The Role of Surface Passivation in Controlling Ge Nanowire Faceting

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Abstract

In-situ transmission electron microscopy observations of nanowire morphologies indicate that, during Ge nanowire growth, Ge facets can rapidly form along the nanowire sidewalls when the source gas (here, digermane) flux is decreased or the temperature is increased. This sidewall faceting is accompanied by continuous catalyst loss as Au diffuses from the droplet to the wire surface. We suggest that high digermane flux and low temperatures promote effective surface passivation of Ge nanowires, with H or other digermane fragments inhibiting diffusion and attachment of Au and Ge on the sidewalls. These results illustrate the essential roles of the precursor gas and substrate temperature in maintaining nanowire sidewall passivation, necessary to ensure the growth of straight, un-tapered, <111>-oriented nanowires.

Keywords: Nanowire, Diffusion, *in-situ* Transmission Electron Microscopy, Surface Passivation

The self-assembly of nanowires (NWs) by the vapor-liquid-solid (VLS) process can produce remarkably uniform diameter-controlled wires with enormous aspect ratios¹. This has generated a large field of study, and many exciting possibilities for technological applications². The growth of ideally uniform NWs requires the nearly complete suppression of two competing processes. One process is uncatalyzed growth on the wire sidewalls, which (when not effectively suppressed) leads to uncontrolled and non-uniform widening of the wire. The other is diffusion of the metal out of the catalyst particle. Several important studies have shed light on these competing processes and how they are suppressed, especially for Si³⁻⁷ and Ge⁸ NWs. Yet our understanding of this critical aspect of NW growth remains far from complete.

Here we use *in-situ* transmission electron microscopy (ETEM)^{9, 10} and ultra-high vacuum (UHV) TEM¹¹ to examine the relationship between wire surface passivation, catalyst diffusion, and sidewall facet growth in Ge <111>-oriented NWs grown from liquid Au-Ge alloy catalyst droplets. These techniques permit the measurement of transient effects, including catalyst diffusion⁵ and sidewall facet formation¹² growth phenomena, which are generally inaccessible to *ex-situ* analysis. By combining *in-situ* ETEM and UHV-TEM data, we show that when either the gas-phase growth species (here, digermane, Ge₂H₆) flux is reduced or the substrate temperature is increased, both Au and Ge diffuse away from the alloy droplets and sidewall facets appear on the wire surface. Based upon these results, we suggest that the stability of Ge <111> NW growth is controlled by the Ge precursor flux: this flux not only supplies Ge for wire growth, but also strongly modifies the surface of the wire, suppressing Au diffusion and Ge growth on the sidewalls.

The surface chemistry is thus crucial in determining NW morphology. Wire surface passivation is subject to competition between adsorption and desorption rates of the passivating Ge₂H₆ radicals during growth. High pressure results in high adsorption, and similarly low temperature encourages low desorption of surface passivating radicals, ensuring high passivation coverage of the wire surface. The

similarities in our ETEM and UHV-TEM data suggest that the processes underlying catalyst migration and facet formation are fundamentally the same over three orders of magnitude in Ge precursor partial pressures. In low partial passivation coverage conditions, catalyst diffusion occurs along with the formation of wire sidewall facets. Thus, a continuous supply of Ge_2H_6 at high flux and low growth temperature is needed to maintain surface passivation and ensure the growth of straight (unkinked), untapered, and $\langle 111 \rangle$ -oriented Ge NWs with relatively smooth sidewalls, as required for many applications.

The Ge NW ETEM growth experiments were carried out in an aberration corrected Titan 80-300 ETEM with a Schottky field emission gun electron source operated at 300 kV with a base pressure of 1.2×10^{-6} Torr. The NWs were directly grown on holey carbon Cu mesh TEM membranes. These grids were first covered with ~ 30 nm of SiO_2 by plasma enhanced chemical vapor deposition (PECVD) using a Trion Orion III PECVD system, and then were decorated with Au catalysts. The SiO_2 provides a buffer layer between the carbon and the Au during wire growth. The Au was deposited as a layer ~ 1 nm thick at a rate of 0.1 nm/s using a Kurt J. Lesker PVD 75 e-beam evaporator. This process resulted in the formation of 2 – 10 nm diameter Au crystallites, which we assume are nearly spherical. The samples were mounted in a Gatan Inconel hot stage and transferred in air into the ETEM. A Gatan SmartSet Model 901 Hot Stage Controller was used to control the sample temperature. Temperature was measured by a thermocouple attached to the hot stage: prior work has shown that the measurements are accurate to within $10\text{-}15^\circ$ ¹³. The TEM grid with Au nanoparticles was heated to 350°C and held for 30 min in the ETEM to minimize thermal drift. Ge_2H_6 was then introduced into the microscope at 350°C through a UHV leak valve attached to a gas cylinder containing a mixture of 5.1 % (molar fraction) Ge_2H_6 and He gases (supplier, Voltaix). The pressures given in the text are the partial pressure of Ge_2H_6 , unless the total pressure is specified. The desired pressure ($\sim 10^{-3}$ Torr) was obtained in approximately 1 minute. Upon introduction of Ge_2H_6 , the Au particles absorbed Ge to form metal-semiconductor alloy droplets¹⁴,

¹⁵ then Ge NWs nucleated and grew with liquid Au-Ge catalyst droplets at their tips. A mixture of straight and (occasionally) kinked wires were observed in the ETEM. These wires had diameters between 10 and 30 nm and grew in random directions away from the SiO₂ support, with some growing nearly perpendicular to the incident e-beam direction. The ETEM experiments analyzed below were carried out on three such <111> oriented wires, which grew (based on video measurements) at 1.5 – 2.1 nm/s. After obtaining > 250 nm long NWs, the leak valve was closed and the Ge₂H₆ was pumped out through the ETEM's differential pumping system. From an initial total pressure of 1.2×10^{-2} Torr, a pressure of 1×10^{-5} Torr was reached in 2 – 3 s during purging, and the base pressure was reached in 13 – 15 s. This pressure drop resulted in a series of changes to the NW and droplet morphology over a relatively short time. TEM images (720 × 480 pixels) of the catalyst and NW morphologies were collected at 5 frames per second (fps) using a Gatan Orius CCD camera. We also carried out similar Ge NW growth experiments using an UHV-TEM (base pressure $\sim 2 \times 10^{-10}$ Torr) at lower pressures ($\sim 2 \times 10^{-5}$ Torr total pressure of a gas containing 20 % Ge₂H₆ in 80 % He). Images were obtained at 30 fps while changing pressure and temperature. Experimental details of the UHV-TEM can be found elsewhere¹⁶.

During the changes in pressure and temperature, we measured changes in the NW morphology and droplet size from individual video frames using ImageJ. The droplet volumes V were calculated based on the assumption of a spherical cap shape, using the formula $V = (1/6) \pi h (3(w/2)^2 + h^2)$, where w and h are the Au-Ge droplet width and height, respectively. The width of the droplet is measured as the distance between one trijunction (vapor-liquid-solid three-phase junction) and the other. The height of the droplet is defined as the highest point of the droplet to the middle of the projected liquid catalyst-wire interface.

Both ETEM and UHV-TEM experiments show qualitatively similar results for the effect of pressure and temperature on the Au-Ge alloy droplets and Ge NW morphologies. Figure 1A presents an image of a typical <111>-oriented 18.5 nm diameter Ge NW with a liquid Au-Ge catalyst, obtained

during an ETEM experiment at 350 °C and in 1.5×10^{-3} Torr of Ge_2H_6 . Figure 1B is obtained as the Ge_2H_6 is being pumped from the microscope. After the Ge_2H_6 pressure drops, we observe changes in both the NW and Au-Ge catalyst morphologies. Initially there is a rapid decrease in the size of the Au-Ge catalyst, apparently due to out-diffusion of the Au and Ge, see Fig. 1C. As a result, the droplet contact angle θ (shown in Fig. 1A) decreases as time progresses (Figs. 1C and D), as long as the trijunction remains pinned at the wire edge. There is a minimum stable contact angle¹⁷, and once the observed contact angle reaches this value the Au-Ge droplet de-pins from the corner of the wire (Fig. 1E). As the droplet material continues to diffuse away, the droplet shrinks at constant contact angle, as shown in Fig. 1E. Eventually the wire tip is bare (see Fig. 1F).

An abrupt enhancement in the contrast along the sidewalls of the wire is visible Fig. 1C (indicated by the arrow) once the Ge_2H_6 has been effectively removed from the system. Such a strong change in bright-field TEM image contrast is presumably caused by an element with a higher atomic number relative to Ge (i.e. Au in our experiments) decorating the walls of the wire¹⁸. Furthermore, as the droplet shrinks, strong faceting of the sidewalls is observed, beginning in Fig. 1C, as indicated by the red arrow. The Ge_2H_6 removal, contrast enhancement, facet formation on the sidewalls, and droplet shrinking all occur simultaneously in our ETEM data. The facets initially form near the trijunction and the faceting progresses away from the wire tip down the wire as the droplet decreases in volume.

The plot in Fig. 2 shows the measured Au-Ge droplet volume V as a function of time. This particular set of data is obtained during the growth of a 13.9 nm diameter Ge NW at 350 °C. A video of the wire behavior before, during, and after Ge_2H_6 purging from the system is available here (Supporting Information Movie S1). In the plot, the data points labeled (A) and (B) correspond to the ETEM images of Figs. 2A and 2B, respectively obtained at times 20.2 s (Ge_2H_6 partial pressure = 6.1×10^{-4} Torr) and 33.0 s (after purging Ge_2H_6). The data in Fig. 2 shows that the Ge_2H_6 pressure has a major impact on the

stability of the liquid catalyst: the (linear) rate of decrease in V increases by an order of magnitude, from $6.6 \text{ nm}^3/\text{s}$ to $77.8 \text{ nm}^3/\text{s}$, after removing Ge_2H_6 .

The formation of the sidewall facets is shown in detail in Figs. 1C-F. To understand this process, we compare the sidewalls of a wire before and after the purging of Ge_2H_6 in Figs. 2A and 2B. Initially (Fig. 2A), during growth in $6.1 \times 10^{-4} \text{ Torr Ge}_2\text{H}_6$, the Ge NW has relatively smooth sidewalls. After purging the Ge_2H_6 , conspicuous facets appear on the sidewalls of the wire (Fig. 2B). To determine whether the facets are a result of surface reorganization or accumulation of new material, we overlay the outline of Fig. 2A on Fig. 2B. The resulting composite image in Fig. 2C shows that the facets observed on the wire walls are a consequence of new material added on the sides of the original wire. Red arrows highlight a few locations of clear facet outgrowth in Fig. 2C. The angle between the facets is measured to be 149° , which is equal, within measurement uncertainties, to the angle (150.5°) between (111) and $(\bar{1}\bar{1}\bar{3})$ planes. Our observation is thus consistent with the $\{111\}$ and $\{113\}$ facets previously observed on $\langle 111 \rangle$ oriented Si wires¹⁹.

Because the sidewall facets form immediately after the removal of the Ge_2H_6 flux, we infer that they result from the loss of sidewall passivation. This could lead to direct growth on the sidewall from the vapor, a well-known process. However, in our ETEM wire growth case it appears the dominant source of material is diffusion of Ge from the Au-Ge droplet. This is suggested by the rapidity of the growth and the fact that sidewall growth appears to cease after the droplet disappears. To determine if the volume of Ge in the newly-formed facets is comparable to the Ge dissolved in the liquid Au-Ge alloy, we measured the projected area of the facets and calculated the volume of the facets, assuming that the wires have hexagonal cross-sectional shape²⁰. The details of facet volume calculations can be found in the Supporting Information (S2). For an 18 nm diameter wire (not shown), we estimate that the total amount of Ge in the facets is $840 - 1,690 \text{ nm}^3$; in comparison the maximum amount of Ge available in the Au-Ge catalyst is $\sim 700 \text{ nm}^3$. Given the large uncertainties involved in these volume calculations, we

suggest that a significant contribution to the growth of sidewall facets observed in our ETEM experiments stems from Ge re-deposition associated with the out-diffusion of Ge from the Au-Ge droplet. We do not rule out the possibility that direct sidewall chemical vapor deposition (CVD) of Ge_2H_6 also occurs as a result of gasses that are still lingering in our ETEM, but we emphasize that the Ge dissolved in the liquid droplet likely forms a significant source of Ge for sidewall facet growth in low pressure CVD conditions.

To determine if the general behavior shown in Fig. 1 and 2 occurs across a broad range of conditions, we conducted Ge NW growth experiments at constant temperature and pressure in the UHV-TEM. UHV-TEM experiments allow us to rule out contributions from contaminant gas species that may be present in a higher pressure ETEM experiment. For example, UHV-TEM experiments were helpful in determining the role of oxygen in altering Si NW sidewall surfaces and influencing catalyst diffusion⁴. Figure 3A shows images of a $\langle 111 \rangle$ -oriented Ge NW during growth at constant temperature 330 °C. Decreasing the Ge_2H_6 partial pressure from 4.8×10^{-6} Torr to 1.1×10^{-6} Torr encourages the formation of facets, as indicated by the red arrow (see times 1074 s and 1284 s, Fig. 3A). Upon increasing the pressure back to 4.8×10^{-6} Torr (see time 1826 s, Fig. 3A), the newly grown Ge wire has sidewalls that are not faceted but appear smooth, as indicated by the blue arrow. The return to relatively smooth wire sidewalls indicates that pressure influences the Ge surface morphology of the newly formed wire, as the faceted regions continue to coarsen and grow (see time 1826 s Fig. 3A). This UHV-TEM result illustrates that the catalyst diffusion behavior shown in Figs. 1 and 2 occurs across a broad pressure range, three orders of magnitude in pressure.

Temperature is also a key factor in influencing NW morphology. In Fig. 3B we show temperature effects *in-situ* in the UHV-TEM during growth of a $\langle 111 \rangle$ -type Ge NW from a liquid Au-Ge catalyst in a constant 2.6×10^{-6} Torr. The temperature, initially 330 °C (time 0 s and 443 s, Fig. 3B), increases to 350 °C at time 589 s. At the lower temperature, the wire walls appear smooth. After the temperature is

increased, facets are observed along the wire sidewalls (see time 589 s Fig. 3B) and their size increases with time. After some time the orientation of the NW changes from $\langle 111 \rangle$ to $\langle 110 \rangle$ (see time 1161 s Fig. 3B). When the temperature is reduced again, the growth direction appears to change (time 1221 s, Fig. 3B). The data shown in Fig. 3B suggests that increasing the growth temperature is similar to lowering the pressure (Fig. 3A), as it can lead to the growth of sidewall facets, also affecting the growth direction of the wire.

The time scales associated with the Au-Ge catalyst diffusion process in the ETEM and UHV-TEM experiments are different. In our ETEM data (Fig. 1 and 2) the catalyst diffuses away in tens of seconds at 350 °C (and base pressure 1.2×10^{-6} Torr). In contrast, the migration is relatively slow in the UHV-TEM experiments (Fig. 3) at the same nominal temperature (base pressure 2×10^{-10} Torr): the Au-Ge droplet sizes changes only modestly (on average a 10 % change in the measured projected area) over the course of minutes. Possible reasons for the differences in time scales for droplet migration could be differences in actual substrate temperature in the two experiments (we know that even 20 °C can have a significant effect on kinetics¹⁶) and the difference in base pressure. This could influence the kinetics of catalyst migration, as is known for Si: even 1×10^{-7} Torr partial pressure of oxygen has been shown to influence catalyst diffusion during Si wire growth⁴, while both oxygen and disilane (Si_2H_6) pressure affect Au diffusion on flat Si surfaces²¹.

To account for the observations presented in Figs. 1-3, we propose that the stability of Au-Ge alloy droplets depends on the NW sidewall coverage of atomic hydrogen^{6, 8, 22} or other radicals formed as a result of dissociative chemisorption of Ge_2H_6 during the VLS growth of Ge NWs. For brevity we will refer to H even though the relevant species might be some larger Ge_2H_6 fragment. We speculate that the presence of radicals on Ge surfaces passivates the surface, suppressing growth, and creates a barrier for out-diffusion of both Ge and Au at the trijunction during growth. Prior literature shows that Ge_2H_6 chemisorption on clean $\text{Ge}(100)$ ²³ and $\text{Ge}(111)$ ²⁴ leads to H adsorption on Ge surfaces but the H desorbs

within a few seconds (at 400 °C) after the Ge_2H_6 is removed²³. From *in-situ* Raman spectroscopy studies of Au-catalyzed Si^{6, 25} and Ge⁸ NW growth using Si_2H_6 and Ge_2H_6 respectively, H is known to decorate the walls of the Si and Ge NWs. Therefore, it is plausible that H – whether produced by cracking of Ge_2H_6 at the Au-Ge catalyst and/or direct chemisorption on the Ge surface – also decorates the sidewalls of our Ge NWs.

During the VLS growth of Ge NWs, H is produced by the decomposition of Ge_2H_6 , and can replace the H that is desorbing from the wire's surface. Thus the surface remains continuously passivated by H, which can act as a barrier for Au diffusion and Ge attachment to the sidewalls. When the Ge_2H_6 gas pressure is decreased, the replenishment of adsorbates lost to desorption decreases,²³ resulting in less complete passivation. When the substrate temperature increases the desorption rate increases²³, similarly reducing the passivation. The observed Au diffusion and Ge facet growth in low partial passivation growth conditions in Figs. 1-3 suggest that the bare Ge surfaces have a smaller kinetic barrier to Au diffusion and Ge attachment. The Ge in the liquid alloy catalyst can then leave the catalyst and bind to the un-passivated wire sidewalls. We speculate that diffusion of Au onto the Ge sidewalls is similar to the Au diffusion that has been reported during both Si wire growth³ and the annealing of Au on Si(112), which leads to the formation of {111} and {113} facets¹⁹. The ETEM and UHV-TEM observations we have presented demonstrate the role of radicals on the surface passivation of the wires, which is important for understanding catalyst diffusion^{3, 7}, Au-Si catalyst droplet spreading²⁶, Au catalyst migration in Ge-Si heterostructure wires²⁷, and the wetting dynamics of the catalyst droplet⁵.

The impact of surface passivation removal is vividly observed by the formation of sidewall facets in Figs. 1-3. The data in Figs. 1C-E, 2B, and 3 show that the Au-Ge catalyst at the wire tip can diffuse away at low Ge_2H_6 pressures and high temperatures, implying rapid hydrogen loss under these conditions. Our *in-situ* NW growth data is consistent with prior NW growth studies that show catalyst

migration is generally minimized at high growth pressure and low temperature conditions for group IV wires^{7, 28} and Au migration occurs when Si wires are annealed in vacuum²⁹.

A schematic summarizing our observations and interpretations is presented in Fig. 4. As the NW grows, a surface layer of H (or other radicals) is deposited (indicated by the blue line), Fig. 4A. Once the Ge_2H_6 has ceased flowing, the adsorbates passivating the walls of the wire begin to desorb, Fig. 4B. Consequently, Au migrates to and Ge binds to the un-passivated walls of the wire (Fig. 4B). The loss of the catalyst results in a decreasing contact angle θ , Fig. 4C. During catalyst diffusion, Ge facet formation is also observed in Fig. 4C, resulting primarily from Ge dissolved in the liquid catalyst. In the high pressure ETEM case ($\sim 10^{-3}$ Torr) catalyst migration continues until all of the Au is attached to the wire sidewalls. In the UHV-TEM ($\sim 10^{-6}$ Torr) experiment the loss of the liquid catalyst is considerably slower and, by increasing the pressure again, we were able to resume passivated growth while also enlarging and coarsening the sidewall facets. We infer that the Au must remain on the Ge NW facets after the reintroduction of the gas, catalyzing the breakdown of the Ge_2H_6 gas and resulting in further radial growth of the wire in this region.

In summary, we have shown that sidewall facet growth occurs immediately after reducing the pressure of Ge_2H_6 at a constant temperature, or when increasing the temperature at constant pressure. The formation of these facets is correlated with the diffusion of some Au-Ge away from the catalyst. We suggest that these observations arise from desorption of H and other radicals, produced from the dissociative chemisorption of the Ge_2H_6 at the catalyst and on the wire walls during Ge NW growth. The loss of the adsorbates promotes out-diffusion of Au and Ge from the catalyst, enabling growth of sidewall facets. Our data suggests that the growth of straight, un-tapered Ge NWs with observably smooth sidewalls is optimal under high flux (high production and adsorption of radicals) and low temperature (reduced radical desorption rate) conditions.

Supplementary Information:

S1: An ETEM video of the Ge NW shown in Fig. 2 (but rotated 180°) before and during digermane pumping.

S2: Measurements and calculations summarizing the Ge volume addition to the wire facets and the estimated available Ge in the liquid Au-Ge catalyst particle before digermane pumping.

Acknowledgements:

Research supported at the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

Figure 1: A-F) Bright-field transmission electron microscopy (TEM) images acquired *in-situ* in an environmental TEM (ETEM) at 350 °C (A) during VLS growth of an 18.5 nm diameter Ge NW from a liquid Au-Ge catalyst in 1.5×10^{-3} Torr Ge_2H_6 , (B) while reducing Ge_2H_6 gas pressure, and (C-F) after pumping of Ge_2H_6 from the microscope. The associated plot shows Ge_2H_6 pressure vs. time along with the times at which the images (A-E) are obtained. θ denotes the contact angle between the droplet and the wire. The loss of image resolution in (B) is due to thermal drift caused by a sudden change in substrate temperature upon reducing the gas pressure. Red arrows in (C) show the formation of facets on the sidewalls of the Ge NW. Images (D-E) show a gradual decrease in the size and depinning of the Au-Ge alloy droplet, as well as the appearance of darker (compared to (A)) contrast along the wire sidewalls: both are associated with the migration of Au from the droplet onto the wire sidewalls. (F) Higher magnification TEM image showing the detailed structure of the wire and the sidewalls. This image was obtained after the liquid Au-Ge catalyst has vanished and all of the Au has migrated to the wire sidewalls.

Figure 2: (A, B) Phase-contrast ETEM images obtained at 350 °C (A) during the growth of a $\langle 111 \rangle$ -oriented Ge NW in 6.1×10^{-4} Torr Ge₂H₆. The inset presents an FFT of the wire's body in (A). The reflections in the FFT inset are measured at a distance of 0.33 nm^{-1} which corresponds to the $\{111\}$ plane spacing in diamond cubic Ge. (B) After removing Ge₂H₆, V is calculated using the droplet heights h and widths w , defined in (A), measured from the ETEM images. In the presence of Ge₂H₆, i.e. during the NW growth, V changes very little, from $\sim 1165 \text{ nm}^3$ at time 0.0 s to $\sim 990 \text{ nm}^3$ after 25.2 s. Upon decreasing the Ge₂H₆ pressure at time 25.2 s, V falls rapidly to 30 nm^3 within 11.4 s. The two linear curve fits in the plot have slopes of $-6.6 \text{ nm}^3/\text{s}$ and $-77.8 \text{ nm}^3/\text{s}$, corresponding to growth in 6.1×10^{-4} Torr Ge₂H₆ and during purging/base pressure respectively. (C) A composite image created by superposition of the outlines of the wire during growth from Fig. 2A and the faceted wire in Fig. 2B. The arrows highlight facets, which appear as protrusions with respect to the sidewalls of the wire in (A), indicating that the facets are due to new material being added to the sidewalls, rather than reorganization of existing material.

Figure 3: Bright field TEM images obtained *in-situ* in the ultra-high vacuum TEM (UHV-TEM) during the growth of a Ge NW (growth rate ranging from 0.03 – 0.11 nm/s for the conditions shown here) from a liquid Au-Ge catalyst with a gas mixture containing 20 % Ge_2H_6 and 80 % He. (A) UHV-TEM experiment at constant temperature, 330 °C. From 0 – 360 s NW growth is carried out at 4.8×10^{-6} Torr partial Ge_2H_6 pressure. During 1074 – 1284 s the lowering of the gas pressure results in the formation of facets along the Ge NW sidewalls, indicated by the red arrow. At 1826 s, upon the increase in pressure to 4.8×10^{-6} Torr, the wire sidewalls become relatively smooth once more, as indicated by the blue arrow. (B) UHV-TEM experiment at constant 2.6×10^{-6} Torr pressure. From 0 – 443 s NW growth is carried out at 330 °C and sidewall faceting is minimal. At 589 s, after increasing the temperature to 350 °C, sidewall facets form (red arrow). At 1161 s the wire facets continue to grow and the NW orientation changes from $\langle 111 \rangle$ to $\langle 110 \rangle$. At 1221 s – upon lowering the temperature to 330 °C – growth appears to change direction.

Figure 4: A schematic illustrating the full process of Au migration and facet formation in our experiments. The schematic P and T plots in the bottom figure illustrate the temperature or pressure evolution required to produce the idealized wire morphologies shown. Initially (A) a Ge NW grows with hydrogen and other radicals attaching to the surface, attributed to the Ge_2H_6 gas. The surface passivation layer is indicated by the blue coating along the Ge NW. (B) Once the Ge_2H_6 is reduced (or temperature increased), the radicals begin to desorb (indicated by the faded blue coating on the wire) and (C) the Au migrates down the wire sidewalls. The Ge in the vapor and liquid alloy binds to the wire sidewalls, forming facets. This eventually leads to a total loss of the catalyst at the tip of the Ge wire in our high pressure ($\sim 10^{-3}$ Torr) ETEM experiments without surface wire passivation.

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Supplementary Information

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Section 1: Facet Volume Measurement

In order to estimate the 3D volume of material added during faceting (based on 2D projected TEM data), an expression for volume in terms of wire diameter, the projected area of a newly grown facet, and the symmetry of the Ge NW structure is needed. The volume of material was estimated based on the facet width b , wire diameter d , and the measured projected area of a facet A_{proj} . We estimate the volume of a single facet in terms of the measured projected area on the side of a wire, given by

$$V_f = \frac{1}{6} (2\pi R A_{\text{proj}}) \quad \text{Eqn. 1}$$

Here R is the radius of revolution, which is given in terms of the wire diameter d and facet diameter b : $R = d/2 + b/2$. The $1/6$ term arises since a facet only covers one 6th of the wire based on hexagonal symmetry. A breakdown of the various terms in Eqn. 1 and how they correspond to the geometry of the wire + facet are shown in Fig. S1.

Figure S1: A figure summarizing how the variables in Eqn. 1 correspond to the wire geometry. Note that the projected area (red shaded region of the facet) was measured using ImageJ.

Equation 1 and the measurements described in Fig. S1 were used to estimate the facet volume of the Ge NW in Fig. S2 to determine the volume of several facets. We align the wire sidewalls and liquid-solid NW interface to produce the composite image in Fig. S2. Note that we assume that the liquid-solid interface does not advance dramatically during the Au-Ge diffusion process, which is consistent with our other ETEM video observations. From the volume measurements collected in Fig. S2 we conclude the average measured facet volume is 6.75 nm^3 of Ge. In addition to this, each facet is spaced apart by approximately 6 nm.

Figure S2: The volume of 4 facets for a Ge NW captured during digermane pumping at 350 °C. This wire is the same wire shown in Fig. 2C in the manuscript. The facets are spaced apart by approximately 6 nm in length and the average volume of the 4 measured facets is 6.75 nm³.

Section 2: Catalyst Volume Measurement

Based on the Au-Ge phase diagram¹, approximately 25% of a liquid alloy catalyst should be composed of Ge at 350 °C, the ETEM experimental temperature. Assuming Au and Ge occupy a similar atomic volume, we take the liquid alloy catalyst to also be 25% Ge by volume. Using the spherical cap formula we can estimate the volume V_c of the liquid Au-Ge droplet, Eqn. 2.

$$V_c = \frac{\pi h}{6} \left[3 \left(\frac{w}{2} \right)^2 + h^2 \right] \quad \text{Eqn. 2}$$

Where w is the droplet width and h is the droplet height. We measure the droplet width and height of a growing Ge NW before digermane purging, Fig. S3.

Figure S3: A liquid Au-Ge alloy catalyst droplet at the tip of a Ge NW. The height and width of the catalyst are measured a few seconds before digermene is pumped from the ETEM and subsequent catalyst migration occurs.

With the measurements from Fig. S3 and using Eqn. 1 the total volume of the catalyst is calculated to be $V_c = 2800 \text{ nm}^3$. From the Au-Ge phase diagram at 350°C the equilibrium Ge fraction should be close to 25%. Thus yields a volume of Ge in the catalyst $V_{\text{Ge}} = 700 \text{ nm}^3$.

Section 3: Facet Volume Estimate on Wire Walls

Now that we have an estimate for the amount of Ge in the catalyst, we need to estimate how much Ge has been added to the wire sidewalls after catalyst migration. We examine the same NW in Fig. S3, but at a later time after all of the catalyst has migrated to the wire sidewalls, Fig. S4.

Figure S4: The Ge NW in Fig. S3 after digermene purging. This image is stitched together from multiple frames in an ETEM video. The extent of the faceting is measured to be 250 nm.

In Fig. S4 the wire is faceted along its length. This is presumably the area where Ge was deposited following the disappearance of the liquid Au-Ge (after digermane purging). We can use the length of the faceting and the facet volume estimates obtained earlier in Section 1 to estimate the total amount of Ge deposited on the wire following catalyst migration.

To estimate how much Ge has been deposited on the wire, we examine the length of a Ge NW that appears faceted after catalyst migration, Fig. S2. We measure the faceting extends 250 nm down the length of the wire from the wire tip. In the wire analyzed in Section 1, we estimate there is 6.75 nm^3 Ge in each facet and a facet located every 6 nm. We also anticipate by symmetry there are $3^2 - 6^{3-4}$ protruding facets for a given each wire cross section plane (perpendicular to [111]) by the hexagonal symmetry of the NW (when viewed down the [111]-axis), Fig. S1. This means that for every 1 nm of Ge wire we anticipate there are 3 - 6 facets/6 nm and each facet contains 6.75 nm^3 of Ge. It is then possible to calculate the estimated Ge deposited on the 250 nm length of the NW shown in Fig. S4, see the calculation in Eqn. 3.

$$\frac{250 \text{ nm}}{6 \text{ nm}} \times \frac{3 - 6 \text{ facets}}{1 \text{ facet}} \times \frac{6.75 \text{ nm}^3 \text{ Ge}}{1 \text{ facet}} \approx 840 - 1,690 \text{ nm}^3 \text{ of Ge} \quad \text{Eqn. 3}$$

Since $840 - 1,690 \text{ nm}^3$ of Ge deposited on the wire is in the same order of magnitude as 700 nm^3 of Ge (estimated initially in the catalyst), we conclude that a plausible origin for the facets after digermane pumping is redistribution of the dissolved Ge in the catalyst particle (within the accuracy of these measurements).

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