



HAL
open science

Control of gold surface diffusion on Si nanowires

Martien den Hertog, Jean-Luc Rouvière, Florian Dhalluin, Pierre Desré,
Pascal Gentile, Pierre Ferret, Fabrice Oehler, Thierry Baron

► **To cite this version:**

Martien den Hertog, Jean-Luc Rouvière, Florian Dhalluin, Pierre Desré, Pascal Gentile, et al.. Control of gold surface diffusion on Si nanowires. *Nano Letters*, 2008, 8, pp.1544-1550. 10.1021/nl073356i . hal-00394786

HAL Id: hal-00394786

<https://hal.science/hal-00394786>

Submitted on 11 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Control of Gold Surface Diffusion on Si Nanowires

Martien I. den Hertog,^{*,†} Jean-Luc Rouviere,^{*,†} Florian Dhalluin,^{‡,§} Pierre J. Desré,[§] Pascal Gentile,[|] Pierre Ferret,[§] Fabrice Oehler,[|] and Thiery Baron[‡]

[†]Laboratoire d'Étude des Matériaux par Microscopie Avancée, CEA/DRFMC.

[‡]Laboratoire des Technologies de la Microélectronique, CNRS UMR 5129.

[§]Laboratoire de Photonique sur Silicium, CEA/LETI/DOPT.

[|]Laboratoire Silicium Nanoélectronique Photonique et Structure, CEA/DRFMC.

Laboratoire d'Étude des Matériaux par Microscopie AVancée, CEA/DRFMC, CEA-Grenoble, 17 rue des Martyrs, 38052 Grenoble Cedex 9, France, Laboratoire des Technologies de la Microélectronique, CNRS UMR 5129, CEA-Grenoble 17 rue des Martyrs, 38052 Grenoble Cedex 9, France, Laboratoire de Photonique sur Silicium, CEA/LETI/DOPT, CEA-Grenoble 17 rue des Martyrs, 38052 Grenoble Cedex 9, France, and Laboratoire Silicium Nanoélectronique Photonique et Structure, CEA/DRFMC, CEA-Grenoble, DRFMC, 17 rue des Martyrs, 38052 Grenoble Cedex 9, France

Silicon nanowires (NW) were grown by the vapor-liquid-solid mechanism using gold as the catalyst and silane as the precursor. Gold from the catalyst particle can diffuse over the wire sidewalls, resulting in gold clusters decorating the wire sidewalls. The presence or absence of gold clusters was observed either by high angle annular darkfield scanning transmission electron microscopy images or by scanning electron microscopy. We find that the gold surface diffusion can be controlled by two growth parameters, the silane partial pressure and the growth temperature, and that the wire diameter also affects gold diffusion. Gold clusters are not present on the NW side walls for high silane partial pressure, low temperature, and small NW diameters. The absence or presence of gold on the NW sidewall has an effect on the sidewall morphology. Different models are qualitatively discussed. The main physical effect governing gold diffusion seems to be the adsorption of silane on the NW sidewalls.

Silicon nanowires (SiNWs) have been actively studied during the past decade, as they hold the promise of becoming key building blocks in future electronic and optoelectronic devices. They are compatible with silicon technology and could be most elegantly grown directly on their final position in a device on a wafer. However successful integration of NWs in devices will depend ultimately on the degree of control that can be obtained over structure and physical properties. One important point is whether gold is incorporated at the NW either on the NW surface or in the NW volume. Indeed in many applications, for instance electric applications, it is important to have no gold incorporation, as gold is known to create deep traps.¹ However some applications, like the realization of NW web,² could benefit from the presence of gold clusters on the NW surface, as it would avoid the additional deposition of gold nanoclusters

at the NW surfaces. For a while, it was not clear whether gold was present on the NW surfaces. Hannon et al.³ have shown that the gold catalyst particle can constantly lose an amount of gold and that this gold would form 1–1.5 gold monolayers on the wire surface. The result of a constant loss of catalyst material is that the NW grows tapered, which is incompatible with long narrow cylindrical NWs if no extra gold is provided by the substrate. Other publications present transmission electron microscopy (TEM) images apparently showing no traces of gold on the NW surfaces, but this result is not discussed in these publications.^{4,5} A few publications have reported conditions modifying the presence of gold at the NW surface. Kodambaka et al.⁶ have shown that addition of oxygen during NW growth can alter the gold surface diffusion since the NW surface is modified by the oxygen. However the quality of the wires appears to be reduced. Pan et al.⁷ reported the presence of gold-rich precipitates on the boron-doped regions of SiNWs whereas there was no gold on undoped regions. However, a systematic analysis of the effect of growth parameters on the presence of gold at the NW surface has never been realized. This is the aim of this paper. We will show that the presence of gold at the surface of NWs can be controlled either with temperature or silane

* Corresponding authors, martien.den-hertog@cea.fr and jean-luc.rouviere@cea.fr.

[†] Laboratoire d'Étude des Matériaux par Microscopie Avancée, CEA/DRFMC.

[‡] Laboratoire des Technologies de la Microélectronique, CNRS UMR 5129.

[§] Laboratoire de Photonique sur Silicium, CEA/LETI/DOPT.

[|] Laboratoire Silicium Nanoélectronique Photonique et Structure, CEA/DRFMC.

partial pressure or with the initial size of the gold catalyst. We will not analyze the possible presence of gold within the NW volume as this topic has been addressed by atom probe tomography⁸ and secondary ion mass spectrometry⁹ and is difficultly seen by TEM.

SiNWs were grown by chemical vapor deposition via the vapor–liquid–solid process on a Si(111) substrate in a low-pressure chemical vapor deposition (LPCVD) reactor at a base pressure held constant at 20 mbar. Gold was used as the catalyst and silane (SiH_4) as the Si source. Hydrogen (H_2) was used as a carrier gas. After pretreatment of the silicon wafer material, 2 nm of gold was deposited in a vacuum of 10^{-6} Pa, or gold colloids of 10–100 nm (Ted Pella) were dispersed on the silicon substrate. The substrate was then loaded in the reactor and annealed between 500 and 900 °C under a H_2 flow for several minutes, in order to form nanocatalysts by dewetting of the Au layer. After cooling down the substrate to the growth temperature, SiH_4 was introduced by keeping the total pressure (SiH_4 and H_2) constant. Wires were grown at different silane partial pressures ranging from 0.054 to 1.023 mbar and at temperatures ranging from 430 to 650 °C. In literature partial silane pressures of 0.03–1.6 mbar,¹⁰ 0.1 mbar¹¹ and 6 mbar,^{4,5} and growth temperatures of 435 °C⁵ to 600 °C³ can be found, showing that our growth parameters are mainly in the low partial silane pressure range.

Also experiments were performed where the temperature was modified during growth. To gain insight into the gold surface diffusion rate, experiments were performed where the sample was held at the growth temperature for a certain time (anneal time) after growth had finished. Observation of the mean distance traveled by the gold clusters with respect to anneal time gave insight into the surface diffusion kinetics. The presence or absence of gold nanoclusters at the surface of SiNWs was observed either with a ZEISS ultrascan scanning electron microscope (SEM) equipped with an in-line detector or with a FEI TITAN TEM working in scanning mode, i.e., working as a scanning transmission electron microscope (STEM) at 300 kV. High-angle annular dark field (HAADF) STEM images and energy dispersive X-ray analysis (EDX) measurements were realized on the TITAN microscope to determine the chemical content of the nanoclusters (Figure 1). SEM allows quick and efficient analysis of a great number of samples without special specimen preparations, but the image quality is not as good as that obtained in STEM. For STEM observations, SiNWs were broken by ultrasound in an ethanol solution and deposited on holey carbon grids from the suspension. All observations were performed ex situ, after growth had finished.

By changing the experimental growth conditions as mentioned above, we were able to determine the main parameters that influence the presence or absence of gold nanoclusters on the side of the NW. These are silane partial pressure, growth temperature and wire diameter. In the following, first we describe the shape of the gold clusters when they are present, then we illustrate the effect of the three main parameters through a selection of NW images

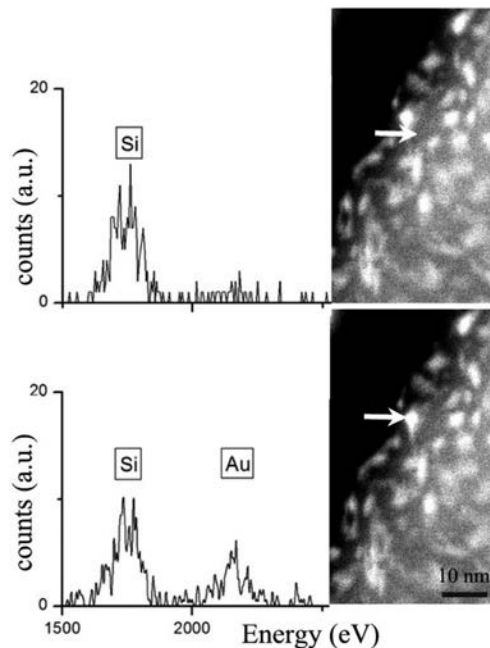


Figure 1. EDX spectra and STEM images of a SiNW grown at 575 °C with 0.077 mbar silane partial pressure. An arrow indicates where the EDX spectrum has been taken. The brighter particles are unambiguously gold rich clusters, as three typical gold lines appear in the EDX spectrum around 2200 eV.

that summarizes what has been observed in many images. Finally, we discuss the experimental results.

Let us start with the gold cluster shape. We find that when gold clusters are present, they always have the same average size and the local dot density can only vary in the presence of large flat facets. Figure 1 shows a characteristic HAADF STEM image of a NW covered with gold nanoclusters. The NW was grown at 575 °C with 0.077 mbar silane partial pressure. The presence of gold in the brighter regions was determined using EDX analysis (see Figure 1). The nanoclusters have a diameter of 3–4 nm and a height of between two and four gold layers, i.e., 0.6–1.3 nm, as measured at the side of the NW (see Figures 1 and 2). The clusters are present under a native SiO_2 layer which forms after growth when the wires are put in the atmosphere. An example is shown in Figure 2: a HAADF STEM image at the side of a NW grown at 575 °C with 0.13 mbar silane partial pressure. Clearly two monolayers of gold can be observed on the wire sidewall. The native oxide layer is just visible (a dotted line is drawn to guide the eye) and has a thickness of ~ 2 nm. Approximately 35% of the wire surface is covered by gold clusters (measured on nine images), implying that the quantity of gold decorating the wire sidewall is equivalent to approximately one monolayer. This number is in good agreement with the value found by Hannon et al.³ Generally the gold coverage is uniform, but a few flat facets of large diameter NWs are sometimes free of nanoclusters. Nanoclusters tend to be trapped at steps and corners (see Figures 1 and 2).

Figure 3 summarizes the effect of silane partial pressure. In Figure 3, two NWs are shown with a diameter of 100 nm, grown under equal growth conditions with the exception

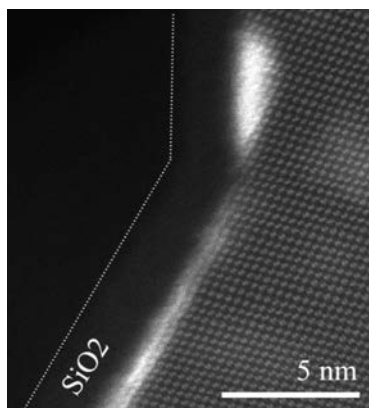


Figure 2. HAADF STEM image on the side of a NW grown at 575 °C with 0.13 mbar silane partial pressure. Clearly two monolayers of gold can be observed on the silicon (111) plane. The silicon oxide layer is not very well visible; therefore a dotted line is drawn to guide the eye.

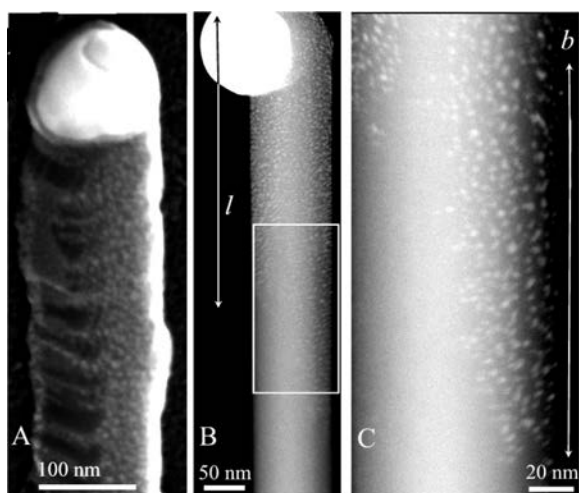


Figure 3. Two SiNWs are shown with a diameter of 100 nm grown at 500 °C with different silane partial pressures. (A) SEM image of a wire grown at low partial silane pressure: 0.0804 mbar. Gold clusters can be observed all over the wire surface. (B) HAADF STEM image of a wire grown at a partial silane pressure of 1.023 mbar. Gold clusters can be observed on the 300 nm region l close to the catalyst particle. (C) Zoom of the marked region in B showing the end of the gold-covered zone. The difference in diffused distance is indicated by b and is approximately 150 nm.

of the silane partial pressure. The growth temperature was 500 °C. At low partial silane pressure (0.0804 mbar, Figure 3A) gold clusters cover the faceted NW sidewalls. At high partial silane pressure (1.023 mbar, Figure 3B) most of the NW sidewall surface is free of gold clusters except a length $l \sim 300$ nm situated near the catalyst particle. This observation will be discussed in the next paragraph. The magnified view shown in Figure 3C shows the transition from gold-covered silicon to a clean wire surface. No faceting on the wire sidewall is observed. Clearly the partial silane pressure has an effect on the gold surface diffusion.

Figure 4 summarizes the effect of temperature and NW diameter. In panels A and B of Figure 4, two NWs are shown with a diameter of 25 nm, grown under equal growth conditions with the exception of the temperature. The partial

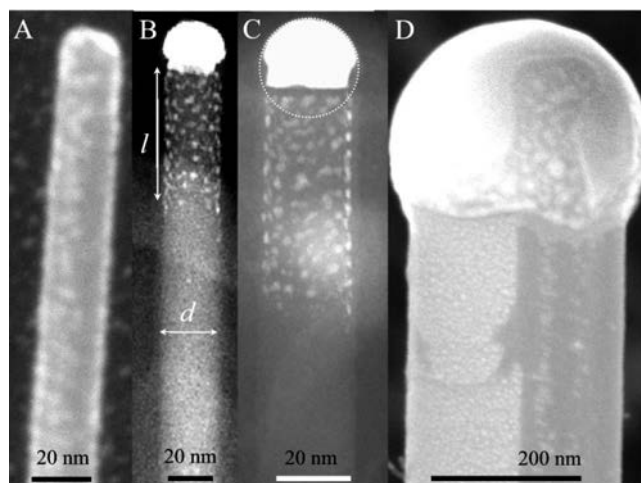


Figure 4. Three NWs are shown with diameters of 25 nm, A and B, and 300 nm in D. Growth conditions were identical except for the temperature. The partial silane pressure was 0.19 mbar. (A) SEM image of a wire grown at 500 °C clearly covered by gold clusters and slightly tapered. (B) HAADF STEM image of a wire grown at 430 °C; gold clusters can be observed on the 60 nm region l close to the catalyst particle. (C) A magnified view of the wire shown in B, a dotted circle is drawn around the catalyst particle to illustrate the deviation from a hemisphere. (D) SEM image of a SiNW grown at 430 °C with a diameter of 300 nm. Gold clusters can be observed all over the wire surface.

silane pressure was 0.19 mbar. The NW grown at 500 °C is covered with gold clusters and slightly tapered (Figure 4A), whereas the one grown at 430 °C has gold clusters only on a length $l \sim 60$ nm near the catalyst particle (Figure 4B). A magnified view of the gold-covered region (Figure 4C) shows that the catalyst particle is not a perfect hemisphere. This will be discussed in the next paragraph. The comparison of panels C and D of Figure 4 summarizes the effect of wire diameter. The NWs of panels C and D of Figure 4 have been grown in similar conditions ($T = 430$ °C $p = 0.19$ mbar). The large diameter NW of Figure 4D ($d \sim 300$ nm) is covered with gold clusters, whereas the small diameter NW of Figure 4C ($d \sim 25$ nm) is not.

First let us analyze why gold-rich nanoclusters are always observed at the top part of our NWs, on a length l (Figure 3B and Figure 4C). Many pieces of information concerning the gold surface diffusion will be extracted from this analysis. The presence of gold clusters near the catalyst is due to a transition regime when the NW growth is stopped, i.e., when silane valves are closed and the heating of the substrate is switched off. This effect is particularly important in our growth chamber which has a large volume and high-temperature inertia. Due to the large volume, it takes 5 min to change the gas composition of the growth chamber and 3 h to reach room temperature. Meaning that after the silane source has been closed, the partial silane pressure is ramping toward zero in 5 min, whereas the temperature remains fairly constant. During cooling down the sample is under constant flow of carrier gas (H_2). Of course the gold clusters can only come from the gold catalyst as the substrate is too far from this top part of the NW. Just after the silane source has been stopped, different mechanisms can happen: (i) NWs continue

growing by decomposing the last amount of silane in the chamber and incorporating the last amount of Si present in the catalyst; (ii) gold from the catalyst starts diffusing over the surface of the NWs; (iii) gold starts forming clusters; (iv) a silicon oxide layer is grown at the surface of the NW and the gold remains at the Si/SiO₂ interface. Since cooling of the sample is done in a H₂ atmosphere, it seems impossible that point iv happens in the chamber in the few minutes after the closing of the silane source. So mechanism iv clearly happens after the other mechanisms. Other facts indicate that mechanisms ii and iii are also separated in time. Diffusion is a random mechanism involving atom diffusion. Since the amount of gold present on the NW surface is approximately one monolayer, it seems probable that at high temperature (during growth) one or more liquid layers of Au or Au/Si are formed on the NW surface by atom diffusion. After a reduction in temperature, the gold starts to form clusters. If the clusters were formed already at high temperature, it would be likely that they would start to form branches at the NW surfaces, each gold-rich cluster becoming a catalyst for a tiny NW that we call branch. Branches on NWs can only be formed if the temperature of the wire is reduced, that is to say only if gold clusters are formed.¹² As far as mechanism i and ii are concerned, the analysis of the STEM images (Figures 3B and 4B) indicate that they do not happen simultaneously but are separated in time. Indeed, if the gold cluster covered zone was growing during the 5 min necessary for the evacuation of silane, the catalyst would lose material in this last growth stage and this part of the wire would be slightly tapered as the diameter of the NW is adjusted to the diameter of the gold catalyst.⁴ Using a simple geometric model,³ where the tapered part of the NW is supposed to have a conical shape characterized by its semiangle β , one finds that

$$\tan \beta = \frac{\Delta d}{2l} = \frac{d}{2l_{\max}} = \frac{4e}{d}$$

where l is the length of the NW grown during the tapered regime taken equal to the length of the covered zone (as indicated in Figure 4B), d is the NW diameter at the beginning of the tapered regime, and Δd is the variation of diameter after the growth of the length l . l_{\max} is the maximum length of the NW if all the catalyst is consumed and if Δd is equal to d . e is the thickness of the gold layer. The last equality of the previous equation comes from the fact that the volume of the gold clusters is taken equal to the volume of the gold wetting layer. Assuming that the thickness e is equal to one atomic gold plane, $e \approx 0.26$ nm, the decrease in wire diameter Δd can be estimated to be 5 or 6 nm for the NWs of Figures 4B and 3B that have diameters of 25 and 100 nm, respectively, and a hypothetical tapered length l equal to the length of the gold cluster covered zone, being 60 and 300 nm, respectively. Such variations of diameter should be visible, which is not the case as the NW diameter remains constant. Furthermore it can be seen in Figures 4C and 6 that the catalyst particle is not a perfect spherical cap fitted to the NW diameter. This clearly indicates that gold surface diffusion (ii) only starts after growth has finished (i).

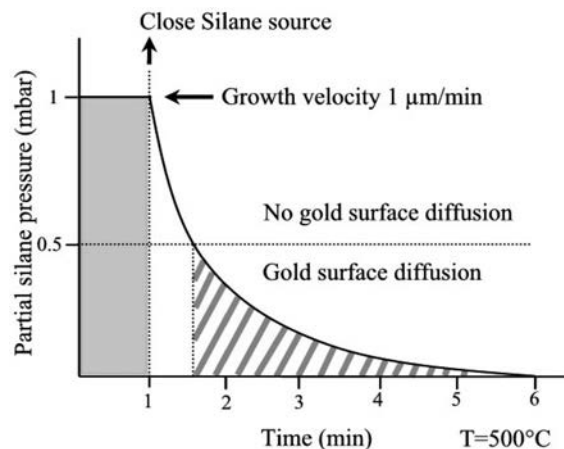


Figure 5. Estimated exponential decay of the silane partial pressure in the growth chamber. The silane flow is closed at time $t = 1$ min. The growth velocity at the starting partial pressure and the partial pressure below which gold surface diffusion can occur at this temperature (for a constant partial pressure value) are indicated. Comparison of the gray surface and the striped surface allows estimating the length the NW can grow, during which time gold diffusion can occur.

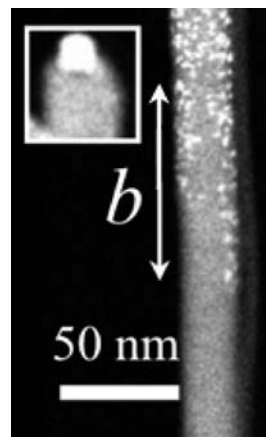


Figure 6. Magnified view of a NW with a diameter of ~ 25 nm, grown under exactly the same conditions as the wire shown in Figure 3B: a growth temperature of 500 °C with 1.023 mbar silane partial pressure. The difference in diffused distance of the gold is indicated by b and is approximately 60 nm. A magnified view of the catalyst particle is shown in the inset: the catalyst particle is considerably smaller than the wire radius. (The length of the gold covered region l close to the catalyst particle is ~ 300 nm (comparable to the wire shown in Figure 3B)).

Another indication to show that the sequence of events is indeed (i) followed by (ii) can be obtained by taking into account the decay of the silane partial pressure after closing the silane source. We estimate an exponential decay of the silane partial pressure after closing of the source at time $t = 1$ min; see Figure 5. From our observations we know that at this temperature (500 °C) gold surface diffusion can occur for wires grown at a partial pressure of 0.5 mbar and lower (for a NW diameter of 50 nm or higher). Also the growth speed at the starting value for the partial pressure is known (1 $\mu\text{m}/\text{min}$). It was shown in ref 13 that the silane partial pressure can be directly related to the growth velocity (at a fixed temperature) since the sticking probability of the feed gas does not depend on the chemical potential of the catalyst

particle. Now we can compare the gray surface (at constant growth velocity, being equal to 1 μm NW length) and the striped surface, being equal to the length the NW can grow during the transition regime when gold surface diffusion should occur. We can estimate the striped surface to be around 600 nm. This explanation implies that the last part of the NW (~ 600 nm) should be tapered. As we have shown in the foregoing this is not the case.

To explain observed influence of growth conditions on the gold surface diffusion, we can consider two explanations. A first possibility can be that the composition of the catalyst particle can be changed in such a way that gold surface diffusion can no longer occur because it becomes energetically unfavorable. We can express a change in chemical potential for gold when going from the liquid catalyst particle to a liquid (mono)layer on the wire surface. We consider the chemical potential of the gold in the eutectic $\mu_{((\text{Au}))}(d)$, this can be written as

$$\mu_{((\text{Au}))}(d) = \mu_{((\text{Au}))}^0 + RT \ln \gamma_{\text{Au}}^* x_{\text{Au}}^* + \frac{4\bar{V}_{((\text{Au}))}\sigma_{(\text{AuSi})}}{d}$$

where $\mu_{((\text{Au}))}^0$ is the standard chemical potential of pure liquid gold at standard conditions, γ_{Au}^* is the gold activity coefficient and can be calculated by assuming the liquid behaves as a regular solution using

$$\ln \gamma_{\text{Au}}^* = -\frac{\lambda(1-x_{\text{Au}}^*)^2}{RT}$$

and

$$\lambda = 4\Delta H$$

(if $x_{\text{Au}}^* = 0.5$), where ΔH is the enthalpy of mixing (-10 kJ mol^{-1}).¹⁴ x_{Au}^* is the gold fraction in the catalyst particle ($0 \leq x_{\text{Au}}^* \leq 1$, 0.77 at 500 $^\circ\text{C}$ for the bulk at equilibrium), $\bar{V}_{((\text{Au}))}$ is the molar volume of liquid gold (1.02×10^{-5} $\text{m}^3 \text{mol}^{-1}$ without taking into account liquid contraction), $\sigma_{(\text{AuSi})}$ is the surface energy of the eutectic particle (1.25 J m^{-2})¹² and d is its diameter (we assume the NW diameter \approx catalyst diameter, taking into account the contact angle does not modify the result of the calculation). The chemical potential of a liquid gold layer $\mu_{(\text{Au})\text{wire}}$ at the wire surface can be written as

$$\mu_{(\text{Au})\text{wire}} = \mu_{((\text{Au}))}^0 + \frac{2\bar{V}_{((\text{Au}))}\sigma_{(\text{Si})}'}{d}$$

where $\sigma_{(\text{Si})}'$ is the surface energy of solid silicon covered by ~ 1 monolayer of gold. Since the surface energy of solid silicon and liquid gold are 1.24 ¹⁵ and 1.25 ¹² J m^{-2} , respectively, this value is taken to be 1.25 J m^{-2} . The energy balance is now given by

$$\mu_{(\text{Au})\text{wire}} - \mu_{((\text{Au}))}(d) = \frac{-2\bar{V}_{((\text{Au}))}\sigma_{(\text{Au})}}{d} - RT \ln \gamma_{\text{Au}}^* \gamma_{\text{Au}}^* = \Delta\mu$$

because $\sigma_{(\text{Si})}' \approx \sigma_{(\text{AuSi})}$. If $\Delta\mu < 0$, gold surface diffusion can occur. For a NW with a diameter ranging from 5 to 300 nm, $\Delta\mu$ increases exponentially from -0.3 to 3.7 kJ mol^{-1} ($x_{\text{Au}}^* = 0.77$, $T = 500$ $^\circ\text{C}$). Taking into account the contact angle of the droplet with the NW, which can be modified by line tension¹⁵ for small diameters, does not change the

calculated values for $\Delta\mu$, if we assume a line tension of $\sim -1 \times 10^{-9}$ J m^{-1} .¹⁵ Modification of the growth parameters silane partial pressure and temperature can change x_{Au}^* and T . For $0.5 \leq x_{\text{Au}}^* \leq 0.99$, $\Delta\mu$ is positive and going through zero for $x_{\text{Au}}^* \approx 0.99$. $\Delta\mu$ does not vary significantly for 430 $^\circ\text{C} \leq T \leq 600$ $^\circ\text{C}$. This analysis shows that gold surface diffusion is not favored energetically under all experimentally observed growth conditions, since $\Delta\mu$ can only become negative if the wire diameter becomes very small, indicating that gold diffusion is possible for very small NW diameters, contrary to the observed effect, or if the catalyst particle is purely gold. In this last case there is no eutectic and therefore no liquid phase. This solution seems physically highly unrealistic. Therefore it is clear that we cannot explain the experimentally observed effects of growth conditions on the gold surface diffusion by taking into account a change in catalyst composition. This explanation is also unlikely because we observe the absence of gold surface diffusion for wire growth during the transition regime at and below a partial silane pressure that is known to cause gold surface diffusion at constant value. This indicates strongly that the observed effect is not related with the relatively fast response of catalyst composition to silane partial pressure (at this growth velocity) but is a slower process.

A plausible explanation seems therefore that the wire surface can be changed in a reversible way due to a change in growth conditions, allowing or inhibiting the gold diffusion. The only component we actively add in larger or smaller quantities is the silane gas itself; therefore we propose that the adsorption of silane gas on the wire sidewall influences the gold diffusion. This hypothesis is consistent with the observed effect of silane partial pressure. According to Le Chatelier's principle, an increase of the silane partial pressure will naturally lead to a mechanism that counteracts the imposed change, being an increase of adsorbed silane. Now we consider the temperature effect. As we already showed in panels A and B of Figure 4, a decrease in temperature can completely block the gold surface diffusion. Furthermore we performed experiments where the temperature was decreased during growth. The result is a NW only partially covered by gold clusters. A decrease in temperature thermodynamically favors adsorption as physisorption or chemisorption are exothermic processes (enthalpy of adsorption ~ 20 – 100 kJ mol^{-1}).¹⁶ Again, using Le Chatelier's principle, the system will favor mechanisms producing energy when the temperature is lowered.¹⁶ So adsorption of silane will be favored when the temperature is lowered. Also a decrease in temperature will lower the mobility of the gold, possibly enhancing the before mentioned adsorption effect. It is evident that an adsorbed layer of silane molecules can exist only if silane decomposition on the wire sidewall (i.e., uncatalyzed growth) is extremely slow. Indeed we find that the uncatalyzed growth rate is negligible at temperatures below 600 $^\circ\text{C}$.

Now we consider the effect of the wire diameter. The effect of wire diameter on gold diffusion might be explained by an increase in chemical potential of the NW surface atoms. The chemical potential of a SiNW can be written¹²

$$\mu_{\text{(Si)}}(d) = \mu_{\text{(Si)}}(d = \infty) + \frac{2V_{\text{(Si)}}\sigma_{\text{Si}}}{d}$$

where $\mu_{\text{(Si)}}(d)$ is the chemical potential of silicon in the NW, $\mu_{\text{(Si)}}(d = \infty)$ is the chemical potential for bulk silicon, $V_{\text{(Si)}}$ is the molar volume of silicon, and σ_{Si} is the surface energy of silicon. The chemical potential will increase for decreasing diameter. However it is unclear if this will affect the silane adsorption (possibly a smaller wire diameter mimics the effect of a step edge on a crystal, which lowers the adsorption energy¹⁷) or rather increases the gold–silicon interface energy, thereby inhibiting the gold surface diffusion. More theoretical studies are necessary to clarify this point.

Interestingly, the edge of the gold cluster covered zone in Figure 3B,C is not straight (perpendicular to the growth direction), but inclined. This suggests anisotropy in the gold diffusion. We can observe a difference in diffused distance b (Figure 3C) to be approximately 150 nm. A wire with a diameter of 30 nm grown under exactly the same growth conditions as the wire in Figure 3C, 500 °C growth temperature with 1.023 mbar silane partial pressure (Figure 6), showed a difference in diffused distance of ~ 60 nm. Since a NW can be regarded as a cylinder in a laminar gas flow, it can be seen intuitively that the larger the diameter, the more important will be the pressure drop when going from the flow side of the NW to the back side. The influence of the carrier gas (after the silane source has been closed) on the NW surface can possibly modify the layer of adsorbed silane molecules. This effect will be increasingly inhomogeneous for increasing diameters. This might explain the anisotropy of gold surface diffusion and its size dependence. This indicates also that the gold surface diffusion can be modified by a change of the NW surface, which in turn is also influenced by the direction of the gas flow. Also Figure 6 shows that the catalyst particle size decreased considerably with respect to the wire diameter. Clearly the NW diameter did not adjust to the catalyst size but remained constant. Confirming gold surface diffusion (mechanism ii) only starts after NW growth has finished (mechanism i).

Now let us consider the gold diffusion rate. Two particular NW growth experiments were realized under the same conditions as the wire shown in Figure 3B (500 °C growth temperature with 1.023 mbar silane partial pressure) except that, after the silane flow was closed, the sample was maintained at the growth temperature during a time $\tau_1 = 5$ min in the first experiment and a time $\tau_2 = 15$ min in the second one, after which the sample was cooled down to room temperature as usual. The length of the gold-covered zone near the catalyst particle was now found to be around $l_1 = 600$ nm and $l_2 = 2500$ nm in the respective experiments. We use the two-dimensional random walk expression for diffusion:¹⁶ the mean traveled distance is $(D\tau)^{1/2}$, where τ is the time interval during which the sample is maintained at the growth temperature and D is the diffusion coefficient. Taking into account that during cooling gold already diffused over a distance of 300 nm, we thus have for the first experiment $l_1 - 300 = (D\tau_1)^{1/2}$ and a similar expression for the second one. This gives diffusion coefficients D of 3×10^{-16} m² s⁻¹ and 5.4×10^{-15} m² s⁻¹ (at 500 °C) for the respective experiments indicating that the gold diffusion is

slower just after the silane flow has been closed, which can be explained by the fact that the remaining silane molecules slow down the gold diffusion. In literature a value for D_0 of $\sim 1 \times 10^{-12}$ m² s⁻¹ can be found¹⁸ for a monolayer or less of gold on Si(111). This again indicates that under our conditions gold diffusion is slower because it is perturbed by the remaining adsorbed silane molecules.

The observation that the gold diffusion only starts after growth has finished indicates that the silane desorption is a rather slow process. The residence half-life of an adsorbed silane molecule can be estimated to be on the order of minutes. This means that the barrier for desorption is significantly higher than that for a physisorption process (~ 25 kJ mol⁻¹),¹⁶ where the residence half-life is predicted around 10 ns at room temperature.¹⁶ Possibly the adsorption process does involve a chemical reaction where the silane molecule is decomposed into an intermediate state where it remains trapped a relatively long time (approximately minutes).

The observation of gold clusters on the doped regions of Si NWs was explained by Pan et al.⁷ as instabilities at the liquid/solid interface, caused by the addition of the dopant gas flow. Since we regard only undoped samples, this explanation is insufficient for our experiment. However since in their experiments the silane gas flow was lowered by 80% for growth of the doped region, this might be the same effect of an increase in silane partial pressure favoring the silane adsorption and inhibiting the gold diffusion on the undoped regions.

It was shown by Ross et al.¹⁹ that the NW sidewall parallel to the growth direction is not flat but shows periodic sawtooth facets. This faceting could be due to the presence of gold on the wire sidewall, since gold is known to induce faceting on silicon surfaces.^{20–22} The surface structure of NWs is of particular importance for applications since transport properties will depend to a great extent on surface roughness. Interestingly, periodic sawtooth faceting of the NW sidewall as described in ref 19 was observed for the completely gold covered wires, but never on the wires showing gold clusters only on a short region near the catalyst particle. If the gold is diffusing during growth, the wire surfaces maintain at the growth temperature until growth is terminated and surface reconstruction can occur. However if the gold is diffusing during cooling of the sample, the energy barrier for surface reconstruction cannot be overcome and no sawtooth faceting can be observed. The absence or presence of gold on the wire sidewall thus has an effect on the sidewall morphology.

Recently an influence of silane partial pressure on the critical wire radius was observed,¹² indicating that small wires (diameter below 30 nm) cannot grow at low partial pressures (< 0.05 mbar) for thermodynamical reasons. It should be noted that the condition of high partial silane pressure, which favors silane adsorption and inhibits gold diffusion, is also a condition that favors very thin wire growth thermodynamically.¹² The growth of thin wires is therefore favored by two decoupled processes resulting from an increase in silane partial pressure (clearly thin wires cannot grow very long if they constantly lose catalyst material). This can partly explain the different results regarding the absence or presence of gold

Table 1. Parameters to Inhibit Gold Diffusion

temperature ≤ 500 °C	partial silane pressure ≥ 1 mbar
---------------------------	---------------------------------------

on the wire sidewall found in literature. Another explanation for these different results is the partial silane pressure itself; in most literature slightly higher partial silane pressure values are used (values of 0.1 mbar¹¹ to 6 mbar^{4,5} can be found in recent literature) and growth is performed at relatively low temperature ($T \leq 500$ °C). These are conditions that inhibit gold diffusion (see Table 1). On the other hand, most literature showing evidence of gold diffusion is performed at very low partial pressures since the growth is carried out under ultrahigh vacuum.^{3,6,23}

In conclusion, we have shown that the gold diffusion on SiNWs can be controlled by two parameters being silane partial pressure and temperature. We propose a qualitative model based on an increased silane adsorption on the wire sidewall, which effectively blocks the gold diffusion. The growth conditions to inhibit gold diffusion are summarized in Table 1.

Also an effect of wire diameter on gold diffusion was observed which might be due to an increase in chemical potential of surface atoms as the diameter decreases. Control of the surface diffusion of gold provides a tool to fabricate long, uniform diameter structures with flat sidewalls and no gold clusters decorating the NW sidewall. Also the possibility exists to modify the sidewall morphology after growth by performing a postgrowth anneal during which the gold can diffuse over the wire sidewalls. In this way gold clusters can be deposited on the NW sidewall, or a part of it, in a controlled and reproducible way, allowing direct functionalization of the NW.

Acknowledgment. The work and results reported in this publication were obtained with research funding from the European Community under the Sixth Framework Programme for the Marie Curie Host Fellowships for Early Stage Research Training (EST) “CHEMTRONICS” Contract Number MEST-CT-2005-020513. The views expressed are solely those of the authors, and the other Contractors and/or the

European Community cannot be held liable for any use that may be made of the information contained herein. This work was also supported by the PREEANS ANR project.

References

- (1) Tavendale, A. J.; Pearton, S. J. *J. Phys. C* **1983**, *16*, 1665.
- (2) Cimalla, V.; Stubenrauch, M.; Weise, F.; Fischer, M.; Tonisch, K.; Hoffmann; Ambacher, O *Appl. Phys. Lett.* **2007**, *90*, 101504.
- (3) Hannon, J. B.; Kodambaka, S.; Ross, F. M.; Tromp, R. M. *Nature* **2006**, *440*, 69.
- (4) Cui, Y.; Lauhon, L. J.; Gudiksen, M. S.; Wang, J.; Lieber, C. M. *Appl. Phys. Lett.* **2001**, *78*, 2214.
- (5) Wu, Y.; Cui, Y.; Huynh, L.; Barrelet, C. J.; Bell, D. C.; Lieber, C. M. *Nano Lett.* **2004**, *4*, 433.
- (6) Kodambaka, S.; Hannon, J. B.; Tromp, R. M.; Ross, F. M. *Nano Lett.* **2006**, *6*, 1292.
- (7) Pan, L.; Lew, K.; Redwing, J. M.; Dickey, E. C. *J. Cryst. Growth* **2005**, *277*, 428.
- (8) Perea, D. E.; Lensch, J. L.; May, S. J.; Wessels, B. W.; Lauhon, L. J. *J. Appl. Phys. A* **2006**, *85*, 271.
- (9) Putnam, C. P.; Filler, M. A.; Kayes, B. M.; Kelzenberg, M. D.; Atwater, H. A. *MRS Fall Proceedings* **2007**, 835.
- (10) Latu-Romain, L.; Mouchet, C.; Cayron, C.; Rouvière, E.; Simonato, J. P. *J. Nanopart. Res.* DOI: 10.1007/s11051-007-9350-3.
- (11) Schmidt, V.; Senz, S.; Gösele, U. *Nano Lett.* **2005**, *5*, 931.
- (12) Dhalluin, F.; Desré, P. J.; den Hertog, M. I.; Rouvière, J. L.; Ferret, P.; Gentil, P.; Baron, T. *J. Appl. Phys.* **2007**, *102*, 094906.
- (13) Kodambaka, S.; Tersoff, J.; Reuter, M. C.; Ross, F. M. *Phys. Rev. Lett.* **2006**, *96*, 096105.
- (14) Hassam, S.; Gaune-Escard, M.; Bros, J. P.; Bunsenges, B. *Phys. Chem* **1983**, *87*, 785.
- (15) Schmidt, V.; Senz, S.; Gösele, U. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *80*, 445.
- (16) *Atkins Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, 2002.
- (17) Olsen, R. A.; Bădescu, S. C.; Ying, S. C.; Baerends, E. J. *J. Chem. Phys.* **2004**, *120*, 11852.
- (18) Slezák, J.; Ondřejček, M.; Chvoj, Z.; Cháb, V. *Phys. Rev. B* **2000**, *61*, 16121.
- (19) Ross, F. M.; Tersoff, J.; Reuter, M. C. *Phys. Rev. Lett.* **2005**, *95*, 146104.
- (20) Seehofer, L.; Huths, S.; Falkenberg, G.; Johnson, R. L. *Surf. Sci.* **1995**, *329*, 157.
- (21) Hild, R.; Seifert, C.; Kammler, M.; Meyer zu Heringdorf, F.-J.; Horn-von Hoegen, M.; Zhachuk, R. A.; Olshanetsky, B. *Z. Surf. Sci.* **2002**, *512*, 117.
- (22) Minoda, H.; Yagi, K.; Meyer zu Heringdorf, F.-J.; Meier, A.; Kähler, D.; Horn-von Hoegen, M. *Phys. Rev. B* **1999**, *59*, 2363.
- (23) Werner, P.; Zakharov, N. D.; Gerth, G.; Schubert, L.; Gösele, U. *Int. J. Mater. Res.* **2006**, *97*, 1008.