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Nanowire growth in the standard $\langle 111 \rangle$ direction is assumed to occur at a planar catalyst-nanowire interface, but recent reports contradict this picture. Here we show that a nonplanar growth interface is, in fact, a general phenomenon. Both III–V and group IV nanowires show a distinct region at the trijunction with a different orientation whose size oscillates during growth, synchronized with step flow. We develop an explicit model for this structure that agrees well with experiment and shows that the oscillations provide a direct visualization of catalyst supersaturation. We discuss the implications for wire growth and structure.

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The vapor-liquid-solid (VLS) and vapor-solid-solid (VSS) growth mechanisms allow semiconductor nanowires to be fabricated with well-controlled structure and composition, paving the way for electronic, optoelectronic, and energy-related applications [1–5]. During nanowire growth, the catalyst remains at the tip, and material is added by step flow [6–8] at the interface between the nanowire and the catalyst [1]. The structure of the catalyst-nanowire interface is key to understanding growth at an atomic level: Interface morphology and step nucleation are thought to determine zinc-blende–wurtzite polytypism in III–V nanowires [9–12] and influence the abruptness of compositional changes at heterojunctions [7,13].

Most studies focus on nanowires growing in the $\langle 111 \rangle$ direction. Until recently, it was assumed for such wires that the catalyst-nanowire interface was planar, meaning that the trijunction (where nanowire, catalyst, and vapor meet) has a simple geometry and provides a unique location for step nucleation. However, two recent experiments show an unexpected geometry, with a truncated edge at the trijunction [14,15]; a similar geometry has been seen in computer simulations [16–18]. Moreover, the degree of truncation varies over the step-flow cycle. Such behavior is of great importance because it overturns our picture of how nanowires grow. In particular, if all edges are truncated, then steps must nucleate away from the trijunction, completely changing the thermodynamics of step nucleation [9,19].

Here we show that this interface behavior occurs in a wide variety of nanowire systems, including both group IV and group III–V materials—indeed, in *all* the VLS systems that we have examined and at least one VSS system. To understand the phenomenon, we examine the thermodynamic and kinetic factors controlling trijunction morphology. We find that, under reasonable assumptions, the presence or absence of a truncated edge is determined

simply by the balance of capillary forces. However, if the edge *is* truncated, the degree of truncation depends on the supersaturation of the catalyst. Truncation thus provides a direct visualization of how supersaturation varies during step flow—a “thermometer” of chemical potential. We develop an explicit model for the oscillations during VLS growth that predicts the time variation of the truncation and is in good agreement with measurements.

Nanowires were grown in an ultrahigh vacuum transmission electron microscope [20]. For Si and Ge nanowires, Si(111) substrates were flash cleaned in vacuum and 0.1–1 nm of Au, Cu, AuGa, or AuAl deposited by thermal evaporation. Substrates were transferred to the TEM, heated to form catalyst droplets (for VLS growth) or particles (for VSS growth), and then exposed to disilane or digermane gases. To examine group III–V nanowire growth, pregrown GaP nanowires on Si substrates were heated *in situ* during exposure to triethylgallium in an excess of phosphine. In all cases, the growth interface and two sidewalls are parallel to the electron beam [20].

Figures 1 and 2 show a selection of nanowire-catalyst combinations during growth. In each case we observe at least one trijunction where the growth interface and the nanowire sidewall do not meet at a sharp angle, but instead the edge appears truncated, as shown schematically in Fig. 3. Furthermore, in all these cases the truncated structure changes periodically during growth. For VLS Si/AuSi in Figs. 1(a)–1(d), for example, the edge is most truncated in (c) and least truncated in (b). Strikingly, we find no evidence that the catalyst-nanowire interface is *ever* a single plane during growth in any of the VLS systems studied. Si/AuAlSi, Si/AuGaSi, and Ge/AuGe [Figs. 2(a)–2(f)] show truncated structures that oscillate with different “maximum” amounts of truncation. Note that the truncation is different on each side of the main facet. Opposite edges are inequivalent, since

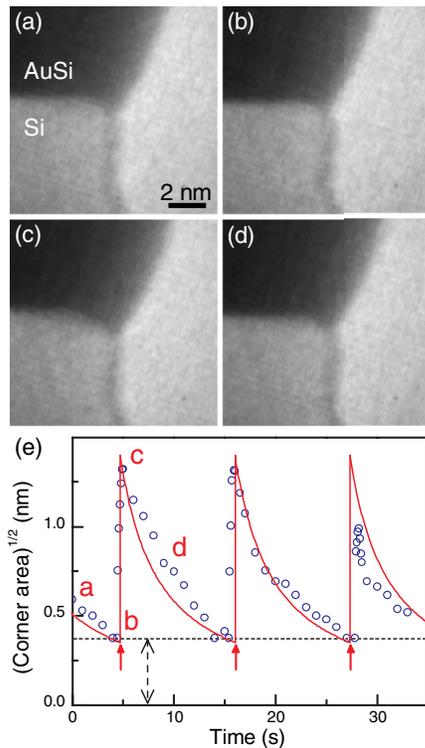


FIG. 1 (color online). Time evolution of nanowire edge morphology. (a)–(d) Bright-field TEM images extracted from a 30 images per second video showing the trijunction morphology during VLS Si/AuSi growth at 550 °C and a partial pressure of 4×10^{-7} Torr Si_2H_6 . (e) The time variation of the truncated area, determined by measuring the area of liquid AuSi below the Si/AuSi interface. Measurements were made over three consecutive cycles, and the data points corresponding to (a)–(d) are labeled. A Si(111) bilayer forms after point b (shown with an arrow for each period) followed by a rapid increase of the truncated area. The horizontal dotted line and dashed arrow indicate that the amount of truncation remains above zero. The maximum truncated volume is 0.2 bilayers at the growth interface, assuming a trigonal hexagon cross section with a 2:1 ratio for the edge lengths and three truncated edges. The solid line is fitted with Eq. (3) with $a_0 = 0.5$ and $a_1 = 1.5$.

the nanowire cross section is a trigonal hexagon with alternating longer and shorter sides [20]. GaP nanowires also grow in the VLS mode and have a similar appearance [Figs. 2(g) and 2(h)]. Oscillation also occurs during growth from a solid catalyst, VSS Si/ Cu_3Si [Figs. 2(i) and 2(j)]. Because of the limited resolution, we cannot reliably quantify the orientation of the edge facet, but we note that its orientation appears different in each system.

It is important to establish that the oscillating trijunction is a reproducible feature of growth. In Fig. 4, we demonstrate its regularity over long periods of steady growth, showing over 50 oscillations for VLS Si/AuSi at several pressures. Figure 4 also shows that each oscillation corresponds to the growth of one Si (111) bilayer (0.31 nm), established by measuring the total nanowire length every few seconds and comparing with the number of oscillations.

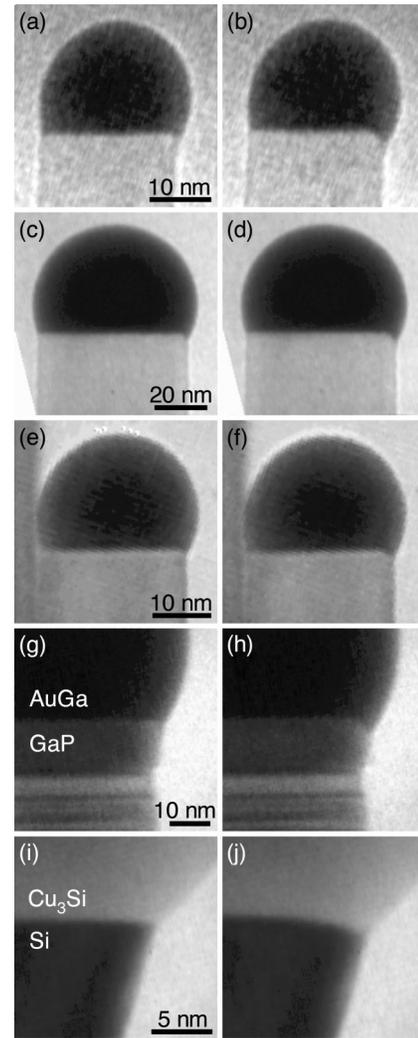


FIG. 2. Video image pairs showing approximately the minimum and maximum truncation in (a),(b) a VLS Si/AuAlSi wire of 23 nm diameter grown at 560 °C and 8×10^{-6} Torr Si_2H_6 . For (b) the maximum truncated volume (assuming trigonal symmetry) is 54 nm^3 or 1.2 bilayers. In (a) the minimum volume is 0.3 bilayers. (c),(d) VLS Si/AuGaSi at 500 °C and 1×10^{-5} Torr Si_2H_6 . (e),(f) VLS Ge/AuGe at 410 °C and 4×10^{-6} Torr Ge_2H_6 . (g),(h) VLS GaP/AuGa at 450 °C and 1×10^{-5} Torr $\text{PH}_3 + 2 \times 10^{-8}$ Torr $\text{Ga}(\text{C}_2\text{H}_5)_3$; (i),(j) VSS Si/ Cu_3Si at 530 °C and 2×10^{-7} Torr Si_2H_6 .

For VLS Si/AuSi [13], Si/AlSi [21], Si/AlAuSi [7], and Ge/AuGe [22], growth is known to take place by the periodic abrupt addition of (111) bilayers. Step flow is too rapid to measure, but from high magnification videos we can identify the moment it occurs [7]. In Fig. 1(e), we show a detailed analysis of a few oscillation cycles. The degree of truncation jumps to its maximum value when the bilayer is added and then decreases in a nonlinear manner during the incubation period between bilayer additions. For VSS Si/ Cu_3Si , truncation is also minimum [Fig. 2(i)] just before step nucleation. These results are consistent with the correlation between oscillations and layer addition established in the two systems examined to date [14,15].

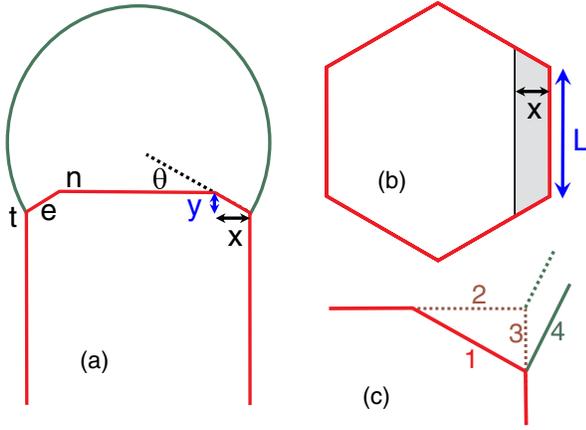


FIG. 3 (color online). Geometry of the catalyst-nanowire interface as viewed (a) from the side and (b) from above. The electron beam is parallel to the nanowire edge, so that the edge shows as a corner in the images, and the corner appears truncated. x and y are the width and height of the truncation, respectively, and $y = x \tan \theta$, where θ is the angle between the two facets. t is the trijunction, e the edge facet, and n the favored nucleation site on the main facet. Only one edge facet is shown in (b) for clarity. (c) Geometrical changes caused by truncating the corner. Contributions to the linear-order capillary term in Eq. (1) are (1) the area of the small facet, (2),(3) the decreased areas of the adjacent facets, and (4) the increase in the liquid-vapor interface length.

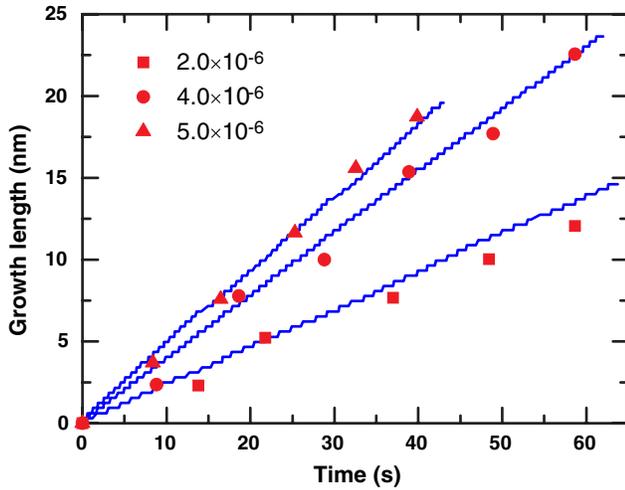


FIG. 4 (color online). The relationship between the nanowire length and cumulative number of oscillations, recorded during VLS Si/AuSi growth at 480 °C and three Si_2H_6 pressures indicated in Torr. The symbols represent changes in the length of the same nanowire measured every few seconds from a fixed point. The staircase graphs represent cumulative oscillations converted to length by multiplying by 0.31 nm. Oscillations are counted whether they are visible at the edge parallel to the electron beam or the other two equivalent edges. The vertical segments indicate the sudden changes in trijunction morphology. In a few cases (three instances over 200 oscillations), a less abrupt morphology change occurred; these are shown as sloped sections.

To understand why the truncated morphology occurs, and why it oscillates, we explicitly calculate the expected structure of a generic nanowire edge during step-flow growth. First we consider a 90° edge of length L and calculate the free energy of an extra facet formed by truncating this edge at angle θ to the main facet, as in Fig. 3. The free energy change E_c of introducing the edge facet (to second order in the linear truncation size y) is

$$E_c = c_1 y L + \frac{1}{2} y^2 (\cot \theta) L (\mu_{\text{cat}} - \mu_0) + c_2 y^2 L. \quad (1)$$

Here, for the quadratic term, we have separated out the contribution from supersaturation, where μ_{cat} is the chemical potential of the growth species (say, Si) in the catalyst and μ_0 is that of a reference system (bulk Si) [16,23]. For a sufficiently small edge facet, E_c is dominated by the lowest-order term, i.e., the linear term with coefficient c_1 . This reflects the capillary forces acting on the edge facet, i.e., the change in interfacial energies with facet size y , illustrated in Fig. 3(c). Changing y also changes the size of the neighboring facets, as well as doing work against the droplet surface tension [Fig. 3(c)]. Thus the value of c_1 is given simply by a geometrically weighted sum of the three crystal facet energies and the liquid surface tension [16,23].

For $c_1 > 0$ the small facet is unstable and will shrink and disappear. Conversely, for $c_1 < 0$ an infinitesimal facet will always grow. In the classic two-phase problem of a crystal in a fluid, $c_1 < 0$ for any facet present in the equilibrium crystal shape [24], so perhaps we should be surprised that there are not *more* facets. However, in the three-phase system, the additional force exerted by the liquid can eliminate facets that would otherwise be present, so a sharp edge is entirely possible. Experimentally, all systems examined show truncated edges indicating that $c_1 < 0$. In cases where we see inequivalent edges on the same wire, one may appear more clearly truncated than the other, but we never see an edge change between sharp and truncated, consistent with this being controlled simply by the sign of c_1 for that edge.

The quadratic terms in Eq. (1) determine the size to which the edge facet will grow when $c_1 < 0$. The first quadratic term describes how the free energy depends on the supersaturation in the catalyst, where $y^2 (\cot \theta) L / 2$ is the volume of the truncated region. All other quadratic contributions are lumped together in the last term, with c_2 independent of supersaturation. The value of y that minimizes E_c is

$$y = \frac{y_0}{1 + \alpha (\mu_{\text{cat}} - \mu_0)}, \quad (2)$$

where $y_0 = -c_1 / 2c_2$ is the degree of truncation for the catalyst at μ_0 and $\alpha = \cot \theta / (2c_2)$. Equation (2) shows how the amount of truncation depends on the supersaturation $\mu_{\text{cat}} - \mu_0$ of the growth species in the catalyst. Alternatively, to infer chemical potential from geometry, we could invert Eq. (2): $\mu_{\text{cat}} = \mu_0 + \alpha^{-1} (y_0 - y) / y$.

To calculate the time dependence of the truncation, we draw on a recent analysis of nanowire step-flow growth [13]. As the growth species arrives from the gas phase, μ_{cat}

risers linearly until a step can nucleate. VLS is a particularly simple case since, as mentioned above, this step flows rapidly to complete the bilayer. This quickly reduces μ_{cat} from its maximum to its minimum value as one bilayer of the growth species is removed from the catalyst. Assuming periodic step nucleation with period t_{step} , and substituting this sawtooth $\mu_{\text{cat}}(t)$ into Eq. (2), we obtain an explicit expression for the time variation of the truncation:

$$y = [a_0 + a_1(t/t_{\text{step}})]^{-1}. \quad (3)$$

Here $a_0 = y_{\text{max}}^{-1}$ and $a_1 = y_{\text{min}}^{-1} - y_{\text{max}}^{-1}$ are determined directly from the measured extremal values of y , circumventing the uncertainties in c_2 and α . With two parameters a_0 and a_1 reflecting the maximum and minimum truncation, this simple prediction agrees well with the data in Fig. 1(e). In particular, the model correctly predicts that, when an edge facet is present, it never shrinks to zero size and that the size varies nonlinearly over the cycle. The excellent fit supports the model and the relationship between truncation and catalyst supersaturation.

The truncated geometry is crucial to understanding several aspects of nanowire growth. Assuming the main facet does not meet the trijunction [labeled “ t ” in Fig. 3(a)], steps on the main facet do not nucleate at the trijunction. Instead, we expect nucleation where the main facet meets the edge facet, labeled “ n .” (This spot is favorable because extending the facet must have lower energy than introducing a step on the terrace—otherwise, the facet would decompose into steps.) While our study of GaP is not systematic or extensive, it clearly suggests that models for III–V nanowire growth and polytypism cannot assume nucleation at the trijunction [9–12]. Furthermore, we note that nucleation at site n is more difficult than at site t , since at t the nucleation barrier is reduced by the catalyst surface tension [9]. Difficult nucleation on the main facet leads to large supersaturations, crucial for understanding VLS growth far below the eutectic temperature, such as in Ge/AuGe [22]. Finally, easier nucleation at t implies that the rate-limiting step is indeed nucleation on the main facet, with the edge facet able to equilibrate quickly, as required in our model [25].

In conclusion, we have shown that the existence of a truncated trijunction structure, whose degree of truncation oscillates in synchronization with the flow of steps across the interface, is a general phenomenon in nanowire growth. We have shown that the trijunction morphology, i.e., whether a given edge is truncated or not, can be understood through the balance of facet energies and droplet surface tension, while the functional form of its time dependence can be understood quantitatively through the time-varying catalyst chemical potential. The trijunction oscillation provides a window into the catalyst composition—indeed, Eq. (2) shows that it is a sort of thermometer for supersaturation which, although certainly uncalibrated, provides a linear measure and which can help extend our understanding of the entire growth process. The truncated geometry itself has far-reaching implications for

understanding both polytypism in III–V nanowires and deep-subeutectic growth in Ge and perhaps other systems. A final consequence is that the oscillation provides a limit on the achievable interface abruptness. On each layer addition cycle, material previously deposited onto the nanowire returns to the catalyst reservoir from the truncated volume. We have observed large truncation volumes, over one Si(111) bilayer [AuAlSi/Si in Fig. 2(b)]. A compositional change could thus be affected by intermixing to this extent. We believe that the demonstration of the generality of the truncated morphology, and the detailed understanding of its time dependence, will help to improve models of step nucleation, heterointerface abruptness, and the control of phases in III–V nanowires.

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