Growth of Silicon and Germanium Nanowires in the Vapour Phase of High Boiling Point Organic Solvents

Department of Chemical and Environmental Sciences, University of Limerick

Hugh Geaney
Supervisor: Dr. Kevin M. Ryan

Submitted to the University of Limerick for the Degree of Doctor of Philosophy
April 2012
Chapter 1: Introduction

1.1 Background
1.1.1 1-dimensional nanostructure background
1.1.2 Silicon NW background
1.1.3 Germanium NW background and comparison with silicon
1.1.4 Metal silicide nanostructures

1.2 Group IV NW devices
1.2.1 Transistors
1.2.2 Li Ion battery anode materials
1.2.3 Photovoltaic applications

1.3 Group IV NW Growth Systems
1.3.1 Laser ablation
1.3.2 Chemical vapour deposition
1.3.3 Supercritical fluid approaches
1.3.4 Non-pressurized, organic solvent based approaches

1.4 Discrete Metal Catalysis
1.4.1 Gold seed catalysis
1.4.2 Alternative metal catalysts

1.5 Alternative Catalytic Methods
1.5.1 Oxide assisted growth
1.5.2 NW growth from bulk metals
1.5.3 Self catalytic growth

1.6 Metal Silicide NW Formation

1.7 Group IV Nanowire Characterization and Properties
1.7.1 NW surface chemistry
1.7.2 NW crystallography
1.7.3 In-situ growth analysis

1.8 References
Chapter 2: Experimental Procedures and Characterization Methods

2.1 Scope of this thesis ................................................................. 64
2.2 General experimental setup ..................................................... 64
2.3 Characterization methods ....................................................... 67
  2.3.1 TEM ................................................................. 67
  2.3.2 SEM ............................................................... 75
  2.3.3 XRD ............................................................... 79
  2.3.4 XPS .............................................................. 81
2.4 References ........................................................................ 82

Chapter 3: Growth of Self Catalytic Germanium NWs within a High Boiling Point Organic Solvent .......................................................... 84
3.1 Abstract .......................................................................... 84
3.2 Introduction .................................................................. 84
3.3 Experimental ................................................................. 86
3.4 Results and discussion ...................................................... 90
3.5 Conclusions ................................................................. 98
3.6 References .................................................................. 98

Chapter 4: Role of Defects and Growth Directions in the Formation of Periodically Twinned and Kinked Unseeded Germanium Nanowires ............................................................................. 101
4.1 Abstract ...................................................................... 101
4.2 Introduction .................................................................. 101
4.3 Experimental ................................................................. 104
4.4 Results and discussion ...................................................... 107
  4.4.1 Straight NW analysis .................................................. 109
  4.4.2 Kinked NW analysis .................................................. 114
4.5 Conclusions ................................................................. 122
4.6 References .................................................................. 123

Chapter 5: High Density Germanium Nanowire Growth Directly From Copper Foil by Self-induced Solid Seeding .................................................. 127
5.1 Abstract ...................................................................... 127
5.2 Introduction .................................................................. 127
5.3 Experimental ................................................................. 129
5.4 Results and discussion ...................................................... 131
5.5 Conclusions ................................................................. 144
5.6 References .................................................................. 146
Acknowledgements

I would first like to acknowledge the excellent support, advice and encouragement given to me throughout my project by my supervisor Dr Kevin M. Ryan. His help and expertise throughout the course of my study was invaluable. It has been a privilege to work within his research team since I joined as an FYP student in September 07.

I would also like to acknowledge my fellow research group members for their efforts over the entire course of my PhD. It has been fantastic to have worked alongside such a diverse and positive group and I have made many friendships which will hopefully continue well into the future. Specifically I would like to thank post doctoral researchers Dr. Robert D. Gunning for expert training, analytical methodology and frequent moments of levity and Dr. Edric Gill for his keen critical eye, precision and lightening wit. I would like to thank past students Dr. Catriona O Sullivan and Dr Chris Barrett for making me feel welcome in the research group and my peer Ajay Singh for his unerring enthusiasm and hours spent mulling over all things synthetic. I would like to thank Emma Mullane for her large contribution to my work as an eager member of the group IV research team. I wish Dervla, Tadhg, Claudia, Tom, Shalini, Michael and all the postgraduates in the physics department, the best for the future.

I would like to recognize the superb training and analysis provided by Dr. Calum Dickinson. His dedication and fervour are an example par excellence. I would also like to thank Dr Fathima Laffir for her expertise on XPS and superb analysis. I would like to thank my parents, brother and friends for their fantastic support. They played a large part in my progression towards becoming ‘Dr. Hughie’.
Declaration

I declare that the work in this thesis has not been submitted for a degree to this or any other university.

Hugh Geaney
05/04/12
Abstract

Herein is presented the development of a versatile glassware based method for the growth of silicon and germanium nanowires. The vapour phase of a high boiling point solvent medium heated to reflux is used as a means of attaining the high temperatures required for the decomposition of organometallic precursors required for nanowire growth.

Initially, the growth of self-catalyzed Ge nanowires on various non-catalytic substrates is presented in Chapter 3. This is followed in Chapter 4 by an in depth study of the various morphologies and defects seen within these Ge nanowires. A temperature related degree of nanowire kinking is presented and is rationalized in terms of changes in the nanowire growth directions. The growth of high density Ge nanowire mats from bulk Cu foil by a self-catalytic process without the need for defined catalyst particles is presented in Chapter 5. The nanowires were found to be catalyzed by an underlying in situ formed Cu₃Ge layer which allowed excellent control over the nanowire diameters formed given the absence of discrete nanoparticle seeds.

Further modification of the synthetic setup allowing the formation of Si nanowires directly on various substrates through catalysis by an evaporated In layer is presented in Chapter 6. Nanowire growth was achievable directly on stainless steel substrates which made the Si nanowires suited for use in Li ion cells. The method represents the first report of Si nanowire growth on substrates within an organic medium. Finally, the growth of Cu₃Si₄ nanowires on Cu foil using the same Si delivery system is presented in Chapter 7. The nanowires possess a tight diameter distribution and are the first nanowires of this Cu silicide phase formed to date.
List of Publications

Publications

First Author Publications


Other Publications


List of Abbreviations:

0-D – zero dimensional
1-D – one dimensional
2-D – two dimensional
3-D – three dimensional
BP – boiling point
CMOS – complementtary metal-oxide-semiconductor
CVD - chemical vapour deposition
DFSTEM - dark field scanning transmission electron microscopy
DPG - diphenylgermane
EBSD - electron backscatter diffraction
EDX - energy dispersive X-ray spectroscopy
EELS - electron energy loss spectroscopy
FET - field effect transistor
FFT - fast Fourier transform
HBS - high boiling point solvent
HPLC - high pressure/performance liquid chromatography
HRTEM - high resolution transmission electron microscopy
ITO - indium tin oxide
k – dielectric constant
NW - nanowire
OAG - oxide assisted growth
PS - phenylsilane
PV - photovoltaic
SCF - supercritical fluid
SEM - scanning electron microscopy
SS - stainless steel
STEM - scanning transmission electron microscopy
TPG - triphenylgermane
VLS – vapour-liquid-solid
VS – vapour-solid
VSS - vapour-solid-solid
XPS - X-ray photoelectron spectroscopy
XRD - X-ray diffraction
Z – atomic number
Chapter 1: Introduction

1.1 Background

1.1.1 1-dimensional Nanostructure Background

Nanomaterials are defined as any material with one dimension less than 100 nm, which can encompass a wide range of geometries from 0-D quantum dots\(^1\) to 1-D nanorods\(^2\) and NWs\(^3,4\), 2-D structures like nanosheets\(^5,6\) and nanodisks and 3-D assemblies of nanocrystals.\(^7,8\) Various geometries have been realized in a variety of elemental and compound nanomaterials, providing massive insights into the fundamental concepts governing nanostructure formation. While the growth of nanomaterials is important from a fundamental crystal growth perspective, the main driving force behind the nanotechnology research area has been the unique size dependent properties exhibited by materials at the nanoscale.\(^1\) Notably, the physical, electrical and optical properties of materials are known to vary strongly with dimension. For example, the melting point of Au can be reduced from 1064 °C to 500 °C when the size is reduced to the nanoscale.\(^9\) The optical properties of quantum dots of compound semiconductors (e.g; CdSe) can also be modified such that their absorbance maximum can be tailored across the visible spectrum simply by altering the nanocrystal diameter. Group IV nanomaterials; which are indirect band gap materials in their bulk form, can be shown to exhibit room temperature photoluminescence when formed in sizes below their excitonic Bohr radii (24.3 nm for Ge and 4.9 nm for Si).\(^10,11\)

A particularly interesting form of nanomaterial is that of the NW. NWs are anisotropic structures with diameters below 100 nm and a long axis leading to aspect ratios typically over 10. As a result of their nanosized diameters, they
retain the diameter-dependent effects associated with quantum dots but their unconstrained lengths make them easily integrable to practical device applications such as transistors, photovoltaic cells and Li ion battery applications.\textsuperscript{12-14} The growth of anisotropic growth using metal catalysts was pioneered by Wagner and Ellis in 1964 with the growth of ‘whiskers’ with micron-sized diameters from a supersaturated gold catalyst.\textsuperscript{15} This pioneering work led to the birth of the vapour liquid solid (VLS) growth mechanism which was the key driving force behind the wave of 1-D nanomaterial synthetic research which followed. The Lieber research group introduced laser ablation as a means of attaining the first NWs with diameters from just 3 nm to 20 nm in 1998.\textsuperscript{4} This report coincided with a marked and dramatic increase in the number of papers dealing with NWs (as shown in Figure 1).\textsuperscript{16} The stark contrast between the dearth of reports prior to 1999 and well over 5000 published articles in 2009 shows the dramatic progress made in the field of NW research.

\textbf{Figure 1:} Number of NW papers/year from 1991-2009.\textsuperscript{16}
This research was facilitated by improvements in synthetic procedures and was aided by the suitability of anisotropic nanostructure growth from supersaturated catalysts. Since its inception, Si and Ge NWs have been at the forefront of the NW research area, with the miniaturization of these elemental semiconductors crucial from both a practical device perspective and in terms of gaining a deeper understanding over the processes which govern NW growth. Si and Ge NWs have been highlighted for a multitude of devices spanning PV applications, biosensing, energy storage, catalysis, and nanoelectronics.

The sheer number of novel materials formed to this day via the VLS method is testament to its general applicability and elegance. Continued advancements in the field of NW research are being aided by improvements to synthetic procedures and a greater understanding over the dynamics of NW growth. For example, NW growth has been extended to the use of solid catalysts (e.g., Cu, Ag, Ni, Bi etc.) allowing the use of cheaper metal catalysts which have been shown to favourably dope the resultant NW.

The newest addition to the wide range of catalytic protocols for the formation of Si and Ge NWs are ‘self seeded’ approaches which facilitate the growth of anisotropic nanostructures without the need for a discrete (or in some cases without any) metal catalyst seeds. These approaches offer great potential for creating high purity NWs while also yielding increased understanding of the fundamental processes which govern 1D nanostructure growth.

The various growth methods and catalytic protocols employed for group IV NW growth will be categorized and discussed in detail later under specific headings.
1.1.2 Si NW background

As the cornerstone material of the semiconductor industry, it is not difficult to understand the immense interest in the growth of 1-D Si nanostructures. The characteristics of Si NWs make them ideally suited to a host of device applications including transistors,\textsuperscript{35, 36} photovoltaics\textsuperscript{37} and lithium ion battery cells.\textsuperscript{19, 38} The use of Si NWs in device architectures has been aided by the wealth of knowledge which exists in Si processing. For example, doping of Si is a well studied phenomenon which allows the electrical properties of the material to be precisely tuned to be p-doped, n-doped or remain i (intrinsic), based on the incorporation of specific dopant atoms into the Si lattice.\textsuperscript{39, 40} This doping can also be realized in Si NWs through careful modification of the Si NW feedstock during growth. For example, precisely controlled p or n doping has been realized by introducing amounts of borane or phosphine gas respectively into the NW growth system.\textsuperscript{41} The precise control over doping achievable within Si NWs is evident in reports detailing with radial and axial p-i-n junctions as shown in Figure 2.\textsuperscript{42}

![Image of Si NW with axial and radial P-I-N junctions](image)

\textbf{Figure 2:} Illustration of axial (upper) and radial (lower) P-I-N junctions within a Si NW.\textsuperscript{42}
1.1.3 Ge NW background and comparison with Si

In comparison to Si, Ge is an ‘old’ semiconductor and was actually the original transistor material of choice in the late 1940s.\textsuperscript{43, 44} However, its lack of a stable oxide and lower natural abundance eventually led to it being replaced by Si. The advent of high $k$ dielectric materials as an alternative to SiO$_2$ coupled with advancements in synthetic protocols has resulted in the revival of Ge, which has been reflected in considerable interest in Ge NW formation.\textsuperscript{45} Logically, Ge and Si will be largely suited to similar devices due to their structural similarities. Compared with Si, Ge has a smaller, indirect band gap of 0.74 eV, a higher carrier mobility, a larger dielectric constant, and a larger excitonic Bohr radius (24.3 nm and 4.9 nm for Ge and Si, respectively).\textsuperscript{46, 47} The larger excitonic Bohr radius of Ge in comparison to Si means that quantum confinement effects are more pronounced at larger NW diameters for the former.\textsuperscript{48} The similarities in crystal structure between Si and Ge mean that they are typically synthesized using similar catalytic and growth procedures with Ge typically suited to lower growth temperatures.\textsuperscript{49}

1.1.4 Metal silicide nanostructures

Transition metal silicides are an extremely broad set of materials which have found application in diverse areas spanning thin film coatings, interconnects and gate materials in CMOS transistors, optoelectronics and photovoltaics.\textsuperscript{50, 51} 1-D silicide nanostructures with sizes matched to nanoelectrical devices would be ideally placed as building blocks for NW based nanoelectronics.\textsuperscript{52, 53} However, the complex nature of the phase diagrams between transition metals and Si has made
the formation of NWs of the defined metal silicide phase far more difficult than simple Si NWs.\textsuperscript{54} This factor is highlighted in Table 1 where the multitude of silicide phases possible for each transition metal is highlighted. In the table, the metal silicide phases successfully formed as NWs are highlighted in bold while the phases yet to be realized are in plain text with Pd and Cu conspicuously poorly examined.

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
</tr>
</thead>
<tbody>
<tr>
<td>KSi</td>
<td>MgSi</td>
<td>Sc\textsubscript{2}Si</td>
<td>Ti\textsubscript{2}Si</td>
<td>V\textsubscript{2}Si</td>
<td>Cr\textsubscript{2}Si</td>
<td>Mn\textsubscript{2}Si</td>
<td>Fe\textsubscript{2}Si</td>
<td>Co\textsubscript{2}Si</td>
<td>Ni\textsubscript{2}Si</td>
<td>Cu\textsubscript{2}Si</td>
</tr>
<tr>
<td>KSi\textsubscript{5}</td>
<td>Se\textsubscript{5}Si</td>
<td>Sc\textsubscript{5}Si</td>
<td>Ti\textsubscript{5}Si</td>
<td>V\textsubscript{5}Si</td>
<td>Cr\textsubscript{5}Si</td>
<td>Mn\textsubscript{5}Si</td>
<td>Fe\textsubscript{5}Si</td>
<td>Co\textsubscript{5}Si</td>
<td>Ni\textsubscript{5}Si</td>
<td>Cu\textsubscript{5}Si</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Si</td>
<td>Y\textsubscript{5}Si</td>
<td>Zr\textsubscript{5}Si</td>
<td>Nb\textsubscript{5}Si</td>
<td>Mo\textsubscript{5}Si</td>
<td>Ru\textsubscript{5}Si</td>
<td>Rh\textsubscript{5}Si</td>
<td>Pd\textsubscript{5}Si</td>
<td>Cu\textsubscript{5}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca\textsubscript{3}Si</td>
<td>Y\textsubscript{3}Si</td>
<td>Zr\textsubscript{3}Si</td>
<td>Nb\textsubscript{3}Si</td>
<td>Mo\textsubscript{3}Si</td>
<td>Ru\textsubscript{3}Si</td>
<td>Rh\textsubscript{3}Si</td>
<td>Pd\textsubscript{3}Si</td>
<td>Cu\textsubscript{3}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSi</td>
<td>Y\textsubscript{2}Si</td>
<td>Zr\textsubscript{2}Si</td>
<td>Nb\textsubscript{2}Si</td>
<td>Mo\textsubscript{2}Si</td>
<td>Ru\textsubscript{2}Si</td>
<td>Rh\textsubscript{2}Si</td>
<td>Pd\textsubscript{2}Si</td>
<td>Cu\textsubscript{2}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSi\textsubscript{2}</td>
<td>Y\textsubscript{2}Si \textsubscript{2}</td>
<td>Zr\textsubscript{2}Si \textsubscript{2}</td>
<td>Nb\textsubscript{2}Si \textsubscript{2}</td>
<td>Mo\textsubscript{2}Si \textsubscript{2}</td>
<td>Ru\textsubscript{2}Si \textsubscript{2}</td>
<td>Rh\textsubscript{2}Si \textsubscript{2}</td>
<td>Pd\textsubscript{2}Si \textsubscript{2}</td>
<td>Cu\textsubscript{2}Si \textsubscript{2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr\textsubscript{5}Si</td>
<td>La\textsubscript{5}Si</td>
<td>Hf\textsubscript{5}Si</td>
<td>Ta\textsubscript{5}Si</td>
<td>W\textsubscript{5}Si</td>
<td>Re\textsubscript{5}Si</td>
<td>Os\textsubscript{5}Si</td>
<td>Ir\textsubscript{5}Si</td>
<td>Pt\textsubscript{5}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr\textsubscript{3}Si</td>
<td>La\textsubscript{3}Si</td>
<td>Hf\textsubscript{3}Si</td>
<td>Ta\textsubscript{3}Si</td>
<td>W\textsubscript{3}Si</td>
<td>Re\textsubscript{3}Si</td>
<td>Os\textsubscript{3}Si</td>
<td>Ir\textsubscript{3}Si</td>
<td>Pt\textsubscript{3}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrSi</td>
<td>La\textsubscript{2}Si</td>
<td>Hf\textsubscript{2}Si</td>
<td>Ta\textsubscript{2}Si</td>
<td>W\textsubscript{2}Si</td>
<td>Re\textsubscript{2}Si</td>
<td>Os\textsubscript{2}Si</td>
<td>Ir\textsubscript{2}Si</td>
<td>Pt\textsubscript{2}Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrSi\textsubscript{2}</td>
<td>La\textsubscript{4}Si</td>
<td>Hf\textsubscript{4}Si</td>
<td>Ta\textsubscript{4}Si</td>
<td>W\textsubscript{4}Si</td>
<td>Re\textsubscript{4}Si</td>
<td>Os\textsubscript{4}Si</td>
<td>Ir\textsubscript{4}Si</td>
<td>Pt\textsubscript{4}Si</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.1:** Table showing the various metal silicide NWs which have been formed are underlined.\textsuperscript{51}
1.2 Group IV NW devices

With Si as the dominant material of the semiconductor industry and Ge the first material from which a transistor was made, it is not hard to envisage uses for group IV NWs. While Si and Ge NWs are ideally suited to use in the electronics industry, they also show massive promise in bulk devices such as photovoltaics and Li ion storage.

1.2.1 Transistors

Si and Ge NWs have attracted considerable interest as building blocks for electronic devices.\(^{35, 36, 47, 55-57}\) Bottom-up grown NWs may be a viable alternative to top-down fabricated devices which may eventually reach a fundamental size limit based on lithographic methods.\(^{58, 59}\) Initially, bottom-up grown single NW devices were investigated in proof of concept experiments.\(^{35, 36}\) The schematic shown in Figure 3\(^{35}\) shows the general approach for single Si NW based FETs with the NW acting as the channel material. These early reports built on synthetic expertise allowing careful modulation of the doping profiles of the NWs. These fundamental studies also provided insight into the central role of NW surface chemistry in determining device efficiency.\(^{35}\) While single NW based devices are an excellent platform for judging the potential of bottom up formed devices, the process of scaling up NWs to functional component scale is far from trivial. A variety of assembly methods have been investigated to allow the potential of bottom-up formed NWs for future large scale device architectures to be realized.\(^{60}\) These include chemical assembly,\(^{60}\) electric\(^{61}\) or magnetic field assembly,\(^{62, 63}\) fluidic alignment,\(^{64-66}\) printing methods\(^{67}\), Langmuir-Blodgett\(^{68, 69}\) and bubble
alignment\textsuperscript{70, 71} methods. The advent of tri-gate transistors which have NW like ‘fins’ is a clear illustration of the immense potential shown by NW and NW-like structures for future electronics.\textsuperscript{72}

\textbf{Figure 3:} Schematic of a Si NW based field effect transistor.\textsuperscript{35}

\subsection*{1.2.2 Li ion battery anode materials}

For bulk applications, high density NW arrays are a required to increase the efficiencies of the devices in question. Such arrays are ideal for use in lithium ion batteries as high performance anode materials. Si has the largest specific Li intercalation capacity of any material (4200 mAh/g) and NWs are ideally suited to replace graphitic anodes (with a capacity of 372 mAh/g) as they can withstand the volume changes associate with lithium cycling better than planar electrodes.\textsuperscript{19, 38}
Ge NWs have also been used in Li ion batteries as they possess higher charge rates than Si NWs, albeit with a lower specific capacity (1600 mAh/g). Group IV NWs can be grown directly on current collector substrates using metal catalysis which removes the need for binders, thus increasing efficiency. As the NWs are grown directly from the current collector, they offer a continuous pathway for electron transport which is much more efficient than that seen in typical disordered cathode materials (Figure 4). High capacity Si NW battery cathodes are now on the cusp of full commercialization and should offer marked improvements in terms of physical weight and storage capacity.
Figure 5: In situ TEM images of the expansion in a Si NW caused by Li insertion.\textsuperscript{77}

A major advantage of Si and Ge NWs for Li ion cells is that they are also suited to various \textit{in situ} analytical techniques, which have allowed the behaviour of the NWs during Li cycling and de-cycling to be examined extensively.\textsuperscript{77-79} TEM analysis of individual NWs during cycling are particularly well established and have shown direct evidence of the volume expansion and phase changes associated with Li insertion. Figure 5 shows an experiment where the volume expansion associated with Li insertion is clearly evident.\textsuperscript{77} The red arrow in each of the figures indicates the lithiation front. Selected area electron diffraction can then be used to investigate the composition of the various segments of the NW.\textsuperscript{79}
1.2.3 PV applications

Crystalline Si is by far the most widely used bulk material for solar cell applications. However, for future generation solar cells, it is envisioned that Si NWs will play a major role in allowing the production of low cost and high performance devices. The intense interest in the use of Si NWs for PV applications is illustrated by the wave of synthetic papers detailing various device architectures exploiting Si NWs. Aside from the cost saving which NWs should provide in comparison to bulk Si devices; a major envisaged advantage is the degree of tunability which exists in NW structures. NWs can be formed in complex heterostructure configurations, allowing efficient carrier separation and maximized quantum yield for the device.

![Figure 6: a) Schematic of a P-N junction solar cell. b) SEM image of the vertically aligned Si NWs.](image)

The schematic in Figure 6 a) shows a p-n junction solar cell fabricated by the Yang research group in 2008. This device showed a relatively low conversion efficiency of 0.5 % which was proposed to be limited by interfacial recombination. Recent reports for Si NW based PV devices have shown efficiencies of between 5 % and 9 % with advancements based on improved cell fabrication expected.
1.3 Group IV NW growth systems

A wide range of synthetic systems have been used for group IV NW growth, with a number of common characteristics across the various systems. The systems all require the decomposition of a precursor species combined with a catalytic aspect to allow anisotropic growth. The various general systems will be examined in the upcoming section while the catalytic protocols employed will be divided into metal-catalyzed and alternatively-catalyzed methods and examined in sections 1.4 and 1.5 respectively.

1.3.1 Laser ablation

The laser ablation method pioneered by Morales et al. allowed the formation of the first NWs. However, the technique requires the use of rather extreme temperatures (1200 °C). In this approach, a catalyst material is co-ablated with the NW monomer material (i.e., Si) and NW growth occurs at least partially in the Ar vapour flow used to transport the material. In the Morales setup illustrated in Figure 7, a laser (1) was focussed on a 90 %/10 % Si/Fe target (3) within a quartz tube in a tube furnace (4). An Ar gas flow was then used to transport the evolving Si NWs to the cold finger (5) where the product was collected. Extremely high reaction temperatures were required to allow a VLS based growth method between Fe and Si which were prohibitively high and thus explain the shift towards CVD based method as an alternative.
1.3.2 Chemical vapour deposition

CVD based methods for Ge and Si NWs have been extremely successful due to their suitability for use with various feedstock and catalyst materials. In the most simple form of CVD (Figure 8), germane (or silane) is fed to a catalyst covered substrate for NW growth. Depending on the precursor and catalyst in question, growth temperatures as low as 275 °C and 290 °C have been reported for Ge and Si NWs respectively. Alternative precursors are typically more stable chlorinated species such as tetrachlorosilane which are less hazardous but require higher decomposition temperatures.

A great advantage associated with the use of CVD is the ability to switch between various gasses during growth. Gasses can also be mixed to produce alloyed structures and introduce dopant atoms into the NW lattices. This has led to
the formation of Si/Ge core shell NWs,\textsuperscript{55, 95} (p-i-n junctions within single Si NWs\textsuperscript{41} and more complex ‘multishell’ NW structures.\textsuperscript{42} Branches and hyperbranched Si and GaN NW structures were formed by performing a straightforward, iterative growth process stemming from a single ‘backbone’. The precise control possible using CVD was shown to allow the formation of kinked NWs with modulated geometries and kink lengths.\textsuperscript{96} p/n junctions formed using CVD methods have been explored as materials for PV devices\textsuperscript{37} and thermoelectronic applications.\textsuperscript{97} The precise synthetic control possible using CVD processes has facilitated the recent surge of interest in group IV NW heterostructures.\textsuperscript{98-101}

CVD processes are also suited to the use of simple elemental precursors. Pure Ge and Si powders have been used for the growth of Ge\textsuperscript{102, 103} and Si\textsuperscript{104, 105} NWs using classical metal catalysis. These methods have been investigated within tube furnaces, which are required to achieve the extreme temperatures necessary for decomposition of the elemental powder precursors. While these methods have been shown to allow the formation of various structures such as nanochains\textsuperscript{103} and NWs,\textsuperscript{102} the operating temperatures (in excess of 800 °C) have curtailed their usefulness.

The main problem associated with the use of CVD processes is their high cost. CVD systems are highly complex and typically require the use of carrier gases, coupled with the use of expensive precursor gasses. A more cost effective alternative is the use of solution based approaches, where liquid precursors are thermally decomposed in organic solvents to form monomers for NW growth.\textsuperscript{3} Solution based approaches also offer far greater potential for producing high yields of NWs\textsuperscript{106} within a medium which allows the production of NW ‘inks’ (i.e.
highly concentrated NWs dispersed in solution). In comparison, CVD grown NWs are, by definition, grown on a solid support framework (Si substrates etc.) which must be mechanically manipulated to yield ‘free’ NWs.

1.3.3 Supercritical fluid approaches

SCFs are an interesting medium for Si and Ge NW growth as they offer a wider temperature range than conventional organic solvent media. As a result, they were the first solution based approaches which allowed both Si and Ge NWs to be readily synthesized. The need for SCF media can be explained by the fact that most conventional organic solvents tend to have boiling points lower than about 300 °C, which are insufficient to thermally decompose both silicon and germanium NW growth precursors. In supercritical fluid reactions, the solvent is taken above its critical point to form a supercritical phase which to date has been used to accommodate VLSand VSS catalyzed NW growth. SCF media possess properties which are intermediate between a liquid and a gas and offer good solubilising properties coupled with facilitating temperatures which are suited to NW growth.

Figure 9: Schematic illustrating a typical SCF setup for Si NW growth.
A typical SCF setup can be seen in Figure 9 which illustrates a few key elements of the setup. The cyclohexane is pressurized by the HPLC pump in the reaction cell into which the DPS precursor is injected. The reaction then ensues on the Au coating on the Si substrate within the reaction. A wide range of modifications have been performed to the core system (flowthrough systems, reaction being conducted solely in the SCF phase, etc.) but the key aspects remain the same. A wide range of solvents have been used for Si and Ge NW including CO\textsubscript{2}, benzene and toluene which have been coupled with the use of various organometallic precursors.\textsuperscript{115-118} The wide range of solvents, Ge and Si precursors and catalyst seeds successfully used in supercritical fluids for NW growth illustrates the generality of the method.

However, SCF media are often highly flammable solvents such as toluene, which is not ideal situation from a safety point of view. An additional problem with supercritical fluids is that they are are know to produce large amounts of particulate by-products due to solvent breakdown at reaction temperature.\textsuperscript{117}

1.3.4 Non-pressurized organic solvent based approaches

A relatively new category of routes to the formation of Ge and Si NWs are those conducted in HBS media which possess boiling points above 400 °C. This interesting set of organic solvents allow the previously perceived barrier to Si and Ge NW nucleation in non-pressurized systems to be overcome.\textsuperscript{119} To date, HBS media have proven particularly suited to Ge NW growth,\textsuperscript{30-33} given the lower temperatures required to form crystalline Ge when compared to Si. Si NWs and nanorods have also successfully been synthesized in HBS systems but required the use of the extremely reactive precursor trisilane.\textsuperscript{120, 121}
The majority of Ge NW growth approaches conducted within HBS have focussed on self-catalytic approaches which will be a major focus of this thesis and will be analyzed in section 1.5.3. These methods have typically been conducted at temperatures close to the boiling point of the HBS solvent in question to facilitate complete decomposition of the Ge precursor and facilitate NW growth. The various synthetic parameters used to date are outlined in Table 1.2. Further inspection of the table yields important information about the requirements for NW growth. It can be seen that high quality Ge NW growth usually requires reactions temperatures of over 380 °C. The two reports which used reaction temperatures of 360 °C and 285-315 °C produced short NWs with large diameter distributions and a high degree of NW kinking.\textsuperscript{30,31} The low reaction temperatures used in these reports also necessitated the prior synthesis of complex, reactive precursors for NW growth. In contrast, reactions carried out at 380 °C typically led to the formation of high quality NWs from simple organometallic precursors such as diphenylgermane and tetraethylgermane. The only custom made precursor used at elevated temperatures was employed as the products of its decomposition passivated the NW surface.\textsuperscript{32}
Table 1.2: Summary of the various HBS based Si and Ge NW growth approaches. Seeded routes are highlighted in blue while unseeded routes are black.

<table>
<thead>
<tr>
<th>First Author</th>
<th>HBS</th>
<th>Precursor(s)</th>
<th>Reaction Temp. (°C)</th>
<th>Proposed Mechanism</th>
<th>Product(s) Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zaitseva[^33]</td>
<td>Trioclyamine Squalene Octocosane</td>
<td>Trichlorogermaine Tetraethylgermaine Tetrabethylgermaine</td>
<td>380-430</td>
<td>Organic mediated VLS mechanism</td>
<td>Ge NWs &lt;110&gt; growth directions</td>
</tr>
<tr>
<td>Zaitseva[^119]</td>
<td>Trioclyamine Squalene</td>
<td>Tetraethylgermaine</td>
<td>380-430</td>
<td>As above</td>
<td>Ge NWs and crystalline Ge nanoparticles</td>
</tr>
<tr>
<td>Ge[^30]</td>
<td>Trioclyamine</td>
<td>GeCl4 + Oleylamine</td>
<td>360</td>
<td>Ge seeded NW growth mechanism</td>
<td>Ge NWs of various diameters</td>
</tr>
<tr>
<td>Gerung[^31]</td>
<td>Octadecene</td>
<td>Ge(DBP)2</td>
<td>285-315</td>
<td>Self seeded mechanism or self assembly (oriented attachment)</td>
<td>Short NW a large degree of kinking</td>
</tr>
<tr>
<td>Hobbs[^32]</td>
<td>Octacosane Repeated in Supercretical toluene</td>
<td>Hexakis(trimethylsilyl)-digermane</td>
<td>400</td>
<td>Oriented attachment or liquid Ge mediated route</td>
<td>Narrow crystalline Ge NWs(&lt;10 nm) with a thick amorphous Si matrix coating</td>
</tr>
<tr>
<td>Heitsch[^120]</td>
<td>Octacosane</td>
<td>Trisilane</td>
<td>430</td>
<td>VLS route with Au or Bi Catalysts</td>
<td>High quality Si NWs. Extended to the formation of Si nanorods[^121]</td>
</tr>
<tr>
<td>Chockla[^122]</td>
<td>Squalene Squalane Octacosane Dotriacontane Trioclyamine</td>
<td>Diphenylgermaine</td>
<td>430</td>
<td>VLS route using Au calayst particles</td>
<td>High quality Ge NWs. Extended to the formation of Ge nanorods[^123]</td>
</tr>
</tbody>
</table>

Other methods using HBS for group IV NW growth were developed in the Korgel research group (highlighted in blue in Table 1.2). They showed that Si and Ge NWs could successfully be synthesized in the solution phase of HBS media using the metal nanoparticle catalyzed routes which had been hitherto confined to SF based approaches. The use of ligand passivation as a means of controlling the NW aspect ratios which had been largely ignored within SCF systems, was fully
realized and led to the formation of Si and Ge nanorods.\textsuperscript{121,123} Their approaches showed the flexibility of HBS for high yield NW formation and also presented the solution-liquid-solid growth mechanism for the first time.\textsuperscript{120}

A common vein within these approaches is that NW growth was conducted at the HBS boiling point and thus confined to the solution phase of the media.\textsuperscript{30-32, 120-123} While these approaches have shown major promise for high quality NW formation, they are spatially restrictive and thus are not particularly amenable to NW growth on substrates, which may limit their suitability to future applications. Ideally HBS based NW growth routes should be extended such that they allow high density growth from a variety of substrates.

1.4 Discrete Metal Catalysis

Metal catalysis has been the major driving force behind group IV NW growth dating back to the discovery of the VLS growth mechanism. A large portion of NW growth procedures have relied on the use of predefined Au nanoparticle seeds to induce anisotropic growth. The VLS mechanism has been analyzed in detail through the use of \textit{in-situ} TEM methods\textsuperscript{124} and complex modelling,\textsuperscript{29} but in essence it is quite a simple concept. The ‘V’ component consists of a vapour growth source (e.g., silane for Si NWs of germane for Ge NWs). This monomer is fed into a liquid catalyst particle (‘L’) which, upon saturation, allows a solid NW (‘S’) to be extruded. The simplicity of this approach allows it to be applied to a wide range of catalysts and precursor feedstocks. The length of the resultant NWs can be controlled by mediating the NW monomer supply while precise control over monomer has even allowed the formation of
axial heterostructures with varying composition along the length of the NW (Figure 10). \(^{125}\)

**Figure 10:** Axial heterostructure NW with Si and SiGe segment along the length of the NW. \(^{125}\)

Recently, significant focus has centred on the nature of the NW catalyst during NW formation. The VLS employs a liquid NW catalyst with additions to the growing NW occurring at the liquid/solid interface of the existing NW segment and the catalyst seed. \(^{126}\) In comparison, the VSS growth mode uses a solid catalyst particle with monomer being supplied to the growing NW via a solid particle (see Figure 11 a and b). \(^{127}\) The VSS growth mode often depends on the prior formation of a silicide (or germanide for Ge), which upon further monomer saturation, leads to the extrusion of a solid crystalline group IV NW.
The use of solid catalysts has been shown to possess several advantages over the typical VLS mechanism. It has been found that solid catalysts can facilitate sub-eutectic growth temperatures (meaning more moderate reaction temperatures), albeit at slower rates.\textsuperscript{27, 128} Solid catalysts also possess benefits in terms of forming NW heterostructures with abrupt compositional interfaces as they do not suffer from the ‘reservoir effect’ associated with liquid catalysts.\textsuperscript{99} This effect is caused by the much higher solubility of Si (or Ge) atoms in the liquid catalyst in comparison to solid catalysts. Solid catalyst particles offer potential for circumventing NW diameter range broadening, caused by catalyst agglomeration which is well known for VLS methods.\textsuperscript{129, 130} Recent reports also suggest that solid catalyst particles may be useful for finely controlling the defect content\textsuperscript{131} and growth directions\textsuperscript{128} of the resultant NWs which is extremely promising for tailoring the NWs towards specific devices.

\textbf{Figure 11}: a) Schematic illustrating the VLS growth mechanism. b) Schematic showing the VSS method with a faceted, solid particle on the tip of the NW.\textsuperscript{127}
1.4.1 Gold seed catalysis

Au is the archetypal catalyst material for both Si and Ge NW growth. The key factor behind this is its simple phase diagrams with both Ge and Si. The eutectic composition for Ge is 28% at 361 °C (Figure 12 a)). Its eutectic composition with Si shows a single, dominant eutectic point with Si content 18.6% at a temperature of 363 °C as seen in Figure 12 b). The relatively low eutectic temperatures facilitate NW growth at temperatures which are suitable for CVD systems. The majority of pioneering approaches illustrating Ge and Si NW growth were conducted through the use of Au colloids or thin films. The use of Au as catalyst to induce growth in various systems has been aided by a number of factors such as the ease of nanoparticle and evaporated layer formation, its nontoxic nature and its stability in air.

![Figure 12](image)

**Figure 12**: Phase diagrams for a) Au/Ge and b) Au/Si.  

Despite the wide ranging successes of Au-catalyzed NW growth, numerous issues exist. Au is expensive but more importantly from a device perspective, it is a known electron trap within semiconductors, making its use within Si and Ge NWs extremely unfavourable. While the removal of Au from the NW tips has been mooted as a means of overcoming this issue, it is highly probable that Au contamination within the NW bulk will persist. The
The diffusion of Au atoms from the catalyst seed into the resultant NW lattice has already been illustrated by advanced characterization methods such as atom probe tomography.\cite{135,136} These issues associated with the use of Au catalysis have led to a recent drive for the use of alternative metal catalysts for both Si and Ge NW growth which would not negatively impact the efficiency of CMOS devices.\cite{127,137,138}

### 1.4.2 Alternative metal catalysts

The search for suitable metal catalysts to effectively replace Au has led to the use of a wide range of metals with the transition metals in particular being well examined. To date, transition metals such as Cu,\cite{128,139-143} Ni,\cite{27,28} Co,\cite{113} Fe,\cite{4} Mn,\cite{145} and Ag,\cite{146,147} have been extensively investigated. These have been supplemented by $p$-block elements such as In,\cite{148-153} Ga,\cite{155-158} and Sn,\cite{152} while the use of lanthanide and actinide catalyst materials such as Pr\cite{159} and Dy\cite{160} illustrates the versatility of catalyst driven NW growth.

In general, there are three types of NW catalyst which can be categorized based on the interaction of the NW and the catalyst material (see Table 1.3).\cite{29}

- **Type A** are ‘goldlike’ catalysts with a single eutectic point with high Si or Ge % (such as Au, Al and Ag). Type B again possess a single eutectic points, but with a much lower Si content (typically <1 %) such as In,\cite{148-153} Ga,\cite{155-158} and Bi.\cite{120,121}
- **Type C** are the silicide (or germanide for Ge) forming metals which exhibit far more complex phase diagrams, often with the presence of multiple silicide (germanide) phases.\cite{29}

As mentioned, Au is the classical NW catalyst and has been used in the majority of the Type A based catalytic reports. In comparison, Ag\cite{147} and Al\cite{136,143},
have been sparingly explored as catalysts but show promise due to the simplicity of their phase diagrams with respect to both Si and Ge. In comparison to gold, the eutectic temperatures between Ag/Si and Al/Si are much higher (at 577 °C\textsuperscript{147} and 836 °C\textsuperscript{161} respectively), which explains why the majority of NW growth processes using Ag and Al catalysts are VSS based. While Ag may also lead to the incorporation of electron trap states in the resultant NWs, they should be less deleterious than those caused by Au due to their position with respect to the Si band gap.\textsuperscript{147} Furthermore, Ag has a lower chemical stability when compared to Au which means it should be more easily removed from NWs post-synthesis. However, like Au, Ag is expensive and it remains to be seen if post-synthetic treatments would be sufficient to remove Ag contamination from within the NW lattice. Al is an interesting candidate catalyst as its position in group 13 of the periodic table means that the incorporation of Al atoms into the NW lattice may induce p-type doping.\textsuperscript{161} However, Al is prone to oxidation to Al\textsubscript{2}O\textsubscript{3} which complicates synthetic protocols due to the difficulty of removing residual O\textsubscript{2} in CVD systems.\textsuperscript{162}

Table 2: Table illustrating the three typical types of NW catalyst for Si and Ge. Dopant atoms are highlighted in green.\textsuperscript{29}
Type B catalysts are an interesting catalyst set which to date are the most sparingly examined. Growth from Zn was initially probed by Heath and co-workers and allowed the formation of Si NWs with sub-25 nm diameters.\textsuperscript{163, 164} However, the Zn impurities within the resultant NWs were found to be similarly problematic as those introduced by a Au catalyst. In this regard, In and Ga are the most promising type B catalysts as they should impart p type doping into the NW lattice.\textsuperscript{29, 49} This is reflected in the relative abundant nature of reports detailing In\textsuperscript{49, 148-154} and Ga\textsuperscript{157, 165, 166} seeded Si and Ge NW growth. The use of In and Ga as catalyst materials is also strengthened by the extremely low eutectic temperatures (156 °C and 30 °C respectively) which are well below the lowest temperatures for CVD based Si and Ge NW growth.\textsuperscript{149}

\textbf{Figure 13:} Phase diagram between Ti and Si.\textsuperscript{29}
Type C catalysts are the broadest class of NW catalysts and tend to possess complex phase diagrams with both Si and Ge. However, these silicide (or germanide) forming metals have an increasing prevalence as NW catalyst materials due to the advantages of solid catalysts. Type C catalysts typically offer control over the growth mode (i.e., VSS or VLS) by simply choosing the correct reaction temperature. This is illustrated in Figure 13 where for Ti seeded Si NWs, a temperature threshold of 1330 °C defines whether growth will proceed via solid or liquid catalysis. The increased use of type C catalysts is particularly evident in the reports detailing Ni, Cu seeded NWs. Interest in the use of Ni catalysts can be ascribed to the advantageous p-type doping of the resultant NWs coupled with the precise size control which can be exerted over Ni nanoparticles. In comparison, Cu is primarily has been examined due to its widespread use in the CMOS industries. Copper has been particularly well studied for the growth of Ge NWs with growth temperatures as low as 200 °C reported.
1.5 Alternative Catalytic Methods

1.5.1 Oxide-assisted growth

OAG of Si NWs was first proposed by Zhang et al. as a complimentary technique to the classical VLS mechanism.\textsuperscript{168,169} It was found that SiO\textsubscript{2} could play a similarly central role to NW growth as that noted for metal induced VLS growth. A mixture of Si and SiO\textsubscript{2} powders were used in a laser ablation or thermal evaporation system for the growth of high quality Si NWs.\textsuperscript{168} The mechanism is highlighted in Figure 14\textsuperscript{168} where a semi-liquid SiO\textsubscript{x} layer is responsible for anisotropic growth. The system is useful as it provided a means of attaining high yields of Si NWs free from metal contamination using readily available powder precursors. The main drawbacks associated with the use of OAG are the high reaction temperatures required for Si NW growth (> 800 °C) and the requirement for a SiO\textsubscript{2} layer as a sheath over the NW surface.\textsuperscript{168} Its main limitation is the inability to accurately control the NW diameter, due to the absence of defined catalyst particles.

![Figure 14: Schematic comparison of OAG and VLS growth.\textsuperscript{168}](image)
1.5.2. NW growth from bulk metals

An emerging departure from the use of defined Type C nanoparticle seeds is the use of bulk metal substrates as catalysts for NW growth. In 2004, Matur et al. showed the growth of Ge NWs directly from a bulk Fe substrate (Figure 15) by the formation of an ‘Fe epilayer’ which was essentially a catalytic Fe germanide. This report was important as it showed the potential for the growth of well controlled NWs from a metal without a defined catalyst size. This report was recently supplemented by further reports of NW growth from bulk substrates. More recently, Barrett et al. showed the formation of Si NWs from the reactor walls of a stainless steel, supercritical fluid reaction vessel (Figure 16). In this method, the formation of a reactive Fe silicide was proposed to be a prerequisite for NW growth. This claim was further strengthened by the introduction of a stainless steel substrates into the reaction system. After a typical reaction, Si NWs were shown to have nucleated directly from the stainless steel. The synthetic patchway responsible for NW growth is shown in Figure 16 b.

Figure 15: Schematic illustration of Ge NW formation from Fe substrates.
Figure 16: Si NW growth from stainless steel induced by ‘epilayer formation’ a) SEM image showing Si NW growth from a stainless steel. B) Mechanistic schematic for silicide ‘epilayer’ formation.

The growth of NWs directly from metal substrates offers real potential in relation to applications such as Li ion cells, which would benefit from NW growth directly from the current collector. Prior to this thesis, the role of germanide formation in inducing anisotropic NW growth was not extensively studied. A greater understanding over the dynamics of these systems is crucial if these self-driven NW growth mechanisms are to replace those governed by defined nanoparticle seeds.
1.5.3 Self-catalytic growth

The vast majority of Group IV NW fabrication methods have either required the use of metal catalysis or extremely high temperatures (as in OAG growth). Ideally, Ge and Si NWs could be formed using metal catalyst free solution based approaches similar to those used for the growth of compound semiconductors such as CdSe and CdS. However, self-catalytic growth of group IV NWs has been sporadically examined due to the high crystallization temperatures typically required for Ge and Si. Despite this, these emerging routes are an extremely promising set of NW growth methods which have the potential for producing ‘pure’ NWs. Self-catalyzed NWs (i.e., those which do not require metal catalysis) should provide an excellent comparison to metal catalyzed NWs, offering a system to gauge the impact of metal contaminants on the NW properties. They also have potential for shedding further light on the fundamental driving forces which govern NW growth.

Figure 17: a) ‘Unseeded’ Ge NWs grown by Zaitseva et al. b) NW emerging from polymer agglomerate. c) Schematic of the proposed unseeded NW growth mechanism.
The concept of ‘unseeded’ NW growth was proposed by Zaitseva et al. in 2005.\textsuperscript{33} There they described the growth of Ge NWs in a HBS without the use of metal catalyst particles. They proposed an analogue of the classical VLS mechanism where a saturated organic particle acts to induce anisotropic growth. They drew these conclusions from the presence of TEM beam sensitive organic droplets on the NW tips which possessed similar diameters to the resultant NWs (Figure 17 a). The catalytic process proposed is shown in Figure 9c where the polymerized organic solvent acts as a sink for Ge monomer incorporation and thus facilitates NW growth.

\textbf{Figure 18:} Schematic of the self seeded Ge NW growth mechanism proposed by Ge et al.\textsuperscript{30}
Various growth methods have been reported as ‘non-seeded’, ‘seedless’, or ‘self seeded’, but in essence these terms are describing metal free growth. An absolute understanding of this type of seeding is still at a fledging stage as it is difficult to identify minute (sub 1-nm), non metal particles using spectroscopy or microscopy. An alternative hypothesis put forward for self-seeded NW growth by Ge et al. was that catalytic Ge nanoparticles formed as an intermediate step in the reaction medium (Figure 18). Depending on the size of these nanoparticles and the reaction temperature being used, these would be liquid due to size-related depression of the Ge melting point. These particles would then act as a seeds in a similar way to the conventional VLS or VSS mechanisms.

![Figure 19](image)

**Figure 19:** Self-catalyzed Ge NWs presented by Gerung et al. a) Ge mediated VLS mechanism proposed. b) Evidence for an agglomeration based NW growth mechanism.
Gerung et al. showed the formation of crystalline NWs from a complex Ge precursor formed \textit{in situ} in octadecene.\textsuperscript{31} Again, they proposed that the NWs formed due to either a ‘self-seeded’ mechanism or an assembly method based on the agglomeration of smaller Ge nanorods. They suggested that both had approximately the same probability of occurrence given the evidence seen from TEM. In Figure 19 a they showed that the ‘seed’ seen was epitaxially connected Ge with a common (111) plane relative to the extruded NW. This possibility represents a Ge-mediated VLS or VSS mechanism with similarities to that previously mentioned.\textsuperscript{30} Their second suggestion was an oriented attachment process whereby Ge fragments agglomerated to form anisotropic NWs. Their logic for this was based on the appearance of short Ge fragments framing some of the NWs (Figure 19 b).

\textbf{Figure 20:} Catalyst free, CVD method for Si NW growth illustrated by Kim \textit{et al.} Nanocrystalline seeds (left hand side) were proposed to allow the growth of Si NWs upon exposure to a Si flux.\textsuperscript{34}
The only approach utilizing silane and germane CVD methodology for catalyst-free growth of Ge and Si was proposed by Kim et al. (Figure 20). They suggested that a VS mechanism was responsible for NW growth, whereby a silicon-rich oxide (SiOₓ) formed on Si wafers was saturated with Si or Ge to form nanocrystalline seeds. These seeds then extrude crystalline NWs along thermodynamically favoured directions rather than forming bulk crystals or thin films. They showed that the reactive SiOₓ layer was crucial to NW growth, with no growth noted at all on typical SiO₂ coated substrates. They showed high density Si NW growth but found that their Ge NWs were quite tapered.

![Figure 21: Temperature related NW diameter control as illustrated by Hobbs et al.](image)
The most recent variation of non-metal catalyzed growth was presented by Hobbs et al. who prepared core shell Ge/amorphous Si NWs in a HBS medium. They used a single source, hexakis(trimethylsilyl)digermane precursor with a silicon functionality which was deemed to be crucial to the formation of the Ge NWs. They suggested that the amorphous Si caused segregation of evolving Ge nuclei and allowed anisotropic growth to proceed. Importantly, their work showed a temperature related NW diameter variation (Figure 21) which they attributed to a Ge melting point depression. They discounted a Ge driven, VLS mechanism and ultimately suggested that an oriented attachment mechanism was responsible for NW growth. Their reactions were conducted within glassware vessels and typical SS reactors with comparable results, indicating that metal catalysis was not responsible for NW growth.
1.6 Metal Silicide NW Formation

The formation of metal silicide NWs often rely on similar CVD processes to those employed for Si NWs. However, the catalytic processes involved for silicide formation are different due to the requirement for a continuous metal supply which cannot be provided by a discrete metal nanoparticle seed. The synthetic methods for forming silicide NWs generally fall into four categories: 1: Si NW silicidation, 2: silane reactions with metal substrates, 3: metal reaction with silicon substrates, and, finally, 4: a co-delivery of metal and silicon sources via CVD methodology as illustrated in Figure 22. The first approach involves the silicidation of preformed Si NWs, typically through the evaporation and subsequent annealing of a metal layer directly on the NW surface. This method is a convenient means of creating silicide NWs as the Si NW backbones used may be conveniently formed using the VLS approach. However, strict control over the phase produced in the NWs (i.e., \(\text{Ni}_2\text{Si}\) vs \(\text{NiSi}\)) is often challenging. This method was pioneered by the Lieber research group and is particularly suited to the formation of \(\text{Ni}_x\text{Si}\) NWs due to the high diffusivity of Ni within Si.

![Figure 22: Illustration of the various approaches for silicide NW formation.](image)
Delivery of Si to metal substrates as a means of synthesizing metal silicide NWs has the advantage of exploiting the well established Si based CVD methods which have been central to the formation of pure Si NWs. This method is only well established for the formation of Ni silicide NWs, with the absence of other metal silicides again attributed to the extremely high level of diffusivity within the Ni/Si system.\textsuperscript{51} The proposed mechanism for Ni\textsubscript{2}Si NW formation is highlighted in Figure 23. In step (a), Ni foil was subjected to a silane flux, resulting in the formation of Ni\textsubscript{2}Si nanocrystals. Upon further Si flow (b), these nanocrystals start to become elongated and anisotropic NWs were formed. This point of NW extrusion was proposed to occur at the point when the diffusion based Ni incorporation rate into the structures equaled the rate of Si addition leading to the formation of thin untapered NWs.\textsuperscript{173} The NWs continued to grow until the point where Si flux was halted (d). This method is extremely convenient as it is a one pot, ‘self-catalyzed’ process which does not require the introduction of defined catalyst nanoparticles.

**Figure 23:** Proposed growth mechanism for Ni silicide NWs formed by delivering a silane flux to Ni foil. a) Ni silicide islands starting to form after initial Si exposure. b) elongation of the structures upon further Si flow. c) Initiation of Ni silicide NW growth from crystals. d) NW growth commences until Si flux was halted.\textsuperscript{173}
Delivery of metal or metal halide species to Si substrates as a means of forming silicide NWs has been widely successful. While the mechanism for NW formation is less understood than the metal substrate based alternative, it is widely accepted that NW growth occurs through a vapour solid (VS) process. To date the method has been suited to a wide ranging set of materials including various silicide phases of Fe,\textsuperscript{174, 175} Ti,\textsuperscript{176} Co\textsuperscript{177} and Cr.\textsuperscript{178} Metal silicide NW formation from the co-delivery of both metal and Si species to a substrate is another method which does not seem to have a straightforward growth mechanism. Despite this, the method, in conjunction with chemical vapour transport has been useful for the formation of NWs of FeSi,\textsuperscript{179} CoSi\textsuperscript{51} and MnSi\textsubscript{1.8}.\textsuperscript{52} Conventional CVD processes using two sources have only been successful for the formation of titanium silicide NWs.\textsuperscript{180}
1.7 Group IV NW Characterization and Properties

1.7.1 NW surface chemistry

Si surface chemistry is extremely well understood and has been routinely modified due to its central role in conventional CMOS processing. After synthesis, Si NW surfaces will typically oxidize quite quickly in ambient conditions to form a thin (sub-5 nm) SiO₂ coverage.¹⁸¹⁻¹⁸³ These oxidized Si NWs have been successfully implemented into a variety of devices applications indicating that this inherent oxidation is not problematic.³⁵, ³⁶ In fact, SiO₂ is a well known passivant which has been used to inhibit surface recombination for Si NW solar cells and is useful in Si based FET devices.¹⁸⁴

Figure 24: Modification of the Si NW surface chemistry. Upper image) Si NW with ‘native’ oxide coverage. Lower image) Amine functionalized NW showing a different amorphous coating thickness.¹¹⁸
The NW surfaces are also suitable for various chemical modifications which are typically used on bulk Si wafers, allowing a large degree of control over the NW surface chemistry. Si NWs have typically been modified post synthesis. The SiO$_2$ covering on theNWs can be etched using dilute solutions of HF, yielding an H terminated surface which is essentially a ‘blank canvas’ for further modification. These surfaces have been subsequently modified with organic molecules which may increase their oxidation resistance and change their solubility in organic solvents. A recent one-pot synthesis approach in a SCF medium, allowed the integrated growth and passivation of Si NWs as shown in Figure 24. They showed that introducing an amine molecule into the reaction vessel caused the NWs to be passivated in situ, removing the requirement for post-synthetic modification. The functionalization of Si NW surfaces with pharmaceutically active moieties has even been used to extend their scope into the realm of nanomedicine, showing the wide ranging applications of Si NW surface chemistry modification.

Figure 25: Modification of Ge NW surfaces with various thiol molecules.
In many ways, control over the surface chemistry of Ge NWs is a more pressing issue than for Si NWs. The unstable interface between Ge and Ge oxides makes them unsuitable for use in Ge NW transistors due to large hysteresis caused by adsorbed water molecules.\textsuperscript{192} Furthermore, the Ge/GeO\textsubscript{x} interface is known to possess a high density of surface states which impact upon the electrical properties and are even more pronounced for NWs in comparison to bulk surfaces.\textsuperscript{193, 194} Ge is also not suited to thermal oxidation as it leads to the formation of a variety of oxide species (1\textsuperscript{+}, 2\textsuperscript{+} and 3\textsuperscript{+}) rather than the desired GeO\textsubscript{2}.\textsuperscript{195} The lack of understanding of the Ge surface chemistry in comparison to that of Si has resulted in concerted research aimed at gaining a greater understanding of the Ge surface. The implementation of high $k$ dielectric materials such as HfO\textsubscript{2}\textsuperscript{196} and ZrO\textsubscript{2}\textsuperscript{197} has allowed the excellent hole and electron mobilities of Ge to be fully exploited for device applications. Ge NWs are also suitable for H,\textsuperscript{198} Cl\textsuperscript{198} and organic monolayer (e.g., thiol modification as shown in Figure 25)\textsuperscript{68, 192, 194} passivation along similar pathways detailed for Si NWs.
1.7.2 NW crystallography

Like in their bulk states, Si and Ge NWs typically possess a diamond cubic structure with space group Fd-3m. To date, a variety of growth directions have been reported for Si and Ge NWs, which can impact upon their properties.\textsuperscript{199} The electrical properties of the NWs are particularly dependent upon their growth direction but can also be influenced by defects.\textsuperscript{129, 200} For the majority of cases, NWs will possess <111>, <110>, or <112> growth directions, often in various percentages depending on the growth method and catalyst type used.\textsuperscript{29, 100} While there does not seem to be a definitive means of predetermining the growth direction of the NWs, there are certain tendencies which have been reported. Si NWs with diameters below 20 nm will tend to possess <110> growth directions, while those above 50 nm will tend to have <111> growth directions.\textsuperscript{29} Ge NWs grown at high temperatures (i.e. above 500 °C) will tend to favour <111> growth directions, while low temperature methods will tend towards <110> oriented NWs.\textsuperscript{200}

**Figure 26:** Kinked NW with a defined 73° angle between the segments due to the angle between the [-21-1] and [110] planes of Ge.\textsuperscript{200}
Another interesting phenomenon observed within Si and Ge NW growth systems is the formation of kinked NWs. The NW shown in Figure 26\textsuperscript{200} possesses a kink with a defined 73° due to a change in growth direction from <110> to <112>. These changes in growth direction are typically attributed to the NW growth being disturbed but have also been deemed to be due to the presence of crystallographic defects.\textsuperscript{200}

![Formation of a controllably kinked NW.\textsuperscript{96}](image.png)

**Figure 27:** Formation of a controllably kinked NW.\textsuperscript{96}

One such example was illustrated for Si NWs, where an abrupt decrease in NW substrate temperature or increase in Si precursor gas pressure resulted in the formation of controlled NW kinks.\textsuperscript{201} By interrupting the growth of individual Si NWs in a precise manner, the formation of multiply kinked NWs with precise kink lengths was achieved by an iterative process which exploited the angular difference between short <110> and long <112> sections (Figure 27\textsuperscript{96}).
Crystallographic defects have been frequently observed within Ge and Si NWs. Defects seem to be an inherent property of the majority of NW growth systems, with the majority of defects occurring on the (111) planes. Control over the defect content within NW yield has often proven elusive, but a recent report showed the potential for transferring crystallographic defects from a solid Ag catalyst seed to a Ge NW (Figure 28). This study is important as the role of the catalyst seed in determining the NW crystallography has often been overlooked. It is also widely expected that NWs with defect will exhibit different electrical properties to those exhibited by their defect free analogues.
1.7.3 In-situ growth analysis

A versatile means of obtaining information about NW growth dynamics and the role of the catalyst is through the use of *in situ* TEM studies within a dedicated, modified microscope (Figure 29). In Figure 29 a), the capillary is used as a means of introducing the NW feedstock to the heated specimen holder. In that case, the Si NWs were grown from a Si substrate (Figure 29 b) which allowed the epitaxial growth to be monitored with time. The use of *in situ* methods allows the NWs to be viewed at each stage of the growth process from nucleation to growth and finally, termination. Real time studies can be easily used to accurately monitor the growth rates of the NWs, while also observing the state of the NW catalyst (i.e., whether it is a liquid or a solid).

![Figure 29: a) Schematic of methodology for in situ TEM analysis of Si NWs. b) Schematic showing the Si NWs growing epitaxially from a Si substrate. c) TEM image of the evolving Si NWs with the catalyst tips clearly visible.](image)

124
More in-depth information can also be obtained through the use of real-time TEM studies. HRTEM images taken at the interface between a Cu$_3$Si seed and an evolving Si NW provided evidence for a ‘ledge flow’ growth mode as shown in Figure 30.\textsuperscript{140} The black arrow present in Figure 30 b), c) and d), respectively, indicates the point at which the Si atoms are adding to the growth interface over time. The ability to monitor NW growth \textit{in situ} has widely improved understanding of the role of catalysts in initiating NW growth,\textsuperscript{99, 140, 143} sub-eutectic NW growth\textsuperscript{19} and NW growth kinetics.\textsuperscript{143, 206}

![Figure 30: In situ TEM images taken from the growth interface of a Cu$_3$Si seeded Si NW over time. The black arrow indicates that the growth is occurring as a ‘ledge’.\textsuperscript{140}](image)
1.5 References:


166. Zardo, I.; Yu, L.; Conesa-Boj, S.; Estrad, S.; Alet, P. J.; Rassler, J.; Frimmer, M.; Roca i Cabarrocas, P.; Peir, F.; Arbiol, J., Gallium Assisted Plasma


Chapter 2: Experimental procedures and characterization methods

2.1 Scope of this thesis

The main motivation behind this project was to fully investigate the potential of HBS organic solvents as growth media for group IV elemental and compound NWs. While these media have previously been shown to allow Ge and Si NW growth, they have either required the use of metal catalysis\textsuperscript{1-3} or been confined to the solution phase of the solvent\textsuperscript{4-8} (limiting their potential for substrate based growth). This thesis shows that by carrying out NW growth within the area in contact with the vapour phase of the HBS media, Ge and Si NWs can be grown directly on various substrates.

The first results chapter (chapter 3) deals with the self seeded growth of Ge NWs from squalene vapour on Pyrex\textsuperscript{®}, quartz and ITO substrates. This is the first self-catalyzed report of Ge NWs on various substrates with consistent NW growth noted across the study. In chapter 4, a detailed morphological study of the NWs is described. This is the first report detailing the defect content of self catalyzed Ge NWs and one of very few detailed for Ge NWs in general.\textsuperscript{4}

Growth of Ge NWs from a bulk, Type C catalyst substrate (Cu foil) using the same system is presented in chapter 5. Interestingly, a catalytic Cu$_3$Ge layer formed on top of the Cu substrate which allowed NW growth to proceed \textit{via} a VSS growth mechanism. This was evident from the presence of Cu$_3$Ge tips on each of the NWs. NW growth directly from metal substrates had previously been investigated,\textsuperscript{10-12} but the prior formation of a germanide (or silicide in the case of Si NWs) had never conclusively been shown to be a prerequisite to NW growth before this study.
Having shown the potential for Ge NW growth within HBS media, the synthetic focus was shifted to the growth of Si NWs in chapter 6. Si NW growth within HBS has previously been limited by the high thermal stabilities of organosilanes. This thermal barrier was overcome by conducting the NW growth within the heated vapour of squalane, and through the use of In as a catalyst material. This method represents a versatile, glassware based, Si monomer supply system and was further extended to the growth of Cu$_{15}$Si$_4$ NWs from Cu foil substrates (presented in chapter 7). The wide range of materials produced using the HBS vapour based system is a clear indication of its versatility. Suggestions for further study are detailed in chapter 8.

2.2 General experimental setup

Each of the methods described herein were conducted within the same glassware based system. The setup has several key features which facilitate the formation of various nanostructures (Figure 1). The reactions were carried out within a three-zone furnace which allowed accurate temperature control in the various reaction zones. Thirty centimetre long custom-made round flasks of either Pyrex® or quartz were used as the reaction vessels with all reactions carried out under Ar flow. In all the reactions undertaken, the HBS medium of choice was heated to beyond its boiling point to create a HBS vapour within the flask. This vapour then served as a decomposition and transport medium for the in situ formed NW feedstock. The reaction temperatures used (between 420 and 460 °C) were sufficient to allow the thermal decomposition of organometallic precursors for NW growth which were injected through a septum cap at the reaction temperature of choice. In the case of self catalyzed Ge NWs directly on the flask
walls, the growth was found to be thermally localizable (Figure 1, inset), by switching off zones in which growth was not desired.

**Figure 1:** Schematic of the experimental setup used in this study. The inset image shows a Ge covered round bottomed flask.

NW growth on various substrates was achieved by placing the substrate of choice into the reaction vessel before the reaction was started. NW growth was found to occur best on the portion of the substrate which was not submerged in the HBS media. Specific growth conditions are provided in each research chapter but it is worth noting that new glassware was used for each different material (and for each new catalyst material) to avoid contamination.
2.3 Characterization methods

2.3.1 TEM

TEM can be used to image the morphology of nanostructures, gain HRTEM images which allow phase identification, perform diffraction analysis, highlight Z contrast differences (using DF-STEM) and is also suited to the use of various analytical techniques such as EDX and EELS. Due to the small de Broglie wavelength of electrons, they are ideal for obtaining crystal lattice resolved images of materials. The various parts of a typical TEM are shown in the schematic in Figure 2. Starting at the top, the electron source is typically a LaB₆ filament or a field emission source. This source of electrons is focussed onto a thin specimen using a series of lenses producing a transmitted image which is captured on an imaging plate.

Figure 2: Schematic of a typical TEM instrument with EDX and EELS detectors.\textsuperscript{5}
Electrons are also scattered as they pass through the material in question, which allows the formation of diffraction patterns. Diffraction allows determination of the crystallinity of the material and also whether it is polycrystalline or single crystal. A typical diffraction pattern is shown in Figure 3 where the distance from the central spot to the various other spots can be used to create a fully indexed pattern for the crystal structure. The generated pattern is in reciprocal space meaning that larger lattice spacings will appear as smaller distances and vice versa. The angles between the spots in the diffraction pattern will also correspond to the angles between the various lattice planes for the material.

![SAED pattern taken from a Ge NW looking down the [111] zone axis.](image)

**Figure 3:** SAED pattern taken from a Ge NW looking down the [111] zone axis.\(^4\)
The diffraction pattern obtained will differ depending on the orientation of the sample relative to the beam. In fact, diffraction patterns may not be complete (i.e., diffraction spots will not appear) if the sample is misaligned. This is particularly true for NWs which can be flexible and may not lay complete flat to the surface of the TEM grid. Kikuchi lines are an effective tool for ensuring that NWs are on the desired zone axis. These patterns are generated by electrons which are diffusely scattered by the sample. Each intersection in the pattern will represent a different zone axis for the material. Using a double tilt TEM holder allows these intersections to be manipulated such that they are in the centre of the electron beam. An example of a kikuchi pattern with an area off-axis (a) and on-axis (b) can be seen in Figure 4.

![TEM image of a NbSe₂ NW with inset kikuchi patterns.](image)

**Figure 4:** TEM image of a NbSe₂ NW with inset kikuchi patterns.⁶
When a sample (particularly a NW) is on zone axis, a full diffraction pattern will be obtained. Nanobeam diffraction can also be used to obtain diffraction patterns of much smaller areas than those allowed by typical SAED, meaning that different regions in the same NW can be analyzed. This is particularly suited to the investigation of NWs which possess catalysts which may be of the order of just several nm.\(^7\) Having a NW on zone axis also has benefits in terms of obtaining high quality TEM images. NWs which are slightly off-zone axis will tend to give images with 1-D lattice fringes while those on-zone axis can give 2-D fringing (Figure 5 a and b, respectively). HRTEM images can effectively be used to work out the growth direction of the NWs. In the case of NWs showing 1-D fringing, the fringes must run parallel to the growth direction. An example is shown in Figure 5 a where the spacing of 0.328 nm corresponding to the (111) spacing for cubic Ge runs along the NW, indicating a \(<111>\) growth direction for the NW. In the case of HRTEM images with 2-D lattice fringes visible, FFTs are a convenient means of elucidating the growth direction. FFTs can be thought of in a similar way as SAED patterns of the corresponding NW. They are patterns which are generated in reciprocal space due to the spacings of the lattice planes which can be indexed in a similar means as diffraction patterns. In the illustration shown in Figure 5 b, the inset FFT was used to determine the \(<110>\) growth direction for the NW. The use of FFTs for HRTEM images of NWs showing 1-dimensionality will only yield one set of spots (corresponding to the NW growth direction) and is often insufficient to fully confirm the composition of the NW.
TEM analysis is also suited to the use of analytical techniques such as EDX which analyzes the characteristic X-rays emitted by a sample when it interacts with the electron beam. EDX allows determination of the elemental composition of a sample at defined locations and is suited as a complimentary technique to SAED. EDX can be effectively used to identify contaminants within samples and is also capable of producing quantification of the various elements present in a sample. For example, one report detailed the role of Cu contamination in a HBS medium in terms of inducing Ge NW growth (Figure 6). This was simple achieved by performing an EDX survey scan on the NWs dispersed on a Ni coated TEM grid.

**Figure 5:** a) HRTEM image of a Ge NW with 1-D lattice fringes corresponding to the (111) spacing. b) HRTEM image of a Ge NW showing 2-D lattice fringes with, inset, an SAED pattern.
Figure 6: EDX profile of the inset Ge NW showing the presence of Cu at the NW tip.¹

EDX can also be used to measure the spatial distribution of elements within samples. Mapping of elements (Figure 7) can reveal information about the nature of NW/catalyst interfaces.¹⁰ The TEM image shows an Au/Cu alloy nanoparticle seeded Ge NW which was analyzed using EDX mapping. The EDX maps show that the Cu and Au signals are almost exclusively confined to the catalyst region evident in the TEM image, while the Ge signal is shown to be non-zero in the body of the catalyst. This is a good indication of the reservoir effect commonly known for NW growth¹¹ and may also indicate the formation of Cu germanide species within the catalyst tip.
Figure 7: TEM image of a Cu/Au alloy nanoparticle seeded Ge NW with corresponding EDX maps for Cu, Ge and Au.\textsuperscript{10}

EDX can also be employed to scan in a line profile mode to analyze chemical junctions. Again, this method is extremely useful for measuring the composition of NW/catalyst interfaces but it particularly suited to the analysis of segmented NW heterostructures.\textsuperscript{12} In Figure 8 a, a TEM image of a Si-SiGe NW with a $<112>$ growth direction is shown. While TEM can often be used to distinguish between materials based on differences in Z contrast (as seen here for the Au seed), the slight compositional variance present in the NW cannot readily be identified on standard TEM mode. Dark-field STEM is more sensitive to Z contrast differences and provides a much clearer indication of the segmented nature of the NW (Figure 8 b). The EDX line profile shown in Figure 8 c quantifies the compositional fluctuations along the length of the NW.
Figure 8: a) TEM image of Au seeded Si-SiGe NW. b) DFSTEM image of a similar NW with EDX line profile c.\textsuperscript{12}

Annular dark-field STEM images are formed by very high angle, incoherently scattered electrons which results in the high sensitivity to variations in the atomic number of elements in the sample (Z-contrast images). The technique can be used to identify small quantities of metal contamination on the surface or within the crystalline lattice of NWs. In Figure 9 (a and b)\textsuperscript{13} the diffusion of Au islands down the sides of a Si NW is shown using STEM. The detection of Au atoms within the NW lattice is even more important given its role as electron traps for Si. Again, this can be achieved using DF-STEM as shown in Figure 9 c where the Au atoms were found to accumulate at a twin defect in the Si NW.\textsuperscript{14}

Figure 9: DFSTEM image as a means of identifying Au contamination on the surface\textsuperscript{13} (a and b) and within (c) NWs.\textsuperscript{14}
2.4.2 SEM analysis

SEM analysis is often used as a complimentary technique to TEM to gain understanding of the 3D morphology of materials. A filament is used to create a beam of electrons in a similar manner to that employed in the TEM as shown in Figure 10. These electrons are then scanned over the specimen, generating an image of the sample surface. SEM analysis is more flexible than TEM as it requires little sample preparation. Nanomaterials grown on substrates can immediately be analyzed without the need to externally prepare the sample (i.e., on a TEM grid) while those formed in solution can simply be dropcast onto a substrate of interest. In this regard, SEM can provide more in-depth information in terms of the nanomaterial orientation as prepared and is particularly useful as a tool for surveying a larger area than that possible with TEM. Figure 11 shows a cross-sectional SEM image of Si NWs grown vertically from a Si wafer. SEM samples can also be easily rotated and tilted to allow different viewing perspectives on the materials which can be allow visualization of the orientation of materials from the underlying substrate.
Figure 10: Schematic illustration of a typical SEM instrument.\textsuperscript{15}

Figure 11: SEM image of vertically grown Si NWs from a Si wafer. The scale bar is 1 micron.\textsuperscript{16}
The use of a backscatter detector in conjunction with SEM can be used to detect Z-contrast differences within samples and as a result is useful for the analysis of metal-catalyzed NWs. The image in Figure 12 shows ZnO NWs which are decorated with Au nanoparticles (as small as 5 nm in diameter) which can clearly be identified due to the use of the backscatter detector. SEM analysis is also compatible with the use of various analytical techniques such as EDX and EBSD. EDX analysis allows compositional data to be obtained in much the same manner as that employed in the TEM and is suited to quantification, point compositional analysis and mapping. An EDX map generated in an SEM for bi-metallic NWs can be seen in Figure 13 where the localization of Ag and Cu to the various segments of the NWs was identified.
Figure 13: SEM/EDX mapping for bimetallic Ag/Cu NWs. a) SEM image of a bi-metallic NW with corresponding EDX map in b). c) Additional SEM image showing a thinner Cu NW with Ag decoration and EDX map d).

SEM-based EBSD analysis is an extremely useful means of identifying crystalline phases present within the sample at the micro scale. As a result, it can be used in conjunction with XRD analysis (a macro analytical technique) to fully understand the crystallography of a sample. For example, EBSD can be used to identify the crystal phase of individual NWs as shown in Figure 14 a. The interaction of the SEM beam with the sample produces kikuchi bands similar to those seen in TEM (Figure 14 b) which can be detected using a phosphor screen. The generated pattern can then be indexed for the corresponding crystal phase as shown in Figure 14 c where the kikuchi bands are indexed for the cubic crystalline phase of Si. EBSD analysis can also be used to obtained detailed maps across phase boundaries or used to distinguish between various phases in samples which contain more than one crystalline phase.
2.4.3 XRD analysis

XRD is a widely used technique for obtaining information of the crystal structure of materials. The wave like nature of X-rays is exploited to obtain a series of reflections which are characteristic of the crystalline planes which exist within a material. The method is described by Bragg's relationship \( \lambda = 2d \sin \theta \), where \( \lambda \) is the wavelength of the incident X-rays in nm, \( d \) is the distance between the atomic planes and \( \theta \) is the diffraction angle. A typical setup for XRD diffraction is shown in Figure 15.\(^{21}\) The source (typically Cu K\( \alpha \) radiation) and detector are typically moved in goniometric measurements using motorized arms. XRD can provide simultaneous information on all the phases present within a sample. Figure 16 shows an XRD diffractogram taken from Au-catalyzed Si NWs with the corresponding reflections indexed. XRD can also be used to quantify the percentage of different phases present by performing Rietveld analysis by comparing the intensity of the reflections of the various constituents.
Figure 15: Schematic of XRD operation.\textsuperscript{21}

Figure 16: XRD diffractogram obtained from Au catalyzed Si NWs.\textsuperscript{22}
2.4.4 XPS analysis

XPS is an extremely useful technique for determining the surface chemistry of materials. The sample in question is bombarded with monochromated X-rays which induce the emission of photoelectrons. These photoelectrons are then analyzed using a detector which can provide information on the elements present and the oxidation states of the constituents. XPS analysis is extremely useful in determining the surface passivation of NWs due to its typical depth penetration of between 1 and 6 nm.\textsuperscript{23, 24} Figure 16 shows XPS analysis of Ge NWs with various surface coatings.\textsuperscript{25} The absence of Ge oxide on the NWs after exposure to air and boiling water caused by thiol and alkene functionalization is shown in Figure 16 a-d. The appearance of GeO\textsubscript{2} due to exposure to H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2} is shown in Figure 16 e-h.

![Figure 16: XPS analysis of Ge NWs passivated with thiols (red) and alkenes (black) after 1 week exposure to air (a,b), boiling H\textsubscript{2}O for 1 hr (c,d), 2.5M H\textsubscript{2}SO\textsubscript{4} for 1hr (e,f) and 30 % H\textsubscript{2}O\textsubscript{2} for 1hr.\textsuperscript{25}](image-url)
2.5 References


Chapter 3: Growth of self catalyzed Germanium NWs within a high boiling point organic solvent

The contents of this chapter appear in *Chemical Communications* 2011, 47, 3843-3845

3.1 Abstract:

High yields of single-crystalline Ge NWs were synthesized in the vapour phase of a high boiling point organic solvent without the need for metal catalyst particles. Thermal decomposition of diphenylgermane allowed the formation of germane gas which acted as a feedstock for Ge NW growth. The germane dissolved in organic vapor allowed thermally localizable, self seeded growth on the reaction flasks. The system was extended to the growth of high density, perpendicular arrays of Ge NWs from ITO-coated substrates. The approach represents a convenient route toward orientated arrays of catalyst-free Ge NWs. The NWs were examined using TEM, SEM, SAED, XPS and X-XRD.

3.2 Introduction:

Group IV semiconductor NWs have been incorporated into a variety of novel device architectures including high performance field effect transistors, lithium ion battery anodes and next generation solar cells – due to their unique size-dependent properties.\(^1\)\(^3\) A particular benefit of group IV NWs is their inherent compatibility with CMOS technologies. In recent years the use of Ge in electronic and optoelectronic application has garnered significant interest due to its larger Bohr exciton radius and higher carrier mobility compared to Si.\(^4\)\(^5\) A variety of techniques – including CVD, laser ablation and various
solution protocols – have been employed in their synthesis. The archetypal and best-studied approach is the Au nanoparticle-seeded route which takes advantage of the low eutectic temperature between Au/Si and Au/Ge. While this route has been widely adopted in the controlled synthesis of NWs, its viability for device applications has been limited due to inherent Au contamination of the resultant nanostructures, prompting interest in the use of alternative metal catalysts. Concurrently, the more recent discovery of routes to Ge NWs grown without metal catalyst particles deemed as ‘unseeded’ or ‘self-seeded’ processes offers even higher purity NW formation. These methods utilise the decomposition of organometallic precursors in organic solvents with boiling points above the minimum nucleation temperature required to induce anisotropic Ge growth. Despite the success of these methods, the maximum attainable temperature within the system is limited by the boiling point of the solvent used. This factor along with the inherent confinement of material growth to the high boiling point solution has precluded the extension of these techniques to the catalyst-free growth of Ge NWs from substrates.

Herein, we describe a simple method for catalyst-free Ge NW growth via the thermal decomposition of an organometallic precursor specifically in the vapour reflux of a high boiling point solvent, squalene. No growth occurs in the liquid phase of this system in contrast to previous high boiling point solvent approaches due to the higher temperatures attainable in the solvent vapour. NWs are shown to grow vertically in high density from substrates placed above the liquid mensicus of the high boiling point solvent without the need for catalyst particles. The unique combination of condensing high boiling
point solvent at a surface and decomposing germanium precursor acts as a nucleation zone for anisotropic wire growth. The simple round-bottomed flask based approach presented is extended to the perpendicular growth of Ge NWs from transparent conducting metal oxides (ITO) which is desirable for optoelectronic applications.15

3.3 Experimental:

Materials and supplies:

All chemicals were used as received unless otherwise stated. The high boiling point solvents, squalane (99 %) and squalene (≥ 98 %), were received from Sigma-Aldrich. Diphenylgermane (DPG) (97 %), tetramethylgermane (TMG) (> 95 %) and tetraethylgermane (TEG) (> 95 %) were supplied by Gelest Inc., all of which were stored and dispensed from a nitrogen-filled glove box (BOC Ltd. Pureshield). All NW fabrication was carried out using custom designed long-neck round-bottomed flasks, constructed from quartz and Pyrex® by Technical Glass Products, Inc. All experiments were conducted using an Applied Test Systems, Inc., Model 3210 3-zone heating furnace, which was employed to regulate the temperature of each reaction within the round bottomed flasks to an accuracy of +/- 5 °C.

Substrate preparation:

ITO-coated glass substrates were produced by depositing an approximately 150 nm thick layer of ITO onto borosilicate glass slides (VWR) via magnetron sputtering (ATC ORIOM sputterer). The operating conditions involved
the use of Ar flow at a pressure of 3 mTorr, with a deposition height of 15 mm and a power (RF) of 100 W.

**Ge NW synthesis:**

The synthesis of Ge NWs was achieved through the thermal decomposition of diphenylgermane in the presence of a high boiling point solvent, at reflux (415 °C) for 2 minutes. In a typical synthesis of NWs, a custom-designed long neck reaction flask was loaded with 10 mL of squalene, fitted to a water condenser and sealed within a 3-zone furnace (Figure 1a). This solvent was degassed at 120 °C for 30 minutes with a 30 mTorr vacuum, prior to back-filling with Ar gas (Pureshield BOC Ltd.) and ramping to a reaction temperature of 415 °C. Once stabilised at the desired temperature, 250 µL of DPG was rapidly injected into the system by means of a glass syringe, through a septum cap located at the top of the condenser. Reactions were generally allowed to proceed for up to 2 minutes at which point the furnace was opened and the flask was rapidly cooled to room temperature. Upon completion, a strong pink to purple colour could be observed from the walls of a flask, which is typical for Ge NWs of diameters below its excitonic Bohr radius of ~ 24 nm. All samples were extracted with sonication in toluene or chloroform and cleaned prior to analysis, according to a previously reported method by successive precipitation and redispersion.\(^{12}\) Parallel reactions using reaction flasks cleaned with *aqua regia* solution prior to use yielded identical results.

**NW purification and characterization:**

The Ge NWs were extracted through the addition of 50-100 mL of toluene with the aid of sonication. To 15 mL solutions of Ge NWs dispersed in toluene,
10 mL of acetone was added, which was then followed by 15 minutes of sonication in a 25 °C water bath. Samples were then centrifuged for 10 min at 4000 rpm, after which the supernatant was discarded and the remaining precipitate re-dispersed with 15 mL of toluene and 5 minutes of sonication. These steps were repeated twice more before the precipitate was again re-dispersed in 20 ml of toluene for analysis.

The SEM images of the synthesised Ge NW samples were obtained with a Hitachi SU-70 system, operated at 3-20 kV. The TEM images of samples and the corresponding SAED patterns were taken on a JEOL JEM-2011 electron microscope operated at an accelerating voltage of 200 kV using a LaB₆ filament. The STEM was conducted with a JEOL JEM-2100F field emission electron microscope and was used for HAADF imaging. Additional TEM analyses were carried out using a 200kV JEOL 2000FX electron microscope, equipped with a thermionic LaB₆ source and a 200 kV JEOL 2200FS electron microscope, equipped with a Schottky field-emission source, Cesium correction and an in-column energy filter. EDX analysis was performed with both an EDAX Genesis XM4 and an Oxford Instruments INCA PentaFET-x3 system during TEM and SEM analysis, respectively. Analysis with both systems was conducted with a Sapphire Si(Li) detector using a 30 mm² detecting crystal. X-ray diffractograms were recorded on a PANalytical X’Pert PRO MPD (multi-purpose x-ray diffractometer), using a Cu-Kα radiation source and an X'Celerator detector. XPS was performed by Dr Fathima Laffir (MSSI) in a Kratos AXIS 165 spectrometer using monochromatic Al Kα radiation of energy 1486.6 eV. C 1s at 284.8 eV was used as the charge reference to determine core level binding energies. For
construction and fitting of synthetic peaks of high resolution spectra, a mixed Gaussian-Lorenzian function with a Shirley-type background subtraction were used. Raman spectra were recorded on a Dilor XY Labram spectrometer equipped with a 20 mW ArHe laser ($\lambda = 514$ nm) and a Peltier cooled CCD detector (nominal resolution $2 \text{ cm}^{-1}$).

**Figure 1** Schematic (a) outlines the synthetic strategy for catalyst-free growth of Ge NWs. Photographs (b) and (c) show flasks after a typical synthesis where the NW growth was thermally localised.
3.4 Results and discussion:

The schematic outlined in Figure 1 a highlights the reaction setup and growth chemistry used in this work. DPG was thermally decomposed by injection into the vapour reflux of the high boiling point solvent squalene to form germaine gas which was transported to the heated sidewalls of the reaction vessel (or growth substrate) by the refluxing solvent, allowing self-seeded Ge NW growth. NW growth was clearly evident from the pink colouration of the reaction flask sidewalls post-synthesis (Figure 1 b and c). Growth in the case of this system does not occur in the liquid solution unlike conventional high boiling point solvent synthesis methods. Rather, NW growth is possible across the inner surfaces of heated quartz/Pyrex® long necked flasks in contact with organic vapour. The organic vapour acts as a carrier for the resultant germaine gas, allowing NW formation. The reaction times necessary for growth were found to be very short, as high NW yields could be achieved after only 2 minutes, with no significant increase in yield given longer reaction times of up to 2 hours (likely due to the Ge monomer source being exhausted). Localized heating experiments were conducted where either zone 1 or zone 2 of the furnace was left inactive while the globe of the flask in zone 3 was continuously heated. Post-synthetic photographs of the system (Figure 1b and c), show that the NW growth could be fully localized, with no growth occurring in the non-heated zones. It can also be seen that no crystalline material was produced in the liquid portion of the high boiling point solution.

The SEM image seen in Figure 2 a shows a dense bundle of Ge NWs sonicated from the sidewalls of a reactor and drop cast onto a Si wafer. The high aspect ratio of the NWs is clearly illustrated from the high resolution
micrograph inset, with some possessing lengths in the tens of microns. Figure 2 b shows a powder XRD collected from Ge NWs synthesised using squalene as the solvent. The resultant diffractogram gave strong peak reflections at $2\theta = 27.29^\circ$, $45.43^\circ$ and $53.81^\circ$, corresponding to the (111), (220) and (311) peaks for diamond cubic germanium.

**Figure 2** SEM image (a) of NWs with magnified image inset. (b) XRD pattern for the NWs indicating crystalline Ge. (c) TEM image showing a selection of Ge NWs with the corresponding SAED pattern (inset). (d,e) HRTEM images of NWs exhibiting $<111>$ and $<112>$ growth directions respectively. The interplanar spacing of 3.27 angstroms for the $<111>$ NW is shown in (d) while an indexed FFT is shown in (e).
TEM analysis of the NWs showed that they were non-tapered with a diameter range between 7 and 15 nm (Figure 2 c). A small 1-2 nm thick oxide layer is also visible at the periphery of the NWs. The corresponding SAED pattern (Figure 2 c, inset) obtained from a collection of NWs shows a polycrystalline ring pattern from which the maximum intensity rings give \( d \) spacings of 0.327, 0.199 and 0.170 nm, respectively. These spacings can be matched to the (111), (220) and (311) type planes expected for the diamond cubic crystal structure of Ge and are consistent with the XRD analysis. It was noted that in a typical synthesis, 80% of the NWs exhibited a \(<111>\) growth direction (Figure 2 d)) while the remaining 20% showed a \(<112>\) growth orientation (Figure 2 e)). The interplanar spacing for the \(<111>\) NW in Figure 2 d was measured at 3.27 angstroms which is consistent with the (111) plane of Ge. The indexed FFT in Figure 2 e was used to determine the \(<112>\) growth direction. The predominance of the \(<111>\) growth over \(<112>\) is consistent with previous reports on both metal catalysed and catalyst-free techniques.\(^{13,17}\)

XPS was used to examine the surface chemistry of the NWs. A low-resolution survey scan (Figure 3) of the NWs on an oxidized silicon substrate, yielded peak positions for Ge, O, C and Si. The C, O and Si peaks were attributed to the presence of residual organic solvent, surface oxidation of the NW surface and Si oxides on the substrate, respectively. The Ge 3\(d\) spectrum (inset) has two peaks corresponding to Ge and a third peak assigned to O 2s. The Ge 2\(p_{3/2}\) spectrum is fitted with a peak at 1217.1 eV which corresponds to elemental Ge and the two other component peaks at higher binding energies correspond to GeO\(_x\), due to oxides on the NWs.\(^{18}\)
**Figure 3.** XPS spectra obtained from samples of as synthesised Ge NWs, with higher resolution scans from both the Ge 3d and Ge 2p$_{3/2}$ spectral regions highlighted in the insets.

**Figure 4.** Raman analysis from Ge samples showing the peak position for squalane synthesised NWs (a) to be slightly down-shifted compared to that of squalene based samples (b).
Raman analysis (Figure 4) also gave confirmation of the presence of nanocrystalline Ge shown by the downshifted vibrational mode peak position of 298.1 cm$^{-1}$ when compared to bulk Ge (circa 300 cm$^{-1}$).\textsuperscript{19}

**Figure 5.** Schematic illustrating the experimental setup used for the growth of Ge NWs on ITO

Having successfully grown the NWs from quartz and Pyrex\textsuperscript{®} flasks, the viability of oriented Ge NW growth on substrates was probed. The synthetic procedure used is highlighted in Figure 5. ITO was chosen as a suitable substrate due to its compatibility with solar and optoelectronic applications. SEM cross-sectional analysis shown in Figure 6 a, conducted at a 70° tilt, shows the nature of Ge NW growth on an ITO coated substrates. The circa 150 nm layer of ITO can be readily identified beneath the extremely dense arrays of perpendicularly grown Ge NWs, covering an area of over 10 µm$^2$. This highly ordered array grown directly from the substrate is further magnified in Figure 6 b. The NWs can be seen to be individual and freestanding up to approximately 1 µm from the substrate before becoming intertwined into a dense mesh. High resolution imaging found the NWs to be untapered along their length from root to tip, with no evidence of metallic seed particles being identified.
Figure 6. SEM images (a) and high resolution image (b) highlighting the large-scale perpendicular arrays of Ge NWs, grown from an ITO surface. (c) XPS analysis of the Ge NWs grown on from an ITO coated substrate.

XPS analysis was used to examine the surface and interfacial chemistry of the Ge NWs on the ITO growth substrate in an effort to investigate potential seeding of the NWs by elemental In as highlighted in previous studies.\textsuperscript{20, 21} The high resolution spectrum of In $3d$ (Figure 6 c) is composed of an asymmetric doublet with In $3d_{5/2}$ appearing at a binding energy of 444.5 eV, characteristic of indium present in ITO as In$_2$O$_3$. The broad structures at ~ 440 and ~ 450 eV can be attributed to GeO$_x$ auger electrons. Elemental indium, if present would appear at a lower binding energy of 443.6 eV.\textsuperscript{22} A chemical shift of 0.9 eV from that expected for elemental indium supports that indium oxides exist at the interface of these materials. This observation, along with the TEM analysis findings that the NWs were identical to those grown on glass suggests strongly that NW growth from the ITO does not proceed via a metal seeded mechanism.
Figure 7. a) XRD analysis conducted on a blank annealed ITO substrate with as deposited ITO (inset) b) Diffractogram collected for the NWs grown on ITO with the addition of a peak at 27° 2θ attributed to the Ge NW growth.

XRD analysis was conducted on the reaction substrates at various stages. The inset in Figure 7 a shows the as sputtered ITO layer on glass. The layer can be seen to be poorly crystalline with no distinct reflections. The main XRD diffractogram in Figure 7 a shows the substrate after it was subjected to a blank reaction (without the addition of DPG in the described route). It can be seen that the high temperatures of the reaction HBS have resulted in an anneal of the ITO layer on the substrate. The defined reflections present are consistent with the cubic bixbyite structure of crystalline ITO. The XRD diffractogram (Figure 7 b) taken from the Ge NW covered substrate shows one additional broadened peak at 27° 2θ which is consistent with the high density Ge formation.

The key difference between this study and previous metal catalyst-free approaches is that Ge NW growth is uniquely facilitated by the vapour phase of the organic solvent growth medium, with no material formation in solution. The absence of solution born NWs in this study is in good agreement with previous work that observed NW growth in squalene solution only in the presence of metal
catalyst seeds of Au or Cu when using DPG as the precursor. We propose that Ge NW nucleation most likely occurs via an organic/self-seeded protocol as reported previously by Zaitseva et al. In their study, liquid droplets were viewed as sinks for vapour molecules which allowed for accelerated decomposition of the Ge precursor and subsequent 1D growth. In comparison, their work focused on precursors which did not form germane gas upon thermal decomposition. The key difference here is that germane gas is formed in the vapour phase of the system. Through the placement of a substrate in the vapour phase portion of the reactor, precursor gas is allowed to saturate the organic medium allowing the self-seeded growth of NWs, forming extremely high density perpendicular arrays.

The use of a solid nucleation surface in our study allows higher density NW formation than that possible in previous solution-based methods. This is due to the substrate acting as a site for organic droplet formation. The < 50 nm size of the NW diameters presented here is consistent with the previous organic seeded report while our tighter diameter distribution is likely due to the more precise temperature control feasible within the three zone furnace used. The consistency of NW diameter across the three substrates used in this study (i.e., Pyrex®, quartz and ITO) is consistent with the formation of organic droplets of a defined size as opposed to surface defect driven growth. The density of the NWs formed on the flask was found to depend on the concentration of DPG injected into the reaction. However, the nature of the NWs produced (i.e., average diameter and length) was found to be independent of both reaction time and concentration. The absence of an increased yield with respect to time can be linked to the Ge monomer source being exhausted within the reactor.
3.5 Conclusions:

In summary, we have presented the vapour phase based, catalyst-free growth of Ge NWs using the thermolytic decomposition of an organometallic precursor. The growth was investigated in both pyrex and quartz reaction flasks and extended to the perpendicular growth of Ge NWs from ITO coated substrates. We believe that NW nucleation occurs via a self-seeding organic based mechanism and represents a significant step forward in catalyst-free Ge NW synthesis.

References


21. Ying Xiang, L. C., Sonia Conesa-Boj, Sonia Estrade, Jordi Arbiol, Francesca Peiro, Martin Heiß, I Zardo, Joan R Morante, Mark L Brongersma and


**Chapter 4: Role of Defects and Growth Directions in the Formation of Periodically Twinned and Kinked Unseeded Germanium Nanowires**

The contents of this chapter appear in *Crystal Growth & Design* 2011, 11, 3266-3272

4.1 Abstract:

Here we show the impact of preferred growth directions and defects in the formation of complex Ge NW structures grown by a simple organic medium based synthesis. Various types of NWs are examined including: straight defect free NWs; periodically bent NWs with precise angles between the NW segments; NWs with mutually exclusive lateral or longitudinal faults; and more complex ‘wormlike’ structures. We show that choice of solvent and reaction temperature can be used to tune the morphology of the NWs formed. The various types of NWs were probed in depth using TEM, SEM, SAED and DFTEM.

4.2 Introduction:

The unique size-dependent properties associated with 1-D Ge nanostructures have generated a wave of synthetic research based on Ge NW growth. Specifically, they are of interest due to their potential as anode and charge carrier paths in lithium ion batteries, use in photoresistors and suitablity for next generation solar cells. Furthermore, a renewed interest in the utilization of Ge has emerged in the semiconductor industry due to the succesful introduction of hafnium oxide as a dielectric lowering the encumbrance to non-silicon material integration. Notably, crystalline Ge possesses greater intrinsic carrier mobility
and a larger excitonic Bohr radius than Si, making it a more promising candidate material for NW based MOSFET technology.8,9

Synthetic methods for the preparation of Ge nanowires are varied and include such techniques as: laser ablation, molecular beam epitaxy, CVD and a variety of different solution based processes.10-13 These methods are catalytic in nature requiring a metal nanoparticle seed with NW growth occurring by the well established VLS14, 15 and VSS16, 17 protocols. An alternative strategy for Ge NW growth is the metal catalyst free, HBS based approach.18,19, 20 Recently, we have developed a method which facilitates the growth of high yields of crystalline wires directly on substrates within the vapor phase of the HBS.21 The growth morphology of NWs produced by unseeded approaches is less understood than their seeded analogues, representing a barrier to broad application.

A wide variety of growth morphologies have been noted in metal seeded NWs. Factors such as NW growth direction and kinking are important when tailoring NWs for applications ranging from transistors to sensors.22, 23 The growth direction for Si and Ge NWs has been widely studied and modulated.24-26 Typically, VLS grown group IV NWs exhibit <111> growth directions while growth in <110>, <100> and <112> directions has also been observed.24, 27, 28 Careful control over the growth orientation is particularly important when epitaxial growth from crystalline substrates is desired.29, 30 Structural variations within NWs, such as lamellar twinning faults, have been noted in a number of seeded approaches and must be understood and controlled as they can impact the electrical and optical properties of the NWs.31 Faults parallel and perpendicular to either the <111> or <112> growth direction of Si and Ge NWs have been shown in a number of studies31-33 while more complex morphological variations such as
NW kinking often occurs as a result of a change in growth direction in single crystal NWs. Such NW kinking has been controllably initiated by abrupt modification of the synthesis parameters such as pressure in a number of studies,\textsuperscript{29, 30} while it has been seen as an inherent occurrence in others.\textsuperscript{34} For example, the Lieber research group deliberately induced acute kinking in a semiconductor wire, which coupled with alternate doping of the arms, allowed electrical probing of biological cells.\textsuperscript{25} While extensive reports on kinking and growth defects exist for Si NWs, there is little information on similar phenomena of Ge NWs, particularly unseeded Ge NWs.

Here we present the morphological details of Ge NWs grown \textit{via} an organic vapour phase-based, catalyst free route.\textsuperscript{21} Examples of, and reasoning for, lateral, longitudinal and more complex faults seen in the NWs are presented and an increase in their relative frequency as a function of reaction temperature and solvent is detailed. Tortuous NWs are examined and NW kinking is found to originate from interplay between NWs tending to grow along preferred crystallographic axes and NW defects being perpendicular to the NW growth direction. The study provides insight into the impact of growth direction changes and defect formation on the morphology of unseeded Ge NWs.
4.3 Experimental

Ge NWs were synthesized by thermally decomposing DPG (> 95 % Gelest Inc.) in either squalene (≥ 98 % Aldrich ltd.) or squalane (≥ 98 % Aldrich ltd.) in custom made quartz round bottomed flasks in a similar setup to our previously reported method. In a typical synthesis, 10 mL of squalene (or squalane) was weighed out into a flask and connected to a schlenk line via a water condenser. The setup was placed inside a 3 zone furnace and the system was heated to 125 °C using a ten minute ramp period under vacuum. The system was subsequently subjected to a vacuum of at least 100 mTorr for 30 minutes. Following this step, the system was filled with Ar and a constant flow of gas was established. The setup was ramped to reaction temperature in 15 minutes. As soon as the temperature had stabilized, 0.25 mL of DPG was injected via a septum cap into the organic medium at reflux. The reaction was allowed to proceed for 5 minutes before quenching by opening the furnace. An example of a reaction flask after the synthesis can be seen in Figure 1. After allowing the reaction to cool to room temperature, the products were collected in toluene via sonication for analysis. The toluene solutions were then dropcast onto lacey carbon TEM grids.
Reactions at various temperatures were analyzed. The reaction temperature used was dependent upon the solvent of choice. Squalene has a boiling point \( \approx 395 \, ^{\circ}\text{C} \) while squalane boils at \( \approx 415 \, ^{\circ}\text{C} \). As reactions were carried out in the reflux vapor of the system, reaction temperatures were carried out at temperatures above the boiling point. Lower reaction temperatures (\( \approx 400 \, ^{\circ}\text{C} \)) were seen to hamper NW growth. This is consistent with previous reports where Au catalysis was required to induce crystalline Ge formation at \( T < 400 \, ^{\circ}\text{C} \).\textsuperscript{35} We found that temperatures more than 30 \( ^{\circ}\text{C} \) above the respective solvent boiling point were unfavourable as they led to solvent decomposition and were thus avoided. This meant that, practically, squalene reactions could be to run at 425 \( ^{\circ}\text{C} \) while squalane reactions could be run at 425 \( ^{\circ}\text{C} \) or 450 \( ^{\circ}\text{C} \). The high boiling point solvents used were chosen such that the attainable temperatures allowed decomposition of the DPG. These two solvents are non-coordinating and therefore would not be expected to play an active part in influencing the crystal structure or
morphology of the wire. Their only influence is to allow modulation of the reaction temperature. Increased reaction temperatures resulted in the formation of a greater amount of large diameter NWs (as evidenced by the increase in relative abundances of type II and type III NWs). The increase in the amount of larger diameter NWs at higher temperature is consistent with the observations of Zaitseva et al. who investigated the formation of unseeded germanium nanowires in the liquid phase of high boiling point solvents. While increased reactions temperatures were found to alter the relative percentage of each type of wire, the diameter ranges of each wire type remained constant.

TEM analysis was conducted using a 200 kV JEOL 2000FX microscope with a LaB₆ emission source. Additional analysis was performed using a 200 kV JEOL JEM-2100F field emission microscope. SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 10 kV. Samples were prepared by dropcasting the Ge NW sample from solution onto blank Si wafers with a native oxide. XRD analysis was conducted by dropcasting a sample of the NWs on a zero background holder in a PANalytical X’Pert PRO MRD instrument with a Cu-\textit{K\textsubscript{a}} radiation source (\(\lambda = 1.5418 \, \text{Å}\)) and an X’celerator detector.
4.4 Results and discussion

Figure 2 a shows a TEM image of the product of a typical squalene reaction carried out at 420 °C. The majority of the NWs were found to be straight with diameters typically between 7 nm and 20 nm and large aspect ratios. A small percentage of the wires (highlighted with the arrow) have larger diameter distributions and show a considerable degree of kinking. These kinked NWs were found to possess NW diameters (typically between 15 and 50 nm) which were larger than those seen in the straight NWs. The relative proportion of kinked wires to straight wires was found to significantly increase when a higher boiling point solvent was used or when the temperature was increased. Figure 2 b shows an SEM image of nanowires produced from squalane (BP ≈ 420 °C) showing a greater morphological variation. A portion of these kinked NWs consisted of long (often in the order of microns) sections prior to very abrupt angular kinking (highlighted as area II). These NWs typically exhibited diameters between 15 and 40 nm.

The remainder of the NWs were found to be extremely tortuous, ‘wormlike’ NWs marked III in Figure 2 b with diameters between 30 and 50 nm. Figure 2 c summarises the types of wire growth identified in a typical non-seeded synthesis. Type I are straight wires which have three sub-sets (only revealed in high resolution imaging (TEM)) single crystal (IA), lateral stacking faults (IB) and longitudinal stacking faults (IC). Type II are of similar aspect ratio to type I, composed primarily of straight regions with abrupt, acute kinking and Type III are the larger aspect ratio, worm-like wires. The frequency of each wire type can be manipulated through slight modifications in the reaction temperature or changing the solvent as outlined in Table 1. The progression is such that more faulted and
kinked structures are found with increasing temperature. In our case, there is also a diameter threshold above which the NW may form the more complex structural alternative (i.e., above 15 nm type II can form and above 30 nm type III can form). The following high resolution TEM and SEM study reveals the impact of growth direction changes and defects in determining the morphology for each wire type.

<table>
<thead>
<tr>
<th>reaction solvent</th>
<th>reaction temperature °C</th>
<th>product composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>squalene</td>
<td>420</td>
<td>85% Type IA, 5% Type IB/IC, 10% Type II/III</td>
</tr>
<tr>
<td>squalane</td>
<td>420</td>
<td>60% Type IA, 10% Type IB/IC, 30% Type II/III</td>
</tr>
<tr>
<td>squalane</td>
<td>450</td>
<td>30% Type IA, 15% Type IB/IC, 55% Type II/III</td>
</tr>
</tbody>
</table>

**Table 1:** Table detailing the relative portions of the different NW types noted in this study.

**Figure 2.** (a) TEM image of straight Ge NWs synthesized using squalene as the HBS. The majority of the NWs can be seen to be straight and untapered while the arrow highlights a small area of kinked NWs. (b) SEM image of increasingly kinked NWs synthesized in squalane with specific NW types highlighted. The schematic depicts the 5 different types of NWs discussed within the text IA: straight, defect free NWs, IB: laterally faulted NWs, IC: longitudinally faulted NWs, II: angular NWs and III: more complex, wormlike kinked NWs.
4.4.1 Straight NW analysis

TEM analysis of a single, defect free, type I NW is presented in Figure 3 a. The NW can be seen to be a perfect, defect free, single crystal. A thin amorphous oxide coating is present at the periphery of the NW, which is consistent with all the NWs synthesized in the study. Figure 3 b shows the corresponding indexed FFT from which a <112> growth direction was deduced. The polycrystalline electron diffraction pattern, seen in Figure 3 c, was taken from a bundle of NWs and shows rings consistent with the (111), (220) and (311) type planes expected for the diamond cubic crystal structure of Ge (space group Fd3m with lattice parameter a =5.66 Å). In addition to the straight, defect free NWs produced by this method, straight NWs exhibiting mutually exclusive lateral (IB) and longitudinal (IC) faults were discovered to represent ≈ 5 % of a typical squalene synthesis. The lateral defects which were evident in the type IB NWs were found to occur on the (111) plane. This indicates that lateral defects will tend to occur on NWs with a <111> growth direction, as indicated by the laterally faulted NW in Figure 3 d. This also suggests that the reaction is not purely homogenous in relation to growth directions as there are some <111> NWs amongst the <112> NWs.33
Figure 3. (a) HRTEM image of defect free NW with a <112> growth direction. (b) Indexed FFT used to determine the <112> growth direction. (c) Polycrystalline electron diffraction consistent with the presence of diamond cubic, crystalline Ge taken from a number of NWs. (d) Ge NW with lateral faults along the entire length of the NW and a <111> growth direction. (e) Corresponding indexed SAED pattern showing the twin defects. (f) Lattice resolved image of the faults with the marked angle equal to 141 ° and the FFT (inset) showing the <111> growth direction. (g) TEM image of longitudinally faulted NW with a <112> growth direction. (h) HRTEM image of a NW with faults extending to the tip with marked angle θ equal to 141 ° between the faults. The inset shows an FFT of the NW with arrows indicating the twinned spots. (i) HRTEM image of a NW with longitudinal faults.

As indicated by the selected area diffraction (SAED) pattern in Figure 3 e, the defects correspond to twin defects on the (111) plane. The streaking of the spots along [111] can be attributed to the shape effect of the thin, edge-on, twin
The small (typically below 5 nm) and regular nature of the crystallographic regions, between fault twin planes more likely exerts a large influence on the morphology of the NWs. If these crystal regions were larger, this would lead to the formation of a less linear, zig zagged NW. The atomic image in Figure 3 f is viewed down the [0-11] zone axis. The [-211] direction is perpendicular to the growth direction, which is parallel to the defects (and therefore lies on the (111) plane which explains why longitudinal defects are later found on <112> grown wires. Similarly, if the NW was tilted 90° about the [111] axis, the [-211] zone axis would be visible and the defects would be noted running parallel to the [0-11] direction. This also agrees with the potential formation of longitudinal defects in <110> grown NWs. Three different examples of type IC, longitudinally faulted NWs are presented in Figure 3. Analysis of the NWs with longitudinal defects (as shown in Figure 3 g) reveals that NW growth occurs in the <112> direction with the defects occurring on the (111) type plane. For a NW with a <112> growth direction, defects on the (111) plane can exist parallel to the wire or at either a 20° or 62° angle relative to the growth direction. As a NW constrains crystal growth in two dimensions, there is a greater amount of stress compared to that in a non-constrained crystal.
The stress can be alleviated with the addition of defects. When these defects run parallel to the growth direction, there is no defect termination and the stress is minimized throughout the length of the NW. When these defects are not parallel, they continually terminate at the edge of the NW and so new defects must occur to avoid the stress returning. Therefore, defects found in the $<112>$ grown, straight wires are likely to be parallel to the growth direction and thus, longitudinal. This is in good agreement with previous reports on longitudinal defect formation in Si NWs with a $<112>$ growth direction.$^{31,32,37}$

Theoretically, the formation of longitudinally faulted NWs with a $<110>$ growth direction should also be possible. However, $<110>$ growth is not the most favoured growth in a kinetically controlled system. This has been highlighted in a previous study of Si NWs where $<112>$ NW growth was shown to dominate.$^{33}$ Figure 3 h shows a NW with longitudinal defects which extend to the tip of the NW. The orientation of the twin defects can be clearly seen in this image. Additionally, there are some stacking faults close to the centre of the NW. The
FFT inset shows a pattern which is consistent with a twin defect structure. Figure 3 i is an additional example of a longitudinally faulted NW with a <112> growth direction. The FFT in Figure 3 i indicates that there are periodic stacking faults present (marked on the image by the white arrows) as indicated by the presence of additional reflections. As the FFT suggests, the common plane containing the defects is once again the (111).

In the case of these straight NWs it appears that faults are only present when they originate during nucleation and continue along the entire length of the NW. Faults on the {111} continue longitudinally on NWs with the <112> growth direction, while new faults are continually formed laterally on the {111} planes in the <111> grown NWs. There is no appearance of random angular faults in these type I NWs.

**Figure 5.** SEM analysis of the kinked NWs produced in squalane. (a) Type II NW showing defined $\approx 60^\circ$ angles between growth segments. Type II (b) NW showing multiple turns along the same rotational axis. (c) Highly kinked, type III wormlike NW.
Bulk analysis of the product was performed with Powder XRD (Figure 4) using Cu Kα radiation. The NWs gave peaks corresponding to the (111), (220) and (311) reflections for diamond cubic Ge as expected.

4.4.2 Kinked NW analysis

Figure 5 shows higher magnification SEM images of complex, kinked NWs similar to those presented in Figure 2 b. These wires were observed to make up a large portion of squalane syntheses (see table 1). A type II wire is shown in Figure 5 a with a defined angle of approximately 60° between each of the kinks (offset by a maximum of 3°) resulting in a regular repeating angular geometry. Figure 5 b shows a further type II NW exhibiting extreme kinking, where the NW appears to be bent back on itself. This has resulted from multiple growth direction changes in similar rotational axes. NWs with denser regions on the ends of the NWs are highlighted with arrows in the image. These features could be misconstrued as seeds. However, closer analysis reveals that these areas were actually short, kinked sections. This is further supported by TEM analysis (Figure 6. Tomography was also performed and is available at http://pubs.acs.org/doi/abs/10.1021/cg200510y.
Figure 5c shows a highly kinked, type III, ‘wormlike’ NW where the extreme tortuosity has caused the various segments of the main NW to become intertwined. The type III NW presented here has a diameter ≈ 50 nm, which is consistent with other type III NWs identified throughout the course of this study. TEM analysis allowed the deduction of how these structural features manifest themselves in terms of growth direction changes. Starting with the regular 60° kinked wires (Figure 7a), a change in growth direction from [-112] to [-211] results in an angular distortion (θ = 62°). The defect marked with the dotted line, \( a \), occurs at a projected 60° angle from the [-112] growth direction. At this section of the NW the defect runs longitudinally, which makes it parallel to the [110] direction. While <112> is a more kinetically favourable growth direction in comparison to <110> growth, defects which are neither parallel nor perpendicular
will alleviate less stress than a longitudinal defect. This leads to interplay between the NWs growing along the preferred growth direction and faults forming longitudinally. Faults a and b are parallel to each other as they both occur on the (111) plane. The predominance of projected 60° angles seen in the defect marked b and Figure 7 (a) indicate that NWs tend to switch from one favourable growth direction to another, rather than switching to an unfavourable growth direction. As a result, more angular defects need to form in order to continually remove the stress. Examples of these defects can be seen further in Figure 7 b.

**Figure 7.** TEM images showing kinked NWs. (a) NW with growth direction changing from [-112] to [-2-11] with an evident angle $\theta$ of 118°. (b) Kinked NW with a characteristic 60° bend due to a change in growth direction from [121] to [-112]. (c) A slightly kinked NW with the corresponding SAED (inset) taken along the [1-11] direction showing weak 1/3 type forbidden reflections: (d) and (e) are the corresponding dark field (DF)TEM images from the specific forbidden reflections marked d and e in Figure 4 (c) which highlight specific crystallographic regions.
The observed angles in the NW in Figure 7 (b) can be explained by the cubic nature of Ge where the [-112] and [121] crystallographic planes have an interplanar angle of 60°. The slight discrepancy in the angle from the ideal 60° is consistent with that seen in a previous study on kinked Si NWs where a 2° offset from the ideal angle expected for such a change in growth direction was noted.\(^{38}\) This deviation may be due to a small out of plane component.

Similar changes in growth direction can also be used to explain the nature of the kinking encompassing long straight sections running parallel to each other as seen in Figure 5 b. The abrupt 90° turn of the NW is likely due to the NW changing growth direction from the favoured [112] direction to the unfavoured [1-10] direction. This claim is further strengthened by the short length of this kinked region before a further right angle turn reverts growth to <112> re-establishing preferential growth.

Figure 7 c is a higher magnification of the highlighted section of the Type II NW in Figure 7 b where a more frequent occurrence of defects was investigated through the use of SAED and DFTEM. The kinked area possesses longitudinal faults, however, the short dimension of this region indicates that the favourable growth direction is the dominant factor in determining the morphology of this NW. The SAED pattern (Figure 7 c inset), taken from the kinked NW, which corresponds to the [1-11] zone axis, shows additional reflections at 1/3\{(-224)\}–type positions, which are related to the stacking fault content in this kinked NW. As previously noted by Gibson et al.\(^{39}\) for crystalline Si, a complete diamond cubic unit cell having an AaBbCc stacking sequence, produces diffracted amplitude from each pair of layers that are phase shifted by 120°, resulting in exactly zero intensity at the 1/3 (-224)-type position. However, since a real
specimen may contain $3_{n+1}$ or $3_{n+2}$ layers in some areas, (i.e., a non-integer numbers of unit cells) residual intensity can sometimes be observed at the $1/3(-224)$ position. For the Ge NWs here, the $1/3\{(2-24)\}$-type forbidden reflections present in the diffraction pattern suggests that some of the faulted lamellae have thicknesses that are $3_{n+1}$ or $3_{n+2}$ layers. In the DFTEM micrographs, which were taken from the specific reflections (Figures 7 d and e), the fine brighter regions highlighted along the NW are the faulted bands corresponding to the $3_{n+1}$ or $3_{n+2}$ layers. The appearance of additional reflections is also clearly evident in the FFT and SAED patterns for the longitudinally and laterally faulted NWs presented in Figures 3 and 7, which again can be related to the stacking fault content of the NWs. The noted switching between growth directions is likely facilitated by their larger diameter relative to type I NWs. This may explain why existing research on kinked NWs has largely been conducted on large diameter ($\approx 80$ nm) NWs.\textsuperscript{25}

Type III NWs were also analyzed by HRTEM to investigate if their kinked, worm-like nature could similarly be linked to changes in NW growth direction. Whilst it was observed that NWs with smaller diameters, typically below 35 nm, possessed primarily longitudinal or lateral faults, larger diameter NWs were found to contain more complex, atypical (not parallel or perpendicular) faulting.
Figure 8. TEM images of a torturous ‘wormlike’ NW with (a) faults evident even at low magnification. The inset FFT was taken from the highlighted faulted region. (b) TEM image taken further down the same NW at the <100> growth direction section showing additional faulting. (c) and (d) are higher magnifications of the interface between the <112> and <100> growth area.

The existence of more complex faulting in larger diameter Si NWs has also previously been observed,\textsuperscript{40,41} which is likely to be the case in Ge NWs. In the previous section, large angle kinks were found to be growth direction driven, while small angle kinks were defect driven. The tortuous NW shown in Figure 8 a possesses a <112> and a <100> growth section, however, a higher defect density leads to the formation of a wormlike NW, the shape of which is more likely defect controlled. The highlighted section of the NW, marked in a, consists of a <112> growth section, while the lower portion contains a <100> growth section. As the
NW growth direction switches from <100> to <112>, a large defect free <112> section is formed. This switch also results in the existing stacking faults on the {111} planes becoming longitudinal. Figure 8 b and c show two intersecting faults, one along the [2-1-1] and another along the [211]. The <100> growth section bisects the (111) and (-111) fault planes. The angle between <100> and <112> is 35.7°, which is exactly halfway between the two sets of defects shown (marked angle \( \theta \) in Figure 8 c is 71.4°).

Tortuosity in NWs can occur due to different types of defects. Whilst the example in Figure 8 showed stacking faults occurring in two different {111} planes, Figure 6 shows a type III NW growing along the <110> with a single defect causing a discrete angle change in the NW. A low magnification TEM image of the complex NW with two kinks evident can be seen in Figure 9 a with its <110> growth section highlighted. Again, the faulted areas (a and b) of interest are highlighted and further magnified in Figures 9 b and c. Figure 9 b shows the HR image of the twin faulted region with the indexed FFT insets taken from either side of the fault. The FFTs are both viewed down the [01-1] direction, however, the switching of the (200) and the (111) indexed spots can clearly be seen. Whilst periodic twinning has earlier been observed, like that seen in NW Figure 2 f, this was absent for this NW section.

The single defect is still along the (111) plane, but differs from the earlier nanowires, with the periodic twinning, due to the defect being neither longitudinal nor lateral. The highlighted area in c resembles stacking faults in the region where the NW changes growth direction to <112>. These faults appear to have similar periodicity to those seen in the longitudinally and laterally faulted NWs and this periodicity can be seen in the FFT inset along the (111) plane between the main
spots. However, as this wire is heavily tortuous, this area could equally be a region of inclined twins.  

Figure 9. (a) Torturous NW with highlighted, faulted regions $a$ and $b$ magnified in (b) and (c) respectively. (b) High resolution image of the twinned area with FFT insets taken from either side of the fault. (c) High resolution image of the defected area with the inset FFT taken from the highlighted faulted area showing forbidden reflections as a result of stacking faults or inclined twins.
4.5 Conclusions:

In conclusion, we have analyzed the morphological variation noted in the non-seeded synthesis of Ge NWs grown by the thermal decomposition of DPG in two HBSs. A temperature dependent increase in the degree of NW kinking was noted which was related to the stacking fault content in the NWs. The various NWs were classified into several categories. Type I were divided into three kinds of straight NWs. Type IA were defect free, Type IB possessed lateral faults and Type IC NWs contained longitudinal faults. These mutually exclusive lateral and longitudinal faults were found to be related to faulting on the (111) plane for NWs with <111> and <112> growth directions respectively. Indeed, all of the faults noted in this study occurred on the (111) plane which is the closest packed plane. Kinked and wormlike NWs were differentiated and interplay between preferred NW growth direction and defect orientation was found to dictate the morphology of these NWs. Kinked nanowires (type II) were found to exhibit predominantly growth direction driven, large angle kinks with a small occurrence of defect driven, small angle kinks. Tortuous nanowires (Type III) were observed to have a greater occurrence of complex defect driven, small angle kinks, however, although less common, still possess some growth direction driven, large angle kinks.
4.6 References:


Chapter 5: High Density Germanium Nanowire Growth Directly From Copper Foil by Self Induced Solid Seeding

The contents of this chapter appear in Chemistry of Materials 2011, 23, 4838-4843.

5.1 Abstract

Herein, is described the growth of highly dense Ge NW mats directly on copper foil by a self induced, solid seeded protocol. The existence of Cu₃Ge tips on each of the nanowires indicates that growth proceeds via a solid catalyzed route, dependent on the in situ formation of the germanide intermediate. The nanowires show a tight diameter distribution and typically <110> growth directions resulting from similarities in the d-spacings between the nanowire and the catalyst seed. The nanowires and substrates were characterized using TEM, SEM, XRD, STEM, EDX and EBSD.

5.2 Introduction

Ge NWs have found significant emerging applications spanning the solar, semiconductor and storage industries.¹⁻⁵ The combination of high mobility and large excitonic Bohr radius makes Ge NWs the semiconductor material of choice either for next generation, on-chip gate architectures or as p-n junction absorber arrays in photovoltaics.¹, ² More recently, Ge NWs have shown promise in Li battery anodes due to their ability to withstand volume expansion on lithium insertion coupled with high theoretical capacities (1600 mA h/g) and increased room temperature diffusivity (compared to Si).³ The conventional seeding protocol where a metal nanoparticle forms a eutectic melt with the semiconductor
has several advantages in forming NWs, particularly for discrete applications, as precise control over diameter and in some cases, length is possible.\textsuperscript{4-6} The metal seed acts as a sink for the growth species either as a liquid\textsuperscript{7} (VLS) or as a solid\textsuperscript{8-10} (VSS) with recent work showing that preferred orientations and defects in the metal seed can be transferred to the semiconductor NW.\textsuperscript{11} Recently, metal seeded growth has shifted towards solid catalysts consisting of Cu,\textsuperscript{12} Ni,\textsuperscript{13, 14} and Fe\textsuperscript{15} in an effort to limit the diffusion of metal atoms into the NWs associated with the use of Au, which can severely impact the electrical properties of the NWs.\textsuperscript{16, 17} The emergence of storage and PV applications places new demands on synthetic protocols for Ge NWs, with production directly from the current collector, in high yield and low cost, desirable. In directly seeded growth, high density is difficult to achieve as temperature driven agglomeration can limit the number of catalytic sites available while also leading to a diameter spread in the NWs formed.\textsuperscript{18-20}

The recent emergence of self-catalytic\textsuperscript{15, 21-25} growth systems for Ge NW formation has allowed high yield growth, often from low cost precursors.\textsuperscript{26} Using the correct conditions, spontaneous NW formation with defect free morphologies and tight diameter distributions have been achieved.\textsuperscript{27} Self catalytic approaches (without the direct incorporation of discrete nanoparticle seeds) have also been successfully extended to the formation of Ge NWs directly on Fe\textsuperscript{15}, Ta and W substrates.\textsuperscript{25} The most interesting candidate for NW growth is copper, due to its use as a current collector in lithium ion batteries. While VSS seeding from copper nanocrystals is known, direct growth from bulk copper would be very attractive as it potentially offers a route towards binder free cells at low cost with sufficient gravimetric density for commercial viability.\textsuperscript{28-30}
Here we present the highly dense growth of Ge NWs in a self-catalyzed process through the thermal decomposition of diphenylgermane (DPG) on copper foil in the vapour phase of a high boiling point solvent. The NWs are grown without the incorporation of discrete metal nanoparticles. Rather, we show that the in situ formation of Cu$_3$Ge acts as a catalyst for the formation of extremely dense NW mats with a very low diameter variation. This is the first direct observation of metal germanide tips in a self-induced VSS process from bulk metals, offering important insights into this growth protocol. HRTEM showed both <110> and <112> growth directions in the NWs with the preferential <110> growth directed by the orientation of the in situ generated orthorhombic Cu$_3$Ge nanocrystals.

5.3 Experimental

Substrate preparation and post synthetic treatment.

Cu foil was purchased from Goodfellow ltd. with a 0.25 mm thickness and 99.9 % purity. The Cu was cleaned with 0.1 M nitric acid and rinsed repeatedly with deionized water and then dried before introduction into the reactor setup. After reaction, the NW covered substrates were removed from the reaction flask. The substrates were rinsed with toluene to remove residual HBS and dried under a N$_2$ line prior to characterization.

Reaction setup

Reactions were carried out using a modified procedure to that previously reported.$^{31}$ 5 mL squalene (≥ 98 % Aldrich) was weighed into a custom made Pyrex®, round bottomed flask. The Cu substrate was then placed into the flask which was attached to a Schlenk line setup via a water
condenser. This was then ramped to a temperature of 125 °C using a 3 zone furnace. A vacuum, of at least 100 mTorr, was applied for 1 hour to remove moisture from the system. Following this, the system was purged with Ar (Pureshield BOC Ltd.). The flask was then ramped to the reaction temperature of 425 °C. Once the temperature had stabilized, 0.25 mL of DPG (> 95 % Gelest Inc.) was injected through a septum cap into the system. DPG is known to thermally decompose to germane at temperatures above 380 °C. Thus, germane dissolved in the squalene vapor is the NW monomer source.\textsuperscript{32, 33} A reaction time of 5 minutes was allowed to nucleate and grow the NWs. After which, the furnace was opened and the setup was allowed to cool to room temperature before extracting the NW coated substrate.

Analysis

SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. The Cu foil substrates were untreated prior to SEM analysis. EBSD was carried out at 20 kV and beam current 1.54 nA using an Oxford Instruments Nordlys EBSD detector and HKL Channel 5 software. For TEM analysis, the NWs were removed from the Cu substrates through the use of a sonic bath. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. EDX analysis of the NWs was conducted on Au TEM grids. XRD analysis was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu-K\textsubscript{α} radiation source (\(\lambda=1.5418\ \text{Å}\)) and an X’celerator detector.
5.4 Results and discussion

Figure 1 a shows a schematic of the setup for NW growth. The bulk copper substrate was placed vertically in an elongated round bottomed flask as shown, with squalene as the solvent. 75% of the substrate is above the liquid meniscus and therefore in the vapor phase of the high boiling point solvent during high temperature reflux. Figure 1 b shows a typical post-synthetic substrate from a reaction carried out at 425 °C. Following the reaction, the copper substrate within the vapor phase of the reactor (region I) was found to be a dark brown/purple color. In contrast, the portion of the substrate below the liquid meniscus (region II) was silver colored with a very distinct cut-off line.33 HRSEM (Figure 1 c) confirmed that the distinct coloration in region I was due to high density NW growth which is completely selective to the vapor phase. The NWs can be seen to form in extremely dense meshes which extend over large areas. Here, the NWs were viewed from near the edge of the copper, allowing the underlying substrate to be identified in the foreground of the image. The inset, higher magnification image (i), shows the NWs are untapered along their length and extend to several microns in length. Additional images showing the mat-like nature and high density of the NWs grown directly on the copper are provided in Figure 2. The diameter distribution shown in Figure 1 c, inset (ii) was taken from a count of 100 NWs across different reactions using TEM and shows an average diameter of 13.4 nm and standard deviation of 5.2 nm. Interestingly, outliers with diameters > 25 nm were found to exhibit tortuosity (Figure 3) due to a diameter dependent increase in NW kinking caused by defect driven growth direction changes.27
Figure 1: (a) Schematic outlining the NW growth system used. (b) Typical post synthetic substrate showing the colors which correspond to large scale NW coverage on area I and Cu$_3$Ge layer in area II. (c) SEM image of the highly dense Ge NW mats grown on the Cu substrates. The underlying substrate can be seen in the foreground with inset I showing a higher magnification image of the Ge NW mats. The size distribution of the NWs can be seen in inset II.
Figure 2: Additional SEM images showing the layered nature of the Ge NWs on top of the undulating Cu$_2$Ge surface.

Figure 3: Highly defected, kinked NW with diameter ≈25 nm.
The XRD diffractogram shown in Figure 4, taken from a typical Ge NW covered Cu substrate, is indexed with the expected peaks of Cu, Ge. Interestingly, additional peaks were also observed consistent with Cu$_3$Ge. The Cu peaks, attributed to cubic Cu with space group $Fm\overline{3}m$ and cell parameter 3.6150 Å remain unchanged when compared to the starting Cu substrate (Figure 5). The Ge NWs were found to exist in the diamond cubic form with $Fd\overline{3}m$ space group and cell parameter 5.623 Å. The Cu$_3$Ge was present in orthorhombic form with space group $Pmmn$ and cell parameters $a= 4.578$ Å $b=5.272$ Å and $c= 4.204$ Å. The presence of Cu$_3$Ge on the growth substrates is noteworthy as it suggests that the formation of this alloy is a facilitating step in NW formation. Cu$_3$Ge formation was characterized by XRD in all reactions carried out following this protocol. It was found that the Ge NWs could be removed from the growth substrates by sonication while still retaining the integrity of the Cu$_3$Ge layer.
Figure 4: XRD pattern obtained from postsynthetic, Ge NW covered substrate. The main Ge, Cu$_3$Ge and Cu reflections present have been indexed.

Figure 5: (a) XRD pattern taken from the initial Cu substrate. (b) Indexed XRD pattern obtained from a post-reaction substrate stripped of Ge NWs.
A TEM survey found that each NW possessed a catalyst particle on one end with approximately 95% of the NWs growing along the <110> axis and the remaining 5% showing <112> growth directions. The presence of Cu$_3$Ge tips on the NWs confirms they are formed via a solid seeding mechanism as NW growth was conducted far below the Cu/Ge eutectic point of 644 °C.\textsuperscript{34} The irregular seed geometry observed here has previously been noted for Cu$_3$Ge seeded Ge NWs\textsuperscript{12} and is in contrast to the typically observed, hemispherical seeds for Au seeded NWs.\textsuperscript{32} Upon closer inspection, it was found that the Cu$_3$Ge catalyst seeds had two specific orientations relative to the <110> NWs. The interfacial region between a <110> NW and the Cu$_3$Ge catalyst seed can be seen in Figure 6 a. Inset (i) is an indexed FFT showing spots consistent with the (111) and (2-20) spacings of diamond cubic Ge. The image was taken down the [11-2] zone axis and indicates a <110> growth direction for the NW. The FFT in inset (ii) is indexed for orthorhombic Cu$_3$Ge. In Figure 6 b the NW shows a <110> growth direction and was viewed down the [0-11] zone axis. In both Figures 6 a and b, the heteroepitaxial relationship between the seed and the NW was found to be [100]$_{\text{seed}}$/[110]$_{\text{NW}}$.\textsuperscript{31,32}
Figure 6: HRTEM analysis of Ge NWs showing <110> growth directions. (a). High resolution interface of a Ge NW. The FFT insets i and ii are indexed with spots which correspond to the diamond cubic Ge and the orthorhombic Cu₃Ge seed. (b) Interfacial region of a <110> NW and a Cu₃Ge seed. The indexed FFT insets i and ii correspond to the diamond cubic Ge NW and orthorhombic Cu₃Ge seed respectively. (c) Additional example of <110> NW with lattice resolved NW/seed interface. Inset FFTs i and ii again belong to NW and seed respectively. (d) High resolution interface of NW and Cu₃Ge seed. (e) and (f) HRTEM images of Ge NWs with the less common <112> growth directions. NW in (e) shows longitudinal faults commonly associated with NWs showing <112> growth directions. The interface between the NW and the catalyst seed particle is shown by the dotted line. (f) Perfect single crystal NW with a <112> growth direction.
This relationship is likely facilitated by the similarity of the respective $d$ spacings (0.2289 nm and 0.2000 nm for (200) and (220) of the seed and NW respectively). The other seed/NW relationship noted (Figures 6 c and d) was found to be [001]<sub>seed</sub>/[110]<sub>NW</sub> which is again facilitated by the (002) lattice spacing of Cu$_2$Ge (0.2102 nm) being approximately equal to the (022) spacing of germanium (0.2000 nm). The indexed FFT in Figure 6 c (i) is viewed down the [111] zone axis. FFT (ii) shows that the NW here is orientated to the (001) plane of the Cu$_2$Ge seed. A higher magnification of the interface between a NW and seed with the same orientation is presented in Figure 6 d. NWs with <112> growth directions were found to make up the remaining 5% of the typical product. The scarcity of this growth direction is consistent with previous seeded approaches, giving similar growth direction distributions.\textsuperscript{35, 36} Two high resolution images of <112> NWs can be seen in Figures 6 e and f. Interestingly, the NW in Figure 6 e shows longitudinal faults which continue to the seed. These faults result in a streaking in the inset FFT.\textsuperscript{27} Figure 6 f is a defect free NW with a <112> growth direction. Due to the scarcity of <112> NWs, we were unable to obtain a high resolution image of the NW seed, however, it is likely that the seed orientation is [200]<sub>seed</sub>/[112]<sub>NW</sub> due to the similarity in the $d$ spacings of (400) and (224) (0.1145 nm/ 0.1155 nm respectively). An image of an individual orthorhombic Cu$_3$Ge catalyst tip found at the end of a <110> NW and additional TEM images of NWs showing <110> growth directions can be seen in Figure 7.

SEM analysis of the starting Cu foil and bare post synthetic substrates (Figure 8) showed that the formation of catalytic Cu$_3$Ge leads to substantial roughening of the substrate. The image presented in Figure 9 a was taken at a
70° tilt angle, with tilt compensation, to allow simultaneous EBSD analysis. EBSD point analysis (inset) confirmed that the composition of the entire surface was undulating islands of orthorhombic Cu$_3$Ge. The unindexed EBSD pattern is shown Figure 10. Investigation of the topology and composition of region II of a post-synthetic substrate, as presented in Figure 1b, using SEM and EBSD analysis (Figure 11), showed the formation of more isolated, crystalline Cu$_3$Ge islands on top of the underlying Cu substrate.$^{37}$

**Figure 7:** Lattice resolved image of a Cu$_3$Ge catalyst tip on top of a <110> NW. (b) two NWs with <110> growth directions as shown in the corresponding FFT insets.

**Figure 8:** Representative SEM image of the initial Cu substrates. (b) and (c) are comparative SEM images taken at the same magnification of the pre and post synthetic substrates respectively, showing the increased roughening caused by Cu$_3$Ge formation
Figure 9: (a) Growth substrate after NW removal with inset EBSD pattern confirming that the layer is composed exclusively of Cu$_3$Ge. (b) Dark Cu$_3$Ge island with attached Ge NWs. (c) HRTEM image taken from the highlighted NW in (b) showing the orientation of the $<112>$ NW to the Cu$_3$Ge island. (d) EDX line profile analysis of a single NW showing Ge and Cu signals. The inset STEM image shows the NW analyzed.
Figure 10: EBSD pattern for Cu$_3$Ge taken from a post-synthetic substrate.

Figure 11: SEM image of a reaction substrate conducted at 380 °C showing Cu$_3$Ge island formation on the Cu substrates. Point EBSD analysis confirmed that the flat underlying substrate was composed of cubic Cu (inset i) while the island features present were composed of orthorhombic Cu$_3$Ge (inset ii).

Having confirmed the large scale presence of Cu$_3$Ge as a post synthetic layer on the growth substrates, a sample with dense NW coverage was doctor bladed and placed on a TEM grid to investigate the relationship between the NWs and the catalytic layer. Figure 9 b shows a large region of excised Cu$_3$Ge
with Ge NWs attached. The HRTEM image of the NW in Figure 9c shows the NW growing directly from the Cu$_3$Ge. The inset FFT shows that the NW possesses a <112> growth direction. Line profile EDX analysis conducted on the single NW shown in the STEM image (inset) is presented in Figure 9d. The confinement of Cu to the catalyst tip and non zero Ge signal present (with Cu to Ge ratio of approximately 3:1), again confirms that the tip is composed of Cu$_3$Ge. HRTEM images of a portion of the Cu$_3$Ge layer showed the presence of polycrystalline domains (Figure 12).

**Figure 12:** (a) TEM image of the excised Cu$_3$Ge with the various crystallographic regions separated by the dotted lines. (b) HRTEM image of the individual Cu$_3$Ge region highlighted in (a).

The presence of Cu$_3$Ge tips on the NWs is a clear indicator that a VSS mechanism is responsible for the sub-eutectic growth presented (Cu/Ge eutectic point exists at 644 °C$^{34}$). We have shown that two specific seed orientations are responsible for the <110> grown NWs which is important given the recent interest in the transfer of crystallographic information from solid catalyst seeds to the resultant NWs.$^{11}$ While sub-eutectic, orthorhombic Cu$_3$Ge-catalyzed, Ge NWs have been synthesized from sputtered Cu layers,$^{12}$ our report details the first sub-eutectic growth from bulk Cu. The dominance
of $<110>$ growth is consistent with these previous reports detailing Cu$_3$Ge seeded Ge NWs. However, the self-induced, solid seeding noted here is unique when compared to other Cu seeded approaches as the catalyst seed is an intermediate formed during precursor decomposition on the metal growth substrate. The term ‘self-induced’ refers to the fact that no discrete metal nanoparticles are introduced into the reaction setup at any stage and the Cu$_3$Ge catalyst particles are formed in situ. While NW growth from other metal substrates without the incorporation of discrete metal particles has previously been reported, there appears to be noticeable mechanistic differences from those presented here. Previously, Ge NW growth from bulk Fe substrates via a root seeded mechanism was proposed to be due to the formation of a transition metal rich alloy (Fe$_3$Ge), however, no metal catalyst particles were found on the NWs after removal from the substrate.

Here, the presence of catalytic tips which were unambiguously identified as Cu$_3$Ge on the NWs after removal from the substrate shows that seed sizes of 5 to 40 nm are necessarily formed during decomposition of the DPG in the vapor phase of the organic medium. Although formation of these seeds cannot be identified in situ, the lattice mismatch between the Cu and Cu$_3$Ge is sufficient that the growing Cu$_3$Ge would proceed initially through the formation of isolated catalytic islands which subsequently grow into the polycrystalline Cu$_3$Ge layer noted post-synthesis here and elsewhere. This accommodation of lattice mismatch in 1D systems likely encourages VSS driven, 1-D NW growth parallel to additional Cu$_3$Ge formation on the
substrate. NW diameter is thus determined by the point in Cu$_3$Ge formation where, upon further monomer supply, 1-D Ge growth becomes favored over additional Cu$_3$Ge formation on the substrate. This allows the high density formation of NWs within the critical diameter range noted.

The high density growth of Ge NWs mats directly on a conductive Cu$_3$Ge layer atop a Cu substrate ensures that they are a promising candidate for applications where high density, bound NWs are required, such as Li battery anodes. The intermetallic Cu$_3$Ge, which has excellent electrical properties, has recently been used as an efficient interconnect in Ge NWs transistors, ensuring good electrical contact between the Cu and the Ge NWs here.\textsuperscript{41, 43} While the \textit{in situ} formation of diffusion formed, orthorhombic Cu$_3$Ge at 300 °C has been reported,\textsuperscript{41, 44} ours represents the first report of Cu$_3$Ge formed from the reaction of solid Cu foil and a vapor phase Ge reactant. A similar formation of a catalytic metal germanide layer followed by spontaneous NW nucleation may be possible in other germanide forming metals such as Co and Ni.

\section{5.5 Conclusions}

We have presented the growth of highly dense, crystalline Ge NWs on Cu substrates through a self-induced, solid-seeding process, without the use of discrete metal nanocrystal catalysts. NW growth proceeded on Cu through the spontaneous formation of a catalytic Cu$_3$Ge seeds within a Cu$_3$Ge layer upon exposure to Ge monomer. The layer was thoroughly characterized using EBSD and XRD analysis, and found to be of identical orthorhombic Cu$_3$Ge to that noted on the NW tips, as characterized by TEM and EDX. The NWs formed
were found to exhibit predominantly <110> growth directions and possessed a low diameter spread given the absence of predefined catalyst particles. The seeding process was facilitated by similarities in \(d\) spacings between the orthorhombic \(\text{Cu}_3\text{Ge}\) and the cubic Ge NWs. This report gives an insight into the potential for high quality Ge NW growth from germanide forming metals.
5.6 References:


37. The lack of NW growth in this solution phase of the organic medium is consistent with our previous results, where the boiling point of the medium (385 °C) was insufficient to facilitate NW growth. Reactions conducted at temperatures below 400 °C led to the formation of a homogeneous Cu3Ge layer over the entire substrate.


Chapter 6: High Density Growth of Indium seeded Silicon Nanowires in the Vapor Phase of a High Boiling Point Solvent

The contents of this chapter appear in Chemistry of Materials 2012, ASAP article DOI: 10.1021/cm301023j

6.1 Abstract

Herein, we describe the growth of Si NWs in the vapor phase of an organic solvent medium on various substrates (Si, glass and SS) upon which an indium layer was evaporated. Variation of the reaction time allowed NW length and density to be controlled. The NWs grew via a predominantly root-seeded mechanism with discrete In catalyst seeds formed from the evaporated layer. The NWs and substrates were characterized using TEM, SEM, XRD STEM, EDX and XPS. The suitability of the indium seeded wires as anode components in Li batteries was probed using CV measurements. The route represents a versatile glassware based method for the formation of Si NWs directly on a variety of substrates.

6.2 Introduction

Si NWs have attracted considerable research interest due to their suitability for a wide range of emerging applications from transistor gate channels in the semiconductor industry to high density light trapping antennae in photovoltaics.1-3 More recently, Si NWs have been developed as a viable candidate material for Li ion battery anodes due their ability to withstand the volume expansion associated with Li cycling (not possible in bulk) allowing the
high specific capacity (4200 mAhg\(^{-1}\)) to be exploited.\(^4\) Practical integration of Si NWs in energy conversion and storage applications requires their formation in both high density and at low cost if grid competitive devices are to be realised.

A wide range of metal-catalyzed protocols have been developed in conventional CVD processes which facilitate Si NW growth by VLS or VSS mechanisms.\(^5\)-\(^7\) These reports can largely be divided into three general categories based on the state of the NW catalyst. Type A catalytic materials possess a single eutectic point with high Si solubility (typically > 10 %) and include Ag\(^8\), Al\(^9\) and the archetypal NW catalyst, Au\(^10, 11\). Type B catalysts (e.g. In, Ga)\(^12\) also show one dominant eutectic point, however, the composition is typically < 1 % Si whereas type C catalysts are silicide-forming metals with complex phase diagrams which allow either VLS or VSS growth depending on the reaction temperature.\(^13\) Indium in particular is an attractive type B catalyst for Si NW growth as its melting point, of just 156.6 °C, facilitates low reaction temperatures, while the incorporation of In atoms into the NW lattice can also be used to impart p-type doping.\(^14, 15\) The incorporation of dopants also increase the electrical conductivity of the NWs which can improve their suitability for Li ion cells due to enhanced charge/discharge rates versus their undoped analogues.\(^16\)

While vacuum-based CVD processes allow precise tuning of dimensions,\(^17\) composition\(^18\) and doping of the nanostructures,\(^19\) more recently developed organic solvent based syntheses have gained attention for their potential to produce high density NWs at low cost.\(^20, 21\) The challenge is that the boiling point of conventional solvents provides for a very narrow temperature window (typically < 400 °C), limiting this technique mainly to compound semiconductors which nucleate at lower temperatures.\(^22\) This obstacle can be
overcome by operating within pressurized supercritical fluid systems, or alternatively, by selecting a suitable metal catalyst and conducting the NW growth within a HBS. While Ge NWs can be routinely nucleated in HBS systems, Si NW growth is more difficult and the only success to date involved the use of a highly reactive precursor (trisilane) in the solution portion of HBSs in the presence of Au or Bi particles.

We have recently developed a Ge NW growth system which utilizes the vapor phase of the solvent as the reaction medium to form the NWs, rather than in the HBS solution phase. The system is advantageous as it is amenable to higher temperature growth, with the NWs forming directly on substrates (placed in the vapor zone), at higher temperatures than in solution in a thermally localizable process. Here, we show that this HBS vapor system can be adapted to allow controlled growth of Si NWs directly on various substrates through the use of an evaporated, catalytic In layer. The method represents a simple, glassware based approach for the formation of Si NWs which exploits the in situ formation of discrete In seeds from the low melting point metal layer. The growth method allows good control over the length of the NWs from 1-5 µm. Through CV measurements, both the Si NWs and the oxidised In (In$_2$O$_3$) are shown to cycle Li, highlighting the potential of these nanostructures as a hybrid composite where the catalyst is actively involved in the subsequent device.
6.3 Experimental

Substrate preparation and post synthetic treatment

In substrates we prepared by evaporating 99.999 % In (Kurt J. Lesker Company) in a glovebox-based evaporation unit. The nominal In film thicknesses investigated were between 5 and 100 nm. Optimal growth was achieved for In thicknesses of between 20 and 30 nm. The substrates were stored in an Ar glovebox (< 0.1 ppm O₂ and H₂O) prior to reactions and contact with O₂ was minimized. After synthesis, the substrates were simply rinsed with toluene, to remove excess HBS, and dried using a nitrogen line. No additional cleaning steps were required.

Reaction setup

Reactions were carried out in custom made Pyrex®, round-bottomed flasks. The growth substrates were placed vertically in the flask which was attached to a Schlenk line setup via a water condenser. This was then ramped to a temperature of 125 °C using a 3 zone furnace. A vacuum, of at least 100 mTorr, was applied for 1 hour to remove moisture from the system. Following this, the system was purged with a constant flow of pure shield Ar (BOC Ltd.). The flask was then ramped to the reaction temperature. Reactions were conducted at 450 °C. At the correct reaction temperature, between 2.0 x10⁻³ moles and 6.0x10⁻³ moles of the liquid precursor PS (97 % Aldrich Ltd.) was injected through a septum cap into the system. Various reaction times were investigated. To terminate the reaction, the furnace was opened and the setup was allowed to cool to room temperature before extracting the NW coated
substrates.

**Analysis**

SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. The In substrates were untreated prior to SEM analysis. For TEM analysis, the NWs were removed from the growth substrates through the use of a sonic bath. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. EDX analysis of the NWs was conducted on Au TEM grids. XRD analysis was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu-Kα radiation source (\( \lambda = 1.5418 \) Å) and an X’celerator detector. XPS was performed by Dr. Fathim Laffir (MSSI) in a Kratos AXIS 165 spectrometer using monochromatic Al Kα radiation of energy 1486.6 eV. C 1s at 284.8 eV was used as the charge reference to determine core level binding energies. For construction and fitting of synthetic peaks of high resolution spectra, a mixed Gaussian-Lorenzian function with a Shirley-type background subtraction were used.

**Electrochemical measurements**

The electrochemical performance was evaluated by assembling two electrode split flat cells in an Ar filled glovebox. The cells consisted of In seeded Si NWs or a 20 nm evaporated layer of In on SS substrates as the working electrode, lithium foil as the counter and reference electrode, a porous polyethene separator, and an electrolyte solution of 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 v/v). The CV measurements were carried out using an Autolab PGSTAT100 at a scan rate of 0.5 mV/s in the potential range of 0.01V - 1.5V versus Li/Li⁺.
6.4 Results and discussion:

Figure 1 a shows a schematic of the reaction set up where In (20 nm layer) coated substrates were placed into the reaction flask with the growth area in the vapor portion of the solvent system (squalane, 450 °C). SEM analysis Figure 1 b shows high density wire growth directly from the Si substrate with an average diameter of approximately 50 nm seeding from larger In particles of ~ 200 nm. The TEM image in Figure 1 c further confirms the seed/wire diameter ratios of 4:1 with the crystalline nature of the Si NWs evident from lattice fringing. The average In seed to NW diameter ratio was 3.6 with a standard deviation of 0.4. (Figure 2 a). The mean NW diameter was 54.6 nm with a standard deviation of 19.8 nm (Figure 2b). Measurements were taken at the interface between the In seed and the Si NW to avoid the impact of any tapering.

Figure 1: (a) Schematic illustrating the synthetic methodology undertaken for Si NW growth. (b) SEM image of Si NWs. The In seeds can be seen to have larger diameters than the corresponding NWs. (c) TEM image highlighting the Si NW and In catalyst.(d) High resolution image of a crystalline Si NW.
Figure 2: a) Size distribution taken from 150 NWs. b) Measure of the ratio of the In catalyst particle to the resultant Si NW.

Figure 3: SEM images showing Si NW aspect ratio and density variation. a) Short Si NWs with lengths < 1 µm with higher magnification image inset. b) Longer Si NWs (up to 5 µm in length) grown in 30 minutes with higher magnification image inset. c) Higher density NWs grown in 1 hour with higher magnification inset.
The lengths and density of the Si NWs formed on the substrate could be controllably altered by modifying the reaction dwell time as shown in Figure 3. Initially, 5 minute reactions were investigated with a $6 \times 10^{-3}$ moles PS concentration, leading to the formation of straight NWs with lengths between 0.5 and 1 micron lengths with relatively low size polydispersity (Figure 3 a and inset). An increase of reaction time to 30 minutes, increased the density and the average NW length to ~ 5 µm (Figure 3 b. Notably when the aspect ratios increased above 25, the wires showed an increase in growth defects and directional changes leading to an intertwined mesh. Further increases in reaction time (Figure 3 c) correlated with greater densification for this mesh that can be attributed both to additional nucleation events (unreacted metal particles are evident after short reaction times inset Figure 3 a or further elongation.

Figure 4 a shows a discrete Si NW with a 42 nm crystalline core and thin (circa 2 nm) oxide coverage with growth occurring in the $<111>$ direction (Figure 4 a, inset) Although this represented the dominant growth direction, NWs were also identified with a $<112>$ growth directions as in Figure 4 b with inset FFT. Although this wire had a smaller diameter (35 nm) further analysis determined that both $<111>$ and $<112>$ growth directions occurred independent of NW diameter (Figure 5). HRTEM images, Figure 4 c-d, show that the NWs tend to taper over 60 nm as NW growth is terminated. Growth defects are evident in the HRTEM images and further HRTEM analysis showed evidence of stacking faults commonly observed in Si and Ge NW systems (Figure 6).[28-31]
Figure 4: a) HRTEM image showing the NWs <111> growth direction as indicated by the inset FFT. b) HRTEM image with inset FFT showing a <112> growth direction. In both a) and b) the thin surface oxide (between 1 and 2 nm) can be seen. c) TEM image showing the tapered tip of a Si NW. d) HRTEM image (and inset FFT) taken from the tip of the NW showing the consistent <111> growth direction to the end.

Typically, these defects will occur on the {111} planes for these diamond cubic crystals, manifesting as lateral faults in NWs possessing <111> growth direction and longitudinal faults in NWs with <112> growth directions.
Figure 5: Additional HRTEM images showing the mixture of NWs with $<111>$ and $<112>$ growth directions.

Figure 6: HRTEM images of three defected Si NWs.
Figure 7: DF-STEM images taken from a bundle of Si NWs. (a) DF-STEM of a bundle of NWs. The In seeds can be seen as the bright white spheres due to their increased Z contrast. (b) Higher magnification of the highlighted NW seen in (a) showing the growth of a smaller, secondary Si NW segment. (c) Additional DF-STEM image of a branched Si NW with bright In clusters clearly visible. (d) DF-STEM taken from the tip of a Si NW showing a bright In area. (e) Corresponding EDX line profile taken from d showing the localization of In to the tip.

DF-STEM (Figure 7) was found to be a useful technique to exploit the Z contrast difference between In and Si for investigating the role of In in NW catalysis. The bundle of NWs shown in Figure 7 a was removed from a post reaction substrate by sonication. Again, large In particles with diameters between 2.5 and 4 times the diameter of the resultant NWs were noted. Higher magnification images of the three highlighted NW portions in a) are presented in Figure 7 b-d. The NW in b) has a narrow secondary branch grown from the main NW. This can be seen to be due to a small In particle at the interface between the two NWs. This secondary growth may have been caused by In migration along the NW during growth or by In from the substrate coming into contact with the growing NW. This highlights the potential for forming more complex, branched Si NW structures through the use of In catalysis. Smaller In particles below ~ 30 nm (like that noted on the branched structure here) were found to induce the
growth of NWs with diameters closer to the catalyst size. The thin Si oxide coating (circa 2 nm) on the NWs is consistent with the XPS analysis. An additional branched Si NW structure with multiple small regions of In can be seen in Figure 7 c. The branching did not appear to follow any regular pattern suggesting that each branch was not crystallographically aligned with the host wire. Interestingly, a NW possessing symmetrical indium tips is highlighted in Figure 7 d suggests the possibility of root and tip growth co-existence in a small number of the NWs. A line profile taken from the NW in d confirms the dumbbell structure of metal-semiconductor metal.

**Figure 8:** SE-STEM images taken from In seed. a) SE-STEM Image of an In seed with primary (i) and secondary (ii) Si NW growth. b) STEM image taken from the end of a Si NW with the In tip removed by sonication. (c) HRTEM image of the same NW with the In area clearly visible at the NW tip with the inset FFTs highlighted for Si section. (d) HRTEM image of the interface between Si and In showing the remnants of the NW/seed interface.
Secondary electron STEM (SE-STEM) images collected from the Si/In seed interface are shown in Figure 8. In comparison to DF-STEM, SE-STEM allowed clearer identification of the In/Si interface as it was not as sensitive to the Z difference between In and Si. The large In particle in Figure 8a can be seen to be responsible for the growth of the main NW and also for the shorter secondary NWs. Where multiple NWs were grown from individual In seeds, the main NW had a much larger diameter than the multiple, shorter secondary NWs. The prevalence of multiple NW growth from individual In seeds was noticeably higher in longer reaction times as the additional time facilitated additional Si NW nucleation events from the In seed. Upon increasing the sonication time for the NWs to one hour, it was found that the large In catalyst tips could be fragmented and almost entirely removed from the NW. The STEM image in Figure 8b shows the end of a Si NW from which the In has been almost entirely removed with only residual In on the NW can be seen as bright regions. This concomitant decrease in the volume of In allowed atomic lattice resolved HRTEM images of both the NW and interface (Figure 8c). The difference in contrast between the Si NW and dark In region is clearly evident. The inset FFT (i) is indexed with spots which correspond to the spacings for cubic Si. The Moiré fringes seen in In region of Figure 8d prevented indexing. However, an example of an elemental line scan taken from a similar In/Si confirmed the presence of In (Figure 9).
Figure 9: a) STEM image of a In/Si interface showing the contrast difference. b) HRTEM image of the interface with inset FFTs showing the cubic of the NW and tetragonal In catalyst particle. c) Elemental line profile taken along the direction of the NW shown in a).
Si NW growth using In catalysis was found to be independent of the underlying substrate material with successful formation on Si, glass and SS steel. XRD analysis of the NWs grown on glass gave reflections consistent with the (011), (002), (110), (112), (020) and (121) spacings for tetragonal In, (111) for cubic Si and the (222) reflection for In$_2$O$_3$ (Figure 10 a). The presence of In$_2$O$_3$ is likely due to the partial oxidation of some of the catalytic In after removal from the reaction flask as the pre reaction substrate showed no sign of oxidation (Figure 9 b).

**Figure 10:** a) XRD diffractogram obtained from a post-synthetic reaction on a glass substrate with reflections for cubic Si, cubic In$_2$O$_3$ and tetragonal In. b) XRD diffractogram of the as deposited In layer on glass showing the (011) reflection for tetragonal In.
Figure 11: a),b) SEM images of the Si NWs grown on SS. C) EDX profile obtained from the post-synthetic substrate with a large Si signal from the NWs, In from the catalyst particles and Fe, Ni, and Cr from the underlying stainless steel.

Figure 12: a) XPS analysis for In showing the 3d peak at 443.8 eV. The prominent shoulder to the principle peak may be assigned to In$_2$O$_3$.b) XPS analysis of the Si NWs showing the characteristic Si peak centred at approximately $\approx$ 99 eV and the broader SiO$_2$ peak at $\approx$103 eV.
Si NW growth on SS was done to show the suitability of the NWs for Li ion cells and to allow XPS analysis. SEM analysis showed that the Si NWs grown on SS were similar to those grown from the Si substrates (Figure 11). XPS was used to investigate the Si NW surface chemistry and oxidation of the In catalyst as noted in the postsynthetic XRD diffractogram. For In (Figure 12 a) the 3d peak at 443.8 eV is characteristic of metallic In. The prominent shoulder to the principle peak may be assigned to In$_2$O$_3$ which is consistent with the XRD analysis. The resultant analysis for Si (Figure 12 b) confirmed the presence of SiO$_2$ and a small portion of sub-oxide SiO$_x$ on the NW surface.

To investigate the potential of the Si NWs as a suitable anode material for next generation Li ion batteries, a two electrode test cell was assembled using the as grown Si NWs on stainless steel as the anode and Li metal as the cathode. CV measurements were carried out to study the electrode reaction processes occurring during charging and discharging. In order to distinguish between the peaks associated with the lithiation/delithiation of Si and the lithiation/delithiation of In, a second two electrode test cell was assembled with a 20 nm evaporated layer of In on SS as the anode and Li metal as the cathode. Figure 13 a shows a CV of the In layer on stainless steel overlaid with a typical CV of the Si NWs on stainless steel. The cathodic branch of the In CV has two peaks at 0.54 V and 0.42 V which are due to the alloying of Li with In, where each peak is a result of the formation of a different Li$_x$In phase. Two corresponding oxidation peaks exist in the anodic branch at 0.48 V and 0.68 V which are due to the dealloying reaction. These peaks also exist in the CV of the In seeded Si NWs, which are evidence of the fact that that the In seeds play an active role in the charge and discharge
Figure 13: (a) CV curves of In seeded Si NWs on SS and of a 20nm layer of In on SS at a scan rate of 0.5 mV/s in the voltage range of 0.01-1.5V vs Li/Li+. (b) The first three CV curves of In seeded Si NWs on stainless steel using the same scan rate and voltage range as (a).

processes of the electrode. The shape of the CV curve is consistent with results for In previously reported by Yang et al.\textsuperscript{35}

The In seeded Si NW CV in Figure 13 a shows additional peaks to the In CV which are due to the lithiation and delithiation of Si. The charge current associated with the alloying reactions of Li with Si occurs below 0.35 V. The peaks at 0.33 V and 0.18 V and the rapid increase in charge current below 0.10 V are due to the formation of amorphous Li\textsubscript{x}Si phases.\textsuperscript{36} Two oxidation peaks are
observed at 0.32 V and 0.43 V in the anodic branch which corresponds to the reverse of this process. The shape of the section of the curve relating to the alloying and dealloying of Li with Si is comparable with previous studies carried out on Si electrodes.\textsuperscript{4,37,38} Figure 13 b shows a CV of the first three cycles of the Si NW electrode. The magnitude of the current peaks associated with charging and discharging grow with each cycle due to an activation phenomenon caused by the gradual breakdown of the crystalline Si structure with each cycle which activates more of the material to react with lithium.\textsuperscript{37} The cathodic peaks at 0.33 V and 0.18 V do not appear in the first cycle but evolve with subsequent cycles due to this phenomenon and are the result of the formation of a series of Li-Si phases.\textsuperscript{39}

6.5 Conclusions

In conclusion, we have shown the direct growth of high density Si NWs in a HBS medium from a catalytic In layer. The route represents a convenient means of growing crystalline Si NWs on a variety of device suitable substrates (e.g., SS for Li ion anodes) and is the first time that Si NWs have been grown on substrates \textit{via} a simple glassware based, HBS approach. The growth occurs by a root seeded mechanism and allows optimal control of NW length as a function of growth time. The Si delivery method within a HBS vapor offers a viable low cost alternative to established approaches and is amenable to scalable device application. We show that the In seeded Si wires are viable hybrid composite anode materials for Li ion batteries offering potential for even higher capacities due to the combined catalyst and Si charging.
6.6 References


Chapter 7: Growth of Cu$_{15}$Si$_4$ NWs from bulk Cu using *in situ* Formed Silane Vapor

7.1 Abstract

Here, we report the formation of Cu$_{15}$Si$_4$ NWs using a simple HBS based method. The reactions were carried out using Cu foil substrates as the Cu source with NW growth dependent upon the prior formation of Cu$_{15}$Si$_4$ crystallites on the surface. The high diffusivity of Cu in Si was proposed to result in the growth of compositionally homogenous silicide nanowires in high yields on the substrates. The method shows that simple Si delivery to metal foil can be used to grow high densities of nanowires with a tight diameter spread at reaction temperatures of 460 °C.

7.2 Introduction

Metal silicide NWs have attracted considerable research attention due to their low resistivities, which make them well suited for use as interconnects and gate materials in nanoelectronic devices.$^1$ To date, a variety of metal silicide NWs have been formed including NiSi$_2$,$^2$FeSi$_3$ and CoSi$_4$. The wide range of stoichiometries achievable within silicide NWs is evident in the well studied Ni/Si system where NWs of six different phases have been produced.$^5,7$ The first reported synthesis of silicide NWs was achieved by evaporating a Ni layer onto a pre-formed Si NW backbone, which upon annealing, led to the formation of a Ni silicide NW.$^8$ Silicide NWs have since been formed by the co-delivery of metal and Si atoms to substrates,$^9,10$ through the interaction of a metal flux with Si substrates$^{11}$and by the reaction of a Si flux with metal foil.$^5$ Of these subsets, the
latter is a particularly interesting route due to its compatibility with Si CVD processing.\textsuperscript{12} However, to date this method has only been shown to allow the formation of Ni silicide NWs.\textsuperscript{13,14} This is often attributed to the high diffusivity of Ni in Si which may explain why this method has not been examined for alternative metal foils.\textsuperscript{15}

Cu silicides are an extremely promising material set which offer potential in catalytic application and as interconnect materials.\textsuperscript{16-18} Cu silicide thin films are well studied and have been highlighted for use as Cu ion diffusion barriers and as passivation layers for on chip applications.\textsuperscript{19,20} Despite the widespread interest in Cu silicide thin films and the well studied diffusivity of Cu in Si,\textsuperscript{19,21-23} Cu silicide nanostructures have been only been sporadically examined. Cu powder evaporation has been used to form nanotriangles, nanosquares and short NWs of Cu\textsubscript{3}Si with and without the presence of an Au catalyst.\textsuperscript{16,24}

The formation of a variety of NWs in the absence of pre-formed catalyst particles has recently been detailed. These papers have primarily been concerned with the growth of elemental semiconductors (i.e., Si and Ge) from solid metal catalysts which require the prior formation of a reactive germanide\textsuperscript{25,26} or silicide\textsuperscript{27,28} phase. Conversely, silicide NW formation methods are typically carried out without defined catalyst particles, and as a result, are less understood than NW growth methods reliant on the well established VLS or VSS protocols.\textsuperscript{29-32}

Here we present the growth of Cu\textsubscript{15}Si\textsubscript{4} NWs through the delivery of Si to bulk copper foil using a simple glassware based approach. The Si flux required for growth was formed by thermally decomposing PS in a HBS medium. The use of HBS media for NW growth has recently been shown to allow reaction
temperatures of over 400 °C which are suitable for the growth of silicide NWs.\textsuperscript{33-36} The method allows the growth of large arrays of NWs with a low diameter spread. The NWs were shown to nucleate from underlying, \textit{in situ} formed Cu\textsubscript{15}Si\textsubscript{4} crystallites which were a prerequisite for anisotropic growth. The report represents the first growth of Cu silicide NWs through the delivery of a Si vapour to a metal foil.

7.3 Experimental:

\textbf{Substrate preparation and reaction setup}

Cu foil was purchased from Goodfellow Ltd. with a 0.25 mm thickness and 99.9 % purity. The Cu was cleaned with 0.1 M nitric acid and rinsed repeatedly with deionized water and then dried before introduction into the reactor setup. After reaction, the NW covered substrates were removed from the reaction flask. The substrates were rinsed with toluene to remove residual HBS and dried under a N\textsubscript{2} (Pureshield BOC Ltd.) line prior to characterization.

Reactions were carried out in custom made Pyrex\textsuperscript{®}, round-bottomed flasks. The Cu growth substrates were placed vertically in the 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 3 zone furnace. A vacuum, of at least 100 mTorr, was applied for 1 hour to remove moisture from the system. Following this, the system was purged with Ar (Pureshield BOC Ltd.). The flask was then ramped to the reaction temperature. Reactions were conducted at 460 °C. Upon reaching the reaction temperature, 0.5 mL (4.06 x 10\textsuperscript{-3} moles) PS (Aldrich Ltd.). Reaction times of 10 minutes and 30 minutes were investigated. To terminate the reaction, the furnace was opened and the setup was allowed to
cool to room temperature before extracting the NW coated substrates.

**Analysis**

SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. The Cu substrates were untreated prior to SEM analysis. For TEM analysis, the NWs were removed from the growth substrates through the use of a sonic bath. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. EDX analysis of the NWs was conducted on Au TEM grids. XRD analysis was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu-Kα radiation source (λ = 1.5418 Å) and an X’celerator detector. XPS was performed by Dr Fathim Laffir (MSSI) in a Kratos AXIS 165 spectrometer using monochromatic Al Kα radiation of energy 1486.6 eV. High resolution spectra were taken at fixed pass energy of 20 eV. Binding energies were determined using C 1s peak at 284.8 eV as charge reference. For construction and fitting of synthetic peaks of high resolution spectra, a mixed Gaussian-Lorenzian function with a Shirley-type background subtraction were used.
7.4 Results and discussion:

30 minute reaction times were initially carried within the HBS growth system with SEM analysis of the substrate showing dense NW formation across large areas (see Figure 1 a where the NW growth extends over at least 100 µm). The NWs were found to be extremely consistent in diameter given the absence of defined metal catalyst particles. The NWs possessed an average diameter of 108 nm with a standard deviation of 9 nm and were untapered along their lengths (Figure 2). The substrates post synthesis were a grey/brown colour and were obviously altered from the starting Cu foil substrates (Figure 3).

**Figure 1:** a) SEM image showing the large area coverage of the Cu$_{1.5}$Si$_4$ NWs. b) Higher magnification image of the NWs showing the consistent NW diameters.
Figure 2: Diameter distribution taken from a count of 75 NWs

Figure 3: Cu$_{15}$Si$_4$ NW covered substrate post-synthesis
Figure 4: SEM image of a Cu$_{15}$Si$_4$ NW taken on an lacey carbon TEM grid with inset EBSD pattern indexed for the cubic Cu$_{15}$Si$_4$ phase. b) Illustration of the Cu$_{15}$Si$_4$ NWs grown from the underlying crystallites. c) SEM of a portion of the underlying crystalline material with inset EBSD analysis again indicating the Cu$_{15}$Si$_4$ phase. d) XRD pattern taken from a NW covered substrate with the marked reflections corresponding to # Cu$_{15}$Si$_4$ *Cu$_{0.83}$Si$_{0.17}$ and Cu.

EBSD analysis was performed on single NWs mounted on a Au TEM grid. In Figure 4 a, an individual NW across the supporting lace can be seen. The inset EBSD pattern shows that the NW gave a pattern which was consistent with that expected for cubic Cu$_{15}$Si$_4$ with space group I-43d. All the NWs analyzed using this technique indicated that this phase was exclusively present in the sample (see Figure 5 for additional examples).
**Figure 5:** EBSD analysis of additional NWs confirming the presence of exclusively the Cu$_{13}$Si$_4$ phase

**Figure 6:** Cu foil prior to NW growth.
The image in Figure 4 b was taken at a 70° tilt and gives a clearer illustration of the faceted substrate material from which the NWs were grown. This appearance of crystallites across the substrate surface was visibly different from the pristine Cu observed prior to the reaction (Figure 6). EBSD analysis of the substrate (Figure 4 c) gave patterns which indicated the presence of solely Cu$_{15}$Si$_4$ on the surface. XRD analysis (Figure 4 d) of the NW covered substrate gave reflections consistent with the presence of Cu$_{15}$Si$_4$ (indexed with a #), Cu$_{0.83}$Si$_{0.17}$ (indexed with a *) and Cu. The appearance of reflections consistent with Cu$_{0.83}$Si$_{0.17}$ was not expected given that both the NWs and the crystalline material from which they emanate had been shown to be Cu$_{15}$Si$_4$. It is likely that this additional Cu rich phase was present underneath the Cu$_{15}$Si$_4$ crystallites observed. This can be explained by the complex nature of the Cu/Si phase diagram$^{37}$ and also the variety of phases which have been found to exist for other transition metal silicides.$^{14,38,39}$

Figure 7: TEM analysis of a single Cu$_{15}$Si$_4$ NW. a) low magnification image of the NW with $<111>$ growth direction marked on the NW. The inset area is magnified in the HRTEM image in b) showing the crystallinity of the NW. The inset selected area electron diffraction pattern is indexed for the cubic Cu$_{15}$Si$_4$ phase
Furthermore, it has previously been shown that upon annealing, Cu silicide phases will tend to form Cu rich phases by a Si diffusion based reaction.\textsuperscript{40}

TEM analysis was also performed on the NWs. The low resolution TEM image in Figure 7a shows a single NW with a diameter of approximately 98 nm. The $<111>$ growth direction is marked on the NW. A HRTEM image taken from the marked area in a) is shown in b). A \textit{circa} 3 nm amorphous coating can be seen at the extremity of the NW with the 2-D lattice fringes of the crystalline NW clearly evident. The selected area electron diffraction pattern (inset) is indexed with spots which correspond to the spacings for Cu$_{15}$Si$_4$ with space group I-43d. The indexed pattern was used to determine the $<111>$ growth direction.

XPS was performed to examine the chemistry of the copper silicide NWs. A low-resolution survey spectrum identified the presence of Cu, Si O and C. High resolution spectra of Cu $2p$ and Si $2p$ were measured to determine the chemical states of the elements. The Cu $2p$ spectrum is shown in Figure 8a and appears as a narrow doublet peak with $2p_{3/2}$ at 933.3 eV and $2p_{1/2}$ at 953.2 eV. It is clear from

![Figure 8: High resolution XPS spectrum of (a) Cu 2p and (b) Si 2p of Cu$_{15}$Si$_4$ NWs](image-url)
the absence of satellite peaks that copper (II) oxide is not present. The peaks can be assigned to copper silicide or copper (I) oxide whose binding energies are very close.\textsuperscript{41-43} However, due to evidence from the XRD and EBSD for silicidation and the narrow FWHM (full width at half maximum of peak) it is possible to assign the peak to a single compound of copper silicide. The high resolution Si 2\textit{p} spectrum is shown in Figure 8 b. The spectra can be fitted with three sets of doublets. The narrow doublet peaks with 2\textit{p}_3/2 at 99.6 eV can be assigned to silicide.\textsuperscript{42, 43} The two sets of doublets at higher binding energies 101.5 eV and 102.5 eV, also supported by the presence of O are indicative of surface oxidation of the silicide NWs and can be assigned to Si-O\textsubscript{x} (x <2) and SiO\textsubscript{2} respectively.

\textbf{Figure 9:} a) SEM image showing an area of lower NW density and the underlying substrate material. b) Higher magnification SEM image showing the interesting geometry of the NWs. c) SEM image of the slightly undulating surface of the NWs.
In areas of more sporadic NW coverage, the growth of the NWs from the underlying substrate could be more easily examined. In Figure 9 a a large number of distinct pockets of NW growth can clearly be identified. In Figure 9 b it can be seen that the NWs are growing from the underlying crystalline material at defined angles. The growth is reminiscent of tetrapods which have been observed in a number of nanocrystal systems (Figure 10 and 11 for TEM and annular dark field STEM, respectively).\textsuperscript{44-46}

![Figure 10: TEM image of a NW showing three fold geometry.](image-url)
For the widely studied CdSe tetrapod system, the unique shape occurs due to the presence of a zinc blende nucleus with wurtzite arms growing from this central region.\textsuperscript{47, 48} Here, the NWs and the underlying crystallites are of the same cubic phase. In Figure 7 it was shown that the NWs possess $<111>$ growth directions. This suggests that the NWs which exhibit the tetrapod like geometry are growing from the (111) faces of the underlying crystallites. Ge NWs (which also possess a cubic crystal structure) were previously shown to grow epitaxially with $<111>$ growth directions from underlying Ge microcrystals in a similar vein.\textsuperscript{49} In Figure 9 c the SEM image shown was taken at a 70° to allow the NWs growing vertically from the underlying substrate to be identified.
Shorter reaction times (10 minutes) were carried out in an effort to investigate the start of NW nucleation. As previously noted, the NWs grew in high density (Figure 12 a). However, the NWs were noticeably shorter than those previously observed with an average length of approximately 1 µm. The 70° tilted image presented in Figure 6 b shows the orientation of the portion of the NWs which were growing vertically from the substrate. Again, the extremely tight NW diameter is visible. The tetrapod like geometry of the NWs, visible only in the more sporadic areas for the longer NWs (Figure 9), could more clearly be seen (Figure 12 c. The higher magnification image in Figure 12 d shows that the NWs are growing directly from the underlying crystallites.
Figure 13: Schematic of the growth mechanism. a) Si is supplied to the Cu foil substrate upon the decomposition of PS. b) Stranski-Krastanov style growth of a Cu$_{15}$Si$_4$ layer plus discrete islands is allowed by the high diffusivity of Cu in Si. c) Continued Si supply allows the formation of Cu$_{15}$Si$_4$ NWs from nucleation sites on the crystallites.

When considering the growth mechanism for the Cu$_{15}$Si$_4$ NWs in this report, there are noticeable parallels with the mechanisms proposed for the growth of the Ni silicide NWs.$^{14, 38}$ There, the formation of Ni silicide crystallites was assumed to be a prerequisite for NW growth. Here, through the use of EBSD analysis, we have shown the NWs grow directly from crystallites of the same Cu silicide phase as the resultant NWs. The decomposition of PS within the vapour phase of the HBS allows the formation of Cu$_{15}$Si$_4$ crystallites on the substrate from the reaction of the silane vapour with the Cu foil. Continued Si flux then results in the formation of single crystalline NWs from nucleation sites on the crystallites, with the continued formation of Cu silicide NWs rather than elemental Si driven by the high diffusivity of Cu in Si.$^{19}$ The compositional
homogeneity along the NWs as they grow from the underlying silicide phase proves that Cu is actively diffusing from the underlying substrate into the structures. The growth of the tetrapod structures is likely caused by the orientation of the underlying crystallites. The Cu$_{15}$Si$_4$ formation on the substrate appears to proceed via a Stransky-Krastanov type growth,$^{50}$ with discrete island formation on top of the Cu$_{15}$Si$_4$ layer underlying layer (as identified by EBSD in Figure 4c). The proposed NW growth mechanism is illustrated schematically in Figure 13.

The preference for growth of 1-D structures rather than continued bulk crystal formation has widely been linked to the existence of a time point in the reaction where the vapour supersaturation level decreases, such that anisotropic growth is favoured rather than addition to limited surface nucleation points.$^{14, 38, 51-53}$ In the context of the single injection protocol employed here, it is logical that bulk crystallite growth should occur at the initial stage of the reaction where the Si concentration is at its highest. As the silane is consumed by the reaction with the Cu foil, the supersaturation drops such that NW growth is favoured over continued bulk growth. As a result, the use of a single precursor introduction is a convenient means of attaining the supersaturation profile required for NW growth. This system may facilitate the growth of silicide NWs from alternative metals which are known to diffuse within Si (e.g., Fe$^{54}$ Ti$^{55}$ and Cr$^{56}$) which have not been grown by Si delivery to metal foils.
7.5 Conclusions:

In conclusion, we have presented the growth of Cu$_{15}$Si$_4$ NWs from bulk Cu foil for the first time. This method shows that silicide NW formation by simple Si transport is achievable on bulk foils other than Ni. The method was conducted within the vapour phase of a HBS medium, which is a flexible Si delivery system for various Si nanostructure growth. The growth mechanism was dependent on the prior formation of Cu$_{15}$Si$_4$ crystallites, from which the NWs nucleated. The orientation of the NWs from the underlying crystallites was examined, and it was found that the NWs possessed <111> growth directions. The simplicity of the growth system suggests that alternative metal foils may be used to induce the growth of silicide NWs.
7.6 References:


Chapter 8: Conclusions and recommendations for further study

8.1 Overall conclusions
The HBS solvent system developed in this thesis allowed the formation of various Ge and Si NWs directly on substrates. The system represents an intermediate system between classic solution based approaches (which are not suited to substrate based growth) and CVD systems (which allow substrate growth but can be prohibitively expensive). It was illustrated throughout this thesis that the system is particularly suited to the growth of high density NWs directly on technologically relevant substrates (e.g., ITO, Si, Cu and SS) which should ease integration into high density applications.

General conclusions will be divided into those for chapters 3 and 4 (self-seeded Ge NW growth and characterization), chapter 5 (Cu$_3$Ge-seeded Ge NWs), chapter 6 (In-seeded Si NWs) and chapter 7 (Cu$_{15}$Si$_4$ NWs grown from copper). Some recommendations for further study will then be provided.

8.1.1 Conclusions from Chapters 3&4
These chapters detail the growth and morphology of self-catalyzed Ge NWs formed using the newly developed HBS vapor approach. The system was shown to allow the formation of Ge NWs directly on various non-catalytic substrates (Pyrex®, quartz and ITO). In chapter 3, the NWs were confirmed to be Ge of diamond cubic phase with $<111>$ and $<112>$ growth directions and no apparent catalyst tips noted. The NWs also possessed narrow diameters given the absence of discrete nanoparticle seeds. The growth of NWs was also achieved perpendicularly in high yield from ITO substrates.
In chapter 4, the defect content and morphologies of the NWs presented in chapter 3 were analyzed. It was observed that the defect content and percentage of kinked NWs within the sample could be increased by switching the solvent from squalene to squalane (with an associated reaction temperature increase required for the NW growth to be conducted in the vapour phase of the medium). It was also noted that the kinked NWs tended to be of larger diameter than the unkinked NWs. Defects were found to occur primarily on the (111) plane which resulted in the formation of lateral faults in the NWs with <111> growth directions and longitudinal faults within the NWs with <112> growth directions. Kinked NWs with defined angles between the arms of the NW were found to be due to the NW altering growth direction. The angle of the kink was thus related to the relationship between the crystallographic directions of the Ge cubic structure. Heavily kinked NWs were found to possess a higher density of more atypical defects (i.e., non (111)) and sometimes showed portions of unfavoured growth directions (i.e., <100>).

8.1.2 Conclusions from Chapter 5

In chapter 5, the Ge delivery system was adapted to allow the growth of highly dense Ge NW mats directly from Cu foil substrates. For the first time, the role of the germanide in allowing Ge NW growth from bulk metal substrates was clearly identified. The presence of orthorhombic Cu₃Ge on the NW tips was clearly illustrated using EDX line profiling and HRTEM analysis, while the presence of the same material on the growth substrate was verified through the use of XRD and EBSD analysis. This catalyst material was found to play an important role in determining the growth direction of the NWs (which were almost exclusively <110> rather than the mixture of <111> and <112> noted in
chapter 3). This was proposed to be due to the closeness of the lattice planes of the Cu$_3$Ge and the resultant NWs in that direction. The NW mats grown directly on a suitable current collector material (Cu) show potential as a material for Li ion battery applications.

8.1.3 Conclusions from Chapter 6

The growth of In seeded, Si NWs on various substrates was demonstrated in chapter 6. The method showed that solution based Si NW formation methods need not be confined solely to the use of SCF media. By conducting the NW growth within the region of the system in contact with HBS vapor, it was feasible to grow high density NWs over a large area on various substrates (SS, glass and Si). The use of an evaporated In layer was found to be a cost effective approach rather than the use of Au. The incorporation of In was also beneficial from a device perspective as Au seeds are known to result in irreversible capacity losses, while In and its oxide In$_2$O$_3$ are interesting materials from a Li ion standpoint. The NWs were found to have either <111> and <112> growth directions which were found to be independent of NW diameter. The role of the In catalyst was investigated through the use of DFTEM and it was found that a root-seeded, VLS mechanism was primarily responsible for NW growth, with some multiprong growth also noted.

8.1.4 Conclusion from Chapter 7

The Si NW growth system described in chapter 6 was modified to allow the growth of Cu$_{14}$Si$_5$ NWs from copper foil as described in chapter 7. The NWs were the first Cu silicide NWs grown by any method and were the first silicide NWs grown in a simple, glassware-based approach. The NWs were found to grow from underlying crystallites of the same phase which were formed as a
prerequisite on the substrate. The composition of the NWs was confirmed using EBSD analysis and diffraction/HRTEM analysis.

### 8.2 Recommendations for further study

#### 8.2.1 Ge Nanostructures

The self-seeded Ge NW growth appears to be dependent upon the use of phenyl-containing precursors. A full understanding over the growth mechanism for the self-seeded NWs would be extremely useful but may require the use of *in situ* techniques. A much more promising focus for the self-seeded NW growth would be to extend the process to allow growth from other non-catalytic substrates (such as Si wafers, etc.). The use of additional precursors and high boiling point solvent systems may allow greater tuning over the NW length and density.

In a similar approach to the use of Cu as a catalytic substrate, various other metal substrates should be investigated. A comprehensive study could involve the use of type A (Al and Ag) type B (Pb, Sn, Bi) and particularly type C catalysts (Ti, Cr, Fe, Co, Ni). The role of the formation of catalytic germanide species would be extremely interesting for the type C catalysts while it would be interesting to see if type A and B could induce NW growth in the absence of germanide formation. Where applicable, bulk metal foils should be investigated in conjunction with evaporated metal layers as a comparison. Initial studies for the type C catalysts should ideally focus on bulk foil. If a germanide layer was then observed on the substrate after reaction, evaporated metal layers of that thickness should be investigated.
8.2.2 Si Nanostructures

In chapter 7 it is shown that the HBS-based Si delivery system can be used to form Cu$_{15}$Si$_4$ NWs. This report was the first showing the growth of silicide NWs in a glassware based approach. In this regard, the use of the system for the formation of various other metal silicide NWs would be an extremely interesting study. The type C metals which were suggested for investigation with Ge in 8.2.1 should be investigated. This study would provide a greater insight into the mechanistic pathways involved as to date it remains unclear why Cu$_3$Ge should seed Ge NWs (chapter 5) while Cu$_{15}$Si$_4$ nanocrystals seed Cu$_{15}$Si$_4$ NWs.

It would also be of great interest to use the experimental setup in an effort to convert preformed metal NWs on a substrate (i.e., Cu NWs dropcast on a Si wafer) as this may provide a generally applicable route to the formation of metal silicide NWs.

8.2.3 Ge/Si Nanostructures

To date, the formation of Ge/Si alloy or Ge/Si heterostructure nanostructures within the HBS system developed has not been realized. The higher thermal stability of silane compared to germane means that precursor choice is extremely important for the realization of such heterostructures. The use of combined Si-Ge precursors may also be an interesting study. As the most effective catalyst to date for Si NW growth here, In may be well placed to allow Ge/Si heterostructure growth.
8.3 Appendices

8.3.1 Si nanospheres

It was found that amorphous Si spheres could be formed in high yields upon thermal decomposition of PS in the absence of a HBS medium in the reaction flask. An SEM image shown in Figure 1 shows that the spheres are relatively polydisperse, however, this route is an extremely convenient means of creating Si spheres which may be of interest for Li ion battery anodes. The work would require a much finer control over the shape and size of the resultant spheres but would be an extremely good comparative material set to Si NWs to gauge the impact of volume expansion during lithiation. Si sphere formation has typically required the use of SCF setups with the extremely reactive precursor trisilane.$^{2,3}$

![SEM image of Si spheres](image.png)

**Figure 1:** Si spheres formed by the rapid thermal decomposition of PS.

**Nanomanipulation and atom-probe analysis**

Nanomanipulation of the self-catalyzed Ge NW was attempted in an effort to conduct atom-probe (AP) analysis. Atom-probe analysis is an extremely useful technique for NWs as it allows elemental composition to be spatially resolved in a
3-D reconstruction. In a standard setup, the NW is ablated by a laser which allows the constituent elements to be captured by a 2-D time of flight mass spectrometer. To date this technique has been used to identify dopant and contaminant atoms within Si NWs but has never been extended for self-catalyzed Ge NWs. This was the focus of a three month SFI-funded exchange fellowship to IMEC, Leuven, Belgium.

Prior to AP analysis, single NWs were required to be adhered to individual tungsten nanomanipulator tips. The goal of this project was to use Kleindike SEM glue to form a sufficiently strong connection between a Ge NW and a tungsten tip to withstand AP analysis. Kleindike SEM glue is a new product which hardened under an electron beam and would allow adhesion between individual NWs and the metal tips. To allow individual NWs to be analyzed, they first had to be pulled out from NW bundles deposited on a Si substrate. The nanomanipulation was performed using 4 Kleindike nanomanipulators within a Hitachi SEM. In a typical approach, a small portion of SEM glue was placed on one of the 4 nanomanipulator tips. Another tip was then slowly brought into contact with the glue to obtain the minimum amount of glue. This glue was then used to contact to a single protruding NW from the underlying Ge NW covered substrate. The SEM beam was then used to harden the glue by increasing the beam current to 30 kV and focusing on the wet glue for 30 minutes. The NW could then be slowly plucked from the bundle for analysis. The nanomanipulator tips were removed from the SEM vacuum chamber and immediately transferred to the AP instrument for analysis.
Figure 2: Ge NW adhered to a tungsten tip. Residual SEM glue can be seen on the foreground of the tip.

In a typical approach, a small portion of SEM glue was placed on one of the 4 nanomanipulator tips. Another tip was then slowly brought into contact with the glue to obtain the minimum amount of glue. This glue was then used to contact to a single protruding NW from the underlying Ge NW covered substrate. The SEM beam was then used to harden the glue by increasing the beam current to 30 KV and focussing on the wet glue for 30 minutes. The NW could then be slowly plucked from the bundle for analysis. The nanomanipulator tips were removed from the SEM vacuum chamber and immediately transferred to the AP instrument for analysis.

Initial experiments for the Ge NWs proved unsuccessful as no Ge signal was obtained from the atom probe analysis. The tip from Figure 2 was returned to the SEM and analyzed to see if there were any visual explanations for the absence of signal. Upon inspection it was found that there was significant material on the
nanomanipulator tip (Figure 3). This material was identified as residual SEM glue which had migrated during transport to the AP instrument. The lack of stability proved to be a major hurdle to preparing samples, while the fragility of the samples made transport extremely difficult. Numerous NWs were lost in transit (as verified by simply opening and closing the vacuum chamber of the SEM and checking if the NW remained on the tip).

**Figure 3:** SEM image of the nanomanipulator tip shown in Figure 2 after attempted AP analysis.
Figure 4: 3D reconstruction of the portion of a Ge NW analyzed with Ge in blue, C in cyan, Si in red and O in green.

Figure 5: 2D slice of the NW presented in Figure 3. Ge is indicated as the blue and light blue dots, O is green and Si is red.

In one partially successful attempt, 50 nm of a NW was successfully analyzed by AP. The 3D reconstruction shown in Figure 4 shows the Ge core of
the NW (in blue). The oxygen signal can be seen to be primarily confined to the edge of the NW (as would be expected for a Ge oxide coating). The Si signal is likely due to the SEM glue. The 2D slice shown in Figure 10 shows the localization of the Ge to the core of the NW and the oxide coating. The AP of the NWs would have been more successful in the presence of a stronger bond between the nanomanipulator tip and the NW. Ideally, measurements should be conducted in an enclosed system, where NWs can be grown and analyzed without exposure to multiple vacuum and ambient exposures. Nonetheless, it was shown that Ge NWs can be successfully analyzed by AP with a high degree of spatial resolution.

8.4 References:

