Sawtooth Faceting in Silicon Nanowires

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We observe *in situ* the vapor-liquid-solid (VLS) growth of Si nanowires, in UHV-CVD using Au catalyst. The nanowire sidewalls exhibit periodic sawtooth faceting, reflecting an oscillatory growth process. We interpret the facet alternation as resulting from the interplay of the geometry and surface energies of the wire and liquid droplet. Such faceting may be present in any VLS growth system in which there are no stable orientations parallel to the growth direction. The sawtooth structure has important implications for electronic mobility and scattering in nanowire devices.

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As microelectronic device sizes continue to shrink and conventional lithography becomes more challenging, it has become important to find new ways of fabricating nanoscale semiconductor structures. Nanowires grown by the vapor-liquid-solid (VLS) process [1] are natural candidates. They have been proposed for a range of exciting applications in nanoelectronics, including diodes, FETs, logic gates and single electron transistors [2], optoelectronic devices [3], and sensors [4]. During VLS growth, material supplied from the vapor phase diffuses through a liquid eutectic and is deposited on the solid surface. If the eutectic is in the form of a small droplet, the deposit forms a pillar or ''nanowire,'' which may grow several microns long yet have a diameter in the tens of nanometers. The VLS growth process was studied in micron-diameter Si wires four decades ago [1], but a quantitative understanding of the structure and growth of nanoscale wires is needed for the applications of interest today.

One issue of particular importance is the surface structure of the wires. Structures such as wraparound gate transistors [5] or core-shell heterostructures [6] require good control of the wire surface, both to achieve a uniform cross section and to minimize carrier scattering at rough interfaces. It is generally accepted that wires are cylinders or prisms in shape, bounded by sidewalls which are parallel to the growth direction.

Here we study nanowires *during* the growth process, using ultrahigh vacuum chemical vapor deposition (UHV-CVD) in a UHV transmission electron microscope (TEM). We find that Si nanowires growing from a Si-Au eutectic show *periodic sawtooth facets*, which are at an angle to the growth direction. Thus the wire surface is not smooth. Growth occurs at a (111) facet at the end of the wire, and the size and shape of this facet oscillates periodically during growth.

Such oscillatory growth can be explained, at least qualitatively, by considering the role of surface energetics in growth. The surface energies of the wire and droplet both play important roles, but very different ones. Force balance arguments predict that the period and amplitude of the faceting is proportional to the wire diameter. We confirm this directly by analyzing several wires grown simultaneously from droplets of different size. This type of faceting can occur in *any* growth system in which the orientations parallel to the growth direction are not stable, i.e., are not present on the equilibrium crystal shape.

The growth experiments were carried out in a UHV TEM having gas handling facilities and a base pressure of 2×10^{-10} torr [7]. A Si(111) wafer patterned with Au was cut into slices, cleaned with a HF dip and then mounted in the microscope with the Au-covered side vertical. Wire growth was then initiated by heating the specimen (using direct current) and exposing it to disilane gas. Simultaneously, images were recorded with the electron beam parallel to the surface. Uncontrolled agglomeration of the Au led to a range of eutectic droplet sizes and therefore wire diameters; and as wires grew away from the surface, their structure could be observed directly. The growth experiments were carried out at 10^{-8} to 10^{-5} torr disilane and temperatures of 500–650 °C. (This is a lower pressure and higher temperature than is typically used for wire growth, and is limited by the maximum pressure attainable during TEM imaging.) The substrate temperature was calibrated postgrowth using an infrared pyrometer.

There are two advantages to carrying out wire growth *in situ*. First, the structure of the wire and droplet can be obtained under growth conditions, rather than after cooling down and exposing to the atmosphere, during which the droplet crystallizes and the surface oxidizes. Second, we can eliminate any effects due to the direct (noncatalytic) CVD growth which occurs (although at a much slower rate) on the wire surfaces after their formation by the VLS process. Such noncatalytic growth is well known to affect wire cross-sectional shapes [1], and we have observed that it can eventually lead to rough irregular features. Because we focus on the newly grown region near the growth front, direct CVD growth is negligible.

In Fig. 1 we show images of Si wires obtained during growth. The wires grow in the ⟨111⟩ direction, and the

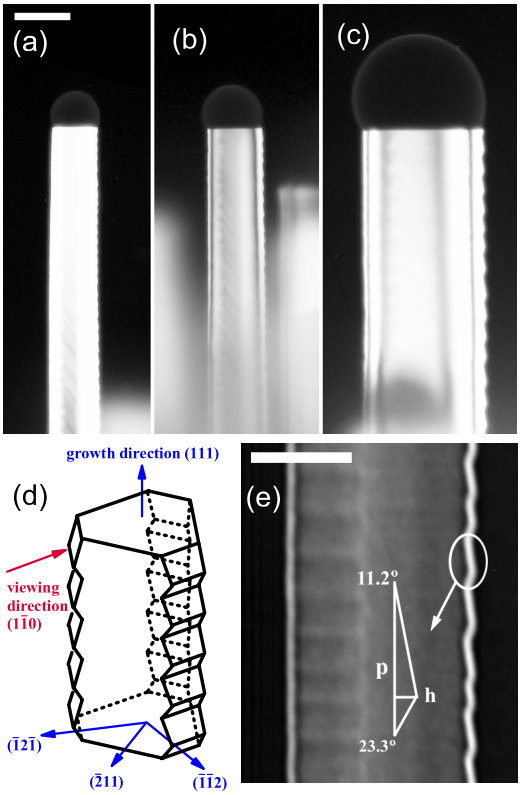

FIG. 1 (color online). (a)–(c) Images of three wires grown at 600 °C and 10^{-6} torr disilane from Au-Si droplets of three different sizes. Scale bar is 100 nm. The faceting along one side of each wire is clearly visible, as is the asymmetrical liquid contact angle and the variation of facet period and amplitude with wire diameter. The viewing direction is $\langle 1\bar{1}0\rangle$ and the growth direction is $\langle 111\rangle$. The dark lines within each wire are thickness fringes in the Si. (d) Schematic of the three dimensional structure of a wire. The cross section of each wire is a trigonal hexagon with three long and three short edges. This asymmetry accounts for the different contact angles seen in profile on the two sides of each wire in (a)–(c). (e) Defocused image of a wire showing the surface structure; scale bar is 50 nm. The facets on three of the sidewalls are visible, and the facet angles are indicated; p and h denote sawtooth period and amplitude.

eutectic droplet and the flat (111) Si/eutectic interface are clearly visible. However, most surprising in these images is the presence of sawtooth-faceted sidewalls with a regular periodicity. Facet angles and period are indicated in Fig. 1(e). TEM tilting experiments and scanning electron microscopy observation show that the wire cross section is hexagonal, with alternating wider and narrower sides, and the sawtooth faceting is clearly visible on the three narrower sidewalls. Faceting is occasionally visible on the three wider sides, but has much smaller amplitude and period so it is hard to resolve; it is not visible in Fig. 1. The specific facets that are present may depend on whether the surface is pristine Si, or includes other atoms such as Au, O, or H. In particular, Au is known to induce facetting on Si(111) and (001) surfaces [8], so it seems likely that the presence of Au determines the specific facets present here.

This sawtooth faceting has not been discussed elsewhere to our knowledge. However, similar faceting is visible in images of the larger wires in the early literature [1,9], and can be detected in at least one more recent nanowire image [10]. Without *in situ* observation, such faceting could perhaps be obscured on smaller wires by postgrowth oxidation or noncatalyzed CVD growth directly on the sidewall. Note that the phenomenon we report here is qualitatively quite different from the ''periodic instability'' observed during growth [11] and during annealing [12] where the wire surfaces are not faceted but instead the diameter changes continuously; this was attributed to continuous changes in contact angle or Rayleigh instability.

While periodic sawtooth faceting may seem surprising and counterintuitive, simple thermodynamic arguments suggest that it could be a rather general phenomenon. At typical VLS growth temperatures, most semiconductors are faceted; and only facets that are present in the equilibrium crystal shape should occur during near-equilibrium wire growth. If there are allowed facets parallel to the growth direction, as for GaN wires in the $\langle 0001\rangle$ direction [13] or Si wires growing in the $\langle 110\rangle$ direction [14], then highly ideal wire growth should be possible. Otherwise, uniform growth is not possible, and steady-state growth can occur only by a periodic oscillation.

We illustrate the thermodynamic arguments in Fig. 2 for the much simpler case of growth in two dimensions. The allowed facets correspond to a wire that is widening or

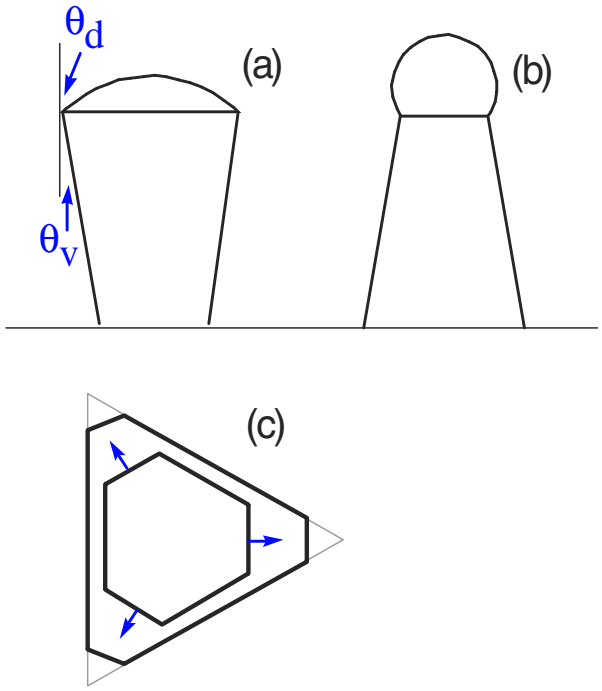

FIG. 2 (color online). Schematic showing the elements of the model.

narrowing as it grows. As the wire grows wider [Fig. 2(a)], the Au-Si droplet is stretched thinner, and meets the Si at a steeper angle. This generates an inward force favoring introduction of the other facet [the narrowing facet of Fig. 2(b)]. Conversely, in the case of Fig. 2(b), the narrowing of the wire eventually leads to the droplet applying an increasing outward force on the wire, favoring introduction of the widening facet of Fig. 2(a).

To analyze the energetics of VLS growth in this 2D case, we assume (as suggested by experiment) that the liquid droplet wets the terminal facet but not the sidewalls. Then the change in free energy per unit length of wire growth is $dE/dz = L\Delta\mu + \Gamma_\nu^{\mathrm{eff}}$, where $\Delta\mu$ is the supersaturation of Si during growth, and

$$\Gamma_\nu^{\mathrm{eff}} = \frac{\gamma_\nu}{\cos\theta_\nu} + (\gamma_d \sin\theta_d + \gamma_i)\sin\theta_\nu \qquad (1)$$

is the surface energy contribution. Here L is the wire width at the terminal facet; ν is an index labeling the different stable facets (i.e., those present in the equilibrium crystal shape); γ_ν is the surface energy of facet ν, and θ_ν is its angle; γ_d is the surface energy of the droplet, and θ_d is its contact angle; and γ_i is the interface energy between the droplet and wire. Angles are defined in Fig. 2(a). The γ_ν term in Eq. (1) represents the sidewall surface energy increase per unit length of wire growth, the γ_d term represents the work done against the surface tension of the droplet, and the γ_i term presents the increase in wire-droplet interface energy per unit length of growth.

Near equilibrium, growth will occur via the most energetically favorable facet, i.e., the facet which minimizes $\Gamma_\nu^{\mathrm{eff}}$. If there is a stable facet that is normal to the growth direction, i.e., having $\theta_\nu = 0$, then we can have the ideal situation of uniform growth from a hemispherical droplet ($\theta_d \approx 0$). However, in general there may be no facet having the required orientation. Then the wire must be either widening or narrowing as it grows.

The droplet volume is effectively constant; so for a widening wire [$\theta_\nu > 0$, as in Fig. 2(a)], the droplet becomes increasingly "taut," with the angle θ_d (and hence $\Gamma_\nu^{\mathrm{eff}}$) increasing as the wire grows. While this raises $\Gamma_\nu^{\mathrm{eff}}$ when ν is a widening fact, it lowers $\Gamma_\nu^{\mathrm{eff}}$ for a narrowing facet, i.e., one having $\theta_\nu < 0$ as in Fig. 2(b). Eventually, the facet having $\theta_\nu < 0$ will become more favorable. Then the new facet is introduced, and the wire thereafter becomes narrower as it grows, until the process is reversed.

Thus the growth may in general alternate between the two facets bounding $\theta = 0$, and the wire width will stabilize at the width where θ_d balances the two facets. If we denote the widening facet by $\nu = w$ and the narrowing one by $\nu = n$, then this balance occurs at $\Gamma_w^{\mathrm{eff}} = \Gamma_n^{\mathrm{eff}}$. As an example, we consider the symmetrical case where the two facets have equal and opposite angle and equal energy γ_ν. Then (or more generally whenever $\gamma_n/\cos\theta_n = \gamma_w/\cos\theta_w$), the balance occurs at

$$\sin\theta_d = -\gamma_i/\gamma_d. \qquad (2)$$

Since typically $0 < \gamma_i \ll \gamma_d$, this would correspond to a droplet that is slightly more than a hemisphere, which indeed is the case typically observed.

The energetic arguments above would lead to rapid oscillation between the two facet types. However, there is always some cost or energy barrier to introducing an edge between facets. We can model this by assuming that switching only occurs at some critical force, i.e., when $|\Gamma_w^{\mathrm{eff}} - \Gamma_n^{\mathrm{eff}}| = \Gamma_c$.

To illustrate the behavior concretely, we calculate the periodicity of the oscillations, for the "symmetric" case mentioned above ($\gamma_n = \gamma_w$ and $\theta_n = -\theta_w$), with a nearly hemispherical droplet given by Eq. (2), and in the limit of small barrier Γ_c. In this case, for a wire of diameter L, the wavelength of the sawtooth is

$$\lambda = L\frac{\Gamma_c}{(2-3\theta_d)\theta_\nu\gamma_d\cos\theta_d(\sin\theta_w - \sin\theta_n)}, \qquad (3)$$

$$\sim L\frac{\Gamma_c}{\gamma_d}\frac{1}{4\theta_w^2}, \qquad (4)$$

showing explicitly the proportionality between wavelength and wire diameter.

The situation in three dimensions is more complex, but still is expected to give sawtooth faceting. Figure 2(c) illustrates (very schematically) the simplest wire cross section that is consistent with our observations and with the symmetry of a ⟨111⟩-oriented Si wire. Let Fig. 2(c) represent (at two successive times) the terminal (111) plane on which the droplet sits, and whose edges are defined by the intersection of this (111) plane with the sidewall facets. If the three edges marked by arrows are growing outward (widening facets), while the other three have a different orientation and so are growing outward more slowly (as shown) or growing inward, then the marked edges shrink, and the terminal plane becomes increasingly triangular. Then the droplet becomes more

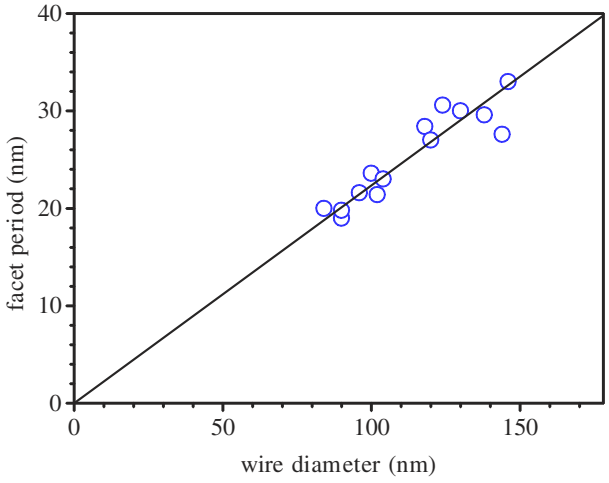

FIG. 3 (color online). The linear dependence of facet period on wire diameter for the growth conditions of Fig. 1.

sharply curved at the three shorter edges, increasing their Γ_w^{eff}. This continues until these facets become unfavorable, and narrowing (or less rapidly widening) facets are introduced.

Even in three dimensions, it remains true (within our near-equilibrium model) that the period and amplitude of the sawtooth faceting are directly proportional to the wire diameter. The only dimensional parameters in the analysis are surface energies, so there are no characteristic length scales, only characteristic angles. We test this prediction by plotting the measured period vs diameter for several wires, which all grew simultaneously from droplets of different size. The result is shown in Fig. 3. The close correlation provides strong support for our general picture.

From Fig. 3, for a wire radius R the period λ of the sawtooth is $\lambda \sim 0.45R$; while from Fig. 1(e), the amplitude ΔR of the oscillations is $\Delta R \sim 0.14\lambda$. So the amplitude of the roughness scales with wire radius as $\Delta R \sim 0.06R$. We expect that this could have important implications for the mobility in nanowire electronic devices. In particular, the rather periodic structure means that scattering may depend strongly on the Fermi wavelength in the wire. In contrast, interface roughness is usually modeled as having Gaussian autocorrelation, giving a smoother dependence on Fermi wavelength.

We note that many aspects of the wire growth are beyond the scope of simple arguments based on near-equilibrium growth controlled by surface energies. We find that much wider wires have a rather different cross-sectional shape than those reported here, and the linear scaling shown in Fig. 3 is less well obeyed. The broken symmetry between opposite sides of the wire also indicates the role of additional factors not considered here. Under different growth conditions, kinetic factors could in principle allow growth of a sidewall with ''forbidden'' orientation, e.g., a sidewall consisting of a vicinal facet with a staircase of atomic steps. (This particular example would be still a sort of sawtooth structure, but with only atomic-scale amplitude.)

Finally, we emphasize that our observations are restricted to growth at relatively high temperature in a UHV environment. It is possible that at lower temperatures, or in growth systems with a background pressure of oxygen or water vapor, different facets may be stable.

In conclusion, we have directly observed sawtooth faceting during VLS growth of Si nanowires and we have proposed a thermodynamic origin which can consistently explain the occurrence of such faceting. Many aspects of the growth are still not understood, and the unexpected complexity highlights the importance of developing a more complete understanding of nanowire growth.

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