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FEATURE ARTICLE**Metal-seeded growth of III-V semiconductor nanowires: towards gold-free synthesis****Kimberly A. Dick,^{*a,b} and Philippe Caroff^c***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

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Semiconductor nanowires composed of III-V materials have enormous potential to add new functionality to electronics and optical applications. However, integration of these promising structures into applications is severely limited by the current near-universal reliance on gold nanoparticles as seeds for nanowire fabrication. Although highly controlled fabrication is achieved, this metal is entirely incompatible with the Si-based electronics industry. In this Feature we review the progress towards developing gold-free bottom-up synthesis techniques for III-V semiconductor nanowires. Three main categories of nanowire synthesis are discussed: selective-area epitaxy, self-seeding and foreign metal seeding, with main focus on the metal-seeded techniques. For comparison, we also review the development of foreign metal seeded synthesis of silicon and germanium nanowires. Finally, directions for future development and anticipated important trends are discussed. We anticipate significant development in the use of foreign metal seeding in particular. In addition, we speculate multiple different techniques must be developed in order to replace gold and to provide a variety of nanowire structures and properties suited to a diverse range of applications.

1 Introduction and background

III-V semiconductor nanowires, which are nanoscale crystals elongated in one direction, have come a long way since the pioneering works of Givargizov on whiskers in the seventies^{1,2}. The transition from (micron-scale) whiskers to nanowires was initiated about twenty years ago with the works of Hiruma and colleagues on bottom-up synthesis and properties of these nanowires³⁻⁶. III-V nanowires have been praised for combining all of the advantages of III-V semiconductors, such as direct bandgap, high carrier mobility, and advanced band-structure engineering, with those of nanoscale objects, such as their free-standing nature, efficient lateral strain relaxation and pronounced quantum confinement effects. Strain relaxation in particular has importance for III-V nanowire materials, in principle allowing them to be combined into lattice-mismatched heterostructures or even integrated directly on Si. Predictions and motivations in the last decade were that they would soon replace their 2D layer counterparts in electronic, optoelectronic and energy applications. However, despite extraordinary proof-of-concept demonstrations at research laboratory level, they have not yet played any significant role in commercial device applications. Indeed, the nanowires' nanoscale dimensions, crystal structure, high surface-to-volume ratio and intrinsic limitations posed by their bottom-up growth mechanisms, proved much harder to control than originally thought.

Recently, research has moved towards harnessing the benefits of the intrinsic advantages of nanowires for novel devices and architectures rather than simply trying to mimic already-performing commercial 2D devices. On a fundamental physics

level, the formation of quantum dots using either InAs/InP axial heterostructures⁷ or metal gates⁸ led to the demonstration of single electron transistors^{9,10}, Resonant tunnel diodes¹¹, and memories¹². Proximity-induced superconductivity using Al leads connected to a III-V nanowire allowed for the realization of superconductor/semiconductor hybrid devices¹³. More recently quantized conductance at non-zero magnetic field has been shown^{14,15}. These key breakthroughs have given transport physics a perfect test-bed for creation of quantum bits (Qbits) and their high frequency manipulations^{16,17}. In addition, in year 2012, III-V nanowires with high electron mobility and large Landé g-factor were used to probe the possible existence of new fundamental particle predicted over 70 years ago¹⁸, with the first experimental signatures of the Majorana fermions, in the form of quasi-particles¹⁹⁻²¹.

The high crystalline quality and large material gain of III-V nanowires have allowed for fabrication of standard light emitting diodes²²⁻²⁴ and quantum light sources to be realized, in the form of efficient single photon emitters²⁵⁻²⁹. Nanowires are also excellent candidates for photon management strategies in solar applications³⁰⁻³⁵, and have been claimed to relax the limitations of the Shockley-Queisser efficiency limit³⁶. Their nanoscale size and the possibility of modulating their surface roughness to reduce thermal transport, combined with low electrical resistivity could lead to breakthroughs in thermoelectricity generation^{37,38}. As Si-based top-down nanowires are already used in the 14 nm technological node fin-field electron transistors (also called Tri-Gate FinFETs) owing to their optimal geometry for electrostatic gate coupling, advanced transistor concepts already demonstrated

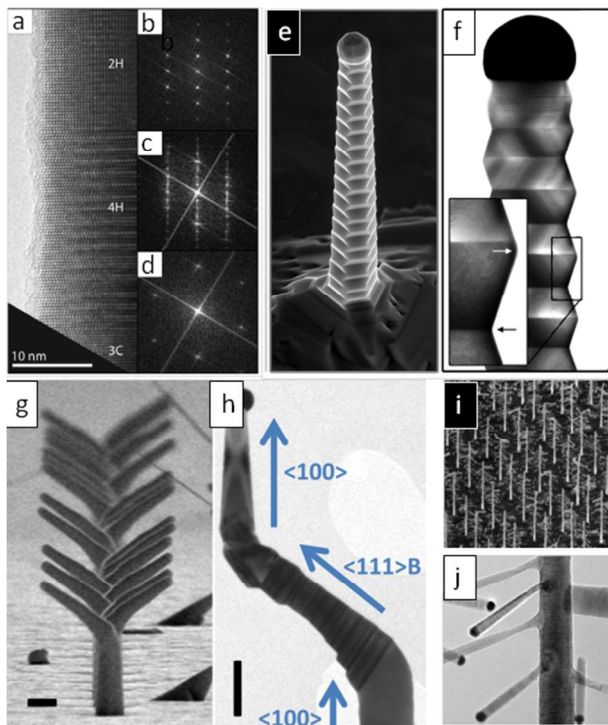


Figure 1: Diversity of crystal structures, growth directions and defect density in III-V nanowires (NWs), along with complex 3D branched geometries. (a) TEM image of an InAs,Sb_{1-x} NW showing a sequence of 3C (ZB), 4H, and 2H (WZ) crystal structures, with associated FFTs in (b) ZB (c) 4H and (d) WZ. Images 1a-d are adapted from Ref. 175 with permission. (e) SEM image of twinning superlattice in GaAs nanowires and (f) associated bright field TEM image along a <110> zone axis. Images 1e,f are adapted from Ref. 227 with permission. (g) SEM image of InP NWs grown on InP (100) substrate with growth direction changing from <100> to <111> [Wang2013], and (h) TEM image along a <110> zone axis of a NW changing growth direction from <100> to <111> and back to <100>. Images 1g,h adapted from Ref. 56 with permission. (i) SEM image of ordered array of GaP nanotrees and (j) TEM image of a nanotree trunk exhibiting five branches, with three different growth directions. Images 1i,j adapted from Ref. 49 with permission.

by Tomioka *et al.* and others^{39,40} are expected to play a significant role in the future technological nodes for a drastic reduction of the power consumption, according to the International Technology Roadmap for Semiconductors⁴¹.

Finally, new capabilities are emerging as the understanding and control of growth processes increase, with the demonstrated possibility of tuning the crystal structures in a unique way with respect to standard layered growth and by going beyond the simple nanowire geometry with branched structures. Various crystal structures including pure wurtzite (WZ), pure zinc blende (ZB), 4H polytypes and artificial twinning or polytypic superlattices can now be grown by design^{1,42-44}, offering additional freedom for electron and phonon bandstructure engineering, complementary to standard heterostructuring. Examples of the control over crystal structure and twinning superlattices that have been demonstrated are shown in Figure 1a-f. Importantly it was shown that forcing GaP nanowires (and

Al_xGa_{1-x}P, GaAs_yP_{1-y} for emission tunability) to adopt the WZ crystal structure changed their bandgap from indirect to direct, with potential for efficient light emission over a large portion of the visible spectrum⁴⁵.

Additionally, branched structures, such as T-shapes and X-shapes⁴⁶⁻⁴⁸, and even nanotrees^{49,50} can now be realized (see Figure 1g-j for examples), offering exquisite engineering freedom for fundamental physics and chemistry studies in multi-terminal devices^{48,51}. In addition periodic or on-demand diameter modulations have been demonstrated⁵²⁻⁵⁴, with potential application in electronics, thermoelectrics, or plasmonics. Finally, “synthetically encoded” nanowire growth directions have been demonstrated first in Si/Ge⁵⁵ and more recently in InP NWs⁵⁶.

However, to reach future commercial viability, most of these applications will require perfectly tunable III-V nanoscale objects to be directly integrated on silicon, for cost-reduction as well as to combine their complementary functionalities.

Although there are in principle many ways to fabricate one-dimensional materials, the advancement of the field of semiconductor nanowires has relied almost entirely on a specific fabrication process, in which gold metal nanoparticles are used as seeds to initiate and guide the growth, directly controlling both diameter and orientation. The details of the process are complex and are described in detail in other works^{57,58}, but in short it is generally understood that precursor species to the solid semiconductor (typically supplied either in vapour or solution) are dissolved in the gold nanoparticle, typically forming a liquid alloy. This liquid alloy ultimately becomes supersaturated with the dissolved species leading to precipitation of semiconductor material at the triple phase boundary⁵⁹⁻⁶¹. The semiconductor surface then provides the lowest-energy surface for precipitation of new material, leading to continuous growth of the semiconductor crystal in one dimension.

The current understanding of this nanowire growth process is in principle general and does not rely on any specific property of gold. Indeed, other metal nanoparticles have been used successfully in this process, as will be described in this Feature. However, the dominance of gold is enormous, with the vast majority of all semiconductor nanowire articles relying on this material in the fabrication. The reasons for the enormous success of gold (relative to other metals) are not fully understood, but it is anticipated that its moderate melting point and formation of low-melting alloys, resistance to oxidation and other parasitic reactions, and the high diffusion coefficients of many other elements in this metal may all play a role⁶². These effects will be discussed in more detail in the Discussion section.

Despite the significant advances and impressive early results on nanowire prototype applications, the near-universal reliance on gold in the fabrication process has presented a significant barrier to the integration of nanowire components into conventional industry. In particular, gold is a forbidden element in CMOS processing, as it forms mid-gap electronic states in Si (which degrade device performance)⁶³, has a very high solid diffusivity, and is extremely hard to remove from exposed fabrication equipment. Any fabrication process that relies on gold will thus be very difficult to integrate with Si electronics beyond laboratory level. The direct effects of gold contamination in III-V materials are less clear, and there is considerable debate on

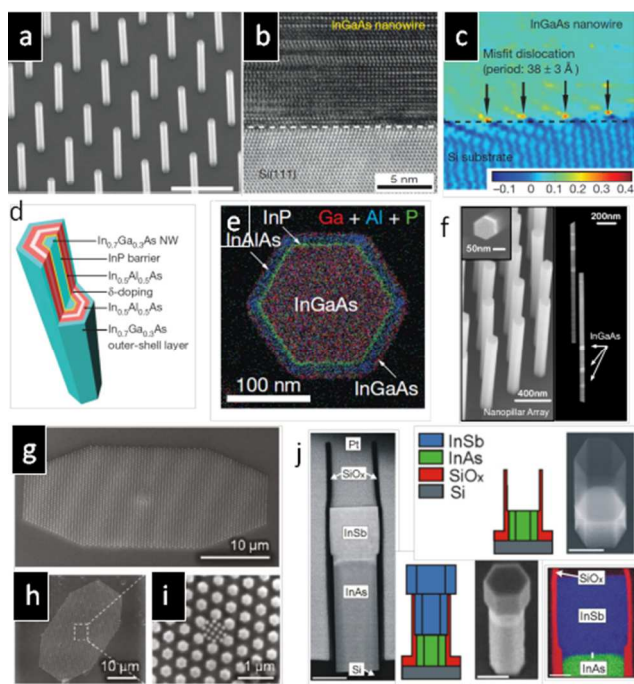


Figure 2: State-of-the-art selective-area epitaxy nanowires (NWs): radial core-multishells and nearly axial heterostructures. (a) Typical SEM image showing selective area growth of {110} faceted InGaAs NWs on Si(111) substrate, using a SiO₂ mask. (b) High resolution TEM images of the nanowire-substrate interface showing a high planar defect density in the nanowires and dislocations at the nanowire/substrate interface. (c) Strain mapping (ϵ_{xx}) estimated from a filtered version of a high resolution TEM image. Misfit dislocations are present at the InGaAs/Si interface with a spacing of about 3.8 ± 0.3 nm. Images 2a-c adapted from Ref. 29 with permission. (d) Schematic of and InGaAs nanowire core is wrapped with InP/InAlAs/ δ -doped InAlAs/InAlAs/InGaAs multilayers. (e) EDX elemental mapping image showing the signal for Ga, Al and P. (f) left: SEM image of a GaAs NW array with axial InGaAs inserts. The inset shows a top view image showing the hexagonal cross section. Right: HAADF STEM image of the NWs where 3 InGaAs axial inserts are clearly visible. Image 2f adapted from Ref. 89 with permission. (g,h) Tilted SEM images of an array of GaAs/InGaAs NWs with an InGaP shell creating a photonic crystal cavity (i) high magnification image of the L1 single defect cavity region of the device. Images 2g-i adapted from Ref. 229 with permission. (j) HAADF STEM image, schematics and SEM images of axial the process to selectively grow axial InAs/InSb NW heterostructures using a SiO_x nanotube template on Si substrate, adapted from Ref. 229.

whether gold atoms unintentionally dissolved in GaAs nanowires^{64,65} degrade the optical or electrical performance^{66,67}. Indeed, despite concerns presented by Breuer *et al.*⁶⁷, most recent reports indicate that the optical properties of gold-seeded GaAs NWs can be excellent⁶⁸. However, it is clear that for devices relying on purity of the optical channel, contamination of this type is best avoided. In addition, gold is among the most expensive stable elements found on Earth, and upscaling of any device fabrication process would be better served by finding cheaper, naturally abundant alternatives.

In this Feature we will review three main categories of gold-

free III-V nanowire synthesis: *selective-area*, *self-seeded*, and *foreign metal-seeded*, with the primary focus on the latter case. Gold-seeded growth is an example of the foreign metal-seeding, but here we refer exclusively to foreign metals other than gold. In brief, selective area growth is an alternative to the seeding technique described above, and instead relies entirely on growth conditions to stabilize certain crystal facets and enhance growth in only one dimension^{69,70}. Self-seeded growth is a type of seeded growth, but uses one of the components of the semiconductor rather than a foreign metal. For III-V materials, the group III species have low melting points and high boiling points, and thus serve well as liquid alloy seeds. Foreign metal seeding, as already stated, refers to the use of an alloy particle composed of a metal distinct from the final product of the synthesis. This foreign metal will in most cases form liquid alloys or solid intermetallic phases with the group III and V constituents, with one of the constituents (group III in the case of gold) typically in excess. In some cases the group III constituent may dominate in volume over the foreign metal, as will be discussed in Section 4. It is also worth noting that the phase of the metal particle formed during growth, and its properties such as interfacial energy with the semiconductor, surface energy/surface tension, and diffusivities of growth species, will have important implications for the properties of the resulting nanowire, including growth rate, growth direction and crystal structure⁶¹.

Before reviewing the current status and future prospects of each category, it is important to emphasize that development of gold-free synthesis techniques may present significant advantages, rather than simply avoiding gold itself. Expanding the possibilities of the fabrication process allows for the expansion of the parameter space, which can be expected to in turn expand the range of achievable material properties. Possibilities may include alternate crystal directions, shapes and crystal structures, increased possibilities for combining semiconductor materials into heterostructures, and direct effects on material properties by intentional incorporation of trace foreign elements. These possibilities will be discussed in detail in later sections.

2 Selective Area

Selective-area epitaxy (SAE) is a growth technique that was and is still used widely to improve the crystal quality of layers grown on a substrates with significant lattice and thermal mismatches. By favouring growth conditions for lateral overgrowth of pillars/pyramids on a substrate partially masked by SiO_x/Si_xN_y dielectric layers, threading dislocations can be blocked or made to terminate at sidewalls, and when these single crystals merge to form a layer, a significant reduction of dislocation density is obtained. This technique and its variations, sometimes referred to as epitaxial lateral overgrowth (ELOG), lateral epitaxial overgrowth (LEO), or Pendeo-Epitaxy, are applied in the case of layers mostly for the GaAs/Si, GaN/Al₂O₃ and GaN/Si systems⁷¹⁻⁷⁴. The selectivity between exposed III-V layers and the mask is greatly enhanced when using metalorganic precursors rather than elemental fluxes, therefore favouring growth techniques for SAE that use these source materials; the vast majority of published works use metalorganic vapour phase epitaxy (MOVPE) reactors for SAE.

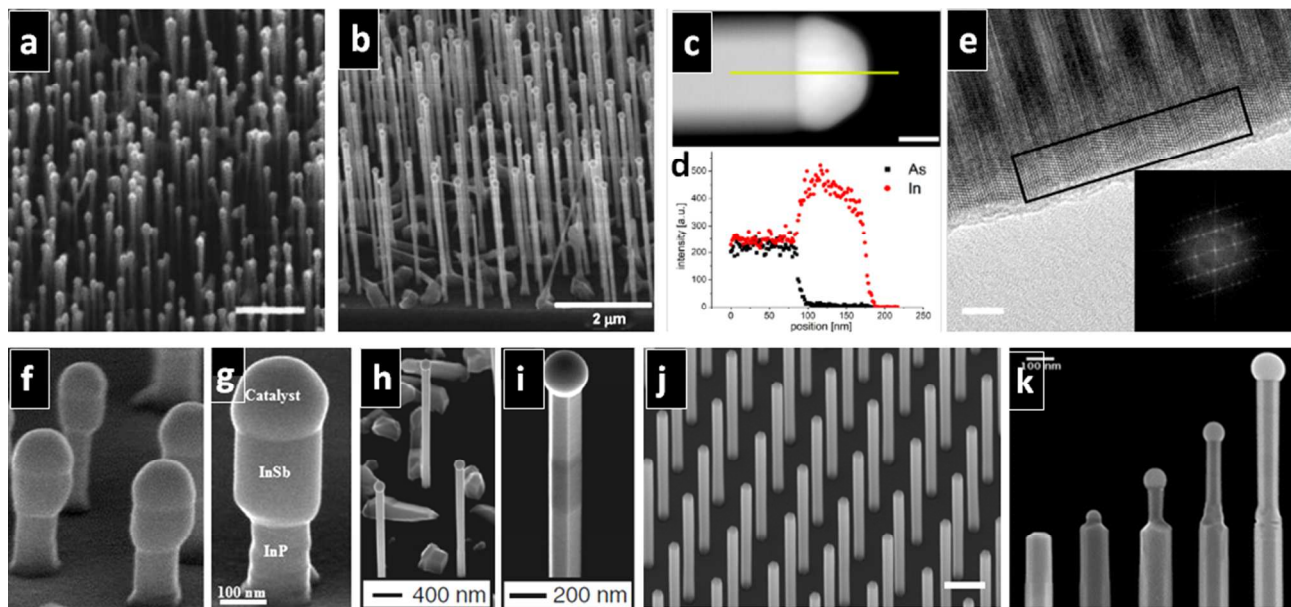


Figure 3: Self-seeded nanowires: state-of-the-art nanowire structures, along with position and diameter control. (a) Early demonstration SEM image of vertically-aligned In-seeded InP nanowires, adapted from Ref. 102. (b) Early demonstration SEM image of vertically-aligned Ga-seeded GaAs nanowires, adapted from Ref. 112 with permission. (c) HAADF-STEM image and (d) corresponding EDX line scan showing the composition of an InAs nanowire with an In seed particle at the tip. (e) High-resolution TEM image with inset FTT, showing periodically twinned zinc blende crystal structure. Images 3c-e adapted from Ref. 108 with permission. (f,g) SEM images of In-seeded InP-InSb axial heterostructure nanowires, adapted from Ref. 114 with permission. (h,i) SEM images of Ga-seeded GaAs-GaAsSb-GaAs axial double heterostructure nanowires, adapted from Ref. 126 with permission. (j) SEM image of position-controlled Ga-seeded GaAs nanowire array on Si substrate, adapted from Ref. 129 with permission. (k) SEM image of Ga-seeded GaAs nanowires where the diameter has been tuned along the growth axis by varying the growth conditions, leading to selective change of the Ga particle size. Adapted from Ref. 143 with permission.

In the early 2000s, the same growth mechanism was used to design arrays of so-called pillars (see Figure 2a), aiming at creation of photonic crystals⁷⁵⁻⁷⁸. Growth conditions were modified to reduce lateral overgrowth and instead favour axial growth along a $\langle 111 \rangle$ direction. Ikejiri *et al.* identified the experimental conditions favouring either axial or radial growth and found that the crystal shape was the consequence of the relative surface energies of the crystal planes, with adatom incorporation being controlled by diffusion length and binding energies^{69,70}.

The reported pillar-shaped micro- and nano- structures could already have been called nanowires at the time^{77,79,80}, but this naming convention came later when diameters were reduced below 100 nm, in the pioneering works of the group led by Fukui^{81,82}. The authors built upon previous works by Tetsuko *et al.*⁷⁵, who grew GaAs pillars using SA-MOVPE, and of Poole and Fraser who grew V-shaped double InP nanowires by CBE⁸³. SAE-grown nanowires on III-V substrates developed at a fast pace, with demonstration of ternary nanowires^{81,84}, radial heterostructures (GaAs/AlGaAs⁸⁵, InAs/In(As)P^{86,87}) and even (mostly) axial heterostructures [GaS/InGaAs; GaAs/AlGaAs]⁸⁸⁻⁹⁰.

The true potential of SAE for nanowire applications was revealed when integration on Si was demonstrated (see Figure 2b-c), as in the early work on non-vertical NWs grown on Si[001]⁹¹, but mostly when the first position-controlled arrays of SAE-grown InAs NW arrays were shown⁹², followed by GaAs/AlGaAs⁹³ and finally InGaAs⁹⁴. Promising field-effect transistors and solar cell prototypes have been realized since

then^{39,30,32,35}. Example of state-of-the art SAE nanowire heterostructures and arrays are shown in Figure 2d-j.

Further advancement in this field will need to overcome a very critical limitation: in all of the reported works, the crystal quality of the NWs is insufficient, with heavily twinned ZB or mixed WZ/ZB crystal structures (see Figure 2b). In addition it was shown that elastic relaxation at the Si/III-V interface was limited to low lattice-mismatches and small diameter^{92,93}. The reason for the high density of stacking faults is not entirely clear, but the relatively high growth temperatures necessary for obtaining untapered nanowires with a high aspect ratio, could play a significant role in favouring the formation of twins or stacking faults, a high density of which leads to polytypism. Suppressing these defects is of utmost importance for future devices. Encouraging early results show some control over the crystal quality of InP NWs by means of standard growth parameter tuning, and interestingly, twin-free SAE-grown free-standing homoepitaxial GaAs membranes have been shown recently⁹⁵. Variability of stacking defect density with temperature has also recently been shown for GaAs nanowires⁹⁶. However, compared to the control obtained using gold seeds, this growth technique has to date lagged behind in demonstrating control of crystal phase, and it remains to be seen whether such control can be obtained.

3 Self-seeded

Growth of III-V nanowires can be achieved by using the low melting temperature group III metallic elements (Ga/In) as seeds. This growth mechanism is called “self-catalyzed” or “self-seeded” (erroneously also sometimes “catalyst-free”), because no foreign element is necessary to initiate nanowire growth. Since the material of the seed particle is also a constituent of the nanowires, this technique can provide extremely clean growth processes, but the droplet can naturally also be consumed depending on the growth conditions and desired application. Fine tuning of temperature and V/III ratio are therefore of utmost importance to keep the dynamic balance between consumption and accumulation of group III species.

This growth mechanism first received attention following the works on In-seeded nanowires in particular for InP nanowires grown by MOVPE, but truly took off after the pioneering works on Ga-assisted nanowire growth by molecular beam epitaxy (MBE) from A. Fontcuberta i Morral *et al.*^{97,98}. In this section we review first In-seeded growth with an historical perspective and then focus on some key works from the broader literature concerning Ga-seeded NWs. Examples of both In-seeded and Ga-seeded nanowires are shown in Figure 3.

3.1 In-seeded III-V nanowire growth.

The first reports of chemically synthesized nanowires were rather uncontrolled and non-epitaxial, such as In-assisted GaN nanowires in anodic alumina template in 2000⁹⁹, In-assisted InAs nanowires by decomposition of a GaAs substrate in closed furnace tube by He *et al.*¹⁰⁰, or Ga-assisted GaInP spectre-like micro/nanostructures on polycrystalline InP substrates in 2004¹⁰¹. First reports of controlled growth using an MOCVD reactor appeared as early as in 2005-2006, with demonstration of single-crystalline, vertical homepitaxial In-nucleated InP nanowires on InP(111)B by Novotny and Yuin in 2005¹⁰² (see Figure 3a). Importantly, Mattila *et al.* showed in 2006¹⁰³ that this In-seeded mechanism could produce ternary In(As)P on SiO_x-covered Si(111) with a defected wurtzite (WZ) crystal structure and reasonable optical properties, although not yet with controlled epitaxial growth directions. Later Yu *et al.*¹⁰⁴ reported similar InP nanowires, but having a highly twinned ZB crystal structure, on native oxide-covered Si(001).

These authors and others revealed the growth dynamics of these nanowires and illustrated the critical roles played by temperature and V/III ratio on the InP and InAs nanowire morphology and dimensions^{102,103,105-107}. In particular Woo *et al.*¹⁰⁵ then Zhang *et al.*^{106,107} showed that the particle could be suppressed at high V/III ratio or different growth temperature, leading to alternative morphologies such as needle-shaped nanocones or nanopillars. Although the crystal structure of these nanowires remained highly defected with a high density of stacking faults in predominantly WZ crystal structure or rotationally twinned ZB crystals, Grap *et al.* showed recently¹⁰⁸ that self-seeded InP nanowires could be also grown as regular twinning superlattices (TSL), comprised of regularly-spaced single twins in an otherwise pure ZB crystal (see Figure 3c-e). Observation of TSL in self-seeded InP nanowires can also be made by studying the SEM images in the work of Dayeh *et al.*¹⁰⁹,

although the authors did not comment on its relevance in that article.

Indium was also used to demonstrate non-epitaxial self-seeded InSb nanowire growth on quartz substrate using direct antimonidization of molten indium droplets¹¹⁰. Later heteroepitaxial growth of InSb wires on various III-V (111)B substrates was shown¹¹¹. In this work, Mandl *et al.* interestingly showed that the crystal structure could evolve from pure ZB to 4H and pure WZ when terminating the growth and cooling down. The same year Zhou *et al.*¹¹² and Ngo *et al.*¹¹³ showed the first examples of ternary InP_xSb_{1-x} antimonide nanowires. Pozuelo *et al.*¹¹⁴, from the same group, also demonstrated that InP/InSb axial heterostructures could be formed via the In-seeded growth mechanism (see Figure 3f-g). Self-seeded antimonide nanowire growth remains however still in its infancy.

3.2 Ga-seeded III-V nanowire growth.

In parallel to In-seeded III-V nanowire growth, Ga was also found to allow for VLS-growth of Ga-based III-V nanowires. Early works date back to the 1960s, where Barns and Ellis demonstrated Ga-assisted micron-size GaAs and GaP whiskers and plates and proposed a VLS mechanism¹¹⁵. GaAs nanowires were also observed in “failed growth” of GaAs layers, for instance by Arthur and LePore¹¹⁶ using MBE. It was however the pioneering works from the group of A. Fontcuberta i Morral in 2008^{97,98} that opened the way to high quality Ga-seeded GaAs nanowires, grown epitaxially on GaAs(111) and GaAs(001) substrates by the intrinsically high purity MBE technique (see Figure 3b). These works triggered a rapid interest from the MBE growth community, and a few months later epitaxial growth of these nanowires on Si was demonstrated, nearly simultaneously by Paek *et al.*¹¹⁷ for growth on Si(111) and by Jabeen *et al.*¹¹⁸ for growth on cleaved facets of Si(100).

Demonstrations of good control of the growth and properties of Ga-seeded GaAs nanowires happened much faster than for In-seeded nanowires, and rapidly GaAs/AlGaAs core-shell heterostructures were obtained^{119,120} and their optical properties studied by photoluminescence¹¹⁹, Raman spectroscopy¹²¹ and cathodoluminescence¹²⁰. Controlled n and p-type doping was demonstrated by Colombo *et al.*¹²² and Dufouleur *et al.*¹²³. First axial heterostructures, consisting of GaAs/In_xGa_{1-x}As^{124,125} and GaAs/GaAs_xSb_{1-x}^{126,127} followed (Figure 3h-i). Finally the first arrays of self-seeded GaAs nanowires directly grown on silicon (111) were shown by Plissard *et al.* in Ref. 128 and refined in Ref. 129 to reach a vertical yield of about 95% (see Figure 3j).

Although these nanowires primarily exhibited ZB crystal structure, the possibility to obtain some degree of WZ/ZB polytypism and isolated twin defects triggered interests in fundamental optical studies of the WZ bandstructure and WZ/ZB band-alignments¹³⁰⁻¹³⁸. Recently twin-free ZB phase in GaAs nanowires has also been demonstrated¹³⁹⁻¹⁴¹, having exceptional optical quality¹⁴². Finally a unique possibility of controlling the diameter of the seed particle and density *in-situ* was highlighted independently by Priante *et al.*¹⁴³ and Somaschini *et al.*¹⁴⁴ in 2013, with promises in future growth developments and applications (see Figure 3k).

The Ga-seeded growth mechanism has therefore proven its value for optoelectronic applications based on the GaAs material

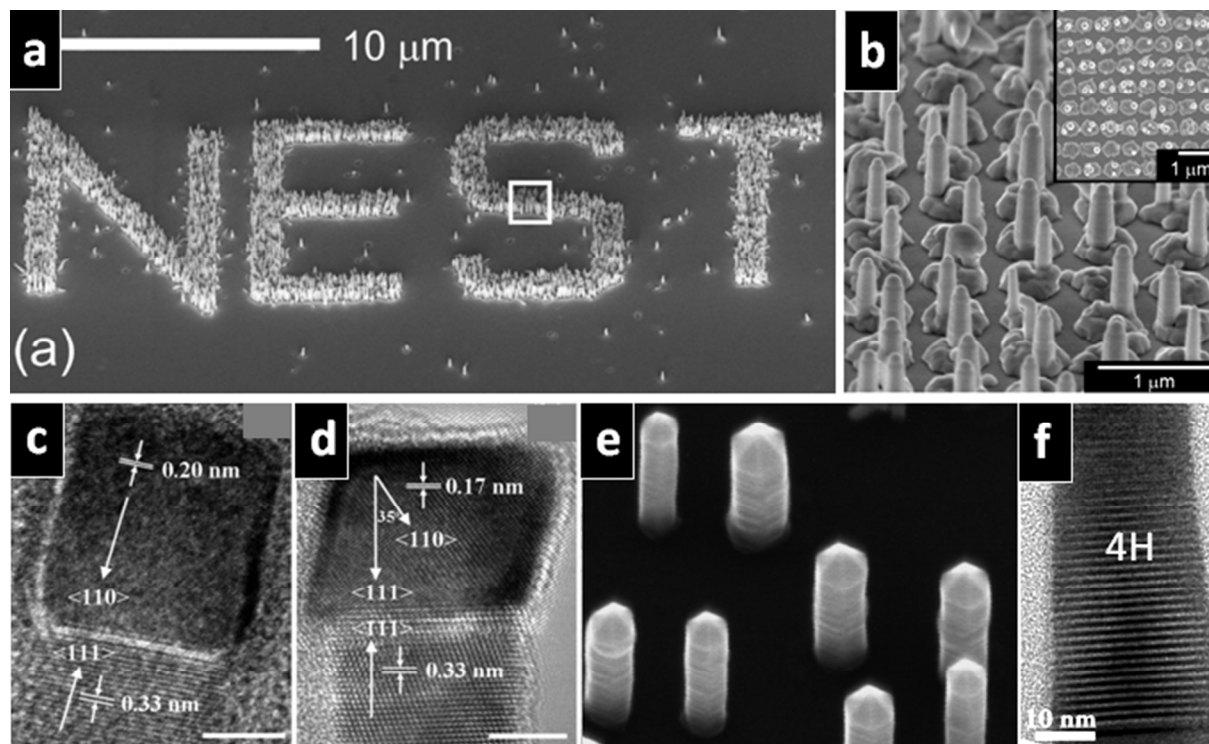


Figure 4: Foreign metal seeded III-V semiconductor nanowires. (a) SEM image of a position-controlled vertically-aligned array of Pd-seeded InAs nanowires, adapted from Ref. 163 with permission. (b) SEM image of a position-controlled vertically-aligned array of nominally Ag-seeded InSb nanowires, adapted from Ref. 176. (c,d) TEM images of Ni-seeded GaAs nanowires where the crystal phase of the $\text{Ni}_x\text{Ga}_{1-x}$ particles is shown to directly correlate with the resulting crystal phase of the grown GaAs nanowires. Adapted from Ref. 162 with permission. (e) SEM image of vertically-aligned Cu-seeded InP nanowires, adapted from Ref. 171 with permission. (f) TEM image showing an extended segment of 4H crystal phase in a Cu-seeded InAs nanowire, adapted from Ref. 44 with permission.

system, thanks to controlled doping and heterostructuring, and brought the highly interesting possibility of seamless integration on Si(111). However, other Ga-seeded materials such as GaP and GaSb have scarcely been reported to date^{145,146,110}. Note however the interesting demonstration of Ga-assisted GaSb nanotrees by Yan *et al.*⁵⁰, showing ultralow reflectivity in the 500-1700 nm spectral region.

4 Foreign metal seeded III-V nanowires

Selective-area and self-seeded nanowire growth both offer obvious advantages in terms of simplicity and cleanliness of the fabrication process. By avoiding the introduction of any additional species beyond those directly used in the fabricated material, it is possible to entirely avoid any unintentional contamination arising from such additional elements. On the other hand, the parameter space is by definition limited for both of these techniques. For SAE, complete suppression of growth in lateral dimensions is not possible, and the aspect ratio of the nanowires will never be unlimited. In addition, even with optimum conditions and very high aspect ratios, diameter will always increase with time. This has important implications for heterostructure growth, since radial and axial growth can never be fully isolated. Self-seeded growth may in principle allow for complete suppression of lateral growth, but it relies on a careful balance of growth conditions to maintain a group III droplet that

does not change size with time (unless this is intentionally induced). Any change in growth parameters will therefore directly affect diameter, limiting the extent to which parameters (and thus properties) can be tuned.

Nanoparticles composed of foreign metals, such as gold, are less sensitive to small changes in parameters since the volume of the foreign species in the seed particle is fixed. In the classic case of this type of growth, the foreign metal species is dominant species in the seed particle and therefore diameter will be insensitive to growth conditions (although under certain conditions one of the III-V components may dominate over the foreign seed metal, as will be discussed below). There is also minimal risk of the seed particle being fully consumed, as can easily occur for group III droplets if the group V precursor supply is too high. Considering foreign seed particles as a group, the parameter space is thus enormously broad compared to other techniques: using gold-seeded growth of GaAs by MOVPE as an example, nanowire growth has been reported from at least 300 to 600°C, with precursor V/III ratios from as low as 1 to as high as 1000. This gives a much greater freedom for tuning properties such as axial/radial selectivity, crystal phase, growth direction and growth rate – all of which are influenced by growth parameters. In all of these cases, it may be considered that there is no single optimum, but different applications may require different extremes in each category. For example, high growth rates may be desired for high-throughput synthesis of single nanowire materials, while low growth rates are associated with

sharper heterostructure interfaces and more controlled crystal phases. This much greater flexibility accounts for much of the continued dominance of gold-based synthesis despite the impressive development of SAE and self-seeded techniques.

However, advances beyond what can be achieved with gold can also be anticipated. For example, it has long been observed that semiconductor nanowires exhibit a very strong preference for growth in the specific crystal direction $\langle 111 \rangle_B$ ¹⁴⁷. However, early results from several alternative foreign seed metals show that this preference may be less prominent with certain alternatives. Additionally, several examples have been reported of crystal phases achieved with alternative foreign seed metals that have not been achieved using gold. Similar effects have also been achieved for Si and Ge nanowires, as will be discussed in Section 5. Examples of foreign metal seeded III-V nanowires are illustrated in Figure 4.

4.1 Nickel

Nickel is in principle compatible with Si electronics and is considerably less expensive than gold, making it is reasonable choice for an alternative seed particle metal. On the other hand, it has a higher melting point than gold, and forms stable oxides in air – both of which may be factors in determining the suitability of a metal for nanowire growth. Interestingly, it also forms mid-gap electronic states in GaN¹⁴⁸, which is the III-V material for which it has most often been used as a seed for nanowire growth.

Nickel has been used a seed particle metal for GaN for more than a decade¹⁴⁹⁻¹⁵¹, making it the second most-common seed particle material after gold. Unlike gold, however, the use of Ni has been almost exclusively restricted to GaN nanowires. Ni-seeded GaN nanowires have been growth by MOVPE and MBE, on a variety of substrates including sapphire¹⁵² and Si^{151,153}. Vertical epitaxial alignment is also routinely demonstrated¹⁵²⁻¹⁵⁵. Various growth directions are reported¹⁴⁹ but for growth in hexagonal $\langle 0001 \rangle$ directions (parallel to the cubic $\langle 111 \rangle$ directions), high densities of stacking defects are often reported¹⁵². Extensive analysis of the growth process and composition of this system has been performed, and it is generally accepted that the Ni seed particles have a solid phase during nanowire growth^{156,157}.

Several recent reports have also shown the growth of GaN and GaN-InGaN heterostructure nanowires using Au-Ni alloy particles^{158,159}, representing some of the first attempts to grow III-V nanowires with particles contain two foreign metals. The authors report that formation of epitaxially-aligned nanowires is easier with alloy particles than with pure Ni, and attribute the difference to faster nucleation with the addition of gold.

Ni has additionally been used as a seed particle for both GaAs and InAs nanowires^{160,161}, using a furnace technique with evaporation and deposition of the semiconductor material in zones of different temperature. High growth rates were reported, and here as well it is proposed that Ni nanoparticle seeds are active in the solid phase¹⁶¹. One very intriguing observation for GaAs nanowires was that that crystal structure of the solid NiGe intermetallic compound was found to correlate with the crystal phase of the resulting GaAs nanowire¹⁶² (see Figure 4c-d). This provides rather convincing evidence that the selection of seed particle material will have a direct impact on the resulting

properties of the nanowires.

4.2 Palladium

Palladium is a noble metal with a high melting point, and resistance to oxidation that is comparable to gold, but forms more favourable electronic states in Si. It is also a versatile catalyst, which may help to improve growth control by allowing for preferential decomposition of precursor species near the growth front. On the other hand, it is among to most expensive of metals.

Pd-seeded growth of InAs nanowires has been demonstrated by two groups using CBE and MOVPE, with epitaxial alignment demonstrated¹⁶³. Both have proposed that nanowire synthesis by Pd-based liquid and solid particles may occur simultaneously^{164,165}, indicating that Pd is an interesting test case for understanding the differences and similarities of liquid and solid-based growth mechanisms. It has also been demonstrated that nanowires may grow in alternate crystallographic directions (other than $\langle 111 \rangle_B$) when using Pd seeds, and that the interfacial energies between the seed metal and the semiconductor play a role in determining the favourable directions. In addition, Pd seeds can be obtained in the form of a precursor which happens to be also a direct-write electron resist, elegantly allowing for simple processing of position-controlled nanowires¹⁶³ (see Figure 4a).

Pd-seeded growth of GaAs nanowires has also been demonstrated, with the primary claim being that morphology is significantly more difficult to control than Au-seeded nanowires grown under identical conditions⁶².

4.3 Platinum

Platinum has many properties similar to Palladium, but is considerably more expensive. It has not been reported to have detrimental effects on the electronic properties of Si or any III-V materials, and is chemically stable in a variety of environments. There is one report of the use of Pt as a seed particle material for GaN nanowires¹⁶⁷. The resulting nanowires have very high crystal quality but do not show epitaxial alignment with the substrate by the technique used. The authors indicate that the barrier to nucleation of GaN nitride is higher from a Pt seed particle than from Ni, limiting the growth rate. They also report that both optical and electrical properties are better for Pt-seeded nanowires than for Ni-seeded, which they directly attribute to the detrimental effects of incorporated Ni atoms on the electronic properties.

4.4 Manganese

Manganese has been used to as a seed particle material for both InAs and GaAs nanowires using MBE¹⁶⁸⁻¹⁷⁰, with the specific purpose to incorporate Mn atoms into the grown material and change the properties, aiming towards magnetic semiconductors. The growth was reported to occur within a very narrow and low temperature window, and the authors conclude that the seed particles remain in a solid state during growth. It is pointed out that the growth parameters and resulting nanowires are very similar to gold-seeded nanowires in the growth system used, leading the authors to speculate that the seed particle material is

not a major influence on properties in this case. Nanowires are shown to exhibit both zinc blende and wurtzite phase together with stacking defects, making them structurally similar to gold-seeded nanowires. Epitaxial alignment with the substrate has not yet been demonstrated for this system.

4.5 Copper

Copper is a period IB metal, like gold, and as such has similar electronic structure. This is reflected in its relatively low reactivity with many gas species, but also in the creation of unfavourable states in Si. Cu is however generally considered easier to remove from fabrication equipment than gold, and is cheaper by as much as five orders of magnitude. Unlike gold, Cu oxidizes in air, but is easily reduced in a moderate reducing environment.

Cu has been demonstrated as a seed particle material for InP and InP-InAs heterostructure nanowires using MOVPE (see Figure 4e-f). Growth was demonstrated within a much smaller parameter space than for gold, and with a notably lower growth rate for identical growth conditions. It was concluded that under most conditions Cu primarily acts as a solid-phase seed. However, under In-rich conditions, an alternative liquid-phase seed was reported with very high In content (similar to self-seeded growth). Nanowires growth with In-rich liquid-phase seeds had notably higher growth rates. Here the Cu was proposed to act only as a collection site for the In species. Epitaxial alignment with the substrate was shown for both solid-phase and liquid-phase seeds.

It was also shown that InAs nanowires for certain diameters consisted of long segments of 4H crystal polytype (Figure 4f). This polytype has not been reported for gold-seeded InAs nanowires despite extensive mapping of the parameter space for crystal structures; indeed reports of 4H in III-V nanowires are extremely scarce, with segments longer than a few nanometers reported only in self-seeded InSb as mentioned above and as a transient phase following the formation of certain ternary antimonide materials.

4.6 Silver

Silver exhibits many properties very similar to gold, including crystal structure, melting point, self-diffusivity, ductility, and resistance to oxidation, making it in many ways a logical alternative to gold. It is among the more expensive and rare metals on Earth, but still cheaper than gold by as much as two orders of magnitude. However, its electronic structure is also very similar to gold, with the consequence that it also forms mid-gap states in Si.

Growth of InSb nanowires with Ag seed particles using chemical beam epitaxy (CBE) has been reported by Vogel *et al.* (see Figure 4b). It was demonstrated that epitaxial alignment of InSb nanowires with a substrate is possible, even at temperatures below 400°C. Interestingly the nanowires were also shown to exhibit high densities of defects and inclusions of hexagonal wurtzite phase. Although such stacking defects and polytypism are very common in most III-V materials, they have never been shown for InSb or GaSb using gold seeds. This supports the suggestion that the crystal phase of the grown

nanowires may be influenced by the seed particle material, and that the use of alternatives may expand the parameter space for material design.

Vogel *et al.* reported that InSb nanowires could be grown directly on InSb substrates, which has not been reported for gold. They speculate that the lower surface mobility of the Ag directly affects this possibility. They also note that the concentration of In is very high in the droplet, relative to the amount of Ag. As with Cu-seeding above, this observation makes it difficult to draw a sharp distinction between foreign metal-seeding and self-seeding, and the growth mechanism cannot be definitively identified as one or the other. Such findings will be useful in understanding the role of the seed particle and how self-seeded growth is related to seeding with a foreign metal, as will be discussed further in the Discussion section.

As well, InP nanowires grown using Ag seeds on Si substrates by MOVPE have been shown, for comparison with Au seed particles in order to gain insight into the growth mechanism. Very little data on the Ag seeded growth is given, but it is noted that nucleation yield is high compared to Au seeded nanowires under the same growth conditions.

4.7 Bismuth

Bismuth is a group V element, but does not form solid binary compounds with either Ga or In. It therefore represents an alternative “self-seeded” type of seed particle with limited solubility in the semiconductor material. It is also a low-melting element that can form liquid alloys with all growth species at suitable temperatures. Since it is a group V species, it is not directly harmful to electronic properties of either III-V or Si materials. On the other hand, trace amounts of Bi dissolved into binary III-V materials can have dramatic effects on the bandstructure, making this a potentially interesting element for tuning the nanowire properties by intentional incorporation of seed particle atoms.

Bi nanoparticles have been used as seeds for solution-based growth of III-V nanowires. Since the synthesis technique differs considerably from the vapour-phase methods used for all other alternative metals (and the vast majority of gold-seeded nanowires), it is difficult to directly compare the results. However, it is noted that nanowires of all investigated III-V materials exhibited a very high crystal quality, free from stacking defects.

4.8 Iron

Iron is among the most abundant and inexpensive metals found on Earth, and exhibits minimal biological or environmental hazards. It is also a ferromagnetic material and can be expected to add increased functionality if incorporated in small quantities in nanowires. Like gold, it forms mid-gap electronic states in Si, and unlike gold, is highly sensitive to oxidation.

Fe has been demonstrated as a possible seed metal for GaAs nanowires in MOVPE. It was demonstrated that nanowires grow in several possible crystallographic directions, giving further evidence for the potential of controlling crystal direction with particle material. Growth in this system was attributed to a solid-phase seeding mechanism due to the absence of a suitable

low-temperature eutectic. Fe has additionally been used as a seed particle material for GaN, also using MOVPE¹⁴⁹. In this case the authors also noted a variety of different simultaneous growth directions and a different predominant growth direction for Fe than for Au.

5 Foreign metal seeding of Si and Ge nanowires

The investigation of alternative foreign seed particle materials is somewhat more mature for Si and Ge than for III-V nanowires. This is partly historical, and builds on early knowledge from growth of micron-scale Si whiskers using gold and other metals as early as the 1960s¹⁸². However, although there are a few reports of catalyst-free Si nanowire synthesis¹⁸³, the lack of an alternative equivalent to liquid-alloy self-seeding for group IV semiconductors has likely also contributed to the drive to develop alternative foreign seed particles. Finally, the potential to predict and to understand the effects of an alternative foreign metal is somewhat more straightforward for semiconductors consisting of one component, rather than two. Here we present a summary of the most important findings and trends in the growth of Si and Ge nanowires with alternative seed particles. We emphasize that the aim is not to exhaustively review the growth of Si and Ge nanowires with alternative seed particles, but to look for trends with potential for extrapolation to III-V nanowire Growth.

Most of the metals that have been used for III-V growth, including Cu¹⁸⁴⁻¹⁸⁹, Ag¹⁹⁰, Pd¹⁹¹, Mn¹⁹², Fe¹⁹³, Ni¹⁹⁴⁻¹⁹⁶, Pt^{197,198}, Ga¹⁹⁹ and In²⁰⁰⁻²⁰³, have also been demonstrated as potential seed particles for Si and/or Ge nanowires. In addition, significant development has been reported for Co^{204,196}, Ti²⁰⁵, Sb²⁰¹, Al²⁰⁶⁻²⁰⁸, Sn^{209,210,211,203}. Binary alloys and compounds consisting of two different foreign metals have also shown significant promise for Si and/or Ge nanowire growth, including AuAl²¹², AuAg^{213,214}, AuCu²¹⁵, and AuGa^{216,217}.

The growth of micrometer-scale Si whiskers using seed particles of other metals than gold was demonstrated as early as the 1960s¹⁸². The first demonstration of Si nanowire growth with an alternative metal was however presented in 2001 using Ti²⁰⁵. It was demonstrated that Ti forms solid silicide compounds that can act as seeds for nanowire growth, representing the first demonstration that nanowire growth does not in principle require a liquid alloy seed particle. Of the wide variety of alternative seed particle metals that have subsequently been reported for Si nanowire growth, the majority are not believed to form liquid alloys under growth conditions. For example, Pd, Pt, and Cu have all been reported to result in nanowire growth from solid compound particles^{188,191,197}. This has been supported by *in-situ* TEM experiments using Pd and Cu^{191,187}, showing that solid-phase seeding is indeed a viable growth mechanism. The effect of particle phase on the resultant properties of the nanowire is not yet fully understood, but there is evidence that considerable control is possible with suitable selection of seed particle material.

In-situ TEM has resulted in considerable advances in the general understanding of the dynamics of seeded nanowire growth, and in recent years there have been a number of studies that have considered alternative seed particle materials^{191,187,212,213}. One important point is that the stability of

the particle under growth conditions is material-dependent, and of course critical for the success of the growth²¹³. The dynamics of the growth itself also seem to depend considerably on the phase and/or material of the seed particle^{187,191}. Comparative studies of Si nanowires grown with Au (liquid alloy) and Pd (solid compound) particles have shown that similar growth rates are in principle achievable, and have given considerable insight into the key parameters. It is indicated that the limiting step in the growth process (such as diffusion through the seed particle or nucleation at the interface) will have considerable influence on the resulting nanowire properties, and will directly result from the properties of the selected seed material. For example Pd and Ni are predicted to result in different rate-limiting steps, with implications for, among other things, the growth rate and amount of foreign atoms dissolved in the nanowire¹⁹¹. It has similarly been suggested that the incorporation rate of material at the interface, when this step is limiting, is determined by the seed particle material – for example, it was indicated that this process proceeds faster with Pt seeds than with Au when both are in liquid alloy form¹⁹⁸.

Compositional grading at heterointerfaces is a pervasive problem in many types of seeded nanowire growth, and has proven difficult to address in the Si-Ge material combination. It was demonstrated that the addition of Al to Au seed particles in order to change to a solid-phase growth mechanism could directly lead to considerably sharper heterointerfaces, attributed to a much reduced solubility for the growth species in the solid phase^{212,213}. It was also shown that selective alloying of Au with Ga also resulted in reduced solubility and sharper heterointerfaces, even in liquid phase²¹⁷.

Epitaxial alignment of Si and Ge nanowires with alternative (solid) seed particle materials has proven difficult¹⁹², indicating an important role of particle-semiconductor interface formation in nanowire alignment¹⁹⁵. Conversely, epitaxially aligned nanowires are more commonly reported with liquid alloy seed particles, including Pt¹⁹⁸ and Cu²¹⁸. However, it was reported that epitaxially aligned Si nanowires could be achieved using solid-phase Al particles²⁰⁶. It is less clear what role, if any, that particle material/phase has in determining the growth direction. Si and Ge nanowires, much like III-V nanowires, most often adopt the <111> growth direction regardless of substrate orientation. However, reports of alternative directions, in particular <112> and <110> are not uncommon using either gold or alternatives⁵⁵. It is therefore difficult to reach conclusions from existing data, although existing results indicate that diameter plays a key role¹⁹⁵.

The role of particle material in crystal phase is clearer, though presently not more understood. Unlike III-V nanowires, which typically exhibit a moderate to high density of stacking defects and phases not present in bulk materials, Si and Ge nanowires with <111> growth direction are, with the exception of two very recent reports²¹⁹⁻²²⁰, free of rotational stacking defects. Conversely, it has been reported that Si and Ge nanowires grown with alternative seed particle materials including Cu¹⁸⁴, In²⁰⁰, Ga¹⁹⁹ and Ni¹⁹⁵ may exhibit frequent stacking defects and segments of hexagonal diamond phase, which is not stable in bulk. It has also been reported for AuAg solid alloy seed particles that the composition of the alloy determines the density of defects

formed, with the potential to selectively tune crystal structure by seed particle engineering²¹⁴. At present there is no predictive explanation for which metals will result in which nanowire crystal properties, but it is clear that there is a connection between the two.

Finally, the potential for self-doping by intentional incorporation of atoms from a suitable seed particle material has been shown to be viable. It has been demonstrated that the level of intentional doping directly from the seed particle material can exceed the equilibrium solubility by orders of magnitude, making this a leading technique for tuning the nanowire properties directly²²¹.

6 Discussion and Conclusions

Selective area growth and self-seeding are relatively mature growth techniques, which nevertheless still have some room for optimization to yield maximum control of the fabrication process. By comparison, foreign metal seeding of III-V nanowires remains underdeveloped, particularly in comparison to foreign metal seeding of Si nanowires. We therefore see this area as particularly promising for significant development and improvement, and major breakthroughs may be anticipated. Currently there is an almost complete lack of understanding of the role of specific seed metal properties on nanowire growth and the resulting material properties. For example, there are indications in the data above that the growth direction and crystal phase are affected/determined by the type of seed. However, presently there is little indication how this can be used in a predictive way to select seed particle metals to give the desired properties.

One important point will be to clarify, and perhaps to challenge, the distinction between self-seeded and foreign metal-seeded growth. There have been several reports, including those by Hillerich *et al.* and Vogel *et al.* mentioned above^{172,176}, which show growth using foreign metal seeded nanowires where the group III species in the particle far exceeds the amount of the foreign metal. Similar examples have been shown for nominally gold-seeded nanowires under certain conditions (specifically, very low V/III ratio)^{50,109,222}. In these cases it is not straightforward to assign the growth to either foreign metal seeding or self-seeding. It should be emphasized that all foreign metal seeds contain during growth a certain amount of both III and V species (though it may range from <1% to >99%) – the amount will change the growth behaviour, material properties and parameter space, but we speculate that the fundamental mechanism remains the same. Foreign seed particles may then act just to collect and control a suitable supply of the III and V species at the growth front. It might then be imagined that self-seeding is just an extreme case of seeded growth, where the amount of foreign element reaches zero. In this case, of course, additional steps are needed to attain maximum control of growth, for example by pre-patterning the growth substrate with a mask.

We envisage that, while significant development is needed to eliminate the use of gold in nanowire growth, there will be no single “solution” developed; that is, no single alternative will be selected as a replacement. Self-seeded and selective area growth have significant limitations in terms of parameter space and independent length/diameter control, but are clearly unbeatable in

terms of cleanliness and purity of the resulting materials. With further development, an even higher degree of control may be cautiously anticipated for self-seeded, and potentially also selective area. This may make these the techniques of choice for applications where the highest purity is needed, or in the case of selective area, when mostly radial heterostructures are desired. On the other hand, the significantly increased design space for foreign metal seeding may lead to the development of a variety of distinct crystal phases and growth directions that can be selected according to the desired application. As another example, intentional incorporation of trace levels of elements from the seed particle might be desirable for a variety of applications, promoting the selection of for example Sn for self-doping, Mn for magnetic properties or Bi for bandstructure engineering.

In developing a variety of alternative techniques for nanowire synthesis, and in particular when selecting alternative foreign metal particle materials, it will therefore be necessary to define more precisely the nanowire parameters that are critical to the chosen application. With a view to the literature it can be stated that very many metals can in principle facilitate some degree of one-dimensional growth; it may be hypothesized that virtually any solid or liquid element could in principle be used in this way. The important thing is then to define the resulting nanowire properties that are desired in order to deem the foreign metal as “successful”. To begin with, cost of the metal in question must be considered when aiming towards upscaling in device applications. Practicality in forming controlled, size selected nanoparticles or droplets that are stable under reasonable semiconductor growth conditions is another important point. Gold is a malleable metal with a moderate melting point, which easily forms both solid size- and shape-controlled nanoparticles, and also forms liquid alloys with low vapour pressure when combined with semiconductor components. It is also highly resistant to oxidation, making it practical to handle and transfer through a variety of processes. On the other hand, its relatively high diffusion rate and length on many surfaces will limit the stability of droplets under some circumstances^{223,224}.

Practicality may be an important consideration for high-melting temperature elements in particular, especially if epitaxial alignment with a substrate is an important parameter for the desired application. Metals that form intermetallic compounds with one or more growth species may be advantages in this respect: this process necessarily results in reshaping of the solid material under growth conditions, increasing the probability of forming well-oriented size- and shape-controlled particles. Indeed, most or all of the elements shown to be viable for solid-phase seeding of Si, Ge or III-V materials do indeed form intermetallic compounds with these species.

Important properties of the resulting nanowire growth may include growth rate, resistance to kinking, selected crystal phase and growth direction, and incorporation of atoms from the seed particle. Growth rate may refer to an absolute rate, whereby the practical of the synthesis process in terms of total fabrication time is critical, or to the growth rate relative to competing radial/bulk/surface growth, which will impact the achievable shape and aspect ratio. Growth rate will necessarily be influenced by the choice of particle material, in particular for solid particles where the diffusion of growth species can be limiting, but also for

any materials which can interact chemically with reactant precursors and thereby affect the amount of available growth species. Nucleation at the growth front will also be affected by the interface energy between the semiconductor and the metal seed, which may be limiting in some circumstances.

Resistance to kinking, or spontaneous changes in growth direction, is also a key factor since the majority of applications require nanowires with a well-defined geometry. Most of the reports above that indicated a limited parameter space for selected alternative foreign seed particles define this parameter space by the range in which unknicked nanowires form with high probability. Resistance to kinking is highly sensitive to growth parameters (in particular temperature and precursor pressures), and indeed for gold-seeded nanowires kinking is also prevalent for a wide range of growth conditions. A better understanding of how this process is connected to particle material must be developed in order to assess suitable material choices and to determine the extent to which this morphology can be avoided.

Similarly, selection of growth direction may be an important factor in determining the suitability of certain seed particle materials. For many applications, the very dominant $\langle 111 \rangle$ growth direction may be entirely satisfactory. However, for integration with Si electronics, there is a strong pressure to develop processes for integration on (001) surfaces, which would ideally also mean growth in [001] direction. Despite extensive efforts, there has been very limited success in growing III-V nanowires in this direction using gold, and only InP [001] nanowires have been demonstrated to date.^{225,226,56} An alternative seeding technique that promoted this growth direction would therefore be especially promising.

Control and selection of crystal phase will also be a critical point and one area where improvement relative to gold is clearly needed. For Si and Ge nanowires, as discussed above, pure crystal phase free of stacking defects is the standard when growing with gold seed particles, and other materials provide opportunities for exotic crystal phase engineering. For III-Vs, the situation is almost the opposite: uncontrolled crystal structure with a high density of stacking defects is standard for most of the parameter space explored for gold, for most III-V nanowire materials. Similar results are observed for both selective-area and self-seeded growth. Although impressive control has been demonstrated with the potential to achieve defect-free cubic and hexagonal phases as well as engineered structures, the parameter space for achieving any of these is very small for most III-V materials. Some of the alternative seed particle materials considered have already shown evidence of a wider parameter space for pure crystal phases than has been achieved with gold, and more complex polytypes have also been reported⁴⁴. Here a substantial breakthrough in understanding the relationship between seed particle material and nanowire crystal structure is needed to aid in the development of alternative fabrication processes.

Finally, we envisage that the use of alloys containing two or more foreign elements for growth of III-V nanowires will be an important and exciting area of development in the near future. As noted, alloys of two foreign elements (typically including gold) have already been developed for Si and Ge nanowires, in most cases with the express intent of tailoring the properties of the seed

particle to achieve the desired nanowire results. The potential of this concept is enormous and it is not unreasonable to speculate that all nanoparticle seeds will eventually consist of designed metal alloys with properties specific to the growth and application needs. However, this opportunity depends first on a much enhanced understanding of the effect of properties of single foreign metal seed particles on nanowire growth.

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Notes and references

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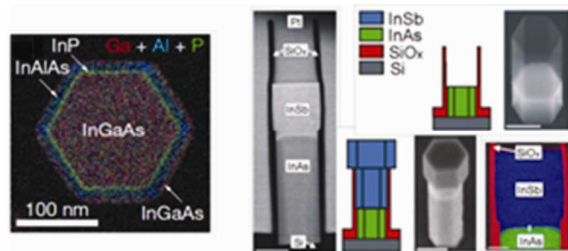
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The progress towards developing gold-free bottom-up synthesis techniques for III-V semiconductor nanowires is reviewed. Three main categories of nanowire synthesis are discussed: selective-area epitaxy, self-seeding and foreign metal seeding, with main focus on the metal-seeded techniques.