**Linear Heterostructured Ni$_2$Si/Si Nanowires with Abrupt Interfaces**

*Synthesised in Solution*

Martin Sheehan,¹ Quentin Ramasse,² Hugh Geaney,¹ Kevin M. Ryan¹#

1 Department of Chemical Sciences and Bernal Institute, University of limerick, V94 T9PX
2 SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury, WA4 4AD, United Kingdom

**Abstract**

Herein, we report a novel approach to form axial heterostructure nanowires composed of linearly distinct Ni silicide (Ni$_2$Si) and Si segments via a one-pot solution synthesis method. Initially, Si nanowires are grown using Au seeds deposited on a Ni substrate with the Si delivery in the solution phase using a liquid phenylsilane precursor. Ni silicide then forms axially along the wires through progressive Ni diffusion from the growth substrate, with a distinct transition between the silicide and pure Si segments. The interfacial abruptness and chemical composition of the heterostructure nanowires was analysed through transmission electron microscopy, electron diffraction, energy dispersive X-ray spectroscopy, aberration corrected scanning transmission electron microscopy and atomically resolved electron energy loss spectroscopy. The method represents a versatile approach for the formation of complex axial NW heterostructures and could be extended to other metal silicide or analogous metal germanide systems.

**Introduction**

Transition metal silicide (TMS) nanowires (NWs) are an interesting material set that have found a number of applications in areas including microelectronics,
photovoltaics and thermoelectrics.\textsuperscript{1-4} Their inherent compatibility with Si makes these materials particularly promising for microelectronic applications,\textsuperscript{5-7} such as multilevel interconnects, where their high conductivities, stable crystal structures and the possibility of forming ohmic contacts to n or p-type Si are desirable.\textsuperscript{8-12} One of the most widely adopted formation routes to TMS NWs is annealing induced conversion of pre-synthesised Si NWs that have been coated with the desired transition metal.\textsuperscript{9,13} By incorporating lithographic processes into this methodology, this conversion can be localised to selected regions of the NWs, resulting in axial heterostructure NWs composed of TMS and Si segments.\textsuperscript{14-16} These structures have been incorporated into single NW transistor devices, with scope for analysing the device performance as a function of channel length by controlling the degree of silicide formation.\textsuperscript{17-20}

An alternative pathway for TMS NW growth is the delivery of Si monomers to transition metal substrates. In this case, two competing processes can occur depending on the conditions, with i) solid phase seeding of Si NWs and/or ii) metal silicide NW formation possible.\textsuperscript{21-23} The Si delivery protocol is attractive as existing setups for Si NW growth can easily be adapted to grow TMS NWs. To date, NiSi,\textsuperscript{24,25} Ni\textsubscript{2}Si,\textsuperscript{26} Ni\textsubscript{3}Si\textsubscript{2},\textsuperscript{11,27} and Cu\textsubscript{0.85}Si\textsubscript{0.17}\textsuperscript{28} NWs have been synthesised by silane (SiH\textsubscript{4}) delivery within chemical vapour deposition (CVD) setups. TMS NW growth in alternative systems has also been demonstrated by Tuan and co-workers who synthesized Cu\textsubscript{3}Si NWs by thermally decomposing phenylsilane in a supercritical fluid based system.\textsuperscript{29} The high boiling point solvent based system that we have developed for Si and Ge NW growth,\textsuperscript{30-35} is also compatible with TMS NW growth and was used to grow Cu\textsubscript{15}Si\textsubscript{4} NWs from bulk Cu foil, using phenylsilane as the Si
A limitation of Si feed approaches to-date is that it has not been possible to introduce more complexity into the NWs. In particular, the formation of linear heterostructures that are desired for microelectronic devices and thermoelectrics has not been achievable. The ability to do this directly from a simple solution based growth method would be attractive as lithographic patterning is relatively low throughput (NW by NW) and process intensive.

Here, we describe the development of a hybrid Si delivery/silicide formation approach to fabricate both Ni silicide NWs and axial heterostructure NWs composed of Ni silicide (Ni$_2$Si) and Si segments within a high boiling point solvent system. In this approach, a thin film of Au is evaporated onto a Ni substrate, to initiate NW growth through the solution-liquid-solid (SLS) mechanism pioneered by Heitsch et al. As a consequence of the high temperatures required for Si NW growth, Ni diffuses out from the substrate into the NWs, forming Ni silicide in the NWs via a solid state reaction. Using this approach, Ni$_2$Si/Si heterostructure NWs and complete Ni silicide NWs can be formed in the same system.

**Experimental Section**

**Growth Substrate Preparation:**

Bulk Ni foil was purchased from Goodfellow with a 0.25 mm thickness and 99.98% purity. The Ni was cleaned with concentrated nitric acid (69% v/v) and rinsed repeatedly with deionized water and then dried. A thin film of Au (~5 nm) was then thermally evaporated onto the Ni foil using a MB-EcoVap Mbraun integrated thermal evaporator. The substrates were stored in an Ar glovebox prior to reactions, and contact with O$_2$ was minimized.

**Reaction Setup:**
Reactions were carried out within a high boiling point solvent system previously reported, with growth occurring via a SLS growth mechanism.\textsuperscript{30-35,37} A 100 ml custom-made Pyrex, round bottomed flask containing 8 ml of squalane (99\% Aldrich) was used as the reaction vessel. The growth substrate was placed vertically in to the round bottomed flask which was attached to a Schlenk line setup \textit{via} a water condenser. This was then ramped to a temperature of 125 °C using a three-zone furnace. A vacuum of at least 100 mTorr was applied for 60 min to remove moisture from the system. Following this, the system was purged with Ar. The flask was then ramped to the reaction temperature. Reactions were conducted at 465 °C, with two of the three zones set at 465 °C and the uppermost zone off. Upon reaching the reaction temperature, 0.75 ml of phenylsilane (98 \% Fluorochem) was injected through a septum cap. In a typical reaction, the growth was allowed to proceed for 60 min. To terminate the reaction, the furnace was turned off and the setup was allowed to cool to room temperature before extracting the NW coated substrates. After the reaction, the NW covered substrate was removed from the reaction flask. The substrate was rinsed with toluene and methanol to remove residual high boiling point solvent (HBS) and dried under a N\textsubscript{2} line prior to characterization.

\textbf{Analysis:}

Scanning electron microscopy (SEM) analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. The NW coated substrates were untreated prior to SEM analysis. For transmission electron microscopy (TEM) analysis, the NWs were removed from the growth substrates using a sonic bath and were dropcast onto Cu TEM grids. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis energy dispersive x-ray spectroscopy (EDS) detector.
Aberration corrected scanning transmission electron microscopy (STEM) work was carried out on a Nion UltraSTEM100 microscope operated at 100 keV primary beam energy. In the conditions used for the experiments, the microscope forms a 0.8 Å probe with a convergence semiangle of 31 mrad. The high angle annular dark field (HAADF) detector semiangular range was calibrated as 82–185 mrad for Z contrast imaging. A Gatan Enfina spectrometer was used to acquire electron energy loss spectra (EELS). Although the native energy spread of the beam delivered by the cold field emission emitter of the microscope is 0.32 eV, the spectrometer was set up so both Ni $L_{2,3}$ and Si $L_{2,3}$ edges could be recorded simultaneously, resulting in an energy resolution (estimated by the full width at half-maximum of the zero loss peak) of 1.5 eV. All EELS data were processed using principal component analysis to minimize the influence of noise. The collection semiangle was 37 mrad for all data presented here. For compositional analysis, Si $L_{2,3}$, Ni $L_{2,3}$, O $K$, and C $K$ edges were integrated over an 80 eV window after the edge onsets, following the removal of the background using a decaying power law function.
Results and Discussion

A schematic illustrating the synthetic protocol used for the formation of Ni$_x$Si/Si NWs within a high boiling point solvent (squalene) is shown in Figure 1a. NW growth occurs in the highest density on the portion of the substrate below the liquid line of the high boiling point solvent (SEM Figure 1b) with no NW growth occurring in the absence of Au. The SEM image in the inset of Figure 1b shows a bare Ni substrate after being subjected to a standard Si growth process. EDS
analysis of the substrates, shown in Supporting Information Figure S1 indicated only trace amounts of Si present. These trace amounts of Si are likely due to residue from the Si precursor on the Ni foil. The lack of any NW growth from bulk Ni foil is likely due to the slow rate of Ni silicide formation when phenylsilane is used as the Si precursor.\textsuperscript{38} In Figure 1c, a DF-STEM image of a heterostructure NW is shown with the Au seed, Si segment and Ni\textsubscript{x}Si segment highlighted. There is an obvious contrast difference axially and the overlaid EDS spectrum Figure 1d shows the formation of Ni\textsubscript{x}Si in the NW with a visually abrupt interface transitioning to pure Si. The EDS maps also confirm the localization of Au and Ni to the seed and Ni\textsubscript{x}Si portions respectively. In all NWs where the partial silicide formation was observed, the intermetallic was at the root with the Si segment closest to the Au tip with an obvious Si/Ni\textsubscript{x}Si transition point visible axially.

In Figure 2a, a low magnification HAADF-STEM image of a Ni\textsubscript{x}Si/Si NW with a diameter of approximately 10 nm is shown. It can be seen that there is a slight broadening of the diameter for the Ni containing portion of the heterostructure NW, consistent with the expansion (up to 30\%) caused by Ni incorporation noted by Weber et al. for silicide formation.\textsuperscript{39} The higher magnification HAADF-STEM image shown in Figure 2b, shows that the interface between the Ni\textsubscript{x}Si and Si segments are visually abrupt. The inset FFT of the highlighted region in Figure 2b is indexed for cubic Si (space group $Fd\overline{3}m$; $a = 5.4305$ Å) and shows twin defects along the <111> direction. HAADF-STEM images of the Ni\textsubscript{x}Si segment of the NW are shown in Figure 2c and Figure 2d with the inset FFT in Figure 2c indexed for orthorhombic Ni\textsubscript{2}Si (space group $Pbnm$; $a = 7.0649$ Å, $b = 5.0012$ Å, $c = 3.7307$ Å). Significant tilting was required to observe
the zone axis of the NW and interestingly there was no direct orientation between the metal silicide and Si segments.

Figure 2. a) Low magnification HAADF-STEM images of heterostructure NW. b) High magnification HAADF-STEM image of the NW interface with the FFT inset of the highlighted area indexed for Si. c) High magnification TEM image of Ni silicide segment with inset FFT indexed for Ni$_2$Si. d) Higher magnification HAADF-STEM image of c) showing lattice fringing.

Figure 3a, shows the spectrum region for EELS analysis of the NW and the arrow represents the scan direction. Interestingly, in the corresponding quantitative EELS line-scan shown in Figure 3b, a region of an intermediate Ni-poor silicide phase, of approximately 10 nm in length, between the Ni$_2$Si and Si segments is visible.
Initially, the relative composition of Ni and Si corresponds to the Ni$_2$Si phase. However, just before the Si segment of the NW, the Ni concentration decreases. At this intermediate segment, the elemental composition corresponds to NiSi. After this intermediate NiSi segment, the Ni concentration dramatically decreases to zero in the pure Si segment as shown in the line scan and EELS map for Ni in Figure 3c. In the overlaid coloured EELS map for Ni/Si/O in Figure 3c, this interfacial region is quite clearly visible. The presence of an intermediate silicide segment has previously been seen in TMS NWs that were fabricated through the conventional silicidation process.$^{18,40}$ In these studies it was observed that the NiSi$_2$ phase would initially propagate through the Si NW,$^{18}$ transforming to Ni$_2$Si with continued diffusion from the Ni source. Here, the Ni diffusion is occurring from the Ni substrate anchor point and it is likely that initially a Ni silicide phase (such as NiSi or NiSi$_2$) forms which eventually saturates to Ni$_2$Si as Ni continues to diffuse from the substrate. This intermediate region was also noted in other NWs in this study with an additional example presented in Supporting Information (Figure S2).
Figure 3. a) HAADF image of heterostructure NW with spectrum region for EELS analysis highlighted. b) Relative composition EELS profile of NW. c) HAADF image spectrum region and corresponding EELS maps for Si, Ni, O and Si/Ni/O overlay.

In Figure 4, the dramatic drop-off in Ni concentration at the interface between the intermediate NiSi and Si segments is further analysed. As seen in the high magnification HAADF-STEM image in Figure 4, the transition from NiSi to Si between the segments is visibly sharp. In the Si segment of the NW, the Si planes are lattice resolved, with the longitudinal twin defect clearly visible. However, the lattice fringing from the NiSi segment is not as obvious. This suggests that this intermediate NiSi segment is slightly disordered, but may also be due to an inability
to simultaneously ensure the correct orientation for the NiSi segment and the Si segment within the NW. In the EELS maps in Figure 4, the sharpness of the interface is confirmed with the pure Si planes stopping within one atomic layer spacing. This is particularly evident from the Ni and composite Si/Ni/O maps. We note that this interfacial abruptness is consistent with previous Ni$_x$Si/Si NW interfaces. For example, Lin et. al. demonstrated that their progressive silicidation progress carried out at 550 °C, led to abrupt interfaces between Ni rich, Ni poor and Si pure phases.\textsuperscript{40} Tang et. al. evidenced an atomically abrupt junction between Ni$_2$Si/Si formed at a more moderate temperature of 400 °C.\textsuperscript{18}

![Figure 4. High magnification HAADF image of heterostructure NW interface with spectrum region for EELS analysis highlighted and EELS maps for O, C, Si and Ni corresponding to the HAADF image spectrum region.](image)
The presence of this intermediate silicide region was also seen in heterostructure Ni$_x$Si/Si NWs with larger diameters. In Figure 5a, a low magnification TEM image of the interfacial region in a NW of approximately 40 nm in diameter is shown. The Ni$_2$Si segment of this NW is slightly uneven; likely a result of the strain associated with the volume expansion during silicide formation.\textsuperscript{40} In Figure 5b, a higher magnification TEM image of the Ni$_2$Si segment of the NW with the inset electron diffraction pattern is indexed for orthorhombic Ni$_2$Si. In Figures 5c and 5d, higher magnification TEM images of the intermediate silicide segment show that the interface of this intermediate silicide segment with the pure Si segment is quite defective and disordered. Interestingly in Figure 5d, it can be seen that the silicide growth front through the NW is not uniform. This could be due to the presence of longitudinal defects which offer channels for Ni diffusion through the NW.\textsuperscript{35} Using EDX spot analysis in DF-STEM shown in Figure 5e, the relative composition of this intermediate silicide region was determined to be 38\% Ni and 62\% Si, which would suggest that this intermediate phase was NiSi$_2$. However, FFTs taken from this intermediate region could not be indexed for any Ni silicide phase. Figure 5f shows EDS elemental maps for Au, Ni and Si of this NW, showing that Ni is confined to the Ni$_x$Si segment of the NW.
Figure 5. a) Low magnification TEM image of heterostructure NW b) TEM image of top region of NW tilted to zone axis with electron diffraction pattern inset indexed for Ni$_2$Si. c) TEM image of interfacial region with higher magnification.
TEM image shown in d). e) DF-STEM image of NW with EDS elemental maps in f).

In addition to axial heterostructure NWs, complete Ni silicide NWs were also observed to grow in this process. Figure 6a shows a low magnification TEM image of a fully silicided NW also including the Au seed with a higher magnification TEM image of the highlighted area in Figure 6b. The electron diffraction patterns inset in Figure 6b are indexed for orthorhombic Ni$_2$Si. Through DF-STEM imaging and EDS analysis of the NWs, shown in Figure 6c (and additional NW in Supporting Information Figure S3), it appears that the composition of Ni and Si is consistent along the length of the NW, suggesting the NW is completely Ni$_2$Si. A schematic depiction of the progressive Ni diffusion mechanism underlying the formation of Ni$_2$Si/Si heterostructure and fully Ni$_2$Si NWs is presented in Figure 6d.

The varying degrees of metal silicide formation that occur in a single synthesis appears to be independent of NW diameter and length. Our observations do show a higher degree of metal silicide formation in NWs where there are clear stacking faults and given that the diffusion is from the substrate, it is plausible that the variation is affected by number and propagation direction of these defects. For instance, in defect free NWs, the diffusion rate of Ni into the Si NW could be lower due to the absence of these defects (diffusion channels), leading to slower growth rate of the silicide. NWs with <111> oriented twin defects orthogonal to the NW growth direction, could allow a channel for Ni to diffuse through.
Figure 6 a) Low magnification TEM image of Ni silicide NW with high magnification TEM image of the highlighted region shown in b). c) DF-STEM image of NW with EDS line scan overlaid. d) DF-STEM image of NW with EDS line scan overlaid.
Conclusions

In this report, a novel approach to the synthesis of axial heterostructure Ni$_2$Si/Si NWs and orthorhombic Ni silicide NWs within a solution based system is outlined. Si NW growth occurs via a Au seeded SLS mechanism, with subsequent Ni diffusion from the substrate resulting in the formation of metal silicide segments of varying length, representing the formation of Ni$_2$Si/Si heterostructure NWs. The Ni$_3$Si segments shows two distinct regions with Ni rich (Ni$_2$Si) and an intermediate Si-rich segment of a corresponding length to the NW diameter (NiSi or NiSi$_2$) close to the transition point to pure Si. Nevertheless, the interface between this intermediate Ni$_3$Si segment and pure Si segment was found to be atomically abrupt. This report is the first route to synthesise both Ni$_2$Si/Si NWs and Ni silicide NWs within a solution based technique without the need for lithographic processing and thereby opens pathways for similar heterostructures in other technologically relevant transition metal silicides or germanides. Future studies on in-situ analysis of Ni$_3$Si formation within Si NWs and deliberate defect incorporation will aim to achieve selectivity for segment length in these novel NW heterostructure systems.

References


**TOC image**

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