

Synthesis of nanostructures in nanowires using sequential catalyst reactions

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Nanowire growth by the vapor-liquid-solid process enables a high level of control over nanowire composition, diameter, growth direction, branching and kinking, periodic twinning, and crystal structure. The tremendous impact of VLS-grown nanowires is due to this structural versatility, generating applications ranging from solid state lighting and single photon sources to thermoelectric devices. Here we show that the morphology of these nanostructures can be further tailored by using the liquid droplets that catalyze nanowire growth as a “mixing bowl”, in which growth materials are sequentially supplied to nucleate new phases. Growing within the liquid, these phases adopt the shape of faceted nanocrystals that are then incorporated into the nanowires by further growth. We demonstrate this concept by epitaxially incorporating metal silicide nanocrystals into Si nanowires with defect-free interfaces, and discuss how this process can be generalized to create complex nanowire-based heterostructures.

The ability to control the fabrication of materials at sub-100 nm dimensions is crucial to tailoring properties and functionalities. The technologies this opens up are highlighted by the evolution of electronic and photonic devices over the last decades. Bottom-up, or self-assembly, approaches to nanofabrication are particularly important because of the demands for increasing diversity of materials, greater structural complexity, and strict requirements for control of the interfaces between the component materials. In this context, the vapor-liquid-solid (VLS) growth mechanism [^{1,2,3,4,5,6}] has been extensively explored. VLS growth is versatile, enabling a high level of control over nanowire composition to form axial and radial nanowire heterostructures, as well as control over nanowire diameter, growth direction and kinking,

branching, periodic twinning, and crystal structure [7,8,9,10,11,12,13,14,15]. Each type of nanowire morphology leads to new applications, with examples including heterostructures with precisely defined surface facets for solid state lighting [16,17]; crystal phase quantum dots, proposed for single photon sources [18], and periodically twinned nanowires for thermoelectric devices [19]. Here, we report an expansion of the catalytic VLS growth concept which opens an additional pathway to tailor complex nano-heterostructures. We supply growth materials sequentially to the liquid droplets that catalyze nanowire growth. This nucleates new phases that form as nanocrystals and can be incorporated into the nanowires with epitaxially perfect interfaces. We use *in situ* transmission electron microscopy (TEM) to directly record each step of this “sequential catalyst reaction” process. We illustrate the concept by forming metal silicide endotaxial nano-inclusions in Si nanowires, and assess its generality and flexibility for creating more complex nanostructured nanowires.

Figure 1 shows an overview of the process by which NiSi₂ nanocrystals can be formed and incorporated into Si nanowires. We carry out the reaction sequence in an ultrahigh vacuum transmission electron microscope (UHVTEM) [20] to provide a controlled growth environment (see Methods). Si (111) nanowires, 20-50 nm in radius and 100-150nm in length, are synthesized using Au as the catalytic metal and disilane (Si₂H₆) as the precursor gas. After cooling (still under UHV), ~1 nm Ni is deposited by evaporation. The sample is then annealed *in situ* for 30 min at 200°C in an O₂ pressure of 1×10⁻⁵ Torr. This oxidation step forms a layer of SiO₂ on the nanowire sidewalls [21] (Supplementary Information, Figure S1), enabling selective introduction of Ni into the catalyst without sidewall reactions. A similar outcome will be described below that makes use of a metal-organic precursor such as nickelocene that incorporates Ni selectively into the droplet without requiring oxidation.

After this oxidation step, the temperature is set to 350°C, a value just below the Au-Si eutectic temperature, and 1×10⁻⁵ Torr Si₂H₆ is introduced (Fig. 1a). The nanowires are slowly heated to 500°C at ~10°C/min. As the temperature passes the eutectic point, the liquid Au-Si droplet reforms (Fig. 1b) as the solid Au abruptly reacts with Si in the nanowire. Simultaneously Ni and Si react. These reactions consume part of the nanowire (Fig. 1b). The outcome of the Ni-Si reaction is surprising. Inside the droplet, bright contrast appears instantaneously as the catalyst becomes liquid, revealing the presence of a solid inclusion. This solid may be a single octahedral nanocrystal, or smaller nanocrystals (as in Fig. 1b) that coalesce into a single octahedral NiSi₂ nanocrystal as the temperature continues to increase (Fig. 1c). Note that the NiSi₂ phase forms in the liquid rather than at the nanowire growth front. Once formed, its volume remains constant but it moves randomly within the liquid droplet (Supplementary Information, Movie 1). Eventually, it “docks” onto the nanowire (Fig. 1d), touching the nanowire growth interface and

forming a defect-free, epitaxial connection (Fig. 1i and j); note the excellent registry ($\sim 0.4\%$ mismatch) between Si and NiSi₂ lattices. During this time, the nanowire continues to grow. Growth is slow due to the low temperature, but initially planarizes the nanowire-catalyst interface. As the temperature is raised, the growth rate increases (~ 2.5 nm/min at 500°C [22]), and the docked nanocrystal is incorporated into the Si matrix (Fig. 1e-h). The result is a nanowire containing an inclusion. We confirm the NiSi₂ phase from the lattice parameter, shape (typical of a cubic phase) and volume (see below), and find that perfect endotaxial incorporation is possible (Fig. 1k-m).

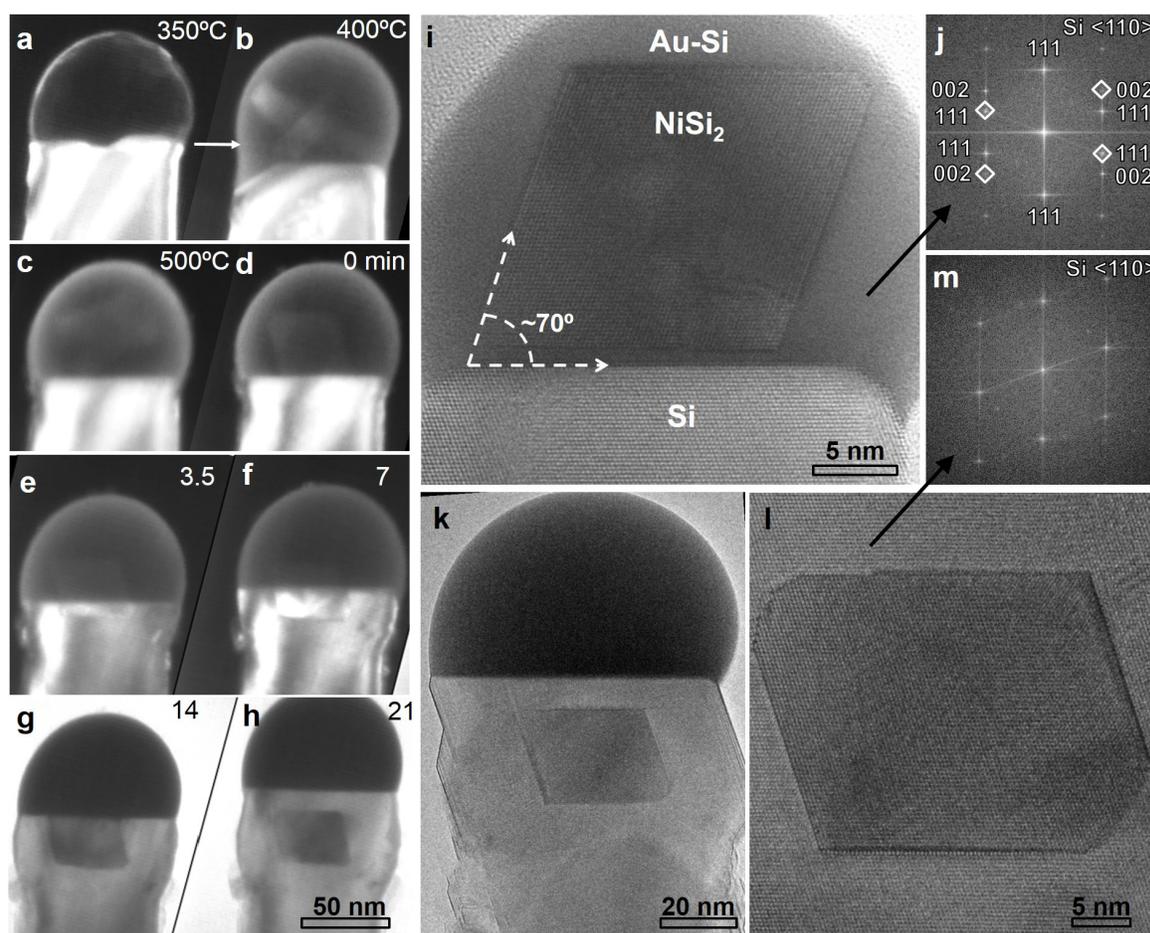


Figure 1: TEM images showing nickel silicide formation and incorporation in Si nanowires. **a-d** Sequence of dark field (DF) images recorded after Ni deposition and oxidation, while raising the temperature to 500°C in 5×10^{-5} Torr Si₂H₆. A NiSi₂ nanocrystal forms inside the Au-Si droplet and makes epitaxial contact with Si. The arrow in **b** shows the initial Au/Si interface. **e-h** Nanowire growth that embeds the nanocrystal as the temperature reaches 500°C. The growth rate is steady, apart from in the first few minutes where it is slower, perhaps by impurities formed at the catalyst surface during oxidation. Bright field conditions are used in **g** and **h** to highlight the structure. The time is given in minutes. **i, j** High-resolution image and Fast Fourier transform (FFT) of a different nanowire showing a nanocrystal in a twinned epitaxial relation with Si. **k, l, m** Image, detail and FFT showing endotaxy in a different nanowire in which the process of silicide incorporation is completed. The dark and bright lines around the nanocrystal in panel **l** are due to diffraction at the crystal interfaces.

The entire sequential catalyst reaction process, from the deposition of Ni to the growth of the nanowire, can be repeated and multiple silicides can be embedded to form a complex silicide/silicon heterostructure (Supplementary Information, Figure S2). The distance between nanocrystals inside the wire is controlled through the growth time between Ni deposition steps, and the size of each nanocrystal is controlled by the amount of deposited Ni. Starting with free-standing nanowires is important in this reaction sequence. For nanowires dispersed on a silicon nitride membrane, NiSi₂ has been observed to nucleate in the Au-Si droplet [23], but the nanocrystal does not move or dock to the nanowire, presumably because the membrane acts as a preferential nucleation site.

How is it possible to have such good epitaxy between Si and the NiSi₂ nanocrystal, given that the nanocrystal forms in the liquid phase and appears to touch and “dock” to the Si surface in one step? Images such as those in Fig. 1 and Movie 1 cannot resolve the atomic level details of the docking process. In Fig. 2 and Movie 2, we therefore show the process as observed in an aberration corrected environmental TEM (ETEM) equipped with gas handling capabilities for Si₂H₆ [24] and a fast camera (see Methods). The sequence shown in Fig. 2 was observed in several instances. First, the octahedral particle makes contact with the Si (111) growth interface by touching at a single edge; second, it completes the epitaxial connection via rotation around the [110] axis (Fig. 2a). The angle between the silicide nanocrystal and Si is readily measured (Fig. 2b) through FFT of the image series. Rotation takes place in a stepwise manner and a single increment can occur in less than 0.1 second (Fig. 2c). The driving force of this two-stage mechanism presumably is based on minimization of interface energies of the two crystals. By analogy to what has been observed for axiotaxial structures [25], even when only one family of planes is aligned, there is an energy gain sufficient to align the nanocrystal with the nanowire. The subsequent stepwise rotation can be understood by noting that the nanocrystal shape appears unchanged during rotation, but the Si surface shows steps that flow readily during rotation. The Si rearranges to accommodate the silicide, apparently by moving atoms from the right side to the left: Si layers on the right of the silicide retract and a new layer appears on the left (Fig. 2d). At each rotation increment, a step moves (Movie 2) increasing the contact area forming the low energy epitaxial connection. During subsequent nanowire growth that fully incorporates nanocrystals, we observe rapid step flow (Movie 3), similar to that observed in conventional nanowire growth [26,27]. We suggest that the mobile nature of the Si surface during docking and subsequent nanowire growth enables the production of highly perfect crystal structures in which silicides can be endotaxially incorporated without any evidence of dislocations.

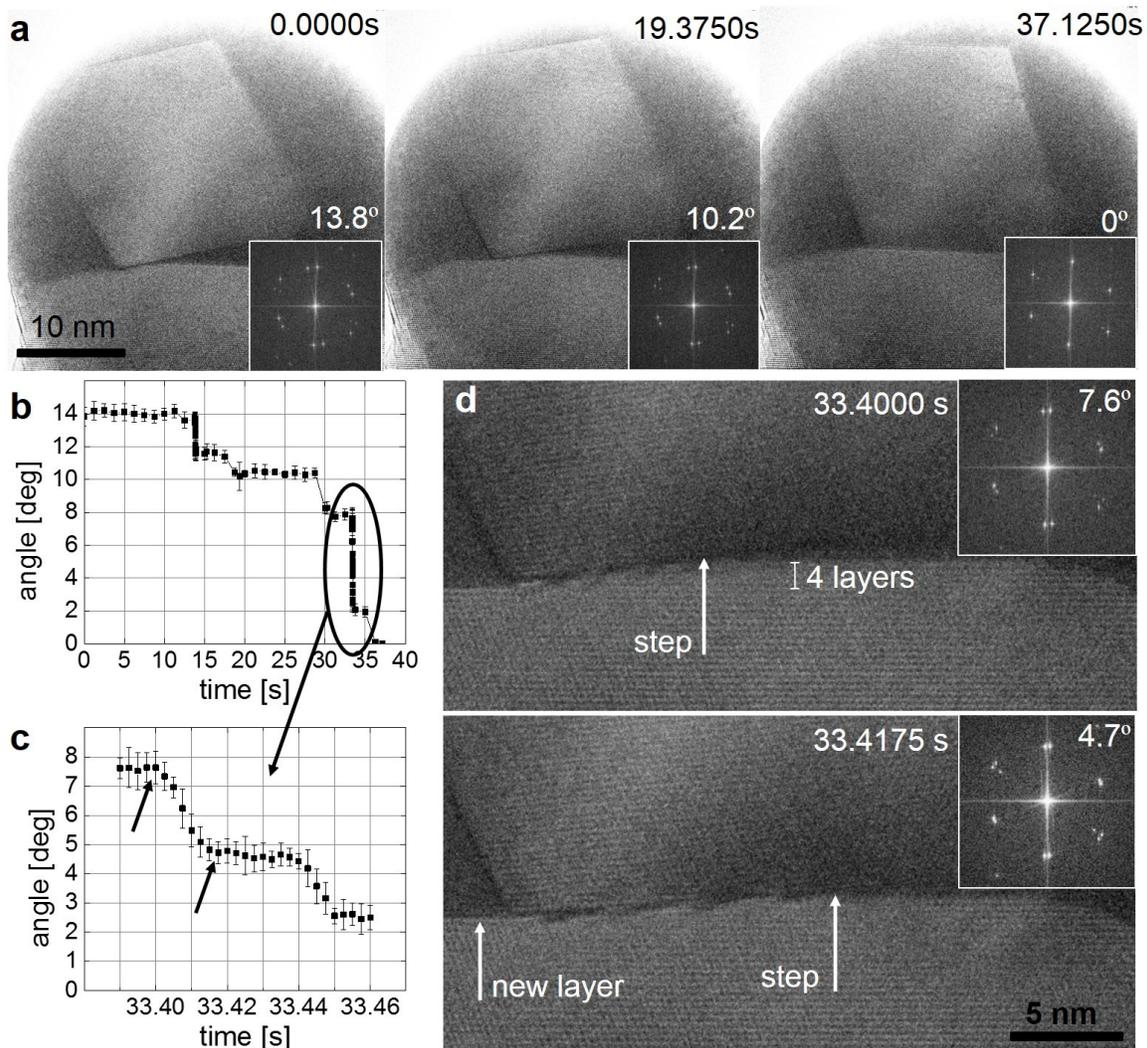


Figure 2: The docking of a silicide particle with its nanowire. **a** Sequence of atomically resolved, 400 fps TEM images recorded at 400°C. The insets show the FFT of each image with the angle between the two crystals indicated. **b** The rotation angle measured from the FFT of the image series in **a** and Movie 2. **c** Detail of **b** showing one larger rotation occurring in two distinct increments; arrows indicate the data corresponding to the images in **d**. Error bars in **b** and **c** represent the standard deviation calculated by measuring the angles between six pairs of spots in the FFT. **d** Detail of the sequence in **a** showing rearrangement of the Si surface during silicide rotation. The insets show the respective FFTs.

The docking process does not always result in perfect endotaxy. Occasionally nanocrystals make contact with the Si surface in an apparently unfavourable orientation and do not reorient before the nanowire starts to grow. An example is shown in Movie 4 (Supplementary Information), where Si grows around a misoriented nanocrystal. The Si growth front remains planar. Defects are visible at the silicide/Si interface but the surrounding Si appears defect-free. This suggests that each Si ledge nucleates at the periphery of the growth front (as in conventional VLS, [26]) rather than at the interior junction surrounding the silicide, and hints that it could be generally possible to grow high quality Si by VLS around inclusions, even if they are not well matched to or aligned with the Si lattice.

A key feature of the sequential catalyst reaction concept is the formation of a single, faceted nanocrystal which later attaches to its nanowire. We presume that the liquid-mediated reaction helps to allow easy coalescence if multiple nuclei form initially, and easy rearrangement of the new phase into a well-defined, low energy shape. But why does the nanocrystal form in the liquid (or at its surface), rather than at the Si interface, especially in this case, where there is an excellent lattice match between NiSi₂ and Si? Experiments such as that in Fig. 1 cannot address this question: NiSi₂ forms too quickly to resolve as the temperature is raised, since Si is present in excess (from the nanowire). We therefore designed experiments where Si is added more gradually to metal particles, slowing down the reaction sequence so that we can understand the Au-Ni-Si system better by examining the phases and nucleation sites in more detail.

In Fig. 3, Au and Ni were deposited sequentially on an electron transparent, inert membrane and annealed in vacuum to agglomerate into crystallites (see Methods). Then the temperature was raised to a constant value and Si₂H₆ was supplied. Figs. 3a, b and Movie 5 show the resulting sequence of phases observed respectively in the ETEM (Fig. 3a and Movie 5) and UHV-TEM (Fig. 3b). This fairly complex sequence can be understood by comparison with the reaction of pure Au with Si under similar conditions [28,29]. In that case, the initial reaction of Si with an Au crystallite forms liquid Au-Si at the Au surface. The reaction front then propagates inwards [28]. Once all the Au is consumed, but Si is still being supplied, the Au-Si eutectic becomes supersaturated with Si. Eventually solid Si nucleates at the periphery of the droplet [29,30].

In Figures 3a and 3b, however, a new phase forms before any substantial reaction of Au with Si. (A thin liquid layer would not be visible.) It is clear from the size of this phase (Fig. 3c) that its volume is fixed by the initial amount of Ni. We assume therefore that it is a Ni-silicide. Only after its growth is complete does the solid Au react with Si to form Au-Si. The initial Ni-silicide is elliptical in projection. However, once the Au is consumed, and presumably Si starts to supersaturate the liquid, the silicide increases in volume (Fig. 3c) by a factor of ~2 and becomes a well-faceted octahedron. This final phase is unequivocally NiSi₂; the initial phase is presumably a Ni-rich silicide, which we cannot identify unambiguously because of the large number of Ni-rich silicides in the Ni-Si phase diagram (Table S1 in Supplementary Information). Eventually, solid Si nucleates and grows at the periphery of the droplet. And crucially, the NiSi₂ and Si come into contact only at the end of the sequence.

The timing of the transition from Ni-rich silicide to NiSi₂ appears to depend on the conditions used: the data in Figs. 3b and 3c is consistent with a transition occurring after all Au has reacted to form Au-Si, while in Fig. 3a the characteristic NiSi₂ faceted shape is visible earlier, even when crystalline Au is still present. However, in all cases, the phase that makes the

epitaxial connection to Si is NiSi₂. The size of this phase can be accurately controlled by adjusting the amount of Ni deposited (Fig. 3d and 3e) and the smallest we have realized is < 3 nm in radius (Fig. 3a).

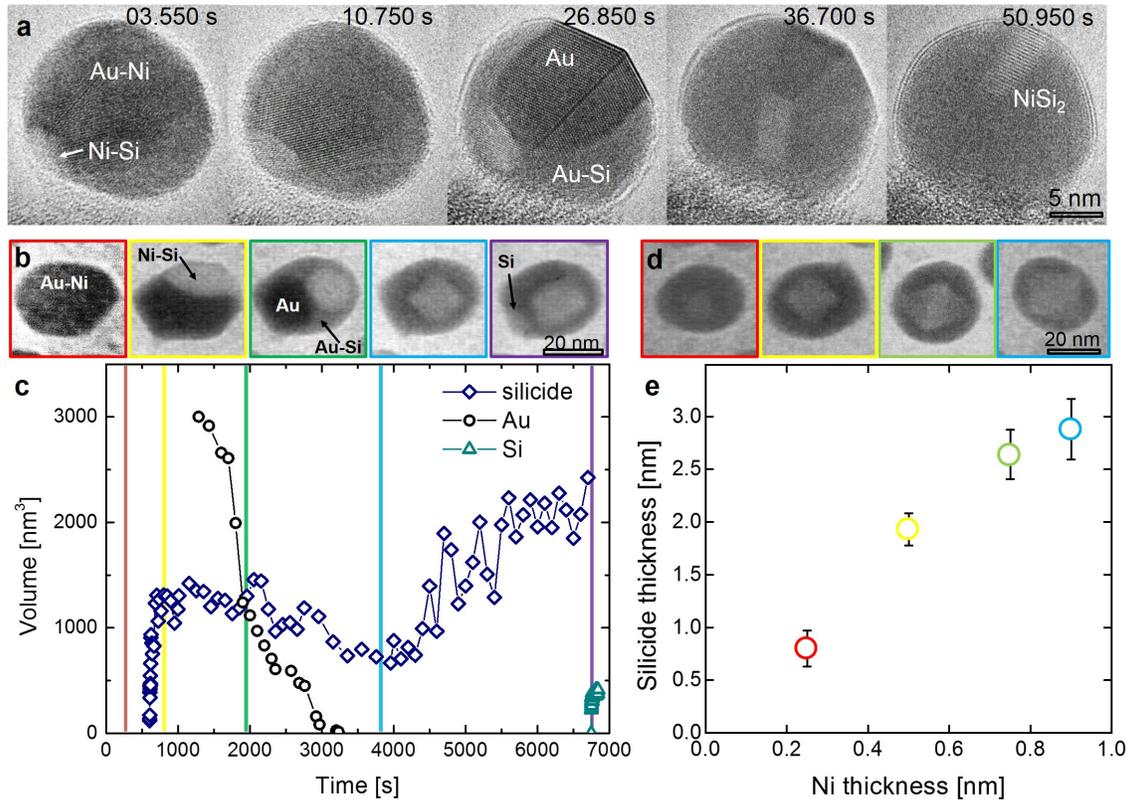


Figure 3: Ni-silicide nucleation in Au-Ni nanocrystals deposited on Si nitride membranes. **a** The sequence of phases observed *in situ* in ETEM during exposure of a 7nm radius polycrystalline Au aerosol particle covered with 0.1 nm of Ni to 3.5×10^{-5} Torr of Si₂H₆ at 400°C. The characteristic shape of NiSi₂ is first visible in the fourth image. **b** Sequence observed in UHVTEM during exposure of a 15 nm radius polycrystalline Au-Ni crystallite to 3.5×10^{-8} Torr Si₂H₆ at 490°C. 2.5nm Au followed by 0.5 nm Ni were evaporated onto a silicon nitride membrane (see Methods). **c** Volume versus time of each phase in **b**, calculated from the projected area and assuming a height equal to the average diameter. Note that the initial silicide volume is overestimated because its shape is far from the assumed ellipsoid; values obtained after disappearance of solid Au are more likely to be accurate. Colored vertical lines identify the time corresponding to images in **c**. **d** Sequence of images of average size silicides formed after the process in **b**, but starting with different amounts of Ni. **e** Colour-coded data of silicide thickness vs. thickness of deposited Ni corresponding to the images in **d**. Silicide thickness is measured by adding the estimated volume of all the silicide nanocrystals recorded in a frame and dividing by its area. Error bars represent the standard deviation calculated by measuring the silicide thickness in 5 different frames.

Overall, the data in Fig. 3 shows that a silicide forms before Si reacts with Au. The fact that the reactions in Fig. 1 take place at a nanowire tip rather than in an isolated Au particle, as in Fig. 3, therefore does not play a role in the overall process. Indeed, if we hold nanowires below the eutectic temperature, so that Au-Si liquid can not form quickly, we observe silicides nucleating even though the Au at the nanowire tip remains solid (Fig. S3). If an initial silicide

forms and attaches only after it has transformed to NiSi_2 , then the final quality of the silicide/Si epitaxy is determined exclusively by the liquid-mediated contact process described in Fig. 2.

We finally consider the yield, uniformity and generality of the sequential catalyst reaction concept, central in developing applications of these nanostructured materials. Yield and uniformity in *in situ* experiments are expected to be poor, because of the small growth area, uncontrolled catalyst sizes and shadowing during the shallow angle Ni evaporation. Even so, nanowires of median size ($r \sim 40$ nm) reliably produce nanocrystals in over 90% of droplets. However, yield loss occurs because all but 5% of wires kink during the incorporation step. This is unsurprising because cooling Si nanowires, as required here for transfer to the evaporator, is known to cause kinking on regrowth [7]. We have solved this issue by using a gaseous metal MOCVD precursor, nickelocene (bis(cyclopentadienyl)Ni, $\text{Ni}(\text{C}_5\text{H}_5)_2$), to selectively deposit Ni into the droplets without the need for cooling. This avoids kinking, also eliminates the need for the sidewall oxidation step (see below), and is promising for its compatibility with large scale production; its main issue is carbon contamination. We therefore believe that yield and uniformity can be addressed through an optimized gaseous precursor such as Ni carbonyl or an *in situ* metal evaporator, in concert with size-controlled catalysts.

To address the generality of the process, we have investigated several other materials systems. We have nucleated single, well-faceted nanocrystals by supplying Co and Mn to liquid Au-Si catalysts (Figs 4a and b, respectively), analogous to the process for Ni. In Fig. 4a, the CoSi_2 nanocrystal was formed using cobaltocene, (bis(cyclopentadienyl)Co or $\text{Co}(\text{C}_5\text{H}_5)_2$). The sidewalls were not passivated by oxidation, yet showed no visible silicide formation. In Fig. 4b, Mn monosilicide was formed using evaporated Mn; manganocene produces similar results (not shown). For Mn, an epitaxial connection forms (Fig. 4c) but does not lead to incorporation because the nanocrystal detaches as Si ledges start to flow when Si growth is restarted. We suppose that the interface is not particularly low energy due to the mismatch, and speculate that for smaller crystals with lower total strain energy it may be possible to complete the incorporation. Finally, Fig. 4d shows a Ni-Ga nanocrystal formed via nickelocene exposure of an Au-Ga droplet at the tip of a GaAs nanowire.

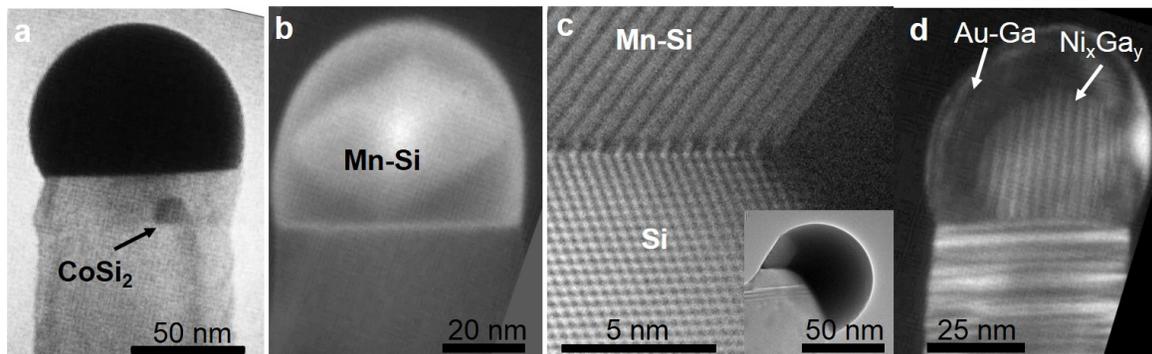


Figure 4: Nanocrystal formation in different materials. **a** CoSi_2 nanocrystal formed after 15 min of exposure to 5×10^{-6} Torr of $\text{Co}(\text{C}_5\text{H}_5)_2$ at 500°C and incorporated into a nanowire after switching to 5×10^{-6} Torr of Si_2H_6 without changing temperature. The Si growth rate after $\text{Co}(\text{C}_5\text{H}_5)_2$ exposure was slower than expected, perhaps suggesting the presence of carbon on the catalyst surface; other metalorganic precursors are known to deposit less carbon at this temperature [31]. **b** Mn-Si nanocrystals formed after Mn evaporation onto the Au-Si catalyst. Similar results are obtained with gas precursor $\text{Mn}(\text{C}_5\text{H}_5)_2$. **c** High resolution image of a Mn-Si nanoparticle in contact with the 111 surface of a nanowire, with the inset showing the whole nanowire. **d** A Ni-Ga nanocrystal formed in a liquid Au-Ga catalyst on a GaAs nanowire after 20 min exposure to 1×10^{-6} Torr of $\text{Ni}(\text{C}_5\text{H}_5)_2$ at 500°C ; image recorded after cooling.

Although the limited number of systems we have explored does not allow us to infer a model that predicts whether a given materials combination will produce endotaxial nanocrystals, we can provide some necessary conditions (Supplementary Information, Fig. S4). The first is the formation of a compact nanocrystal instead of a full layer of the new material. It has already been shown [32] that this requires a specific relationship between the interface energies of the various crystals. Endotaxy implies additional constraints: the new crystal should be completely wetted by the liquid catalyst, and there must be a driving force for attachment, as discussed in the Supporting Information. This simple thermodynamic argument can perhaps guide materials choice, especially in cases where the relevant energies can be estimated.

In conclusion, we have introduced a technique that extends the VLS method of nanowire growth, allowing the formation of nanowires that contain embedded nanocrystals. In essence, the catalyst particle is used not only to grow nanowires, as in the classic VLS process, but in an extended role, to independently nucleate different nanocrystals, whose formation and attachment in the liquid contribute to the high nanocrystal/nanowire interface quality. Using *in situ* TEM, we have explored this process in detail for Ni, embedding NiSi_2 quantum dots within Si nanowires with defect-free interfaces, and with a size and relative position controlled by the amount of Ni supplied and by the growth time between nucleation events. *In situ* microscopy reveals the process by which the epitaxial interface is created, and factors that influence nanocrystal location and phase. We have described how this sequential catalyst reaction concept can apply to other metals and nanowire materials, and introduced a different pathway to selectively supply the metal. In particular for metalorganic precursors, the catalytic droplet can be thought of as a

“mixing bowl” where the order and amount of each ingredient can be programmed to make a desired recipe with the aim of achieving controlled growth of complex nanostructures. This method is complementary to the formation of fully embedded quantum dots by shell growth on axially modulated nanowires [33,34]. Such quantum dots are limited in diameter by the initial nanowire diameter, and only certain materials combinations produce good quantum dot morphologies [32]. Sequential catalyst reactions allow compact quantum dots to be formed with dimensions decoupled from the nanowire diameter, including in materials that do not grow by VLS but present technological interest. The embedded nanocrystals may be located at p-n junctions or compositional interfaces to enhance their functionality.

The materials system on which we have focused has central relevance for microelectronics applications since Ni silicides are the material of choice for contact fabrication in CMOS technology. Ni and Co silicides also have magnetic and plasmonic properties that make them appealing for a wide range of applications. One such application could be in photodetectors. The dielectric functions of silicides show metallic behavior in the infrared and visible ranges and the manufacturing advantages of silicides make them promising materials for infrared plasmonics integrated on microelectronic devices [35,36,37]. Si nanowire based photodetectors [38] are generally coupled with metallic waveguides or nanoparticles to improve their efficiency [39]. NiSi₂ [40] or CoSi₂ [41] nanoparticles embedded at the p-n junction of a photodetector would be expected to enhance light absorption by exciting localized surface plasmon resonances. The method described here can in principle provide the building blocks for such devices. Quantum transport provides another possible application. Nanoscale PtSi clusters in a Si nanowire offer a unique potential for realizing “Coulomb blockade” transistors and other single-electron devices [42]; such silicide quantum dots have been formed accidentally during fabrication of PtSi contacts to the nanowire, but we can now see how to form such structures in a controlled way. High-density memories, semiconductor lasers, and tunnel diodes are other areas of interest. For integrated electronics, epitaxial metallization incorporated into vertically-grown semiconductor heterostructures opens up new possibilities by providing buried interconnects of atomic perfection, along with the capability to engineer a wide range of three-dimensional device structures. We therefore suggest that sequential catalyst reactions will open up exciting opportunities for the controlled growth and device integration of complex nanostructures with tailored functionalities.

Author contributions: FP and YCC performed experiments and data analysis, MCR developed the UHV TEM technique, DZ and EAS performed high resolution ETEM experiments, and SH and FMR designed the experiments and coordinated the analysis.

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Methods: Nanowire growth was performed in a Hitachi H-9000 UHV-TEM having a base pressure of 2×10^{-10} Torr and a maximum pressure during imaging of 2×10^{-5} Torr. The microscope is connected to a cluster of UHV tools where temperature calibration and metal deposition were carried out. The substrates used for nanowire growth were $3 \text{ mm} \times 300 \text{ }\mu\text{m}$ silicon strips cut from a $700 \text{ }\mu\text{m}$ thick (111) wafer, and were imaged with the polished (111) surface parallel to the beam. Each sample was cleaned chemically finishing with an HF dip and was then loaded into a sample holder cartridge that can heat the sample by passing a direct current through it. After introducing the cartridge into the UHV environment, the sample was degassed and any surface oxide was desorbed by heating above 1200°C . The temperature was measured with a pyrometer and an *ex situ* calibration of temperature vs. current was performed. 1-2 nm of Au was then deposited by thermal evaporation and the sample was loaded in the microscope where precursor gas (Si_2H_6) was introduced through a capillary tube at a pressure of 2×10^{-5} Torr. The temperature was raised to 500°C in order to agglomerate Au into droplets and initiate VLS growth. Subsequently, Ni or other metal evaporation was performed in the same UHV tool using an electron beam evaporator. For each metal evaporation step, a crystal monitor was used to measure the thickness of the deposited metal. The crystal monitor reading was calibrated via using medium energy ion scattering measurement of samples with different thicknesses of deposited metal. Alternatively, Ni or other metals could be deposited by exposure to nickelocene or analogous reactive gas precursors, but without any calibration of the amount deposited.

High resolution imaging was carried out in a FEI Titan 300 aberration-corrected ETEM. Samples on which nanowires had been pre-grown and Ni had then been deposited in the UHV-TEM were carried through air, cleaned with an HF vapor etch, then loaded into the ETEM. A shell of SiO₂ remained visible around the nanowires but this could be removed by condensing the intense electron beam spot around the nanowire catalyst droplet while holding the sample at 500°C. Images were recorded using a Gatan K2 camera at 400 frames per second each having 4 mega-pixels.

Nucleation experiments were performed on 50 nm thick silicon nitride windows formed by etching the substrate away over a $\sim 100 \times 100 \mu\text{m}^2$ region in the centre of a $3 \times 4 \text{ mm}^2$ sample that had been diced from a nitride-coated Si wafer. 1-2 nm of Au was evaporated onto such samples and agglomerated by heating, or alternatively, Au aerosol nanoparticles were deposited directly onto the samples. Ni or other metals were then added by evaporation or gas phase precursor, as described above. The membrane samples were heated by direct current with the temperature calibrated by pyrometer.

Supplementary Information

Synthesis of nanostructures in nanowires using sequential catalyst reactions

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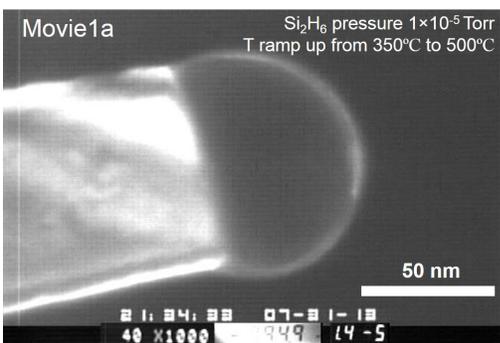
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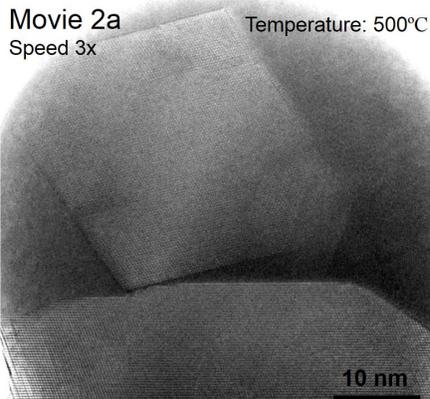
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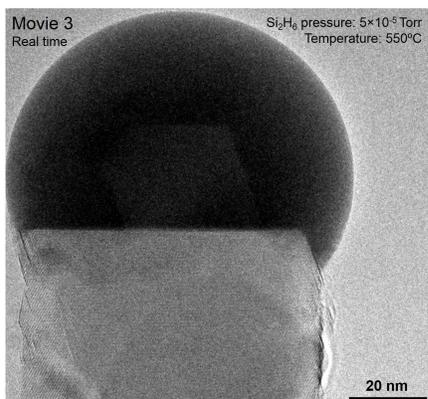
Details of Supplementary Movies 1-5



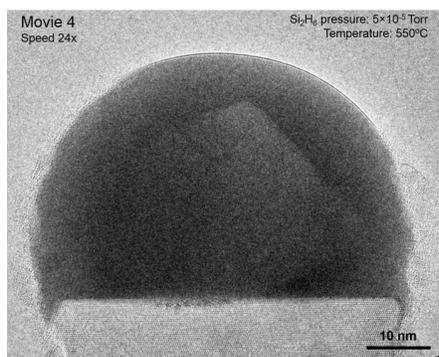
Movie 1: Compilation of sequences that illustrate the formation and incorporation of a NiSi₂ nanocrystal in a Si nanowire, recorded using both dark and bright field conditions in the UHV TEM. **a** Formation of silicide nanocrystals on heating a Si nanowire with 1nm Ni from 350 to 500°C in 1×10⁻⁵ Torr Si₂H₆. **b** Docking of the nanocrystal on the Si(111) interface during exposure to 1×10⁻⁵ Torr Si₂H₆ at 500°C. Real time. **c** Incorporation of the nanoparticle during heating to 500°C in 1×10⁻⁵ Torr Si₂H₆. Speeded up 30×.



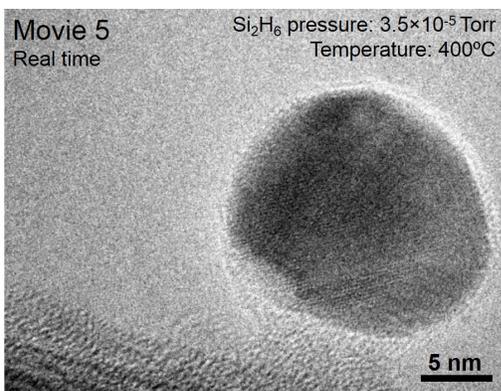
Movie 2: Compilation showing docking of a NiSi₂ nanocrystal on the Si(111) interface, recorded at 400 frames per second in the ETEM. **a** Rotation of the nanocrystal after contact; temperature 500°C. Speeded up 3×. **b** Cropped region showing the interface area in **a**, with ledge flow during rotation of the nanocrystal. Slowed down 30×.



Movie 3: Incorporation of a NiSi₂ nanocrystal into a Si nanowire, recorded at 400 frames per second in the ETEM at 550°C in 5×10^{-5} Torr Si₂H₆. Real time. .



Movie 4: Incorporation of a misoriented NiSi₂ nanocrystal into a Si nanowire, recorded at 400 frames per second in the ETEM. at 550°C in 5×10^{-5} Torr Si₂H₆. Speeded up 30×.



Movie 5: The sequence of phases formed in a 7nm radius polycrystalline Au aerosol particle coated with 0.1 nm of Ni during exposure to 3.5×10^{-5} Torr Si₂H₆ at 400°C. Real time.

2. The importance of the oxidation step

The method described in Fig. 1 includes an oxidation step where the nanowire is exposed to 10^{-5} Torr O₂ before raising the temperature above the eutectic temperature to form and incorporate the NiSi₂ nanocrystal. This oxidation step is necessary to prevent metal-silicon reactions at the nanowire surface. Fig. S1 illustrates the result of carrying out the same Ni deposition and anneal but without the presence of O₂.

The samples shown had 1 nm Ni deposited, then were heated to 360°C (i.e. slightly below the eutectic temperature) in 5×10^{-6} Torr of Si_2H_6 for 10 min. Under these conditions, the $\text{Au}_x\text{Si}_{1-x}$ catalyst is solid (Fig. S1a). The temperature was then increased by 5°C to induce the transformation of solid Au + Si into liquid $\text{Au}_x\text{Si}_{1-x}$ eutectic (Fig. S1b). This phase transition happens within 0.1s, consuming part of the nanowire (note the interface receding between Figs. 1a and b). However, immediately afterwards, the droplet size decreased and Au became visible on the sidewalls (Fig. 1c), suggesting surface migration of Au. This is not a coarsening process but a simultaneous collapse of all droplets. (Au migration out of the droplets could in principle be driven by coarsening [43], but at this temperature the process would be slow.) The final equilibrium shape of the droplet (Fig. 1d) exhibits a small wetting angle ($\sim 30^\circ$) and volume reduced by $\sim 6\times$. Inside the remaining $\text{Au}_x\text{Si}_{1-x}$ liquid, nanocrystals with bright contrast (arrows in Fig. 1d) are visible; these were identified as Ni silicides.

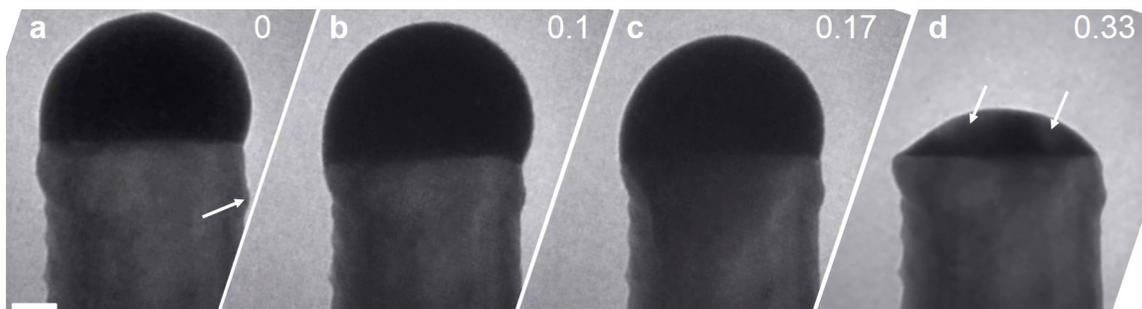


Figure S1: Sequence of bright field TEM images recorded during annealing at 370°C and 5×10^{-6} Torr Si_2H_6 . The Si nanowire is covered by 1 nm of Ni deposited by e-beam evaporation. The time is shown in seconds since the first image. The scale bar is 20 nm. The arrowed feature in **a** is used as reference to align the images. **a** the wires were held for 10 min a few degrees below the Au-Si eutectic temperature, then at $t=0$ the temperature was increased by 10°C. **b** A rapid reaction forms liquid $\text{Au}_x\text{Si}_{1-x}$. **c** Rapidly the $\text{Au}_x\text{Si}_{1-x}$ droplet shrinks and Au becomes visible at the nanowire surface as a dark shadow; **d** Au has mostly diffused away from the droplet. Two silicide nanocrystals (bright contrast) are visible inside the remaining liquid.

We believe that the migration of Au from the droplet is induced by a change in the nanowire sidewall energy that modifies the equilibrium droplet shape. It is well known that the deposition of a few nm of Ni on clean Si by evaporation [44] or sputtering [45] induces the formation of a Ni-Si amorphous intermixed layer, even at room temperature. This layer, after successive annealing steps, crystallizes into a nickel silicide phase: sub-nanometer layers deposited by e-beam evaporation and annealed 450-550°C result in NiSi_2 , while sputtered layers usually form the metastable $\theta\text{-Ni}_2\text{Si}$. Under our deposition and annealing conditions we therefore expect to form a thin NiSi_2 layer on the nanowire sidewalls. Such a layer would have a surface energy higher than silicon [46,47] and could therefore be responsible for destabilizing the droplets

by inducing Au migration. The oxidation step, carried out at 200°C in 1×10^{-5} Torr of O_2 for 30 min, results in a SiO_2 layer at the nanowire surface through the following mechanism: first Ni reacts with Si forming one of the silicide phases; second, the silicide decomposes into Ni + SiO_2 since the reaction of Si with oxygen to form SiO_2 is energetically favorable with respect to NiO; finally the resulting nickel migrates through the silicide layer and reacts at the silicon-silicide interface to form more silicide [48]. On the Au_xSi_{1-x} droplet, the Ni rapidly forms an alloy with Au and reacts with oxygen. However at this temperature the reaction is slow and the complete consumption of Ni requires several days [49].

3. Incorporation of multiple silicides

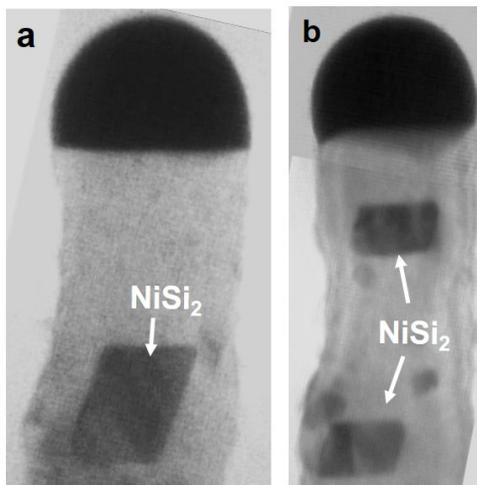


Figure S2: Bright field TEM images showing silicides incorporated into Si nanowires. **a** Single silicide incorporated during growth at 500°C and 5×10^{-6} Torr Si_2H_6 . **b** Same sample in **a** but a different wire after repeating the process of formation and incorporation of silicide nanoparticles.

4. Determination of the Ni-silicide phases

First phase

Growth experiments such as those in Fig. 3b and 3c do not identify the first silicide phase directly because of the relatively low spatial resolution. Instead, we infer the silicide phase from two clues: the time to nucleation of Si, and the volume changes of the silicide.

(a) First consider the timing of the phases in Fig. 3b and 3c. As was done in Ref. 26, the rate at which Au shrinks can be used to determine the arrival rate of Si atoms into the Au particle. The complete reaction of Au and Si to form Au_xSi_{1-x} happens after 2400s at $t=3010s$, and the Au reacts at a rate of $0.9 \text{ nm}^3/s$. This corresponds to a rate of Si introduction into the droplet of 33 atoms per sec (i.e. $0.13 \text{ nm}^3/s$). We assume that Si continues to arrive at this rate throughout the remainder of the experiment (i.e. that the sticking probability is constant). After the Si particle nucleates, its growth rate is $0.16 \text{ nm}^3/s$, consistent with this assumption.

Given this arrival rate for Si, we now calculate the expected time at which Si should nucleate, in the absence of any Ni reactions, based on the compositions at the liquidus lines at the growth temperature [50]. Si nucleation would be expected at $t=4070$ s but was actually observed at $t=6400$ s. Clearly not all of the incoming Si was used to increase the Si content in the Au_xSi_{1-x} . Instead, the additional ~ 2330 s corresponds to ~ 2400 nm³ Si (129000 atoms) and these transform the Ni-rich phase to NiSi₂. The final NiSi₂ volume of ~ 1800 nm³ contained ~ 182000 atoms of Si, so the initial phase contained $182000-129000=53000$ atoms. The ratio is 3.4, consistent with the ratio 4 expected for the transformation from Ni₂Si to NiSi₂.

(b) Another clue comes from the change in volume between the initial Ni-rich phase and the final NiSi₂ phase. In Fig. 3b and 3c, the silicide forms and remains at a constant volume for the first 2500 s then its volume changes by a factor ~ 2.2 after the complete consumption of solid Au. This is consistent with an initial phase of Ni₂Si, which in Table S1 is expected to show a volume ratio of 2.37 with NiSi₂.

Last phase

Two pieces of evidence suggest that the octahedral nanocrystal is the Si-rich silicide phase NiSi₂. First, the octahedral shape composed of {111} facets is consistent with the lowest energy configuration for a crystallite of cubic structure. Second, the lattice parameter and epitaxy with Si are consistent with NiSi₂, as it is the only nickel silicide that is cubic and has a lattice parameter close to Si (0.4% mismatch).

The formation of NiSi₂ at low temperature appears in disagreement with what is generally observed during the solid state reaction of Ni and Si thin films and the respective bulk diffusion couples [51,52]. Both the free energy gain (ΔG) and surface energy gain of silicide formation are presumably altered in the presence of Au. Unfortunately neither the ternary Au-Ni-Si phase diagram nor data about silicide/ Au_xSi_{1-x} interface energies are available. However, alloying Au with Ni is known to favor nucleation and growth of Ni silicides at low temperature [53]. The same has been found for Co [54]. Thus, the presence of the catalyst may allow lower temperature formation of phases than would be possible otherwise. Moreover, the solubility of Au is known to be about 20 times higher in NiSi₂ than in the commonly observed Ni-rich phase, Ni₂Si, at 300°C [55]. The presence of Au may thus favor formation of NiSi₂ by increasing its ΔG with respect to the other phases, due to the increase in the total entropy of mixing of the system.

5. Silicide nucleation before Au-Si reaction

If we hold nanowires similar to those in Fig. 1 below the eutectic temperature, we can observe the phase sequence directly without rapid formation of $\text{Au}_x\text{Si}_{1-x}$ liquid. In Fig. S3 below, the Au remains solid. A silicide forms before the Au has reacted to form $\text{Au}_x\text{Si}_{1-x}$, the same sequence that took place in Fig. 3.

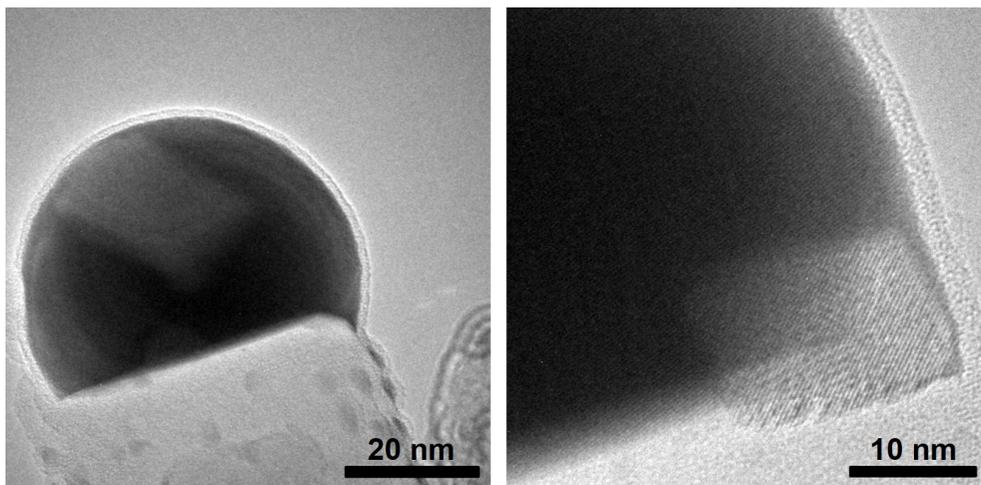


Figure S3: TEM images of Ni-silicides forming in a solid Au catalyst at the tip of a Si nanowire. The nanowires were coated with $\sim 1\text{nm}$ of Ni and annealed for one hour at 300C . Ni-silicide forms while the Au remains solid. Formation at two different locations is shown, at the interface and at the droplet surface.

6. Thermodynamic constraints for endotaxial crystal formation

A necessary condition for the formation of straight (as opposed to kinked) nanowire heterojunctions was developed in Ref. ⁵⁶. Fig. S4 extends this simple model further to address the necessary conditions for creation of nanowires containing endotaxial inclusions. The first requirement is that the system should form a compact nanocrystal instead of a full layer of the new material. This requires a specific relationship between the interface energies of the various crystals, shown in line I. However, for endotaxy the newly formed, compact crystal should be completely wetted by the liquid catalyst otherwise it will form at the nanowire surface. This leads to the inequality in line II. Finally, the attachment and subsequent incorporation of the new crystal requires the inequality relating the interface energy between the two crystals in line III.

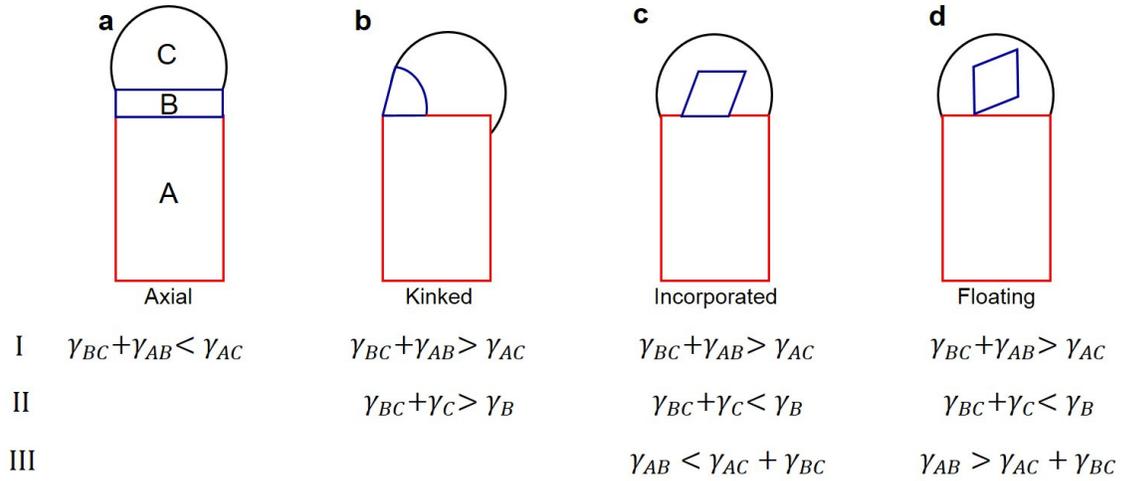


Figure S4: Schematic representing four kinds of heterostructures obtainable as a function of three conditions for the surface energies of the nanowire, droplet and nanocrystal. γ_{AB} is the interface energy between A and B, while γ_A is the surface energy of A, with other terms defined analogously. **a** represents the case of axial heterostructures; **b** the case that induces the wire kinking (both adapted from Ref. ⁵⁶); **c** is the case of the incorporation of a compact nanocrystal and **d** the nanocrystal floating in the liquid.

Phase	Structure/ Group	Lattice			Silicide V per Ni atom (Å ³)	NiSi ₂ /Silicide V (Å ³)
		a (Å)	b (Å)	c (Å)		
Ni	Cubic/Fm3m	3.5238			10.94	3.61
Ni ₃ Si	Cubic/Pm3m	3.5056			14.36	2.75
Ni ₃₁ Si ₁₂	Hex/p3 ₂ 1	6.671		12.288	15.28	2.58
δ-Ni ₂ Si	Orthor/Pnma	4.99	3.72	7.06	16.07	2.37
θ-Ni ₂ Si	Hex/P6 ₃ /mmc	3.80		4.89		
Ni ₃ Si ₂	Orthor/Cmc21	12.29	10.805	6.924	19.16	2.06
NiSi	Orthor/Pnma	5.233	3.258	5.659	24.12	1.64
α-NiSi ₂	Cubic/Fm3m	5.416			39.5	1
Si	Cubic/Fd3m	5.4309				

Table S1: Structure of nickel silicide phases [⁵²]

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