNW crystal lattice into the liquid-phase Au alloys at the liquid-solid interface. The atomic percentage of Si in the Au alloys introduced by dissociation of the vapor-phase Si precursor, which is the rate-limiting step for NW growth, was the same for the thin- and thick-SiNWs, because equal amounts of Si precursor were present in the reactor, in both cases. However, considering the large contact area of the interface between the thick-SiNWs and the Au alloys, it is expected that the number of Si atoms incorporated from these SiNW crystal lattices into the Au alloys should be large. Therefore, the amount of gold silicide in the Au alloys of the thick-SiNWs was larger than that of the thin-SiNWs (Figure 3a). Much more gold silicide was formed on the SiNWs cooled at a rate of 0.271 °C s⁻¹ (Figure 3b) than on the SiNWs cooled at a rate of 13 °C s⁻¹ (Figure 3a). The formation of gold silicide was accelerated during slow cooling because slower cooling of the SiNWs at high temperatures for a longer time facilitated the incorporation of Si atoms from the SiNW crystal lattices into the Au alloys.

The morphology and crystallinity of the SiNWs were characterized by transmission electron microscopy (TEM) analysis. Figure 4a shows a representative low-magnification TEM image of a thick-SiNW developed by fast cooling at a rate of 13 °C s⁻¹. The selected area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) images (bottom insets of Figure 4a) confirmed that the SiNW was single-crystalline and grew along the (111) direction; this was also true for the SiNWs shown in Figure 4b and c (Figure S1 in Supporting Information). The presence of the Au alloy at the top of the SiNW indicated that Au-catalyzed VLS growth occurred. Under fast cooling, the Au alloy at the top of the SiNW was hemispherical and neat, according to the SEM images shown in the inset of Figure 2b. Figure 4b and c show low-magnification TEM images of the thin- and thick-SiNWs, respectively, that were slowly cooled at a rate of 0.271 °C s⁻¹. The morphologies of the Au alloys in these images were distinct from those formed at a cooling rate of 13 °C s⁻¹. The SAED patterns in Figure 4b and c show the crystal pattern of the Au alloys (left of bottom inset) and the ring shape of the outside layer (right of bottom inset), which confirm that the Au alloys of the SiNWs were composed of crystalline gold silicide and were surrounded by an amorphous oxide layer. Because the reactor was not an ultrahigh-

![Figure 4a](image-url)
![Figure 4b](image-url)
![Figure 4c](image-url)

**Figure 4.** TEM images of thick-SiNWs with (a) fast and (b) slow cooling, and (c) a thin-SiNW with slow cooling. TEM images and corresponding EDX elemental maps and cross-sectional EDX elemental line scans of (d) thick- and (e) thin-SiNWs with slow cooling. (a) Top inset: high-magnification TEM image of the Au alloy at the top of the SiNW. Bottom insets: SAED pattern (left) and high-resolution TEM image (right) taken from white square area in (a). (b, c) Top insets: high-magnification TEM image of the Au alloy. Red and blue circles indicate Au alloy and oxide layers, respectively. Bottom insets: SAED patterns taken from the designated areas in top insets.
vacuum (UHV) system, it was possible for oxygen to be present during SiNW growth,[26] which resulted in the oxidation of gold silicide.[26]

The Au alloys at the tops of the thick-SiNWs subjected to slow cooling were distorted, not hemispherical, and appeared to be formed by crystallization of gold silicide in the Au alloys, as shown in Figure 4b. In addition, the oxide layers of these Au alloys were thicker and more clearly distinguishable than those on the SiNWs cooled at the faster rate (Figure 4a). From the XRD patterns in Figure 3, the thick-SiNWs had more gold silicide, which resulted in accelerated oxidation of gold silicide. Consequently, the Au alloys had a thick oxide layer, as shown in the inset of Figure 4b. In contrast, the Au alloys at the tops of the thin-SiNWs formed by slow cooling migrated from the tops to the sidewalls of the SiNWs, and no Au alloys were present at the tops of the SiNWs. Furthermore, the oxide layers of these Au alloys were thinner than those of the thick-SiNWs as shown in Figure 4c. The elemental composition of the SiNWs around the Au alloys was confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis, as shown in Figure 4d and e. In both cases, there were thicker oxide layers around the Au alloys than at the surface of the SiNWs, although thicker oxide layers were observed on the thick-SiNWs.

Figure 5a shows the atomic percentage of Si in the Au alloys (based on EDX analysis) as a function of the diameter of the Au alloys. This plot reveals that the atomic percentage of Si increased with increasing Au alloy diameter. In general, the small amount of Si atoms in the Au-Si eutectic resulted in migration of the Au alloy along the SiNW surface, and spreading of the small Au-Si eutectic over the SiNW sidewalls was energetically more favorable than maintaining the Au-Si eutectic on the top of the SiNWs.[27] Supply of the Si precursors was discontinued during the cooling stage. The Au-Si eutectic formed from the Au alloys at the tops of the thin-SiNWs, having a low percentage of Si as shown in Figure 5a, migrated to retain stable Si atoms from the sidewalls of the SiNWs instead of staying at the tops of the SiNWs. This occurred because the contact area between the interface of the Au alloy and Si crystals of the thin-SiNWs was small and could supply a small amount of Si atoms. Conversely, the Au-Si eutectic of the Au alloys of the thick-SiNWs was more stable than that of the thin-SiNWs, because of the large percentage of Si atoms in Au alloy, and could receive sufficient Si atoms from the Si crystals at the interface of the Au alloy and Si crystals, where the interface had a large surface area. Thus, the eutectic mixture remained at the tops of the SiNWs, and formation of gold silicide progressed via incorporation of the Si atoms from the SiNW crystal lattice into the Au alloys.

The Au alloy tends to migrate or form gold silicide over time at high temperature; therefore, there was little gold silicide at the tops of the SiNWs in the case of fast cooling. In contrast, during slow cooling, the behaviors of the Au alloy were different because the SiNWs were maintained at the high temperatures required for surface migration of the Au alloy or formation of gold silicide for a longer period of time. The mechanism of Au migration for the slowly cooled vertically aligned thin- and thick-SiNWs is illustrated in Figure 5b. In this process, the diameter of the Au alloys is critical as it affects formation of the Au-Si eutectic and migration of the Au alloys along the SiNW sidewalls. During growth of the SiNWs, the Si precursors are incorporated into the Au alloys, and one-dimensional (1D) epitaxial growth of SiNWs occurs by precipitation of Si in the Au alloy at the liquid-solid interface.[27] Thus during this growth stage, the Au alloys remained at the tops of the SiNWs in both cases because there was a continuous supply of Si atoms. However, in the cooling stages, the supply of Si atoms from the Si crystal lattices into the Au alloy was different for the thin- and thick-SiNWs due to the difference in contact area at the liquid-solid interface, resulting in different surface migration behavior of the Au alloy.

The atomic percentage of Si in the Au alloys of the SiNWs is dependent on the diameter of the Au alloy at the top of the SiNW. The amount of gold silicide and the atomic percentage of Si in the large Au alloys were higher than those in the small Au alloys (Figure 3b and 5a), which indicates that there could be two different mechanisms of Au alloy migration for the small and large diameter Au alloys. The slowly cooled Au alloys with small diameter can migrate from the tops to the sidewalls of the SiNWs during the cooling process, thereby lowering the energy of the Au-Si eutectic because of the small atomic percentage of Si in the Au alloys.[27] In contrast, the slowly cooled Au alloys with large diameters remain at the tops of the SiNWs during the cooling process instead of migrating over to the Si surface because the Au-Si eutectic is
stable. Additionally, the formation of gold silicide and oxidation are further accelerated in the thick-SiNWs, leading to thick oxide layers (Figure 4b) that can inhibit the migration of Au alloy from the top to the sidewalls of the SiNWs.

In conclusion, the mechanism of Au alloy migration for vertically aligned thin- and thick-SiNWs grown by CVD via the VLS mechanism was investigated at different cooling rates. Under fast cooling conditions, the Au alloys remained at the tops of the SiNWs because of the SiNWs were maintained at the high temperatures required for Au migration for only a short period of time. However, under the slow cooling regime, the behavior of Au alloy migration along the sidewalls of the SiNWs depended on the size of the Au alloys, which is related to the stability of the Au-Si eutectic in the Au alloys and the accelerated formation and oxidation of gold silicide. The small Au alloys, which had a low atomic percentage of Si, migrated from the top to the sidewalls of the SiNWs to obtain Si atoms because of the small contact area at the interface between the Au alloy and Si crystal. In contrast, the large Au alloys, which had a high percentage of atomic Si, remained at the tops of the SiNWs because of the sufficient supply of Si atoms to the Au alloy through the large contact area at the interface and the accelerated oxidation of gold silicide. These results should facilitate the improvement of the performance of SiNW-based electronic devices, reducing catalyst contamination.

**Experimental Section**

**Chemicals and materials**

Silicon tetrachloride (SiCl₄, 99.998%) and ammonium fluoride (NH₄F, 40% in water) were purchased from Sigma-Aldrich. Hydrofluoric acid (HF, 32–52% solution in water) was purchased from Acros. Acetone and isopropyl alcohol were purchased from Samchun. Finally, Si(111) wafers were purchased from LG Siltron.

**Synthesis of SiNWs**

Vertically aligned SiNWs (v-SiNWs) were synthesized by CVD using SiCl₄ as the Si precursor, which was carried by 10% H₂ in Ar via the Au-catalyzed VLS mechanism. Au film was deposited on a Si(111) wafer with dimensions of 1 cm (width) x 1 cm (length) by e-beam evaporation. The Au-covered Si(111) substrate was placed at the center in a 12 in. horizontal tube furnace (Lindberg/Blue M) equipped with a quartz tube furnace with a 1 in. diameter, as shown in Figure 1a. Before the experiment, the quartz tube was evacuated and flushed repeatedly with 10% H₂ gas in Ar (high purity, 99.999%) to minimize oxygen contamination. Detailed reaction diagrams, which consist of ramping, growth and cooling stages, are shown in Figure 1b and c. The substrate was heated to a growth temperature (T₀) of 860 °C at a rate of 20 °C min⁻¹ in an environment of 10% H₂ in Ar. Once the T₀ was reached, SiNWs were synthesized with the carrier (C) and dilution (D) gas, which were introduced at flow rates of 100 and 750 sccm, respectively. After 5 min of SiNW growth, the supply of the Si precursor was stopped, and the reactor was cooled to a cooling temperature (T₁) with different rates for each SiNW sample. The temperature was decreased from 860 °C (T₀) to 600 °C over a cooling time (t₀) of 20 s or 16 min in an environment of 10% H₂ in Ar, with rates of 13 °C s⁻¹ (fast cooling) and 0.271 °C s⁻¹ (slow cooling), respectively.

To cool down the SiNWs, the reactor was simply moved away from the center of the quartz tube, which held the SiNW samples.

**Characterization**

The morphologies of the synthesized v-SiNWs were characterized using field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7600F) at an acceleration voltage of 15 kV. X-ray diffraction (XRD) patterns of the SiNWs were obtained using a Rigaku diffractionometer (D/MAX-1C) with a monochromatic beam of CuKα radiation. Then, the single-crystalline structures of the SiNWs were analyzed by a JEOL 2010 transmission electron microscope (TEM) using energy-dispersive X-ray spectroscopy (EDX) for chemical analysis. The samples for TEM imaging were made by depositing an ethanol solution of SiNWs prepared by the sonication of the as-synthesized substrate in ethanol onto holey carbon grids on 300 mesh copper (Structure Probe, Inc.).

**Acknowledgements**

This work was supported by Nano-Material Technology Development Program (2012M3A7B40434986) funded by the National Research Foundation and the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT & Future Planning (2012-0009562). Additionally, it was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2015R1A2A2A01005556).

**Keywords:** Au alloys · Au-Si eutectic · cooling rates · nanowires · surface migration · vertically aligned Si nanowires


