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Karla Hillerich  
*Lund University*

Kimberly A. Dick  
*Lund University*

Cheng-Yen Wen  
*Birck Nanotechnology Center, Purdue University*

Mark C. Reuter  
*International Business Machines (IBM)*

Suneel Kodambaka  
*University of California - Los Angeles*

*See next page for additional authors*

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Strategies To Control Morphology in Hybrid Group III–V/Group IV Heterostructure Nanowires

Karla Hillerich,† Kimberly A. Dick,‡,§ Cheng-Yen Wen,§,# Mark C. Reuter,‖ Suneel Kodambaka,⊥ and Frances M. Ross*†

†Solid State Physics, Lund University, Box 118, S-221 00 Lund, Sweden
‡Polymer & Materials Chemistry, Lund University, Box 124, S-221 00 Lund, Sweden
§Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, United States
‖IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598, United States
⊥Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, California 90095, United States

Supporting Information

ABSTRACT: By combining in situ and ex situ transmission electron microscopy measurements, we examine the factors that control the morphology of “hybrid” nanowires that include group III–V and group IV materials. We focus on one materials pair, GaP/Si, for which we use a wide range of growth parameters. We show through video imaging that nanowire morphology depends on growth conditions, but that a general pattern emerges where either single kinks or inclined defects form some distance after the heterointerface. We show that pure Si nanowires can be made to exhibit the same kinks and defects by changing their droplet volume. From this we derive a model where droplet geometry drives growth morphology and discuss optimization strategies. We finally discuss morphology control for material pairs where the second material kinks immediately at the heterointerface and show that an interlayer between segments can enable the growth of unkinked hybrid nanowires.

KEYWORDS: Nanowires, heterostructures, group IV/group III–V, interlayers, in situ TEM, morphology, CVD

Self-assembly of nanowires using the vapor–liquid–solid† and vapor–solid–solid‡ methods provides an opportunity to integrate different materials that are not easily grown together as thin films.3,4 The nanowire geometry allows successful integration of group III–V semiconductors with high mismatch,3,5 since strain is relieved efficiently by lattice relaxation.6 The nanowire geometry also allows integration of chemically dissimilar materials to form “hybrid” nanowires,7,8 that combine segments of group III–V and group IV materials. Here, the limited interfacial area also improves epitaxy by avoiding inversion domains or antiphase domain boundaries in the III–V segment which are known to arise, during thin film growth of III–V materials, from steps on a group IV substrate.9,10

Hybrid nanowires potentially have very interesting functionality, including integration of III–V semiconductors with Si technology, photovoltaic applications, measurement of band offsets, silicide formation and contact physics, and even the growth of magnetic quantum dots of well-defined geometry. It is certainly convenient that both III–V and group IV nanowires can be formed with the same catalyst, Au, and can exhibit the same growth direction, ⟨111⟩. In spite of this, well-controlled growth of hybrid nanowires has not proved straightforward to achieve. We have shown7 that certain hybrid combinations, such as GaP grown on Si (referred to below as Si/GaP, with the first-grown material listed first), lead to excellent nanowire and heterojunction morphology. However, other combinations, such as GaP/Si, tend to kink at or near the heterojunction. Unkinked morphologies are key to applications that require quantum wells and barriers of precise geometry,11 while controllably kinked nanowires are useful for fabricating three-dimensional electronics.12 Hocevar et al.8 demonstrated very recently that a high yield of straight hybrid nanowires is possible in both switching directions with careful optimization of the growth conditions in their metal–organic vapor phase epitaxy (MOVPE) system. To extend this impressive result to other materials and growth techniques, it is necessary to understand fully the processes that lead to kinking in a general hybrid nanowire. Thermodynamic parameters such as interface energies can explain many observations of hybrid nanowire morphology,7,13 but it also appears obvious that thermodynamics cannot be the sole factor determining morphology; growth conditions and technique should play an important role.

Here we investigate heterojunction morphologies in several hybrid combinations, including GaP/Si, GaAs/Ge, and GaAs/Si. Nanowire growth is performed within a very broad...
parameter space using three different growth chambers, to provide information on the general processes determining hybrid morphology. As expected, we find that the overall nanowire morphology depends on both materials and growth parameters. By varying growth parameters for GaP/Si, we identify two distinct types of defect that lead to a kinked nanowire. We then show that similar morphologies can be reproduced in pure Si nanowires by controllable changes in growth parameters. Examining pure Si nanowires allows us to distinguish chemical effects from geometrical effects, revealing a relationship between growth morphology and the geometry of the catalyst droplet at a heterojunction. Our results suggest two strategies for tuning nanowire morphology: controlling droplet geometry through growth conditions, and using an interlayer at the heterojunction. We demonstrate complex multilayered hybrid structures such as GaAs/Ge/Si and GaAs/Ge/Si/Ge using the latter strategy. Hocevar et al.8 applied a similar approach, showing that Si and GaAs can be combined if separated by a segment of GaP. The overall understanding of how geometry and thermodynamics affect nanowire morphology can help develop strategies to obtain desired heterostructure combinations.

Our experiments make use of three growth systems: a conventional low pressure (LP) MOVPE (75 Torr in 6 L/min H2),2 a conventional chemical vapor deposition (CVD) reactor operated under low pressure conditions,14 and an in situ, ultra high vacuum transmission electron microscope (UHV TEM) with capabilities for carrying out CVD at pressures up to 10^-5 Torr.15 By combining results from these growth systems, we can span a wide range of growth conditions to provide general trends in morphology, and we can correlate the final morphology of hybrid nanowires (from MOVPE and CVD-grown samples) with the specific sequence of events that take place during the formation of the interface (from in situ UHV TEM experiments). In the MOVPE reactor, GaAs and GaP nanowires were grown using Si(111), GaAs(111)B, or GaP(111)B substrates on which size-selected aerosol Au particles16 had been deposited. The precursors were trimethylgallium (TMG), phosphine (PH3), and arsine (AsH3) with partial pressures of 7 × 10^-4 Torr, 0.5–0.9 Torr, and 4–8 × 10^-2 Torr, respectively, at growth temperatures of 475–500 °C. The samples were cooled in the group V precursor. On some samples, Si segments were grown in the same reactor (after cooling down) using disilane (Si2H6) with a partial pressure of 10^-3 Torr and a growth temperature of 625 °C. Other samples were transferred through air to grow Si or Ge segments either in the LP-CVD reactor, using undiluted silane at 450–630 °C, or in the UHV TEM, using undiluted disilane at 450–630 °C, or digermane (Ge2H6) at 300–400 °C.

Since growth conditions vary widely between the three di- 

disilane at 450 °C, and 4×10^-2 Torr, we focus on the materials pair GaP/Si (Figures 2 and 3). GaP/Si offers a relatively wide parameter window for Si growth, due to the stability of GaP at high temperatures;23 furthermore, the good lattice match between the materials suggests that strain effects may be neglected. By following the growth in situ in the UHV TEM, we find that the initial deposition of Si on GaP forms a planar layer under all conditions examined, similar in appearance to the earliest stages of Ge growth on GaAs shown in Figure 1. However, we will show that the subsequent morphological evolution depends on parameters such as temperature and gas environment that are expected to affect the steady-state diameter of the Si segment. We then describe two experiments in which “plain” Si nanowires are grown under conditions that also lead to a change in diameter and use the comparison between the Si and GaP/Si results to discuss the relationship between droplet geometry and heterojunction morphology.

Figure 1 to defects such as twins also enables us to conclude that the Ge segment here is defect-free. It is clear from the image sequence that the layer-by-layer deposition of Ge preserves the direction of the growth interface and results in a straight nanowire morphology.

However, it is also clear in Figure 1 that the nanowire diameter changes between GaAs and Ge: the diameter of the Ge segment increases over the first 25 nm of growth before reaching a steady-state value. We often observe such diameter changes in hybrid nanowires. The diameter of a nanowire during steady-state growth is determined by droplet volume and contact angle.17–20 The droplet volume depends on the amount of the seed material (Au, in this case), as well as the amount and nature of the growth elements with which it is alloyed (in this case Ge, Ga, and/or In, see the Supporting Information). The contact angle is a function of surface and interface energy terms, which in turn depend on parameters such as temperature. The droplet volume may change with supersaturation.20 These complex dependencies mean that there is no reason to expect the nanowire to have the same steady-state diameter before and after the heterojunction. Once growth of the second material starts on the area defined by the first material, it appears from data such as Figure 1 that the diameter changes gradually toward the steady-state value. A transition distance is consistent with simulations where an “mismatched” droplet contact angle favors a gradual “correction” by influencing deposition at the trijunction.17,18,21,22

We believe that changes in the steady-state nanowire diameter are a key ingredient for understanding the morphology at heterojunctions. To investigate this hypothesis, we focus on the materials pair GaP/Si (Figures 2 and 3). GaP/Si offers a relatively wide parameter window for Si growth, due to the stability of GaP at high temperatures;23 furthermore, the good lattice match between the materials suggests that strain effects may be neglected. By following the growth in situ in the UHV TEM, we find that the initial deposition of Si on GaP forms a planar layer under all conditions examined, similar in appearance to the earliest stages of Ge growth on GaAs shown in Figure 1. However, we will show that the subsequent morphological evolution depends on parameters such as temperature and gas environment that are expected to affect the steady-state diameter of the Si segment. We then describe two experiments in which “plain” Si nanowires are grown under conditions that also lead to a change in diameter and use the comparison between the Si and GaP/Si results to discuss the relationship between droplet geometry and heterojunction morphology.
Figure 2. Hybrid nanowires with Si grown at low temperature, showing single kinks. (a) A bright field/dark field image pair showing a straight Si segment growing on a GaP nanowire in the UHV TEM. Si was grown for 65 min at 520 °C then 15 min at 600 °C in 1.6 × 10⁻⁶ Torr disilane. The beam was parallel to (211), hence no twin contrast appears in the GaP. (b) Bright field images of Si during growth on a GaP nanowire at 430 °C. The beam was parallel to (211), hence no twin contrast appears in the GaP. Images shown after 115, 140, 147, and 158 min growth in disilane at pressures that drifted between 3 and 5 × 10⁻⁶ Torr (the pressure variation does not appear to affect results). The Si diameter decreases, and the droplet morphology first starts to change after it has decreased by ~2.5%. (c) Postgrowth images of a long kinked Si segment grown on a GaP nanowire, imaged at high resolution with the beam parallel to (110). Si was grown in the LP-CVD chamber for 10 min at 450 °C in 0.2 Torr silane, following a 5 min anneal at 450 °C. Insets show the heterojunction at increasing magnification. The diameter at the heterojunction is 55.7 nm, while the Si after the kink has a 9% smaller diameter of 50.0 nm. (The wider diameter around the kink likely results from movement of the droplet between the different inclined facets; see text.)

Figure 3. Hybrid nanowires with Si grown at higher temperatures, showing inclined defects. High-resolution, postgrowth images of two MOVPE-grown GaP/Si nanowires are shown with the beam parallel to (110). GaP was grown on a GaP substrate for 1 min at 475 °C followed by an air break and then Si grown for 20 min at 625 °C. The stacking faults (arrows) originate in the Si near the GaP/Si interface. (The smaller features are Si side branches grown from catalyst particles added after GaP growth.)

Figure 2a–c shows examples of Si segments grown on GaP in the UHV TEM at relatively low temperatures, from 430 to 520 °C, and pressures spanning a wide range (10⁻⁶ Torr in Figure 2a and b; 0.2 Torr in Figure 2c). Straight morphology for the Si segment is possible (Figure 2a), but other nanowires show a single kink at a distance of the order of 1 diameter beyond the heterojunction (Figure 2b,c). In situ TEM shows intriguing behavior as the nanowire kinks: the diameter of the Si segment decreases compared to the GaP by forming inclined facets, and as it does so, the catalyst droplet increasingly wets the nanowire sidewall at an inclined (111) facet (Figure 2b). After this single kink, the nanowire typically grows without further kinking in an inclined (111) direction (see the LP-CVD example in Figure 2c), with the final diameter of the Si segment a few percent smaller than the diameter at the GaP/Si interface. This mode of kinking can affect the majority of nanowires in a growth experiment. For in situ growths, increasing the temperature appears to increase the number of straight nanowires (compare Figure 2a at 520 °C and Figure 2b at 430 °C). Although it is difficult to obtain good statistics from the relatively small numbers of nanowires examined in a typical TEM experiment, this observation implies there should be an optimum temperature that yields a maximum probability of straight nanowires, consistent with the results of Hocevar et al.⁸

We next examine Si grown on GaP at higher temperatures. In Figure 3 we show Si segments grown by MOVPE on GaP nanowires at a temperature of 625 °C and pressures in the mTorr range. We observe at these high growth temperatures that the diameter of the Si segment increases by a few percent immediately after the heterojunction. We also observe inclined defects within the Si. Additional Si growth forms a segment with a meandering morphology, kinking over small angles. Recent observations²⁴ have shown that inclined faults may affect sidewall geometry and cross section, making it easier for a nanowire to change direction. The formation of inclined defects may therefore affect the subsequent nanowire morphology.

The observations above suggest that, even after initially planar growth of the Si segment, defective morphologies can arise in two distinct ways: formation of a single kink, which we frequently observe for relatively low temperature Si growth and Si segments that narrow, and formation of inclined defects, often observed for higher growth temperatures and associated with Si segments that widen. We now discuss two types of pure Si nanowire growth that lead to similar morphologies, Figure 4, yet with of course no change in chemistry, only a change in droplet geometry. Figure 4a and b shows the growth of a pure Si nanowire in the UHV TEM under conditions that decrease the droplet volume. This was achieved by carrying out Si growth under conditions where Au migration occurs.⁹ Au is known to be highly mobile on the Si surface and its migration leads to Ostwald ripening: Au atoms detach from droplets, diffuse across the surface, and rejoin the same or other droplets. Most droplets decrease in volume (although the largest droplets slowly increase). As droplets shrink, in situ observations (Figure 4a and b) show that the nanowire diameter also decreases, and that it does so by forming inclined sidewall facets. Low angle facets such as {311} can form,²² but to accommodate a more rapid diameter reduction, we find that higher angle (111) facets appear (Supporting Information, Movie 1). Three such facets may be present due to the symmetry of the nanowire tip. These facets are key to the subsequent evolution because they share the same structure as the original (111) growth interface. The droplet appears to
Figure 4. Si nanowires grown under conditions of increasing and decreasing droplet volume. Bright field images obtained during growth in the UHV TEM with the beam parallel to (110). (a) During growth at 645 °C in 1.1 × 10⁻⁶ Torr disilane, migration of Au from the droplet to nearby larger droplets (Ostwald ripening) reduces the droplet volume. The nanowire diameter reduces by forming inclined (111) facets. The first image shows the point where the diameter has decreased by 8%. The second image, 14 s later, shows the droplet first wetting the newly formed facet. (b) A different nanowire with a larger inclined facet; after 51 s, when the droplet is about to dewet the original growth interface; after 152 further seconds; and after 450 further seconds. (c) At a fixed temperature of 515 °C, disilane was switched off, and several monolayers Au were deposited over 20 min, allowing time for Au diffusion to existing droplets. Subsequent growth in 5 × 10⁻⁶ Torr disilane resulted in a diameter increase (here 28%) with inclined stacking faults (arrow).

Figure 5. Schematic diagram showing the outcomes for nanowire morphology in the case of a mismatch between the droplet volume/contact angle and the nanowire diameter. (a) The scenario, based on Supporting Information Movies 1 and 2 and Figures 2 and 4a,b, where the droplet is too small for the diameter at the heterojunction. The nanowire narrows, forms inclined (111) facets, the droplet wets an inclined facet and the nanowire kinks. (b) The scenario based on Figures 3 and 4c where the droplet is too large for the diameter at the heterojunction. The wire widens, and defects form.

liquidus line at the growth temperature. When growth is resumed, the enlarged droplets cause the nanowire diameter to increase gradually, and we frequently (in perhaps half the nanowires) observe inclined faults at the location of the diameter change. Although inclined defects do not form in all nanowires, their presence in some is unsurprising because widening of a nanowire requires addition of material beyond the boundary of the existing growth front. Atoms in this extended region have lower coordination, since no atoms from the growth front are present directly beneath them, and thus may be more prone to stacking errors. Thus, an association of inclined faults with a diameter increase may be a general feature of Si nanowire growth, irrespective of whether a heterointerface is present or not. The scenario of Figure 4c is summarized in Figure 5b.

The two modes of instability we have described for Si nanowires—where a decreasing droplet volume leads to decreasing diameter, inclined (111) sidewalls and a single kink, while an increasing droplet volume leads to increasing diameter and formation of inclined defects—share striking similarities with the modes of instability observed for GaP/Si nanowires. This similarity suggests that a mismatch between droplet volume and nanowire diameter, driving a change in the diameter, may be the cause of the instabilities observed in hybrid nanowires. These morphologies may be distinguished from other modes of kinking, where growth is immediately destabilized by rapid changes in pressure, temperature, or surface chemistry. Because the total pressure, gas chemistry, and temperature may all affect the droplet geometry and hence the droplet/diameter match, we would expect that changing any growth parameter may affect the morphology of hybrid nanowires. It is difficult to make quantitative predictions because of the unknown surface chemistry and droplet composition (for example, the presence of In and Ga in the droplet, as shown in the Supporting Information). We can, however, discuss one particular trend that we might expect to see as the temperature is changed.

A particle with a fixed amount of Au grows a Si segment that has a larger diameter at higher temperature, as shown in the Supporting Information. Thus, for a given GaP diameter and hence amount of Au, a high Si growth temperature should favor a wider Si segment. Based on the discussion above, this would
increase the probability of forming inclined defects. A low Si growth temperature should favor a narrower Si segment. This would increase the probability of the single kinking events that take place as the Si diameter decreases. This is consistent with the experimental observations. It should therefore be possible to control the two types of morphological defects by choosing a Si growth temperature that minimizes the diameter change. It is important to note that the optimum temperature will depend on other growth parameters, the growth technique, precursors, and reactor geometry. However, understanding the morphology in a particular growth experiment helps to predict the direction in which the growth conditions must be tuned, greatly increasing the potential for system-specific optimization similar to that shown by Hocevar et al. In some cases the temperature cannot be chosen arbitrarily; for example, extensive conformal Si growth on the III–V segment occurs if the Si growth temperature and pressure remain high for too long. In such cases, we suggest that gradual temperature ramping after heterojunction formation could be a promising strategy for morphological control.

We conclude by discussing a second strategy for optimizing nanowire morphology. In the materials pairs discussed so far, GaP/Si and GaAs/Ge, the group IV material initially grows as a planar layer. Thus, a thin segment can be grown, for example, to create a narrow quantum well; the kinking and inclined defects described above occur as the segment becomes longer. However, in many materials pairs the second segment grows right from the start as a “compact nucleus”. Examples include key materials such as GaAs/Si (Figure 6a), GaP/Ge, and (under some conditions) Si/Ge. Compact nucleus formation can be understood through considerations of equilibrium interface energy. Once a compact nucleus has formed, its further growth displaces the catalyst asymmetrically, so the nanowire typically kinks and may even fold over to grow back down the previous segment. A different strategy is clearly required to control nanowire morphology in this case.

We have explored the possibility of growing an interlayer between the two segments, using a material that grows as a planar layer on the original segment. In Figure 6 we demonstrate this approach for the kinked hybrid combination GaAs/Si, using Ge as the interlayer. The compact nucleus formed by GaAs/Si (Figure 6a) can be compared with the planar structure GaAs/Ge/Si (Figure 6b and c), while Figure 6d illustrates a four-layer structure, GaAs/Ge/Si/Ge. Each layer is planar, and although the diameter increases, the nanowire morphology is straight. Clearly, an appropriate choice of growth conditions is required for precise control of these structures. Furthermore, the use of alloy or graded SiGe interlayers, rather than the pure materials shown here, should provide a further degree of control.

In summary, we have investigated the formation of interfaces between group IV and group III–V materials in hybrid nanowires, using a combination of in situ and ex situ growth experiments in three different growth chambers, to characterize the general processes that affect nanowire morphology. The group IV material may form a compact nucleus or a planar layer on the group III–V segment. In the former case, exhibited for example by GaAs/Si, the nanowires are known to kink; here we show that adding an interlayer can be successful in suppressing compact nucleus formation and can therefore allow planar layer growth and avoid kinking. For general materials pairs, it may be possible to design an interlayer strategy based on the surfactants already developed for thin film epitaxy. In the latter case, exhibited by GaP/Si and GaAs/Ge, a planar layer forms, but the nanowire is surprisingly still prone to kinking or defects after the heterojunction. Our examination of GaP/Si over a broad range of growth conditions, combined with a study of pure Si nanowires under conditions where the droplet volume changes, suggest that the kinking and introduction of defects are linked to the geometry of the droplet. We suggest that the choice of the match between the nanowire diameter and the volume and contact angle of the droplet is the key parameter in determining the subsequent nanowire morphology. The droplet geometry arguments can apply in principle to any materials pair, although there are perhaps most important in hybrid systems, where the change in droplet geometry may be much more significant than when changing between two group IV or two group III elements. An appropriate choice of growth conditions, for example an optimal growth temperature or the use of gradual temperature changes to control droplet geometry without causing conformal deposition, may form the basis of strategies to optimize morphology and structural perfection.

Many nanowire applications require structural perfection of the individual segments of complex heterostructures. But nanowire growth also provides the exciting opportunity of fabricating structures with controlled morphology, with distinct applications for both straight and kinked geometries. An increased understanding of the factors that determine heterojunction morphology suggests exciting possibilities for designing complex multimaterial structures, as well as integrating dissimilar materials within single nanowires to create novel structure and functionality.

Figure 6. (a) GaAs/Si, showing formation of a compact nucleus. Si was grown during a 120 min ramp from 300 to 470 °C in 8.0 × 10⁻⁶ Torr disilane. Dark field image with the beam parallel to (211), hence no twin contrast in the GaAs. (b) GaAs/Ge/Si showing planar layer formation. Images are shown near the start of Ge growth (5 min at 390 °C in 1.2 × 10⁻⁶ Torr digermane), where the Ge layer is too narrow to distinguish; at the end of Ge growth (25 min, 300 °C); and after Si layer growth (60 min ramping from 300 to 350 °C in 1.1 × 10⁻⁶ Torr disilane). Bright field images with the beam parallel to (110). (c) A different nanowire with the same Ge and Si followed by additional Si grown over 82 min ramping from 350 to 510 °C in 2.0 × 10⁻⁵ Torr disilane). Bright field images with the beam parallel to (211), hence no twin contrast in the GaAs. Growth conditions were Ge (130 min at 330 °C in 1.0 × 10⁻⁶ Torr); Si (23 min at 360 °C in 1.1 × 10⁻⁵ Torr); Ge (73 min at 330 °C in 2.0 × 10⁻⁶ Torr).
ASSOCIATED CONTENT

Supporting Information
(1) Description of Movies 1 and 2 showing nanowire direction changes caused by AuSi droplet shrinking; (2) composition of the catalyst after hybrid nanowire growth; (3) the diameter of a Si nanowire grown from a fixed amount of Au. Movies 1 and 2 (si_002.avi, si_003.avi) show the initiation of a kinking event in a Si nanowire caused by reduction of the volume of the catalytic droplet. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Address: 1101 Kitchawan Road, Yorktown Heights, NY 10598, USA. Phone: (914) 945 1022; fax: (914) 945 2141; e-mail: fmross@us.ibm.com.

Present Address
*Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan.

Notes
The authors declare no competing financial interest.

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