Growth mechanism of silicon nanowires from nickel-coated silicon wafer

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**GROWTH MECHANISM OF SILICON NANOWIRES
FROM NICKEL-COATED SILICON WAFER**

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TECHNOLOGICAL
UNIVERSITY**

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ABSTRACT

Crystalline silicon (Si) nanowires are important building blocks in devices of photonics, quantum-dots, optoelectronics, and energy. Thermal annealing of metal-covered Si wafers gives rise to clean Si nanowires without metallic catalyst at the tip. The process does not need flammable or toxic gases. However, the growth mechanism is yet elucidated. This project grows Si nanowires by adopting the thermal annealing method: nickel (Ni) is sputtered on Si wafers as catalyst and thereafter a layer of carbon is sputtered to protect Si nanowires from oxidation during thermal annealing. Careful studies via transmission electron microscopy and selected area electron diffraction patterns elucidate the growth process and the relationship between the seeding Ni particle and the grown Si nanowire. The seeding Ni particles are embedded in the Ni-Si-O nanoclusters that are connected with the grown Si nanowires at the end of the nanowire growth. The growth orientation of Ni-seeded Si nanowires is not dictated by surface energy of the various nanocrystal planes, but follows specific structure sensitive principle with the seeding Ni nanoparticles to minimize the mismatch in lattice spacing and dihedral angle at the wire/particle interface. It is inferred that the growth orientation of Si nanowires is determined by the ordered planes of the Ni catalyst particle at the wire/particle interface. The various morphologies of the nanowires are controlled by the diameter and vibration of the Ni-Si-O droplet, the distribution of the Ni-Si, Ni-Si-O_y ($y \approx 1$) and Ni-Si-O_x ($x \approx 2$) phases, and the supersaturated content in the Ni-Si-O droplet.

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TABLE OF ABBREVIATIONS

Si	Silicon
a-Si	Amorphous Si
a-C/Ni	Amorphous-carbon/nickel
SLS	Solid-liquid-solid
VLS	Vapor-liquid-solid
SFLS	Supercritical–fluid–liquid–solid
VSS	Vapor-solid-solid
PECVD	Plasma enhanced chemical vapour deposition
SAED	Selected area electron diffraction
FET	Field effect transistors
UHV	Ultrahigh vacuum
MBE	Molecular beam epitaxy
HF	Hydrofluoric
RTA	Rapid thermal annealing
FESEM	Field emission scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
GIXRD	Glancing incidence X-ray diffraction
HRTEM	High resolution transmission electron microscopy
SiO	Silicon monoxide
R _q	Root mean square roughness
FWHM	Full width at half maximum
2D	Two dimensional
FFT	Fast Fourier Transform

Chapter 1. INTRODUCTION

1.1 Background

Crystalline Si nanowires are important building blocks in optical devices, field-effect transistors, lithium batteries, and power generators. Si nanowires are reported to be grown by laser ablation of Si/Fe disk or Si disk in quartz tube, chemical vapor deposition of SiCl_4/H_2 , or SiH_4 ; thermal degradation of diphenylsilane in a supercritical hexane fluid using the size-monodispersed Au nanocrystals as the seeds; thermal evaporation of bulk Si onto metal-covered substrates under ultrahigh vacuum; thermal evaporation of Si-containing powders in quartz or alumina tube; or thermal annealing of metal-covered Si wafers. The freely mobile Si atoms come from powder disks, vaporized powders, gaseous molecules, fluid molecules, or Si-containing bulk materials. These methods suffer from the low production yield (laser ablation), the risk of flammable or toxic precursor gases (chemical vapor deposition), high level of defects (thermal evaporation of powder), surface contamination of hydrocarbon or limited choice of metal catalyst and Si reactant (solution), or limited growth rate and considerable Si film growth (evaporation of bulk Si).

The Si nanowires grown directly from Si wafers through thermal annealing metal-coated wafers could get rid of the metallic contamination at the tip of the nanowires. In the process, there is no need to introduce Si-containing flammable and toxic gases. The freely mobile Si atoms directly come from the eutectic melting of the metal covering and Si wafer. Understanding of the underlying growth mechanisms

could effectively tailor the dimensionality and growth orientations of the grown Si nanowires, thus in turn controls their mechanical, electronic and optical properties. Except for the reported $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ orientations in this technique, however, the growth orientations of the Si nanowires are not comprehensively investigated, especially the origin of the growth orientation of the grown Si nanowires in relation to the seeding metallic nanoparticles. Additionally, the diameter-oscillating, side-by-side biaxial, or nanosphere-entrapped Si nanowires, which are co-existing with the coaxial one, play more important roles in photonics, optoelectronics, quantum-dots-based devices, and energy storage, due to the unique quantum-dots effect, and third-order nonlinear susceptibility. However, their growth mechanisms are not fully elucidated. Two serious controversies are found: (1) The diameter-oscillating Si nanowires are formed by the periodic violation of liquid metal-Si droplet, or by that of the Si nanoparticles. (2) The coaxial, side-by-side biaxial, and the transitional nanowires are Si/SiO₂, or β -SiC/SiO₂. In the reported growth mechanisms, five fundamental flaws exist: (1) The disproportionation of SiO, and the redox reaction of carbon and SiO can't explain the growth of the nanowires, because the reactions only involve the migration of electrons, but no rearrangement of the produced atoms and molecules. The growth is highly possible seeded by Cu-Si and Al-Si eutectic droplets since Cu and Al already exist in quartz as metallic impurities, and could ooze out upon heating; Al could reduce from alumina tube under reduction atmosphere. Si in the nanowire comes from the Si portion in the ejected powder particles. The vaporized atoms/molecules of the powder materials couldn't reach the location where the nanowire grows due to the limited mean free path and comparable difference in diameter and mass with the protective gas molecules, while the ejected micron-sized powder particles could land at the growth location due to the dramatic

difference in diameter and mass with the gas molecules. (2) The growth kinetics or surface energy can't explain the transition from the Si/SiO₂ coaxial nanowire to the side-by-side biaxial nanostructure, because crystallization is an energy-releasing, not an energy-consuming process. (3) In liquid metal-Si droplet, metal and Si couldn't reach supersaturation at the same time. Only one of them could reach supersaturation at certain moment, when the other acts as the solvent. (4) The capillary force can't explain the formation of the Au-nanopeapodded silica nanowire since the silica nanotube has never been observed, the dark core is highly possible Si rather than Au, and the spacing between the Au-nanopeas is not hollow but filled with silica. (5) During thermal evaporation of the SiO powders, the disproportionate SiO₂ molecules are still confined in the ejected SiO particle. SiO₂ melts at a high temperature of 1703 °C, (cf., the growth temperature is only 850-900 °C), thus unable to move around directly to form the oxide sheath of the Si nanowire, not to mention the entrapping of the Au/Si nanospheres in the Si nanowire. The details are discussed in section 4.4.2.

1.2 Objective

This project grows various Si nanowires through thermal annealing of Ni-coated Si wafers beneath sputtered amorphous carbon. The morphology, composition, structure, growth orientations of the grown Si nanowires and the relations to the seeding Ni nanoparticles, as well as the origin of the growth orientations are explored in detail to reveal the underlying growth mechanisms for the various morphologies of the grown Si nanowires.

1.3 Novelty

- 1) Amorphous carbon (a-C) layers of different thickness were sputtered on Ni-coated Si wafers to retard the oxidation of the Ni-Si-O droplets and thus effectively control the core diameter of the crystalline Si nanowires.
- 2) The origin of the morphologies of Si nanowires was elucidated.
- 3) A structure-sensitive principle was discovered to reveal the origin of the growth orientations in Ni-seeded Si nanowires.

1.4 Scope

To realize the objective of this project, the following work has been implemented.

- 1) Cross section, chemical composition, and structure of the as-sputtered Ni-coated Si wafer and a-C/Ni films.
- 2) Growth of Si nanowires through thermal annealing of the as-sputtered films for different duration of time.
- 3) Surface morphology of the annealed films, chemical composition, and the structure of Si nanowires. Structural evolution of the Si nanowires as function of the amorphous carbon layer thickness and annealing duration.
- 4) Various morphologies of Si nanowires and their relationship to the seeding Ni particles, cross sections, growth orientations, and the orientation relationships to the seeding Ni particles.
- 5) Origin of the morphologies of Si nanowires.
- 6) Origin of the growth orientations of Si nanowires.

1.5 Organization

Chapter 1 introduces the background, objectives, novelty, and scope of this project.

Chapter 2 reviews the structure, properties, applications and synthesis techniques of Si nanowires, and the existing problems.

Chapter 3 overviews the project, sets up the experimental flowchart, and introduces the employed characterization techniques.

Chapter 4 presents (1) cross section, chemical composition, structure of the as-sputtered Ni layer and a-C/Ni films; (2) the surface morphology of the annealed films, chemical composition and structure of the grown Si nanowires, and the structural evolution of Si nanowires as function of the a-C layer thickness and annealing duration; (3) cross section and growth orientation of the grown Si nanowires, and the origin of the growth orientations in silicon nanowires; (4) various morphologies of the grown Si nanowires, the relation to the seeding Ni particles, and the origin of the various morphologies of Si nanowires.

Chapter 5 concludes the contributions and gives the recommended future work.

Chapter 2. PRESENT RESEARCH STATUS OF SILICON NANOWIRES

The structure, properties, applications, and synthesis techniques of Si nanowires are reviewed in this chapter. The existing problems are pointed out.

2.1 Structure, properties and applications

The diamond cubic crystal structure is a repeating pattern of 8 atoms that certain materials may adopt as they solidify. The first known example was diamond following the face-centered cubic (FCC) bravais lattice. The lattice describes the repeat pattern: for diamond cubic crystals this lattice is "decorated" with a motif of two tetrahedrally bonded atoms in each primitive cell, separated by 1/4 of the width of the unit cell in each dimension. The atomic packing factor of the diamond cubic structure (the proportion of space that would be filled by spheres that are centered on the vertices of the structure and are as large as possible without overlapping) is $\pi\sqrt{3}/16 \approx 0.34$. Si is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. The atomic number is 14. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of Si dioxide (silica) or silicates. It is of a diamond cubic crystal lattice.[1] The spatial lattice of Si is defined as FCC with a lattice parameter of 5.43 Å as shown in **Fig. 2-1**.

Fig. 2-1 Face-centered cubic Si crystal structure. [1]

As seen in **Fig. 2-1**, each Si atom is surrounded by four other Si atoms arranged at the corner of a tetrahedron. Compared to bulk Si, one dimensional crystalline Si nanowires are of the substantial quantum size effects as long as the diameter reaches 3 nm and below,[2] which could result in the great increase of the band gaps from 1.1 eV to 3.31 eV. **Table 2-1** shows the detailed physical properties, i.e., Young's modulus (E), Fracture strength (σ), Bending strength (σ_b), and Band gap (E_g), between bulk Si and Si nanowires.

Table 2-1 Physical properties of bulk Si and Si nanowires

Properties	Lattice constant (Å)	E (GPa)	σ (GPa)	σ_b (GPa)	E_g (eV)
Bulk	5.43	135-190[3]	22[3]	-	1.1[4]
Nanowire		158-210[3]	12[3]	0.3-0.85[3], 17.5[3]	1.1-3.5[5], 3.31[2]

Dimension and orientation of Si nanowires are the keys in determining the optical,[6] electrical,[2] chemical,[2] and mechanical properties.[7] It is known that quantum confinement effects shift band gap energies as the nanowire diameter approaches the carrier de Broglie wavelength, and generate visible photoluminescence in Si.[2, 6] The dimension of Si nanowires in metal-seeded growth is easily controlled by the diameter of the droplet and duration of growth,[8] e.g., small and uniform Si nanowires can grow through the supercritical fluid solution-phase approach using size-monodispersed Au nanocrystals as seeds in a supercritical hexane fluid.[6, 9] Growth orientation is another crucial variable to regulate the nanowire properties for specific applications. The band gap and electrical conductance are dramatically different for Si nanowires of different growth orientations.[2, 10-13] It is reported that the $\langle 100 \rangle$ Si nanowires exhibit a significantly higher exciton energy than the $\langle 110 \rangle$ oriented ones.[6] The $\langle 110 \rangle$ Si nanowires demonstrate the highest sensitivity to surface modification but display the lowest total energy,[14] whereas the $\langle 111 \rangle$ oriented one is structurally stable to the change of diameter, and the most reluctant to surface modification.[2] The $\langle 110 \rangle$ oriented Si nanowires display a direct transition, Si nanowires with the $\langle 111 \rangle$ axis possess a competitive indirect-direct gap character, and Si nanowires in the $\langle 112 \rangle$ orientation have an indirect band-gap.[12] Tetrahedral Si nanowires oriented in the $\langle 111 \rangle$ orientation are the most stable and best suited for quantum confinement effects.[13] The $\langle 112 \rangle$ Si nanowires exhibit the highest tensile strength of 12.31 GP_a , and the weakest link fracture is a byproduct of orientation-dependent flaw populations. [7]

To date, the rearrangement of the semiconductor atoms to a preferred repeating patterns, i.e., growth orientation, however, is still mysterious, though lots of

physical factors have been reported to affect the growth orientation, including surface chemical treatment of substrate,[15, 16] nanowire diameter,[8, 17, 18] composition of the initial alloy droplet,[19, 20] growth temperature,[21-23] reaction pressure,[6, 24] and precursor molar ratios.[25] Most prospective believes the growth orientation is dictated by the surface energetics at the solid-liquid interface of the nanocrystal emerging from the liquid droplet, which involves surface free energy of various nanocrystal planes,[17, 26, 27] and the effect of amorphous surface oxides,[27] as well as the lattice matching.[28] Metal-seeded nanowire growth, however, involves the formation of the metal-semiconductor eutectic droplet from vapor,[17, 29, 30] solid,[31-34] or solution,[6, 9] and the subsequent crystallization. The former process needs thermal energy, i.e., an energy-consuming process. The subsequent crystallization, i.e., phase transition from vapor, melt or solution to solid, however, is an energy-releasing process.[35] It is reported that 3.04×10^5 J is released when 1 mole vapor Si (at 1000 K, 1 atmosphere) transits into solid, and 5.0×10^4 J is released when 1 mole liquid Si (at 1693 K) transits to solid state. Surface energy quantifies the disruption of intermolecular bonds that occur when a surface is created. For a solid, the molecules on the surface have more energy compared with the molecules in the bulk of the material, otherwise, there would be a driving force for surfaces to be created, removing the bulk of the material. For a liquid, the surface tension and the surface energy density are identical everywhere. As such, energy should not be the determining factor during precipitation of Si nanowires from Si supersaturated metal-Si droplet. In other words, the growth orientation of Si nanowires cannot be dictated by energy.

Si nanowires are of large surface area and possible quantum confinement. The large amount of surface area available to molecular adsorption greatly increases the sensitivity of the nanowire electrical properties to the environment. The small size of Si nanowires can be used to prepare dense arrays of sensors. Si nanowires are semiconducting, and the dopant type and concentration of Si nanowire are controllable, which enables the sensitivity to be tuned in the absence of an external gate. Si nanowires allow the combination of one-dimensional transport and self-assembled processing with the well-known Si technology. Si nanowires can circumvent the pulverization and capacity fading in the application of lithium battery due to the great Si's volume changes upon insertion and extraction of lithium. To date, however, no production-scale Si nanowire applications have shown in the marketplace, but many simple device structures have been demonstrated, such as optical devices,[36-38] biosensors,[39] field effect transistors,[40-43] and lithium battery,[44-46] and power generators,[47-49] exhibiting the great possibility that may be marketable in the future.

2.2 Growth techniques

Two big categories of methods are applied to synthesize Si nanowires, referred to as “top-down” and “bottom-up”.[50] In top-down method, bulk materials of desired composition are carved into the desired nanoscale structure by lithographic techniques. Such methods dominated the material processing over the last century, and are still of principle importance for production of electronic components. However, as the desired length scales of devices and applications shrink, these techniques become more problematic. This is partly a practical problem: techniques to carve out ever-smaller structures are difficult to find. More importantly,

uniformity of bulk crystals on nanometre length scales is not very high, and quality of structures becomes difficult to control. Metal-assisted chemical etching is one of the top-down methods.

“Bottom-up” methods mimic nature’s way of self-assembling atoms to form increasingly larger structures. Such techniques involve controlled crystallization of materials from vapour, liquid or solid sources, typically yielding uniform and highly ordered nanometre-scale structures. Nanostructures can be grown in solution, as particles in a vapor, or on a solid support surface. Vapor-liquid-solid (VLS), fluid-liquid-solid (FLS), vapor-solid-solid (VSS) and solid-liquid-solid (SLS) are the well-known “bottom-up” growth mechanisms. Si is provided by distinct sources in different growth mechanisms,[51] either bulk Si or Si-containing compounds in the form of vapour, gases or fluid. In the latter case a chemical reaction often takes place at the metal-Si droplet.

2.2.1 Metal-assisted chemical etching

Reactive-ion etching could produce vertical Si nanowires out of Si wafers. The nanowire diameter is defined by a lithography step preceded by reactive ion etching. Metal-assisted chemical etching is an alternative to reactive-ion etching,[52] where Si is wet-chemically etched, with the Si dissolution reaction being catalyzed by the presence of a noble metal that is added as a salt to the etching solution.[53] Alternatively, also a continuous but perforated noble-metal film can be used. During etching, this film could etch down into the Si wafer to produce vertical Si nanowires at the locations of the holes in the metal film.[54, 55] In a typical metal-assisted chemical etching procedure,[52] a Si wafer partly covered by a noble metal is subjected to an etchant composed of hydrofluoric (HF) acid and an oxidative

agent. Typically, the Si beneath the noble metal is etched much faster than the Si without noble metal coverage. As a result, the noble metal sinks into the Si wafer, generating pores in the Si wafer or, additionally, Si nanowires. The detailed geometries of the resulting Si structures depend mostly on the initial morphology of the noble metal coverage. Under certain conditions, microporous structures could form in the regions without noble metal coverage.

Fig. 2-2 describes the metal-assisted chemical etching process: (1) the oxidant is preferentially reduced at the surface of the noble metal due to the catalytic activity of the noble metal on the reduction of the oxidant; (2) the holes generated due to the reduction of the oxidant diffuse through the noble metal and are injected into the Si that is in contact with the noble metal; (3) the Si is oxidized by the injected holes and dissolved at the Si/metal interface by HF. The reactant (HF) and the byproducts diffuse along the interface between the Si and the noble metal; (4) the concentration of holes has its maximum at the Si/metal interface. Therefore, the Si that is in contact with the metal is etched much faster by HF than a bare Si surface without metal coverage would be; (5) the holes diffuse from the Si under the noble metal to off-metal areas or to the wall of the pore if the rate of hole consumption at the Si/metal interface is smaller than the rate of hole injection. Accordingly, the off-metal areas or sidewalls of the pore may be etched and form microporous Si.

Fig. 2-2 Schematic diagram of the metal-assisted chemical etching process. [52]

However, there are a lot of unsolved technical problems in the metal-assisted chemical etching process. (1) The injection process of the hole has not been systematically studied. The influence of the intrinsic properties of the Si wafer (i.e., doping type and doping level), surface state of the Si wafer, and the type and morphologies of the noble metal catalyst on the hole injection process remains incompletely understood. Additionally, the proper explanation of some currently poorly understood phenomena, such as different etching behaviours of Si wafers with different doping type and doping level and the different etching behaviours induced by different type of metal catalysts, relies upon the fully understanding of the hole injection process. (2) The origin of the driving force of the movement of the noble metal particles is simply the preferred etching of Si under the particles. The etching path of the noble metal particles and the possible role of the shape of the noble metal particle (sphere, half sphere, or disk) have yet been investigated. The driving force for aligning the movement directions of adjacent particles for longer etching times, which appears to be some kind of cooperative effect, is not presently understood. (3) A systematic study of the relation between the etching

rate, etching direction, and orientation of Si wafers is lacking. (4) A possible influence of the specific dopant element, doping levels, etchants, and noble metals on the morphologies of the etched structures has not been studied. (5) The etching morphologies of these non-Si semiconductors have been well characterized, whereas the detailed etching mechanisms are yet to be explored.

2.2.2 Vapor-liquid-solid growth

The VLS mechanism was first developed by Wagner and Ellis in 1964 to explain the growth process of Si whiskers.[30] The growth process takes place as follows: a small particle of Au is placed on the {111} surface of a Si wafer and heated up to 950 °C, forming a small droplet of Au-Si alloy as shown in **Fig. 2-3(a)**. A mixture of H₂ and SiCl₄ is introduced. The liquid alloy acts as a preferred sink for arriving Si atoms or, perhaps more likely, as a catalyst for the chemical process involved. The Si enters the liquid and freezes out, with a very small concentration of Au in solid solution, at the interface between solid Si and the liquid alloy. By a continuation of this process the alloy droplet become displaced from the substrate crystal and “rides” atop the growing whisker as shown in **Fig. 2-3(b)**. The eutectic point of Au-Si alloy is around 363 °C as shown in **Fig. 2-3(c)**, thus droplet could form during heating the Au-covered Si wafer at 950 °C. The VLS mechanism reflects the pathway of Si, which coming from the vapor phase diffuses through the liquid droplet and ends up as a solid Si nanowire. It represents the core of semiconductor nanowire research, since it does not only work for Si but also for a much broader range of nanowire materials.

Fig. 2-3 VLS growth of the Si whisker.[30] (a) Initial condition with liquid Au-Si droplet formed on the Si substrate. (b) Growing Si crystal with the liquid droplet at the tip. (c) The Au-Si eutectic alloy melts at 363 °C.[56]

The growth of Si nanowires through CVD of the gaseous Si precursors follows the VLS growth mechanism. Depending on the type of Si precursors, it could be separated into high temperature ($>700\text{ }^{\circ}\text{C}$) and low temperature ($<700\text{ }^{\circ}\text{C}$) CVD. The most frequently used precursors are silane (SiH_4) disilane (Si_2H_6), dichlorosilane (Si dichloride, SiH_2Cl_2), and tetrachlorosilane (Si tetrachloride, SiCl_4). The growth temperature ranges from about $800\text{ }^{\circ}\text{C}$, [57-60] to well beyond $1000\text{ }^{\circ}\text{C}$, [61, 62] when SiCl_4 is used; while it is about $400\text{--}600\text{ }^{\circ}\text{C}$, for Si nanowires grown in the presence of SiH_4 . [63-65] The use of a chlorinated silane precursor in the presence of hydrogen would lead to the creation of hydrochloric acid during nanowire growth, causing some desirable or undesirable etching to the substrate, the nanowires, and the equipment. Additionally, chlorinated silanes are chemically more stable than their nonchlorinated counterparts. Thus higher temperature is required to thermally crack the precursor.

2.2.2.1 High-temperature CVD

High temperature CVD is carried out in tubular hot wall reactors. [58, 60, 62] A gas flows typically hydrogen or a hydrogen/inert gas mixtures is directed through an externally heated quartz tube held at about atmospheric pressure. Prior to entering the reactor, a part of the gas is led through a bubbler filled with SiCl_4 (SiCl_4 is liquid at room temperature and atmospheric pressure), thereby supplying SiCl_4 to the reactor. If the Si substrate deposited with some amount of the metallic catalyst is placed in the hot zone of the reactor beforehand, Si nanowires would commence growing.

As shown in **Fig. 2-4**, [58] Cu-catalysed Si nanowire array having nearly 100% fidelity over a large ($>1\text{ cm}^2$) area is grown through an oxide buffer layer to confine

the Cu catalyst to the desired areas in the pattern. A 300 nm oxide was thermally grown on Si (111) wafers and then photolithographically patterned. The oxide within the patterned resist holes was removed by immersion of the samples for 4 min in buffered HF. The desired catalyst islands, now separated by a buffer oxide, were then formed by thermal evaporation of 500 nm of Cu, followed by lift-off of the resist. These samples were then annealed in a tube furnace at 850–1100 °C for 20 min under 1 atm of H₂ at a flow rate of 1000 sccm. Nanowires were then grown for up to 30 min at 850–1100 °C under 1 atm of H₂ and SiCl₄ at flow rates of 1000 and 20 sccm, respectively.

Fig. 2-4 Tilted SEM views of the Cu-seeded Si nanowire array having nearly 100% fidelity over a large area ($>1 \text{ cm}^2$). The scale bar in the inset is 10 μm . [58]

High-temperature CVD was preceded by using a closed reaction vessel instead of a flow reactor. Wagner et al., [66] for instance, obtained their early results by using evacuated and sealed quartz ampoules into which iodine was placed together with Si

and the metallic catalyst materials. Upon heating, iodine reacts with Si to form gaseous silicon iodide products, which then serve as a locally produced CVD precursor. And then, Si nanowire growth takes place at the colder parts of the quartz ampule.

The advantage is the much broader choice of the metallic catalyst materials. However, the high growth rates (on the order of $\mu\text{m}/\text{min}$, [58], or even $\mu\text{m}/\text{s}$ [62]) and the diffusion of the metallic catalysts (Ostwald ripening effect [67, 68]) at elevated temperature often result in the difficulty to control the length and to grow nanowires with well-defined diameters. Therefore, high-temperature CVD suits for the growth of microscopic Si wires rather than nanowires. In dependent of the catalyst material used, the main crystallographic growth direction of the nanowires is the $\langle 111 \rangle$ direction, probably due to the large diameter of the wires. However, Wagner et al. pointed out that $\langle 112 \rangle$ oriented wires showing a twin defect parallel to the wire axis can be found. [66] The introduction of the dopant precursor does influence the wire morphology. Givargizov et al. pointed out that the periodic instability of the wires (a periodic variation of the wire diameter observed at high temperatures and pressures) disappears once AsCl_3 is added to the gas mixture, [61, 69] presumably because AsCl_3 changed the surface tension configuration of the wire and/or the catalyst droplet.

2.2.2.2 Low-temperature CVD

Silane (SiH_4) and disilane (Si_2H_6) are used in low-temperature CVD. Silane could decompose at about 350°C , therefore, the temperature ranging from 363 to 700°C is enough. Disilane is more reactive than silane, as it allows for Si nanowire growth

at much lower pressures. Both silane and disilane are self-igniting gases that are potentially explosive if contact with air. The dominant orientation of nanowires with diameters larger than about 50 nm orientation is $\langle 111 \rangle$. Low pressure, cold wall reactors are used. When Au is used as the catalyst, high-vacuum equipment with a base pressure around 10^{-6} mbar is sufficient for nanowire growth. This is, however, not the case when more sensitive metallic catalysts are used. For instance, as aluminium is sensitive to oxidation, the use of an ultrahigh-vacuum reactor with a base pressure lower than about 10^{-9} mbar is recommended. Yet, if oxidation of Al is prevented, excellent nanowires can be achieved.[70]

The silane partial pressure typically ranges from 0.1 mbarr,[63, 65] to 0.5 mbar,[71], resulting in growth rates on the order of nanometers per second. The growth rate increases approximately linearly with the partial pressure of silane.[71] Au-seeded growth of Si nanowires by using silane as source are usually slightly tapered (cf., **Fig. 2-5**), indicating that the radial growth is slow compared to axial growth. Radial growth rates are about 2 orders of magnitude lower than the axial growth rates. The activation energies for Au-seeded Si nanowire growth are about half as large as those for Si thin film growth: 19 kcal/mol vs 35kcal/mol for silane,[71] and 12 kcal/mol vs 28 kcal/mol for disilane.[72] This reduction by about a factor of two makes the Au droplet a catalyst droplet. Plasma enhanced CVD (PECVD) makes use of the plasma in the nanowire growth reactor,[73] thus the Si precursor, silane in most cases, is partially precracked. Such a precracking could facilitate the supply of Si to the catalyst droplet.

Fig. 2-5 Diameter-dependent nucleation of Si nanowires. (a)-(f) The evolution of a flat Au disk into a hemispherical Au droplet on top of a Si nanowire. Diameters range from 250 nm (a) to 80 nm (f). Scale bars are 100 nm.[71]

The advantages of the low-temperature CVD are that nanowires with a large variety of diameters and length could be grown epitaxially on Si substrates. With the lengths of the nanowires being essentially proportional to the process time, they can be easily adjusted. Nanowire growth at predefined positions on the substrate is possible. Furthermore, the properties of the nanowires could be tuned directly by doping from the gas phase, allowing also for modulated doping profiles. One major problem is that they exhibit a certain variation of the growth direction, especially for diameters smaller than about 50 nm. Another problem is that a certain percentage of the nanowires tend to change their growth direction during growth, resulting in the appearance of a kink. However, kink can be circumvented by growing the nanowires inside a template such as anodic aluminium oxide.[74]

2.2.3 Vapor-solid-solid growth

Vapor-solid-solid (VSS) growth is of reduced processing temperature and more abrupt heterojunction.[75] The interface between the semiconductor and the metallic catalyst provides a preferential interface for the incorporation of adatoms into the growing crystal.[76] The phase of the metallic catalyst may be the same both during and after growth. The growth could be broken down into four steps (cf., **Fig. 2-6**): a) delivery of precursor species to the substrate; b) precursor decomposition; c) diffusion in or on the catalyst particle; and d) incorporation of adatoms into the growing nanowire. Each step introduces specific requirements for appreciable VSS growth to be realized. Firstly, sufficient source material must be delivered to the substrate for growth to occur. Then, selective precursor decomposition at the catalyst can facilitate the anisotropic growth. Next, Si adatoms must be delivered to the growth interface by bulk or surface diffusion. Finally, anisotropic growth requires the preferential incorporation of adatoms at one interface.

Fig. 2-6 VSS mechanism of the nanowire growth. (a) Delivery of the precursor to the nanowire surface, followed by the decomposition of this precursor. (b) Atoms are delivered to the metal catalyst/nanowire interface by surface or bulk diffusion processes. (c) Semiconductor atoms are incorporated at the growth interface (metal catalyst/nanowire interface) leading to anisotropic growth.

Compared to the VLS growth, VSS growth is of the following potential advantages. Firstly, in the same metal system, VSS growth takes place at reduced temperatures compared to VLS growth because the metallic catalyst remains in a solid state. Lower temperatures could reduce the thermal budgets and slow diffusion in the grown structure. Secondly, particle ripening by diffusion could be mitigated if the solid nanoparticles are used, particularly at lower temperatures, resulting in narrow diameter distributions. Thirdly, the crystal structure and orientation of the solid

catalyst may provide a stronger influence on the orientation of the nanowire, leading to opportunities to control orientation and crystallinity independent of the substrate. The choice of metallic catalyst affects the orientation and crystalline quality of the Si nanowires, i.e., $\langle 110 \rangle$ [57, 77], $\langle 111 \rangle$ [57, 77, 78], $\langle 112 \rangle$ [79], $\langle 113 \rangle$ [57], and $\langle 100 \rangle$ [80] orientations, since the phase of the catalyst and the particular semiconductor/catalyst interfaces could strongly influence the surface energies near the growth interface such that nanowires of a particular orientation may be preferred. Fourthly, the incorporation of unintentional impurities, particularly from the metal catalyst, may be reduced due to the reduction in atom diffusivity and solid solubility associated with nanowire growth at lower temperatures. Finally, the growth may yield more abrupt interfaces in axial nanowire heterostructures which are generally difficult to realize with the VLS mechanism.

As shown in **Fig. 2-7**, Si nanowires are grown in a TEM chamber by chemical vapor deposition on a Cu-coated Si (111) substrate through the vapor-solid-solid mechanism [77]. In **Fig. 2-7** (a) and (b), S indicates the nanowires that grow along the surface in $\langle 110 \rangle$ directions. T indicates wires growing off the surface, like those in **Fig. 2-7** (c), with growth directions also $\langle 110 \rangle$. In **Fig. 2-7** (c), the dashed arrow indicates the projection of the vector in the [011] or [101] orientation. The dotted arrow indicates the mirror symmetric directions. In **Fig. 2-7** (d), the growth plane of the nanowire is Si (111), which is labelled as A in the diffraction patterns. And the Cu_3Si (0001) plane is labelled as B. The schematic illustration shows the electron diffraction patterns of Si $[\bar{1}\bar{1}0]$ and Cu_3Si $[1\bar{1}20]$ zone axes, open circles and solid circles, respectively, and the superposition of Si $(11\bar{1})$ and Cu_3Si $(\bar{1}\bar{1}01)$ reflections, labelled O. Averaged over several nanowires, the Cu_3Si [0001]

orientation is 8.3 (0.7° to Si [111]) in the diffraction patterns, while the nanowire growth orientation is 18.4 (0.7° off the Si [111] axis, as expected for a nanowire growing out of plane in the Si [011] or Si [101] orientation. Si nanowires start to grow after exposure to disilane, Si_2H_6 (20% diluted in helium, He). The growth temperature ranges between 470 and 550°C and the disilane partial pressure between 1×10^{-7} and 8×10^{-6} Torr. The Cu_3Si phase serves as the catalyst and the epitaxial growth orientation is predominantly $\langle 110 \rangle$, but depends on the relative orientation of the catalyst and substrate. The real-time observations show that the nanowire growth involves rigid rotations of the catalyst particles and is by repeated ledge nucleation and flow at the $\text{Cu}_3\text{Si}/\text{Si}$ interface, with the ledges propagating in a jumpy manner due to pinning by interfacial dislocations at the growth interface. In comparison with the VLS growth, the nanowires grown by VSS may require more stringent process control, because of the dependence of the nanowire orientation and growth rate on the detail of the catalyst shape and orientation relation.

Fig. 2-7 (a, b) SEM plan-view and grazing angle (10°) images of Cu_3Si -catalyzed Si nanowires after 3 h of growth on Si (111) at 510°C and 1×10^{-6} Torr Si_2H_6 . [77] (c) Bright-field TEM image of Si nanowires recorded during growth at 530°C and

1×10^{-6} Torr Si_2H_6 . (d) TEM image and electron diffraction patterns of a [101] nanowire. (e) TEM image and electron diffraction patterns showing a nanowire and catalyst with another orientation relation, $\text{Si (111)}/\text{Cu}_3\text{Si}(\bar{1}\bar{1}03)$, labelled A and C, respectively. The growth direction is close to Si [111].

The key features of the VSS growth are summarized as follows. Prior to the initiation of growth, the solid seed particles must be formed. Upon exposure of the metal particles to a vapor phase flux of Si, silicides begin to form. The solid silicide phases are expected to form from the metal particles at temperatures as low as $\sim 0.35 \times T_{\text{eut}}$. When excess Si is present, solid Si would crystallize at an interface with the silicide because crystallization of the semiconductor at this metal/semiconductor interface is energetically favourable. The atom diffusion through the particle and the subsequent atom incorporation at the catalyst/semiconductor interface result in the nanowire growth. However, the VSS growth rates of nm/min are 10–100 times slower than that of the VLS growth depending on the catalyst, growth temperature, and precursor partial pressure.[75] The reduced rates can be attributed to slower precursor decomposition kinetics, diffusion through a solid rather than a liquid, and/or slower atomic incorporation at subeutectic temperatures.

2.2.4 Supercritical-fluid-liquid-solid growth

Supercritical-fluid-liquid-solid (SFLS) growth utilizes highly pressurized supercritical organic fluids enriched with a liquid Si precursor, such as

diphenylsilane, and metal catalyst particles,[6] could produce high product yield of Si nanowires. In the original design, diphenylsilane, $\text{SiH}_2(\text{C}_6\text{H}_5)_2$, is used as the Si precursor, which is mixed with hexane and sterically stabilized gold nanoparticles in a high pressure reactor. High pressures of 200-270 bar and a temperature of 500°C are applied to the reaction vessel. Under these conditions, hexane becomes supercritical, which is why this method is referred to as being supercritical-fluid-based. At reaction temperatures above the metal–Si eutectic point, the Si precursor decomposes and Si atoms form an alloy with gold. The alloy droplet in this supercritical–fluid–liquid–solid (SFLS) method starts to precipitate a Si nanowire once the alloy gets supersaturated with Si.

The synthesis is performed in a flow reactor instead of a closed reaction vessel (cf., **Fig. 2-8**). In this case, gold colloid particles together with a well-defined amount of the Si precursor, e.g., diphenylsilane, are fed into the solution as dispersions and transferred into the heated and pressurized reactor, where the nanowire synthesis takes place. Si nanowires synthesized using monophenylsilane,[81] i.e., SiC_6H_8 , and diphenylsilane as precursor differ in that the use of monophenylsilane leads to a higher product yield and additionally to a smaller amount of carbonaceous byproduct as compared to using diphenylsilane. Supercritical fluids such as hexane and cyclohexane disperse high concentrations of sterically stabilized nanocrystals, and precursor concentrations can range from 0.1 to 1.0 mol/L,[82] in contrast with typical values of 4.0×10^{-3} mol/L in CVD.[8] The combination of high concentrations and diffusion coefficients that approach gas-phase values affords fast growth rates and efficient nanowire production. Similar to the VSS growth, growth of Cu-, Ni-, and Co-seeded Si nanowires performed at temperatures well below the melting point of the corresponding metal-Si alloy has been

demonstrated.[83] Au and Bi seeded Si nanowires are demonstrated at atmospheric pressure.[9] Trisilane, Si_3H_8 , which is even more reactive than disilane, is used as the Si precursor. The growth reaction takes place in a vessel filled with a long-chain, low-vapour pressure hydrocarbon. The nanowire growth takes place at temperatures higher than the eutectic temperatures of Au-Si or Bi-Si through the SFLS mechanism.

Fig. 2-8 Schematic of the flow reactors used to synthesize Si nanowires.[82]

In the SFLS growth, bulk quantities of thin nanowires of good crystalline quality and uniform size could be synthesized. The variability with respect to the choice of the precursors offers an additional degree of freedom for optimization. The ability to manipulate the precursor concentration, the metal seed concentration and size, and the solvent strength of the supercritical fluid via pressure and temperature provide flexibility in controlling the nanowire composition, morphology, and orientation. The flow reactor provides the kinetic tenability necessary to minimize undesirable Si particle deposition and to optimize the production of straight nanowires. Si nanowire growth in the supercritical fluid could be mediated by a

solid catalyst particle. However, a controlled, in-place, epitaxial growth is hardly realized. The elements with alloy eutectic temperatures above the boiling point and even the critical temperature of most solvents couldn't use the SFLS technique.

2.2.5 Solid-liquid-solid growth

Solid-liquid-solid growth includes molecular beam epitaxy, laser ablation, thermal evaporation, and thermal annealing using bulk Si, Si-containing powders, and Si wafers as the source materials.

2.2.5.1 *Molecular beam epitaxy*

The molecular beam epitaxy (MBE) growth is achieved by evaporating bulk Si onto the substrate covered by metallic catalyst (cf., **Fig. 2-9**).^[84] An ultrahigh vacuum (UHV) system with a base pressure in the 10^{-10} mbar range is required to satisfy the mean free path for the vaporized Si atoms to reach the substrate. To maintain such low pressures even during the nanowire growth, therefore, parts of the system are often cooled with liquid nitrogen. For Au seeded Si nanowires, Au is deposited onto the substrate. Annealing the substrate at temperatures above the Au-Si eutectic temperature causes the Au film to break up. Au mixes with Si to form Au-Si eutectic droplets on the substrate. And then they act as catalysts for the subsequent nanowire growth. Since the Si atoms in MBE are from the bulk Si, instead of the decomposition of Si compound, the role of the metallic catalyst merely facilitates the crystallization of Si. As there is no chemical reaction involved, the catalyst droplets are not real catalysts anymore from a chemical point of view.

However, Si nanowires grow faster than the substrate by about a factor of 2, indicating that the droplets do have an effect on Si crystallization.

Fig. 2-9 Cross section images of Si nanowires grown on a $\langle 111 \rangle$ Si substrate at 0.5 Å/s for 60 min (a) and 120 min (b) growth time at 525°C. (c) An overview on the arrangement of the Si whiskers in sample (b).[84]

Typically, Si nanowires are grown at the substrate temperatures of 500-700 °C. The evaporated Si diffuses on the substrate surface until it either crystallizes directly or finds an Au catalyst droplet. The main reason for growth at temperatures higher than 500°C is because the nanowire growth strongly relies on Si surface diffusion. Yet, at these temperatures, it is difficult to realize small Au-Si droplet sizes (due to

Ostwald ripening), therefore, the diameters of the nanowires usually exceed 40 nm. Gibbs-Thomson effect might be another potential cause for the fact that only nanowires with diameters larger than about 40 nm can be obtained. The rather slow surface diffusion results in a comparably small growth rate, typically at 1-10 nm/min. The growth rate is inversely proportional to the nanowire diameter. Single crystalline <111> oriented Si nanowires can be homoepitaxially grown on Si substrate at predefined positions. The incoming particle fluxes can be accurately controlled, which is particularly important for a doping of the Si nanowires. Therefore, Si nanowires with well controlled doping profiles could be realized. If additional evaporation sources, for example, Ge exist, axial heterostructures could be formed by switching sources. The main disadvantages are the considerable Si film growth on the substrate and the limited flexibility concerning nanowire diameters and aspect ratios.

2.2.5.2 Laser ablation

Laser ablation ablates the catalyst/Si disk and the Si nanowire growth takes place in the vapor phase. Lieber et al. pioneered this nanowire synthesis method, used a mixed Si/Fe target containing about 90% Si and 10% Fe.[29] They heated the tube furnace to 1200 °C, which is close to the minimum eutectic temperature required for forming Fe-Si droplet. Under these conditions, they ablated Fe and Si from the laser disk by shooting at it with a pulsed, frequency doubled Nd:YAG laser (wavelength 532 nm). The ablated material collides with inert gas molecules and condenses in the gas phase, resulting in Fe-Si nanodroplets, which act as seeds for Si nanowire growth (cf., **Fig. 2-10**). Formation of Fe-Si eutectic droplet takes place at 1207 °C: though this temperature is 7 °C higher than that at the disk, laser

ablation may have produced vapor Fe or Si atoms or nanosized particles thus the size effect operated here, as explained by Lieber et al..[29] As such, Si dissolves into the liquid eutectic droplet. Upon supersaturation, Si precipitates and supplies to the growth of the Si nanowire.

Fig. 2-10 Schematic diagram of the nanowire growth apparatus.[29] The output from a pulsed laser (1) is focused (2) onto a target (3) located within a quartz tube; the reaction temperature is controlled by a tube furnace (4). A cold finger (5) is used to collect the product as it is carried in the gas flow that is introduced (6, left) through a flow controller and exits (6, right) into a pumping system.

In laser ablation, sophisticated gas installations and substrate are no need. The composition of the nanowires can be varied by simply changing the composition of the laser ablation target. The high temperature allows the use of non-gold catalyst materials such as Fe and Ni. The size of the nanowires depends on both the type of metal catalysts and the gases that are streamed through the furnace, such as H_2 , He, Ar or N_2 . [85] However, it is not suitable for the in-place epitaxial growth of Si nanowires and the product yield is low.

2.2.5.3 Thermal evaporation

Thermal evaporation of commercially available Si-containing powders, e.g., Si, SiO₂ or SiO, is a cost-effective method to produce Si nanowires.[86] A two-zone tube furnace connected to an inert gas supply and the above mentioned powders are the basic requirements for the synthesis of Si nanowires. The high-temperature tube has a temperature gradient from about 1350 to 900 °C. As seen in **Fig. 2-11**, Lee et al. believe that it undergoes a disproportionation reaction into Si and SiO₂, i.e., $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, thereby forming the nanowires due to the nonexistence of metal in the nanowire samples even in the case of laser ablation of Si/Fe disk. Later in 2001, the growth was explained by the self-assembling of the unsaturated Si sub-oxide clusters through the formation of the preferred Si-Si bonds due to the highly reactive Si atoms in the clusters,[87] and the concomitant reconstruction and migration of some oxygen atoms to the surface. In the process, the only equipment required is a tube furnace. Thermal evaporation represents the most cost-efficient way of producing Si nanowires. The difficulty in controlling the nanowire diameters, lengths and doping is the main disadvantage. Another drawback is that epitaxial growth on Si substrates is impossible, as the substrate would oxidize rapidly under the prevailing oxygen rich conditions.

Fig. 2-11 Nucleation and growth mechanism of Si nanowires.[88] The parallel lines indicate the $\langle 112 \rangle$ orientation. (a) Si oxide vapor is deposited first and forms the

matrix within which the Si nanoparticles are precipitated. (b) Nanoparticles in a preferred orientation grow fast and form nanowires. Nanoparticles in nonpreferred orientations may form nanoparticle chains.

The experiments carried out by Lee et al. could be grouped into two categories based on the high-temperature tube and the growth atmosphere (cf., **Table 2-2**): (1) Si/Fe or Si disk, and Si/SiO₂ powder mixture were evaporated at 1200 °C in quartz tube under Ar atmosphere; [89-93] (2) SiO powders were evaporated at 1200-1320 °C in alumina tube under Ar+H₂ atmosphere. [5, 27, 94, 95] The “oxide-assisted growth” mechanism can’t explain why Ar/H₂ is used for alumina tube, [88, 91, 92] only Ar is used for quartz tube. The following analysis shows that it is actually not “oxide-assisted growth”, instead, it is still a metal-seeded “solid-liquid-solid” growth process, where the metal could be Cu and Al.

Table 2-2 Key experimental conditions in the “oxide-assisted growth” related articles

Ref/Year	high- temperatur e tube	Atmosphere/flow rate (sccm) /Pressure (Torr)	Furnace temperature (°C)	Growth temperature (°C)	Source materials (Supplier, purity)
[89]/1998	Quartz	Ar/50/500	1200	Unknown	Si/Fe disk made by pressing Si powder mixed with 0.5 % iron
[90]/1999	Quartz	Ar/50//500	1200	Unknown	Si disk made by pressing the Si powder at 150°C for 48 h under a hydraulic press Si powder mixed with
[91]/1998	Quartz	Ar/Unknown/500	1200	930	approximately 70 wt % SiO ₂ (Goodfellow, purity 99.99%)
[92]/1999	Quartz	Ar/Unknown/500	1200	930	Si powder mixed with about 70 wt% SiO ₂ (Goodfellow, 99.99%)
[93]/1999	Quartz	Ar/50/500	1200	920-950	Mixed disk of Si (purity: 99.998%, particle size: ~45 μm) and SiO ₂ powder (purity: 99.995%, particle size: ~50 μm) with a hydraulic press.
[94]/2000	Alumina	5%H ₂ +Ar/50/400	1300	930	SiO powders (Goodfellow, 99.95%)
[95]/2001	Alumina	5%H ₂ +Ar/50/400	1250	950	SiO powders (Unknown)
[27]/2003	Alumina	5%H ₂ +Ar/50/300	1320	Unknown	SiO powders (Aldrich, 325 mesh, 99.9%)
[5]/2003	Alumina	4%H ₂ +Ar/100/200	1200	900	SiO powders (Unknown)

The disproportionation of SiO, i.e., $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, was the backbone of the “oxide-assisted growth”, but there was no SiO to start with in the experiments of category 1, because Si/Fe disk was a mixture of Fe and Si powders; Si disk was made of Si powder; and Si/SiO₂ powder mixture was made by mixing Si and SiO₂ powders. Powders contain large quantities of absorbed or occluded gases. Upon heating, the spontaneous release of gases due to the great volume expansion would cause violent ejection of the evaporant particles.[96] This is why the baffled sources have been designed to inhibit direct line-of-sight transmission from the evaporant to the substrates in thin film technology (cf., **S_Figure 1**). During thermal evaporation of the Si/SiO₂ mixed powders in quartz tube, Si atoms and SiO₂ molecules are sublimated from the particle surface (1200 °C [97]), the micro-particles are also ejected into the atmosphere due to volume expansion of the residual gases. Commercial Si and SiO₂ powder particles are in micron-scale, e.g., around 45 micron in diameter,[93] at least 5 orders of magnitude larger than the diameter of Si atoms, Ar or SiO₂ molecules (around 0.30 nm, cf., **Table 2-3** [98]). The mass of a Si atom (i.e., 4.67×10^{-23} g) is 0.7 times heavier than an Ar molecule, and the mass of a SiO₂ molecule (i.e., 9.98×10^{-23} g) is 1.5 times heavier than an Ar molecule, while the mass of a Si micro-particle is around 1.12×10^{-7} g, 1.69×10^{15} times heavier than an Ar molecule. Si vapor pressure of around 0.837 torr could be produced during thermal evaporation of bulk Si at 1200 °C,[97] under 200-500 torr (cf., **Table 2-3**),[96, 99, 100] however, the mean free path of these vaporized atoms/molecules is lower than 3.11 μm, i.e., a galaxy away from the location where the nanowire grew (i.e., 15 cm downstream[89, 93]). To reach the growth location, the vaporized Si atoms would collide at least 4.8×10^4 times with the Ar molecules. These collisions would scatter the sublimated atoms/molecules, and attenuate or

annihilate the momentum. As such, the vaporized atoms/molecules couldn't reach the growth location to supply the growth of Si nanowires.

Table 2-3 Physical constants of the micro-particles, atoms and molecules

Substance	Diameter of micro-particle, atom, or covalent bond (nm)	Mass (g)	Density (g/cm ³)	Mean free path (μm, at 1200 °C, under 200-500 torr)	Ref
Si					Aldrich,
micro- particle	4.4-4.5×10 ⁴	1.11- 1.12×10 ⁻⁷	2.32-2.34	Nil	Goodfellow, [97]
SiO					Aldrich,
micro- particle	4.4-4.5×10 ⁴	0.95 1.02×10 ⁻⁷	2.13	Nil	Goodfellow, [97]
SiO ₂					Goodfellow,
micro- particle	4.5×10 ⁴	1.04- 1.11×10 ⁻⁷	2.18-2.32	Nil	[97]
Si atom	0.235	4.67×10 ⁻²³	Nil	1.24-3.11	
SiO molecule	~0.30	7.32×10 ⁻²³	Nil	0.76-1.91	
SiO ₂ molecule	~0.30	9.98×10 ⁻²³			[98]
Ar molecule	0.394	6.64×10 ⁻²³	1.4 (87 K)	0.44-1.12	
H ₂ molecule	0.240	3.35×10 ⁻²⁴	0.07 (20 K)	1.19-2.98	

Growth of Si nanowires needs mobile Si atoms: in vapor,[30] melt,[29] or solution.[6] Ref [86] assumed “semi-liquid” SiO_x cluster at the tip of the nanowire

served as nucleation sites thus assisted the growth of Si nanowires in a certain crystalline orientations.[87] The SiO_x clusters were formed by the sublimated Si atoms and SiO_2 molecules after colliding with the Ar molecules. To grow Si nanowires, i.e., Si core surrounded by SiO_2 sheath, ≤ 43 nm in diameter and a few hundreds microns in length,[89] requires thousands upon thousands of mobile Si atoms or SiO_2 molecules to accurately land right at the tip of the lying nanowires. Therefore, it is impossible to grow Si nanowire from the vaporized Si atoms or SiO_2 molecules due to their minute mean free path, and comparable diameter and mass with the Ar molecules. Moreover, even though two SiO_x clusters accidentally fuse together via forming the preferred Si-Si bond, no force could drive the Si-bonded oxygen atoms to the outer surface, and not to mention the growth of the one-dimensional Si nanowires in specific crystalline orientations.

On the other hand, the collisions have negligible impact on the ejected micro-particles due to the dramatic difference in diameter (5 orders of magnitude) and mass (15 orders of magnitude) with the Ar molecules. For reference, the diameter and mass of a basketball (around 246 mm in diameter, and 600 g in mass) are only 6 times bigger and 200 times heavier than a ping-pong (around 40 mm in diameter, and 2.7 g in mass); or there are only 1 order of magnitude in diameter difference and 3 orders of magnitude in mass difference between a basketball and a ping-pong. The collisions could not affect the kinetic energy of the ejected micro-particles, thus it is highly possible that these particles could reach the growth avenue. However, the Si atoms are still confined in the ejected Si particles, and not free to move around to grow into Si nanowires. Supposedly the “semi-liquid” SiO_x cluster in ref [86] represents the mixture of Si and SiO_2 . But Si has a melting point of 1410 °C,[97] and SiO_2 melts at 1703 °C. The growth temperature was 900-950 °C.[5, 91-

95] Melting of Si or SiO₂ is impossible. As the crystalline size reduces to certain degree, its melting temperature drastically reduces. This is called “size effect”. It is reported that the diameter of the as-grown Si nanowires could reach 43 nm.[89] But Si particle has to be less than 20 nm in diameter before it can have any size effect on melting point.[101, 102] And, to melt below 900 °C, Si particle must be less than 10 nm. Commercial Si and SiO₂ powders are reported in micron scale,[93] i.e., 45 μm, 3 orders of magnitude larger than the diameter of the nanowires, thus “size effect” does not work. Consequently, the assumption of the “semi-liquid” SiO_x cluster is of no ground, thus the Si atoms are still confined in the ejected Si particles, not free to move in space to grow into Si nanowires.

With metallic impurities, however, melting point of Si can drastically decrease: in contact with Al, Al-Si eutectic droplet forms at only 577 °C;[56] meeting with Cu, Cu-Si eutectic droplet forms at 802 °C; with Fe, eutectic Fe-Si melts at 1207 °C. In 1996,[103] in 2002,[104] in 2003,[105] and in 2004,[106] it is reported that quartz tube already contains metallic impurities including Al and Cu (cf., **Table 2-4**). To confirm the metallic impurities on the quartz tube wall, a Φ10 mm×800 mm fused quartz tube (UFO Labglass, Singapore), with constriction at the middle point is heated to 1100 °C at a ramping rate of 5 °C min⁻¹, and held for 2 hour in a vertical tube furnace. The tube is filled with flowing gases including 20% methane and 80% nitrogen at a flow rate of 5 standard cubic centimeters per minute (sccm) and under 760 torr pressure. The tube has been used for a long time before. After the heat treatment, the quartz tube is cooled down to room temperature at a cooling rate of 5 °C min⁻¹. The quartz tube pieces are cleaned ultrasonically for 20 min in acetone followed by 10 min in ethanol before characterization on morphology, composition and structure. It is found that a lot of grain boundaries are shown up on the quartz

tube wall (cf., **Fig. 2-12a**, **S_Figure 2**, dark arrows). This is the indication of the crystallization of the fused quartz. The crystallization is double confirmed by the X-ray diffraction peaks (cf., **Fig. 2-12b**), where several characteristic peaks: (100) centered at 20.51° , (101) centered at 26.27° , (110) centered at 35.91° , (102) centered at 39.01° , and (111) centered at 39.65° , (200) centered at 41.72° , (201) centered at 45.04° , (003) centered at 50.14° , (103) centered at 54.71° , (211) centered at 58.90° , (300) centered at 64.56° , (203) centered at 67.20° , (104) centered at 72.64° , (220) centered at 76.15° , and (213) centered at 78.62° are detected, exhibiting the typical crystalline structure of quartz. The X-ray photoelectron spectroscopy core-level spectra detected from the outside tube wall reveals the dramatic increase of the atomic concentration of Zn, Al and Cu (cf., **Fig. 2-12**, c-e), implying the oozing of the metallic impurities from the quartz tube, though the spectra exhibit their oxide states, i.e., 1022.4 eV for Zn $2p_{3/2}$, [107] 934.0 eV for Cu $2p_{3/2}$, [108] and 74.6 eV for Al $2p_{3/2}$. [109] Understandably, Zn, Al and Cu could be oxidized in air, but could still reserve the metallic state in the quartz tube under the Ar atmosphere. To double confirm the crystallization of fused quartz occurring in the first heating, a brand new fused quartz tube is heated up to 1150°C at 5°C min^{-1} , and held at this temperature for 45 min (cf., **S_Figure 3a**), and then cooled down to room temperature at 5°C min^{-1} . Upon heating, the grain boundary does appear on the quartz tube wall, double confirming the crystallization of the fused quartz (cf., **S_Figure 3**, b-e). Three reasons explain the appearance of the grain boundary and the oozing of the metallic impurities: (1) the crystallization of the amorphous fused quartz taking place in the first heating produces the grain boundaries (cf., **Fig. 2-12**, a and b), (2) the $\alpha \rightarrow \beta$ phase transition of the crystalline quartz occurs at 573°C (in the succeeding heating), [110-113] resulting in the

change of the quartz crystals in cell dimension and volume, thus thickens the grain boundaries; (3) the melting of the metallic impurities, e.g., Zn (melting point, 420 °C), [97] Al (melting point, 660 °C) and Cu (melting point, 1083 °C). Though the impurity level may change from supplier to supplier, Al and Cu exist in all the quartz tubes (cf., **Table 2-4**).

Table 2-4 Chemical composition and/or metallic impurities of quartz and alumina tubes from common suppliers

Materials (Supplier)	Purity (%) or grade	Chemical composition (percentage by weight) or trace element content (parts per million by weight)
Fused quartz tube (Quartz Scientific)	99.995	Al (16), Cu (<0.1) , As (<0.4), B (<0.1), Ca (0.6), Cd (<0.01), Cr (0.05), Fe (0.3), K (0.7), Li (1), Mg (0.1), Mn (0.1), Na (1), Ni (<0.1), P (1.5), Sb (<0.4), Ti (1.1), Zr (1.5), OH (<5)
Fused quartz tube (Heraeus)	HQS grade	Al (15), Cu (<0.05) , Ca (0.5), Cr (<0.05), Ca (0.6), Fe (0.1), K (0.4), Li (0.6), Mg (0.05), Mn (<0.05), Na (0.3), Ti (1.1), Zr (0.7), OH (<30)
Fused silica glass (Toshoh)	N grade	Al (8), Cu (<0.01) , Ca (0.6), Fe (0.2), Na (0.6), K (0.1), Li (<0.07), Mg (0.4), OH (200)
Fused quartz tube (UFO Labglass)	Corning 7980 B	Al (40), Cu (<13) , Ni (<7), Zn (<30), Ti (<40), Zr (<30), U (<1), Mg (<25), K (<21), Cr (<1), Fe (<15), Mo (<5), Li (<1), Ca (<20), B (<100), As (<5), (Na<150), V (<10)
High-purity alumina tube (Vesuvius/McDanel)	99.8	Al₂O₃ (99.82%) , Fe ₂ O ₃ (0.025%), SiO ₂ (0.06%), CaO (0.04%), MgO (0.035%), Na ₂ O (0.008%), TiO ₂ (0.004%), Cr ₂ O ₃ (0.003%), K ₂ O (0.001%), B ₂ O ₃ (0.001%)
High-purity alumina tube (Graphtek LLC)	>99.6	Al₂O₃ (>99.6%) , Fe ₂ O ₃ (<0.05%), SiO ₂ (<0.1%), Na ₂ O (<0.1%), K (<0.1%), L (<0.1%)

Fig. 2-12 Surface morphology, structure and chemical state sampled at (I) the unheated fused tube wall, (II) 3 cm away from the heat center, and (III) heat center. (a) Surface morphology. (b) XRD patterns. (c) XPS survey scan. (d) Cu 2p core-level XPS spectra. (e) Al 2p core-level XPS spectra.

A solid evidence of the metallic impurity is readily found as the dark eggs embedded in the amorphous SiO₂ nanowire, i.e., frog-egg-shaped Si nanowire (cf., **FIG.3b** in ref [90], **S_Figure 4a**). The dark “eggs” were declared to be the sites of Si nuclei (precipitated through the disproportionation of SiO) embedded in Si nanowires. In that case, however, there shouldn’t be any contrast between the “Si nuclei” and the “Si nanowire” since they are Si. Actually, the “eggs” were the metallic Cu or Al, highly possible entrapped through the precipitation of the supersaturated metallic Cu or Al, instead of Si, from the oxidized Cu-Si or Al-Si

eutectic droplet, since the metallic catalysts at the tube wall could dissolve into the droplet to reach supersaturation at certain moment, when Si is not supersaturated as a result of the oxidation of the droplet. It is noted that similar metallic nanoparticles were entrapped in Si oxide nanowires during the Au-Si droplet seeded growth, where Au was deposited on the Si films or Si wafers, and the Si atoms came from the Si films.[114, 115] or the ejected Si-containing particles.[116] For instance, the Au₂Si nanospheres were peapodded in the Si oxide nanowires during annealing the Au/a-Si/c-Si film at 1030 °C under 50 sccm N₂ flow and 760 torr atmosphere (cf., **Figs. 1**, a and b in ref [114], **S_Figure 4**, b-c). The Au nanospheres were entrapped in the silica nanowire during heating the Au/SiN_y/Si wafer sandwiched with an Au-coated Si wafer at 530 °C in a gas mixture of H₂ (200-250 sccm) and NH₃ (300-350 sccm) atmosphere under 50-70 torr pressure in a microwave chamber (cf., **Figures 2 e and f** in ref [115], **S_Figure 4**, d-e). The Au/Si nanoparticles were entrapped in the amorphous SiO₂ nanowires during thermal evaporation of the SiO powders at 1050 °C on an Au-coated Si wafer (850-900 °C) in a quartz tube at 50 sccm N₂ and 25 mbar atmosphere by Lee's co-workers, Kolb et al. (cf., **FIG.2** and **FIG.4** in ref [116], and **S_Figure 4**, f-j).[117] Theoretically and experimentally, therefore, the nanowire growth via thermal evaporation of the Si-containing powders in quartz tube is actually seeded by the metal-Si eutectic droplet, where the metal could be Cu and Al, and Si atoms come from the ejected Si particles.

A plausible explanation is that the ejected Si micron-sized particle forms liquid "metal-Si" (where the metal being Al or Cu) eutectic droplet on the quartz tube wall, which seeds the growth of the Si nanowire. The key in the whole process is the availability of Si and metallic impurity that could form metal-Si eutectic droplet. In the case of laser ablation of Si/Fe disk (cf., **Fig. 2-13a**), and in the case of

Si/SiO₂ powder mixture (cf., **Fig. 2-13b**), Si is from the ejected Si particles. In quartz tube,[89-93] metallic Al and Cu already exist as impurity in the tube composition and could ooze onto the tube wall during crystallization of the amorphous fused quartz and the $\alpha \rightarrow \beta$ phase transition of the crystalline quartz. Formation of liquid Al-Si and Cu-Si eutectic droplet respectively takes place at only 577 °C and 802 °C, much lower than the growth temperature (900-950 °C). In case of laser ablation, Fe exists in the disk. Formation of Fe-Si eutectic droplet takes place at 1207 °C: though this temperature is 7 °C higher than that at the disk, laser ablation may have produced vapor Fe or Si atoms or nanosized particles thus the size effect operated there, as explained by Lieber et al..[29] As such, Si dissolves into the liquid eutectic droplet. Upon supersaturation, Si precipitates and supplies to the growth of the Si nanowire (cf., step 4 in **Fig. 2-13**).

As the tube wall is at 900-950 °C, a water-cooled “copper finger” points in the center of the tube, and the tube is evacuated with the Ar gas, the tube center must be colder than the wall (the “*driving force*”), therefore, the eutectic droplet stays at the wall and the wire grows away from the wall towards the center of the tube (thus the catalyst droplet would always be found at the “root” of the wire instead of “atop”). This is confirmed in ref [89], where the nanowires were “formed on the inner wall of the quartz tube at the position surrounding the tip of the copper cold finger”. As such, no metallic trace should be found if the “root” at the wall is not examined (cf., step 4 in **Fig. 2-13**). Meanwhile, as the nanowire freezes out from the liquid “foundation”, it couldn’t stand thus either lies on the surface of the tube wall or on the Mo gird that is placed on the tube wall. The nanowires were either “taken off directly from the produced spongelike web”, [89] or sampled through placing the Mo grid “in the region of the quartz tube where nanowires grew”, [91,

92] therefore, the observed particles or nanowire standing alone on the grid were not the nucleation sites, but the broken end sections of the nanosphere chains or smooth Si nanowires (cf., **Figs. 1 b** and **c** in ref [92]). The seeding of the liquid metal-Si eutectic droplet, i.e., liquid foundation, at the tube wall explains why the Si nanowires either form “spongelike web” on the tube wall,[89-92] rather than stand perpendicularly to the tube wall.

Even in presence of metallic impurities, ref [91] failed to produce any Si nanowires with pure SiO₂ powders in quartz tube at 930 °C, because here the SiO₂ powders didn't contain any elemental Si, and 930 °C could not melt SiO₂ (melting point: 1703 °C [97]). It is not difficult to infer that the vaporized SiO₂ micro-particle in refs [91-93] (cf., **Fig. 2-13b**) did not melt or participate in the growth of the Si nanowire. This also explains why the yield of the Si nanowires didn't show any dependence on the fraction of Si oxides in the Si/SiO₂ mixed powders,[91] (e.g., the nanowire yield was lower than 0.01 mg at 0 wt.% SiO₂; but it became zero when 100 wt.% SiO₂ powder was used.) but dependent on the fraction of Si in the Si/SiO₂ powder mixture. Therefore, the Si oxide sheath is formed via the precipitation of the supersaturated Si oxide from the oxidized metal-Si droplet. Earlier in 2000, Yu et al., (co-workers of Lee et al. in ref [89]) also reported the solid-liquid-solid growth of Si nanowires,[31] double confirming the possibility of forming the metal-Si droplet at the tube wall to seed the Si nanowires through the eutectic melting of the Si-containing micro-particle and metallic catalysts. In our recent nickel-seeded growth of Si nanowires through thermal annealing of a nickel-coated Si wafer beneath sputtered amorphous carbon,[34] the nickel nanoclusters were also found seeding at the root of the as-grown wires, not atop the wire.

Fig. 2-13 Schematic diagrams of the Al-, Cu- and Fe-seeded growth of Si nanowires during (a) laser ablation of Si/Fe disk in quartz tube at 1200 °C under Ar atmosphere, (b) thermal evaporation of Si/SiO₂ powder mixture in quartz tube at 1200 °C under Ar atmosphere, and (c) thermal evaporation of SiO powders in alumina tube at 1200-1320 °C under Ar+H₂ atmosphere. To simplify the mechanism, the slight deformation of the ejected micro-particle, the vaporized atoms or molecules, the size difference between the micro-particles and the droplets, and the oxide sheath in the Si nanowires are ignored.

Whenever the alumina tube was used, H₂ was introduced,[5, 27, 94, 95] and the furnace temperature was held at 1200-1320 °C (cf., **Table 2-2**). Under this condition, nanosized Al could be reduced from Al₂O₃. It is reported that the addition of 5-8 wt.% hydrogen to the steam could cause an exponential erosion rate increase over the steam-only on a Φ3.17 mm×16 mm long alumina rod that is heated in a alumina tube furnace through $\text{Al}_2\text{O}_3(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{Al}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$. [118] At 1277 °C, the 10 m/s hydrogen-steam flow has a penetration rate of 0.1 mm per year, and a weight loss rate of 0.008 mg per hour on the alumina rod. Surface reduction of alumina by H₂ may take place at 450-550 °C through $\text{Al}_2\text{O}_3(\text{surf}) + \text{H}_2(\text{g}) \leftrightarrow 2\text{AlO}(\text{surf}) + \text{H}_2\text{O}(\text{g})$. [119] Theoretical considerations based on the thermodynamic data show that liquid or gaseous aluminium could be formed at 1600 K (1327 °C) or above, by direct reaction between molecular hydrogen and alumina through $\text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{Al}(\text{l, g}) + 3\text{H}_2\text{O}(\text{g})$. [120] Laboratory experiments demonstrate that hydrogen dissolved in molten aluminium could possibly reduce alumina to aluminium at temperature as low as 700 °C through $\text{Al}_2\text{O}_3(\text{s}) + 6\text{AlH}(\text{g}) \leftrightarrow 8\text{Al}(\text{l}) + 3\text{H}_2\text{O}(\text{g})$. [120] It is confirmed that this reaction occurring at 1500 K (1226 °C) is still exothermic with $\Delta H_f^\circ = -475.010 \text{ kJ/mol}$ and $\Delta G_f^\circ = -52.505 \text{ kJ/mol}$, indicating it may have taken place at lower temperatures. Though the experiments in ref [120] used 10% H₂ and 90% Ar at 1200 °C for 24 h, while refs[5, 27, 94, 95] used 4%-5% H₂ mixed in Ar at 1200-1320 °C for 2-7 h, it is highly probable that this reduction have taken place to produce liquid Al at the very shallow surface of the alumina tube wall, i.e., nanosized surface reduction. However, it is technically difficult to prove the superficial surface of the alumina tube has been reduced after the growth since the nanosized Al is easily oxidized in

air, but could maintain the metallic droplet to seed Si nanowires under Ar+H₂ atmosphere.

In 1996,[121] in 2003,[122, 123] and in 2004,[124] it was found that the commercially available SiO powders (around 44 micron in diameter, cf., **Table 2-2**), were not 100% SiO, but an inhomogeneous mixture of amorphous SiO₂ and amorphous Si with SiO phase at the interface (cf., **Fig. 2-13c**, “starting SiO particle”). Upon thermal evaporation of the SiO powders (at 1300 °C,[94] 1250 °C,[95] 1320 °C,[27] or 1200 °C[5]), the SiO micro-particles could eject in space, and then land on the inner tube wall (cf., step 2 in **Fig. 2-13c**). Disproportionation of SiO, i.e., $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, takes place at around 900 °C through the migration of electrons.[122] However, no physical movement of Si atoms or SiO₂ molecules occurs in this redox reaction. It is noted that this reaction needs at least two SiO molecules with intermolecular bonds, thus can only occur in the ejected SiO micro-particle, rather than the space-separated gaseous SiO molecules that are sublimated from the SiO powder particles. After the redox reaction, therefore, the particle becomes a microscopic mixture of Si and SiO₂ clusters. These clusters are not separable, but still confined in the particle, not able to move freely and separately in space (cf., **Fig. 2-13c**, “ejected SiO particle”).

Once Al (liquid) is available, however minute it could be, nanosized Al-Si droplet could form at 577 °C through the eutectic melting the Si portion in the SiO particle (either existed in the starting powder or produced from the disproportionation reaction but still confined in the SiO particle). As the tube wall was over 900 °C, definitely the liquid Al-Si eutectic droplet could form and seed the Si nanowires at the tube wall. Refs [94, 95] placed Si wafers in the alumina tube under H₂+Ar atmosphere and still observed Si nanowire on the substrates.[94, 95] A possible

explanation is that the liquid Al on the “ceiling” (which melts at 660 °C,[97] while the growth temperature was over 900 °C), or the ejected SiO micro-particle getting in touch with the liquid Al on the “ceiling”, dropped from the “ceiling” onto the substrates whereby the nanowire growth took place (cf., **Fig. 2-13c**). Since the SiO₂ portion is confined in the SiO micro-particle (cf., **Fig. 2-13c**), and could not melt to participate in the growth of the Si nanowire, the Si oxide sheath is also formed through the precipitation of the supersaturated Si oxide from the oxidized metal-Si droplet.

In conclusion, the growth of Si nanowires via evaporating Si-containing powders in quartz tube is not “oxide-assisted”; but still metal-Si droplet seeded “solid-liquid-solid” growth. The ejected Si micro-particle (the “*solid*”) gets in touch with metallic Al or Cu that is inherited in the tube to form Al-Si or Cu-Si eutectic droplet (the “*liquid*”) on the tube wall. Si thus dissolves into the droplet. As it is supersaturated with Si, Si precipitates towards the cold tube center (the “*driving force*”), and adds into the Si nanowire (thus “*solid*” again). The oxide sheath is formed through the precipitation of the supersaturated Si oxide from the oxidized metal-Si droplet. The liquid metal-Si eutectic medium, i.e., “foundation”, always seeds at the tube wall, not atop the nanowire, resulting in the “spongelike web” on the tube wall. In alumina tube, the Si nanowire could be seeded by the Al-Si eutectic droplet, where the Si atoms come from the Si portion in the ejected SiO micro-particle (either inherited in the starting SiO particle or produced from the disproportionation of SiO), and the nanosized metallic Al could reduce from Al₂O₃ under Ar+H₂ atmosphere.

2.2.5.4 Thermal annealing

The growth of Si-related nanowires via directly thermal annealing of metal-covered Si wafers was first reported by Yu et al.,[31] who grew amorphous Si-oxide nanowires through heating 40 nm Ni coated Si (111) wafers to 950 °C under an Ar/H₂ atmosphere without supplying a gaseous or liquid Si-containing source materials. **Fig. 2-14** depicts the growth process.

Fig. 2-14 Si-oxide nanowires grown through thermal annealing of a Ni-covered Si wafer. (a) Deposition of a thin layer of Ni on the Si (111) wafer; (b) formation of the Ni-Si eutectic droplets; (c) the continuous diffusion of Si atoms through the substrate-liquid (S-L) interface; (d) final state of the Si-oxide nanowire growth. The smooth surface of the original substrate becomes rough at the end of the Si oxide nanowire growth.[125]

Under the conditions, the specific surface/volume ratio of bulk Si substrate is extremely low compared with that of the micro-sized Si powder target, or in the case of laser ablation. Therefore, the Si concentration in the vapor phase is

negligible at the growth temperature. On the other hand, the Si wafer was covered by a thin layer of Ni. Thus the only possible Si source comes from the bulk Si wafers since no extra Si source was introduced into the vapor phase. The binary Ni-Si diagram shows that the eutectic point of NiSi_2 is 993°C . Due to the melting effect of small-size grains, the eutectic compound NiSi_2 can form at a temperature lower than 993°C . It is proved that the Ni film could react with the Si wafer at a temperature above 930°C , and forms NiSi_2 eutectic liquid alloy droplets. Because of the relatively high solubility of Si in NiSi_2 eutectic droplet, more Si atoms would diffuse through the solid (substrate)-liquid interface into the liquid phase i.e., the NiSi_2 droplets. A second liquid-solid (nanowire) interface will form when the liquid phase becomes supersaturated due to thermal or compositional fluctuations, resulting in the growth of Si nanowires. Because this growth process involves solid-liquid-solid phases, it is called SLS growth which is, in fact, an analogous to the VLS mechanism. After Yu et al., a few groups conducted SLS growth of amorphous Si, SiO_x or crystalline-Si/amorphous- SiO_x nanowires, i.e., c-Si/a- SiO_x , directly using Si wafer as the Si source and adopting Au,[126, 127] Pt/Au,[128] NiO ,[32] Fe,[33] as catalyst in a N_2 or Ar atmosphere. For instance, Park et al. grew c-Si/a- SiO_x nanowires by heating a NiO-covered Si substrate under a reductive environment of WO_3 , C and Ar atmosphere via SLS growth.[32] A tentative mechanism for the growth of the nanowire based on chemical reaction was proposed: CO gas from the carbothermal reaction of WO_3/C reacted with SiO_x to produce SiO and CO_2 , where SiO_2 was formed from Si-Ni-O liquid droplets in the NiO/Si interface. Si and SiO_x were generated through the disproportion reaction of SiO in the film.[32] The c-Si/a- SiO_x nanowire was grown via the phase separation of Si and SiO_x from the super-saturated Ni-Si-O droplets by the cooling

effects of Ar flow. Taking consideration of the oxidation of the droplet at the beginning stage of the growth, Nie et al. developed a mechanism to describe the growth of Si-SiO_x core-shell nanowires during directly heating Fe-coated Si wafers.[33] In the mechanism, the one-dimensional amorphous SiO_x nanowires was grown from the fully oxidized Fe-Si alloying droplets as a result of the continuously feeding Si into the alloying droplets. Partially oxidized large droplet forms Fe-Si alloying core and Fe-O-Si shell, resulting in Si-SiO_x core-shell nanowire.

Amorphous SiO_x nanowires could be grown directly via heating a NiO-covered Si substrate without using WO₃/graphite powder in a tube furnace,[32] or thermal heating Au or Ni coated Si substrates.[129] The residual oxygen is unavoidable in the chamber. The serious oxidation by residual oxygen in the reaction chamber at high temperature should not be overlooked, since the growth is often under an inert gas atmosphere rather than a high vacuum environment. The formation of amorphous all-SiO_x nanowires is attributed to the serious oxidation of the metal-Si droplet. To grow crystalline Si nanowires, the oxidation of grown Si nanowires must be retarded. So far, only <111>,[32] and <110>,[34] and <112> oriented,[130] Si nanowire has been reported in the growth. The comprehensive understanding of the mechanisms is still the main challenge, including the growth orientations, cross section, the lattice structure, the controlling of the size and growth orientations.

2.3 Summary

As summarized in **Table 2-5**, the various “bottom-up” growth methods are quite distinct in their characteristics. Basically speaking, they can be classified into

substrate-tethered growth (nanowires directly grown at a specific position on the substrate) and two-step growth-assembly (nanowire growth is performed in a first step, followed by a subsequent assembly step) approaches. Regarding the former, the top-down fabrication method has competitive controllability, reliability, and size variability. CVD is presumably the closest to the top-down method, as it allows for an epitaxial growth on Si substrates at specific positions, and additionally offers great versatility concerning growth conditions, dimensions and properties of nanowires. MBE, though combining epitaxial growth with a good controllability of composition, lacks the variability of CVD with respect to nanowire diameters and aspect ratios.

Table 2-5 Summary of the various nanowire growth techniques

Mechanism	Techniques	Si source	Advantages	Disadvantages
Top-down	Metal-assisted chemical etching	Si wafers	<ul style="list-style-type: none"> • Controllability in growth orientation, position, and size, • substrate-tethered growth 	<ul style="list-style-type: none"> • Unsolved etching mechanisms, • Time-consuming, expensive and difficult to achieve uniform diameters below 10 nm
VLS	Chemical vapour deposition	SiH_4 , Si_2H_6 , SiCl_4/H_2	<ul style="list-style-type: none"> • Broad choice of the metallic catalysts, • Substrate-tethered epitaxial growth, 	<ul style="list-style-type: none"> • Ostwald ripening effect, • Flammable and toxic gases

			<ul style="list-style-type: none"> • High growth rates, • Good controllability and variability of the composition 	<ul style="list-style-type: none"> • Unable to control the growth orientation in non-epitaxial growth
VSS	Chemical vapour deposition	SiH_4 , Si_2H_6	<ul style="list-style-type: none"> • Reduced growth temperature, • Controllability of orientation, • Mitigated particle ripening, • No unintentional impurities, • Abrupt heterostructural interfaces 	<ul style="list-style-type: none"> • Very low growth rate, • Flammable and toxic gases
SFLS	Supercritical-fluid-liquid-solid growth	$\text{SiH}_2(\text{C}_6\text{H}_5)_2$, SiC_6H_8	<ul style="list-style-type: none"> • Uniform diameter, • Easy to control the orientation by pressure 	<ul style="list-style-type: none"> • High pressure and cost, • Unable to realize in-place epitaxial growth, • Limited choice of metallic catalysts and fluid, • Surface contamination of hydrocarbon
	Molecular beam epitaxy	Bulk Si	<ul style="list-style-type: none"> • Easy to dope other elements, • Substrate-tethered epitaxial growth 	<ul style="list-style-type: none"> • Low growth rate, • High cost due to ultrahigh vacuum, • Considerable Si film growth,

SLS				<ul style="list-style-type: none"> • Limited flexibility for nanowire diameters and aspect ratios
	Laser ablation	Si-containing powders	<ul style="list-style-type: none"> • No sophisticated gas installations and substrate, • Controllability of the nanowire composition, • Wide choice of metallic catalysts 	<ul style="list-style-type: none"> • Not suitable for the in-place epitaxial growth, • Low product yield
	Thermal evaporation	Si-containing powders	<ul style="list-style-type: none"> • Cost-efficient 	<ul style="list-style-type: none"> • Hard to control the nanowire diameters, lengths and doping, • Unable to realize epitaxial growth, • Long growth duration, • Dangerous under hydrogen atmosphere, • High level of defects
SLS	Thermal annealing	Si wafers	<ul style="list-style-type: none"> • No flammable or toxic gas, • Fast growth rate, • Substrate-tethered growth, • Cost-efficient, • No metal contamination at the 	<ul style="list-style-type: none"> • Serious oxidation of the Si nanowires, • Hard to control the diameter and growth orientation of nanowires, • Unclear role of the metal-Si-O droplet,

			nanowire tip, • Unlimited source material	• Hard to control the diffusion rate of Si
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Laser ablation combines a good controllability and variability of the nanowire composition with excellent nanowire quality but small yield. Solution based growth techniques offer a high nanowire yield, which makes this approach especially attractive for large-scale nanowire production. The grown Si nanowires exhibit excellent crystallinity except for the possible surface contamination of hydrocarbon and the limited choice of metal catalysts and silicon reactants. Thermal evaporation which follows the metal-seeded solid-liquid-solid growth mechanism represents the most cost-efficient way of producing Si nanowires. The difficulty in controlling the nanowire diameters, lengths and doping is the main disadvantage. Metal-induced chemical etching is usually time-consuming, expensive and difficult to achieve uniform diameters below 10 nm. The diameter and growth alignment in the VLS growth can be readily controlled by using uniformly distributed metal seeds with well-designed sizes on the substrate. The use of flammable or toxic precursor gases such as SiH_4/H_2 or SiCl_4 is the disadvantage.

The growth of Si nanowires directly from metal-covered Si wafers promises the growth on Si substrates at specific positions, offers great versatility concerning process conditions, nanowire dimensions and properties. The growth employs the wafer as the unlimited source material, thus eliminating to introduce the flammable gas, laser or solution in the growth. The metal catalyst locates at the root of the nanowire, thus eliminating the contamination of the metal catalyst. However, to date, (1) the oxidation of the Si nanowires is hard to retard at too high temperature;

(2) distribution of the growth orientation, the orientation relation between the seeding metal particle and the grown Si nanowire are unsolved; (3) the origin of the various morphologies of Si nanowires is yet elucidated; (4) the size distribution is difficult to control due to the Ostwald ripening effect; (5) the diffusion rate of Si is hard to control due to unlimited Si source. (6) Last but not least, the origin of the growth orientations in all the bottom-up growth couldn't be explained by surface energy of the various crystal planes since the crystallization is an energy-releasing process.

Chapter 3. **EXPERIMENTAL DETAILS**

3.1 Project overview

Si nanowires are reported to be grown via laser ablation of Si and Fe powder mixture, chemical vapor deposition of SiCl_4/H_2 , or SiH_4 gases, thermal evaporation of Si/ SiO_2 powder mixture in quartz tube or SiO powder in alumina tube, evaporation of bulk Si on metal-covered substrates, or thermal degradation of diphenylsilane in a supercritical hexane fluid using the size-monodispersed Au nanocrystals as the seeds. Laser ablation or thermal evaporation needs Si containing powders, and often suffers from the high level of defects. Chemical vapor deposition introduces the flammable and toxic gases. The growth via evaporation of bulk Si takes place only under ultrahigh vacuum. The solution method requires the degradation of specific Si precursor in particular supercritical fluid under high pressure, limited the choice of the metal catalyst and Si reactant.

Si nanowires are also reported to be grown through thermal annealing of Ni-covered Si wafers without introducing any special source materials in the form of vapor, solution or powder. Si in the nanowire comes from the Si wafers. During annealing, Ni melts with the Si wafer at the Ni/wafer interface to form the Ni-Si eutectic droplet. Si atoms therefore continuously diffuse into the droplet. Upon supersaturation, Si is precipitated from the droplet to grow into nanowires. In the growth, Si is from the Si wafer and the liquid metal-Si droplet acts as the medium. However, the detailed growth mechanisms are yet to be elucidated. This project grows Si nanowires of various morphologies and structures via thermal annealing

of Ni-coated Si wafers beneath sputtered amorphous carbon (a-C). Issues including composition and microstructure of the deposited films, the surface morphology of the annealed films, the morphology, composition, structure, growth orientations of the grown Si nanowires, and their relation to the seeding Ni particles, are carefully studied.

3.2 Experimental details

The project schedule, or in other words, the contribution of this project is listed in **Fig. 3-1**. They are: (1) the oxidation retardation by the surface covering; (2) the origin of the growth orientations of Si nanowires; (3) the origin of the morphologies of Si nanowires. The project is carried out in the following steps. Firstly, the single layered Ni film and a-C/Ni double layered films are deposited by magnetron sputtering. The Si nanowires are grown through thermal annealing of the deposited films for different duration of time at 1100 °C. Secondly, the cross section, composition and microstructure of deposited films are characterized by field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), glancing incident X-ray diffraction (GIXRD) and Raman spectroscopy. Thirdly, the surface morphology of the annealed films, the morphology, composition, structure, growth orientation of the grown Si nanowires, and the relations to the seeding Ni particles are examined through careful studies of FESEM, transmission electron microscopy (TEM), selected area electron diffraction (SAED) patterns, and electron dispersive x-ray spectroscopy (EDS).

Lastly, the retardation oxidation of the surface covering, the origin of the growth orientations and the morphologies of Si nanowires are elucidated.

Fig. 3-1 Contribution of this project.

3.2.1 Deposition of Ni and a-C/Ni catalyst films

The single layered Ni and double layered a-C/Ni films were deposited in an E303A magnetron sputtering system (Penta-Vacuum, Singapore).[131] N-type Si (100) wafer was used as the substrate (10 mm×10 mm in area, 475 μm in thickness and 0.5 nm in R_q). Before loading into the sputtering chamber, the substrate was ultrasonically cleaned in acetone for 20 min, followed by 10 min in alcohol. Once the base pressure reached 1.0×10^{-3} Pa, Ar gas was introduced at a flow rate of 50 standard cubic centimeters per minute (sccm). High energy Ar^+ ions were generated at a substrate bias of -300 V for substrate cleaning for 15 min to further clean the

surface contamination. A 5-min sputtering of Ni target (99.99% in purity) in 0.47 Pa pressure at room temperature resulted in a thin layer of Ni catalyst on the substrates. Afterwards, Si and C were subsequently co-sputtered from Si and graphite target (99.999% in purity) on the Ni layer under the same pressure. a-C films of around 130 nm and 570 nm in thickness were co-sputtered for 15 min and 60 min, respectively. The sputtering power densities for Ni, Si and C were respectively RF 1.85 W/cm², RF 2.47 W/cm² and DC 12.22 W/cm².

3.2.2 Growth of Si nanowires

The as-sputtered films underwent rapid thermal annealing (RTA, Jipelec Jetfirst 100 rapid thermal processor) in an Ar ambient at 1100 °C for 60 s and 180 s, respectively. The RTA chamber was purged 10 times with Ar (99.999% in purity) at 2000-sccm before ramping up to 600 °C at 58 °C/s. After dwelling for 6 s at 600 °C, the chamber was further ramped up to 1100 °C at 42 °C/s, and then held for 60 s and 180 s, respectively. After annealing, the chamber was cooled down to 500 °C at 43 °C/s, and then followed by natural cooling to room temperature. During the whole annealing process (ramping, holding, and cooling), the inflow of the Ar gas was kept at 2000 sccm to maintain the chamber pressure at around 1.08×10^5 Pa.

3.2.3 Characterization

Sample characterization includes the cross section, chemical composition, microstructure of the deposited films, the surface of the annealed films, the morphology, composition, structure, growth orientation of the grown Si nanowires,

and the relation to the seeding Ni particles by various characterization techniques.[132] Detail illustration is summarized in this section.

3.2.3.1 Cross section and surface morphology

Field emission scanning electron microscope (FESEM, JEOL JBM-7600F, JEOL Ltd., Japan) was employed to observe the cross-section of the films and the surface morphology of the annealed films. The films are cut through the cross section into small pieces for observation. The working principle of FESEM is summarized below. Under vacuum atmosphere, the electrons generated by a field emission source are accelerated in a field gradient. The electron beam passes through electromagnetic lenses, focussing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor.

3.2.3.2 Chemical composition

The surface chemical states of the films were determined by X-ray photoelectron spectroscopy (XPS, Kratos) using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71 eV) radiation (10 mA and 15 kV) and a hemispherical electron energy analyzer. The mechanism of XPS is summarized as follows. Under ultrahigh vacuum, the sample surface is excited by photons (Al X-rays). Then photoelectrons are emitted either from a core level or valance band of

the atoms near the sample surface. Photoelectrons are counted then separated according to their energy. Energy of photoelectrons is related to atomic and molecular environment. Number of electrons emitted is proportional to the concentration of the emitting atom on the surface. In this study, the base vacuum of the chamber was 2.67×10^{-7} Pa. The spectra of binding energy were used to determine the elements, relative quantity of each element as well as the chemical state of the elements. Survey spectra in the range of -1 - 1200 eV with a step size of 1.0 eV on a scan spot with $300 \mu\text{m} \times 700 \mu\text{m}$ in area were recorded to determine the elements present in the films, followed by high resolution spectra at 0.1 -eV scanning step size covering the binding energy range of the detected elements. The respective core-level XPS curve fitting was performed after a Shirley background subtraction by nonlinear least square fitting using a mixed Gauss/Lorentz function after charge-correcting by positioning C $1s$ peak to 284.6 eV. The atomic concentration of each element was determined by the ratio of the corresponding fitted core-level peak area over the sum of the fitted peak area of all the elements. The depth profiling of the films were obtained by recording the XPS spectra after sputtering by an ion gun (Kratos MacroBeam) with an accelerating voltage of 4 keV. A spot of $220 \mu\text{m}$ in diameter was scanned.

3.2.3.3 Microstructure of the films

X-ray diffractometry is a good way to investigate the crystal structures of the coating. Information like diffraction pattern, lattice plane spacing, lattice constant and grain size can be determined from the diffraction spectra.

The mean crystallite dimension is calculated by Scherrer formula,[133]

$$D = \frac{C\lambda}{\beta \cos \theta} \quad (3-1)$$

Where, D is the mean crystallite dimension normal to diffracting planes. C is a constant ($C = 0.91$), λ is the X-ray wavelength, β is the full peak width at half-maximum peak height and θ is the Bragg angle.

The mean crystallite dimension is also calculated by Williamson–Hall Plot while considering the micro strain.[134]

$$\beta_i \frac{\cos \theta_i}{\lambda} = \frac{K}{D} + \frac{4\varepsilon \sin \theta_i}{\lambda} \quad (3-2)$$

Where, β_i is the integral breadth (in radius 2θ) of the i th Bragg reflection positioned at $2\theta_i$.

In this study, the microstructure of the films is investigated using glancing incidence X-ray diffraction (GIXRD, PANalytical B.V., Almelo, Netherlands) with monochromatic copper $K\alpha$ radiation (40 kV and 40 mA) at wavelength of 0.15406 nm using an incidence angle of 1° . The scanning range is conducted from 40° to 120° at step size 0.02° and 1 second per step.

3.2.3.4 Carbon bonding structure

Raman Spectroscopy is widely used, being a routine, non-destructive way to characterize the detail bonding structure of the amorphous carbon material system through the peak shift and width.[135] Diamond has a single Raman active mode at 1332 cm^{-1} , which is a zone center mode of T_{2g} symmetry. Single crystal graphite has a single Raman active mode, which is the zone-center mode at 1580 cm^{-1} of E_{2g}

symmetry labelled 'G' for 'Graphite' (There is a second Raman active E_{2g} mode at 42 cm^{-1} due to interplane vibrations). Disordered graphite has a second mode at around 1350 cm^{-1} of A_{1g} symmetry labelled 'D' for 'Disorder'. It corresponds to breathing vibrations of rings at the K zone boundary. An unusual and significant fact is that the Raman spectra of most disordered carbons remain dominated by these two G and D modes of graphite, even when the carbons do not have particular graphitic ordering. Therefore, it is possible to find the structural information of carbon and the sp^3 fraction from Raman spectra.

Renishaw Raman Spectroscope RM1000 using a He-Ne laser source with an excitation wavelength of 633 nm, and the scan area about $3.14\text{ }\mu\text{m}^2$ is used for the carbon bonding structure characterization. The data acquisition region is from $3000\text{--}800\text{ cm}^{-1}$, and the laser power used is 50 mW. In order to decrease the noise, three scanning accumulations are used. After data acquisition, the spectra is deconvoluted into two Gaussian peaks for band intensities in terms of counts, and peak positions in terms of wave number (cm^{-1}) by the GRAMS/32 program. The ratio of the peak intensity of D-band over that of the G-band, I_D/I_G , had the same trend as the ratio of the area under the D-peak over that under the G-peak, A_D/A_G . Either of the ratios is the signature of the atomic bonding structure of the carbon coating. The I_D/I_G ratio could be used to estimate the sp^3 fraction in the amorphous carbon.[136, 137]

3.2.3.5 Nanostructures

High resolution transmission electron microscope (HRTEM, JEOL 2010, 200 kV, JEOL 2100F, 200 kV), and selected area electron diffraction (SAED) were used to

determine the nanostructure of the Si nanowires. The TEM is constructed with an electron gun, condenser lens, object, object lens, intermediate lens and projective lens. During the observation, a beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

The composition of the nanostructure was characterized by electron dispersive x-ray spectroscopy (EDS, EDAX Inc., US) cross-sectional elemental mapping that is installed in the TEM. As the electron beam of the TEM is scanned across the sample, it generates X-ray fluorescence from the atoms in its path. The energy of each X-ray photon is characteristic of the element which produced it. The EDS microanalysis system collects the X-rays, sorts and plots them by energy, and automatically identifies and labels the elements responsible for the peaks in this energy distribution. The growth orientations of Si nanowires were determined by SAED patterns by comparing with the standard database of Si. The lattice constant d of Si nanowires is calculated by the Bragg Equation, i.e., $\lambda L = Rd$, where λL is the diffraction constant or camera constant, and R is the distance between the pattern and the diffraction center. In SAED, normally, spot patterns belong to single crystal materials, ring patterns are from polycrystalline, while diffused rings are from amorphous ones.

3.3 Summary

The key points of this chapter are summarized as follows.

- (1) The surface coverings, i.e., Ni film, and a-C/Ni films with different a-C thickness, are sputtered from Ni and carbon targets. The nanowires are grown through thermal annealing of the as-sputtered films for different duration of time.
- (2) The evolution of the chemical composition, carbon bonding structure, and microstructure of the films is determined by XPS, Raman spectroscopy and GIXRD.
- (3) The morphology, composition, structure, growth orientations of the grown nanowires are characterized by FESEM, TEM, EDS, and SAED.

Chapter 4. **RESULTS AND DISCUSSION**

4.1 Properties of the surface covering

The as-sputtered and the annealed Ni and a-C/Ni thin films were studied using different characterization techniques, including FESEM, XPS, and GIXRD. The results and discussions are presented in this section.

4.1.1 Cross section

The typical cross section of the a-C film of 570 nm and 130 nm in thickness are respectively shown in **Fig. 4-1** a and b. The 30-nm-thick Ni layer is clearly observed between the a-C top layer and Si substrate as shown in **Fig. 4-1b**. However, it is not very clearly seen in **Fig. 4-1a** due to the low contrast between the thick carbon top layer and the Ni interlayer. But the white colour of the Ni layer is also seen as highlighted by the arrow at the interface. The thickness of the single Ni film is around 50 nm as shown in **Fig. 4-1c**. The detailed parameters of the as-sputtered a-C/Ni and Ni film are summarized in **Table 4-1**.

Fig. 4-1 Cross sections of the (a) 570-nm a-C/30-nm Ni film, (b) 130-nm a-C/30-nm Ni film, and (c) 50-nm Ni film.

4.1.2 Chemical composition

4.1.2.1 Surface chemical state

Fig. 4-2 a and b show the XPS survey scan spectra of the as-sputtered and the 3-min annealed 570-nm a-C film. Note that no signal for Ni 2p with binding energy ranging from 885.0 eV to 847.9 eV is detected in the spectrum except for Si 2p, Si 2s, O 1s, O 2s, C 1s, which means that Ni still locates at the bottom of the film. As seen, upon annealing, the signal of C 1s is dramatically trailed off, while the intensity of O 1s, O 2s, Si 2s and Si 2p are greatly boosted up. Before annealing, the C 1s content (79.34 at.%) is ultrahigh in comparison with that of the Si 2p (4.16 at.%) and O 1s (16.50 at.%). The amount of Si in the film is very small. After

annealing, there is a dramatic decrease in the C 1s content (5.2 at.%) and a sharp increase in the content of O 1s (67.10 at.%) and Si 2p (27.69 at.%).

To evaluate the chemical state of Si in the as-sputtered films and the oxidation of Si after annealing, the Si 2p core-level peaks of the film before and after annealing are illustrated in **Fig. 4-2** c and d. The five oxidation states of Si^{n+} ($n=0, 1, 2, 3$ and 4) corresponding to the five chemical structures of Si, Si_2O , SiO , Si_2O_3 and SiO_2 , respectively [138], exist in nonstoichiometric SiO_m ($0 < m < 2$) films. The position of the five synthetic peaks of Si 2p is determined thus: 99.6 eV in Si^0 , 100.6 eV in Si^{1+} , 101.6 eV in Si^{2+} , 102.6 eV in Si^{3+} , and 103.6 eV in Si^{4+} . [139, 140] The full width at half maximum (FWHM) of each peak is fixed to be 1.90 eV during the fitting process. After charge correcting the Si 2p peak by positioning the major component in C 1s peak to 284.8 eV, the above peak positions are used to fit the Si 2p core-level lines. A variation in the position of each peak of ± 0.1 eV is considered acceptable. With the possible existence of the five oxidation states in mind, after subtracting an integrated Shirley function background, the curve fitting is conducted by decomposing the spectrum into the $\text{Si } 2p^{1/2}$ and $\text{Si } 2p^{3/2}$ partner lines for the 5 oxidization states without any pre-adjudication. Although the spin-orbit splitting and the $\text{Si } 2p^{1/2}$ and $\text{Si } 2p^{3/2}$ intensity ratio are not fixed in the fitting, the fitting yields reasonable results. The fitting yields that the spin-orbit splitting is 0.6 ± 0.05 eV and the intensity ratio is equal to the statistical value of 1:2 for all of the oxidation states.

Fig. 4-2 XPS spectra of the 600-nm a-C/Ni film (a) as-sputtered, (b) 3-min annealed; deconvolution of Si 2p core-level spectra of the (c) as-sputtered, and (d) 3-min annealed.

As seen in **Fig. 4-2** c and d, prolonging the annealing to 3 min, the atomic concentration of the Si⁴⁺ component is up-shifted and the atomic concentration of sub-oxide components is decreased. Note that Si⁰ and Si¹⁺ peaks don't appear in the whole process indicating Si⁰ does not exist in the a-C film. Huge difference of the atomic concentrations of the other four Si environments is that: for the as-sputtered film, the content of Si³⁺ (38.73 at.%) and Si²⁺ (57.26 at.%) are high in comparison with Si⁴⁺ (4.01 at.%); for the annealed one, there is a great increase in the content of Si⁴⁺ (59.79 at.%) and sharp decrease in the concentration of Si³⁺ (29.53 at.%), Si²⁺ (10.68 at.%). Upon annealing, the film is transformed from a random bonding model structure into distinct mixtures of graphitic carbon and SiO₂-like. The

reasons are summarized as follows. The annealing system is not a high vacuum device thus the presence of residual oxygen is unavoidable. In addition, even if the chamber pressure with Ar (1.08×10^5 Pa) is a little higher than the outside atmosphere (1.01×10^5 Pa), a small amount of oxygen could still be introduced into the chamber. Therefore, the additional oxygen might have come from the leakage of and the residual oxygen in the annealing system. The presence of the additional oxygen and the high annealing temperature result in the removal of carbon and corresponding increase of oxidization in the films. This, taken into consideration with an increase in the Si 2p binding energy, intimates the formation of oxidized coatings which are more $\text{SiO}_{m>1}$. To summarize, upon annealing, the Ni layer remains at the bottom. The amount of Si in the deposited film is very small, thus thereafter the a-C: Si film is termed a-C film. The annealed film has a close chemical composition to stoichiometric SiO_2 . Si^0 doesn't exist in the as-sputtered film.

4.1.2.2 Elemental depth profiling

XPS elemental depth etching profiling is applied to evaluate the surface chemical state of the Si wafer before and after sputtering Ni, **Fig. 4-3** shows the XPS elemental depth etching profiling for the 50-nm Ni film in **Fig. 4-1c**. The etching rate was calculated to be 2.5 nm per min by dividing coating thickness of 50 nm into the etching time of 20 min till detecting the signal of Si 2p. The chemical composition of the Ni film was uniformly distributed except for the contamination on the film surface: Ni 2p (25.11 at.%), O 1s (27.06 at.%), Si 2p (0.00 at.%), C 1s (47.83 at.%), and the slight oxidation at the film/substrate interface: Ni 2p (83.34

at.%), O 1s (7.71 at.%), Si 2p (8.95 at.%), C1s (0 at.%). There were inevitable oxygen contaminations on the top surface of the film (O 1s: 27.06 at.%) and at the film/substrate interface (O 1s: 13.35 at.%) due to the exposure in the ambient environment. Moreover, the Ni/Si diffusion interface was confirmed with a diffusion depth for Ni 2p around 100 nm by taking the etching rate of 2.5 nm per min. The deep diffusion interface is suggested to facilitate the formation of Ni-Si-O droplet during the subsequent thermal annealing process.

Fig. 4-3 XPS elemental depth profiling of the 50-nm Ni film.

4.1.3 Microstructure

4.1.3.1 Crystalline structure

Fig. 4-4 shows the GIXRD patterns of the as-sputtered Ni film, where five characteristic peaks respectively centered at: 44.51° for Ni (111), 51.85° for Ni (200), 76.37° for Ni (220), 92.94° for Ni (311), and 98.45° for Ni (222) are detected, exhibiting the typical FCC polycrystalline structure of the Ni film. These peaks are consistent with the standard database of Ni with PDF#04-0850 (cf., External database Data 1).

Fig. 4-4 GIXRD peaks of the 50-nm Ni film.

4.1.3.2 Carbon bonding structure

Fig. 4-5 shows the transformation of carbon sp^2 bonding structure after 3-min annealing of the 570-nm film at 1100°C under Ar atmosphere. The Raman spectra are deconvoluted into D band (at $\sim 1350\text{ cm}^{-1}$ A_{1g} mode) and G band (at ~ 1580

cm^{-1} , E_{2g} mode) using a mixture of Lorentzian and Gaussian functions.[141, 142] D peak is the breathing mode of those sp^2 sites only in rings.[141] Its intensity is directly dependent on the presence of the six-fold rings. G peak is attributed to the in-plane stretching vibration of any pair of sp^2 bonded carbon atoms, either in C=C chains or in aromatic rings.[141] I_D/I_G increases as the number of rings per cluster increases and the fraction of chain groups falls.[143]

Fig. 4-5 Carbon sp^2 bonding structures in the (a) sputtered, and (b) 3-min annealed 600-nm a-C/Ni film.

After annealing, G peak is upshifted from 1533 cm^{-1} to 1588 cm^{-1} . The corresponding I_D/I_G increases from 0.98 to 1.77. The second order bands at approximate 2643 cm^{-1} and 2908 cm^{-1} are extruded. The band at 2643 cm^{-1} is the most intensive one and attributed to the first overtone of the D band (around 2 times of 1350). [144, 145] An additional higher order band at 2908 cm^{-1} has been assigned to a combination of the G and D modes characteristic for disturbed graphitic structures. Raman active mode for Si is observed at around 520 cm^{-1} . [146] In the sputtered film, it is generated from the doped Si. In the annealed film, it comes from both the doped Si and the grown Si nanowires. To summarize, once the temperature surpasses a certain point, the graphitization inclination and the crystallinity is dramatically accelerated and strengthened. The great increase of I_D/I_G , the huge upshift of the G-band position, the appearance of the second-order bands at high Raman shift centers are attributed to growing sp^2 clusters and the conversion from sp^3 to sp^2 bonding configuration during the rapid thermal annealing process.

4.1.4 Summary

From studies in this section, some key points can be summarized as follows.

- (1) Through co-sputtering of carbon and silicon targets, the 570 nm and 130 nm a-C: Si films are respectively sputtered on the pre-deposited 30 nm Ni layer on Si (100) wafer substrates. The Si in the top films could be ignored due the small amount and the oxidized state.
- (2) A 50-nm-thick Ni film is sputtered on the Si (100) wafer substrates, exhibiting a FCC polycrystalline structure. Due to the exposure in the ambient environment,

the interface at the Ni film/Si wafer substrate (O 1s: 13.35 at.%), and the film surface (O 1s: 27.06 at.%) are oxidized .

(3) Upon 3-min annealing of the 600-nm a-C/Ni film,

- a. The signal of C 1s is dramatically trailed off, while the intensity of O 1s, O 2s, Si 2s and Si 2p are greatly boosted up. Before annealing, the C 1s content (79.34 at.%) is ultrahigh in comparison with Si 2p (4.16 at.%) and O 1s (16.50 at.%). The amount of Si in the film is very small. After annealing, there is a decrease in C 1s content (5.2 at. %) and sharp increase in O 1s (67.10 at.%) and Si 2p (27.69 at.%).
- b. The amount of Si in the as-deposited film was very small, thus the film is termed a-C. The Ni catalyst particle remains at the bottom. The as-annealed film has a close chemical composition to stoichiometry SiO₂. Si⁰ doesn't exist in the as-sputtered film.
- c. During the thermal annealing, the growing sp² clusters and the conversion from sp³ to sp² bonding configuration result in the increase of I_D/I_G from 0.98 to 1.77, the upshift of G-band position from 1533 cm⁻¹ to 1588 cm⁻¹, and the appearance of the second-order bands respectively at 2643 cm⁻¹ and 2908 cm⁻¹.

4.2 Oxidation retardation by the surface covering

This section investigated the surface morphology of the annealed films, the composition, structure of the grown nanowires, and the effect of the carbon top layer and annealing duration on the structure of the grown nanowires.

4.2.1 Surface morphology of annealed films

Fig. 4-6a shows the surface of the 600-nm a-C/Ni film after 3-min annealing at 1100 °C under Ar atmosphere. The grown nanowires are located at the white region as magnified in **Fig. 4-6b**, while the dark region is the a-C film without covering nanowires. As seen in **Fig. 4-6c**, the nanowires are around 70 nm in diameter, up to 10 μm in length, entangling with each other. The nanowires become inhomogeneous with bright and transparent outer sheaths and a white inner core indicating a heterogeneous structure. **Fig. 4-6d** shows bundles of nanowires growing from the cracked film. **Fig. 4-6e** shows the nanowires grown after 3-min annealing of the 160-nm a-C/Ni film at 1100 °C under Ar atmosphere. The nanowires are of homogeneous structure and of round ends, lying on the film surface entangling into each other. **Fig. 4-6f** shows the nanowires grown via 3-min annealing of the single layered Ni film without the a-C layer on the top. In summary, wire-like nanostructures grow during annealing of the a-C/Ni/Si-wafer and Ni/Si-wafer samples. The Ni particle doesn't appear at the tip of the nanowire.

Fig. 4-6 Nanowires grown via 3-min annealing of the (a-d) 600-nm a-C/Ni film, the white arrow indicates the center of the nanowire, (e) 160-nm a-C/Ni film, and (f) 50-nm Ni film.

4.2.2 Composition of the grown nanowires

Fig. 4-7a shows a coaxial nanowire grown through 1-min annealing of the 600-nm-thick a-C/Ni film at 1100 °C under Ar atmosphere. The grown is of 14.5-nm-diameter core and 17.6-nm-thick sheath. The study via the cross-sectional element mapping reveals the nanowire consists of Si and O only. The intensity of Si and O exhibits almost the same parabolic function along the cross-sectional route, not only indicating stable atomic concentration ratio (1:2) between Si and O along the route, i.e., Si/SiO_x ($x \approx 2$), but also implying the cross section is very round. Particularly, the intensity of O has a small plateau while that of the Si continues to increase while approaching the core of the nanowire, which could be regarded as an implication of the Si core. The nanowire diameter equals to that of the Si core plus two times of the thickness of the SiO_x sheath. **Fig. 4-7b** shows another triple-concentric nanowire grown through the same process. It is constructed with a 33.3-nm-diameter core, a 14.1-nm-thick interlayer, and a 17.6-nm-thick outer sheath. The EDX cross sectional elemental mapping reveals the core is Si, the interlayer is SiO_y ($y \approx 1$), and the outer sheath is SiO_x, i.e., Si/SiO_y/SiO_x. Due to the drift of the nanowire during EDX cross sectional element mapping, the signal is not sharp enough to clearly distinguish the interfaces of core/interlayer and the interlayer/sheath. However, it is known that the EDX intensity is related to the atomic number and atomic weight of the element. In **Fig. 4-7b**, the intensity of Si and O exhibits almost the same parabolic function as the signal proceeds into the outer sheath, indicating the atomic concentration of around 1:2 between Si and O since the ratio of the atomic weight between Si and O is 2:1. As the signal proceeds into the interlayer, the intensity of the O doesn't keep increasing, while that of the

Si continues to increase. This can indicate the round cross section of the nanowires and also the decrease of the atomic concentration of O in the interlayer. It shows that the intensity ratio between Si and O is close to 2:1, therefore, the atomic concentration between Si and O in the interlayer is estimated to be 1:1. In the center area of the nanowire, the intensity of O only comes from the outer sheath and the interlayer, thus almost keeps constant. The intensity of Si comes from the core, interlayer and outer sheath, thus it keeps increasing to the maximum of the parabolic curve in the center. In conjunction with the thickness of the core, interlayer and outer sheath, the composition of the triple-concentric nanowire is estimated, i.e., Si core, SiO_y ($y \approx 1$) interlayer, and SiO_x ($x \approx 2$) outer sheath, or $\text{Si}/\text{SiO}_y/\text{SiO}_x$ structure.

Fig. 4-7 Chemical composition of the grown nanowires via 1-min annealing of the 600-nm-thick a-C/Ni film, (a) Si/SiO_x (x≈2) coaxial nanowire, (b) Si/SiO_y/SiO_x (y≈1) triple-concentric nanowire, through EDX cross sectional element mapping spectra.

4.2.3 Structure of the grown nanowires

Fig. 4-8a shows a nanowire consisting of a dark Si core (12.3 nm in diameter) surrounded by a grey SiO_x sheath of 21.2 nm in thickness. The ratio of the core diameter over the sheath thickness is 0.6. The nanowire is of uniform and smooth morphology along the growth direction. To determine the correct growth direction, the diffraction patterns should be indexed for specific zone axis of Si. This requires the electron beam perpendicular to specific cross section of the Si nanowires along the nanowire length, which could generate the symmetric spots, i.e., SAED patterns. In the process, tilt is used to by rotating the nanowire along x- or y- axis of the sample holder. The tilt range is around $\pm 35^\circ$. The SAED patterns in this thesis were generated by careful adjusting the tilt angle along the x- and y- axis, i.e., rotating angle, to match with the standard database. The inset shows the corresponding SAED patterns of the nanowire. A unit cell of cubic structure (lattice parameter=5.43 Å) was consistent with the diffraction pattern. Indexing of the SAED pattern shows the [111] zone axis of the single crystalline Si, suggesting that the nanowire is constructed with crystalline Si growing along $[\bar{1}10]$ orientation,[147] surrounded by amorphous SiO_x sheath (i.e., c-Si/a-SiO_x). **Fig. 4-8b** shows a smooth-surface Si/SiO_y/SiO_x triple-concentric nanowire. It is constructed with a 31.8-nm-diameter Si core, a 15.7-nm-thick SiO_y interlayer, and a 17.8-nm-thick SiO_x outer sheath. The detailed structure of the rectangle is highlighted in **Fig. 4-8c**. There is 24.6° anti-clockwise drift due to the strong bombardment of the electron beam on the Si nanowires lying on the copper grid at too high magnification. It shows that the highly crystalline Si core is surrounded by the amorphous SiO_y interlayer, followed by the amorphous SiO_x outer sheath. Note that, the thickness of the SiO_x

outer sheath shrinks from 17.8 nm to 10.1 nm due to the great bombardment of the electron beam. **Fig. 4-8d** shows the atom-resolved crystalline Si core surrounded by the amorphous SiO_y interlayer. The two dimensional (2D) Fast Fourier Transform (FFT) of the atom-resolved Si core is indexed for Si [102] zone axis (cf., **Fig. 4-8c**, right inset), determining the nanowire grows along the [21 $\bar{1}$] orientation. The orientation is double confirmed in the atom-resolved crystalline Si core, which clearly shows the (2 $\bar{1}\bar{1}$) atomic planes (spacing, 2.22 Å), the (020) atomic planes (spacing, 2.72 Å) and their dihedral angle (65.9°). In short, the separation of the Si, SiO_y and SiO_x phase does exist in Si nanowires, and follows the sequence of crystalline Si, amorphous SiO_y and SiO_x from the core to the sheath.

Fig. 4-8 TEM images of nanowires via 1-min annealing of the 600-nm a-C/Ni film.

(a) A Si/SiO_x coaxial nanowire grows along the $[\bar{1}10]$ orientation. The inset shows the SAED pattern of the Si core. (b) The smooth Si/SiO_y/SiO_x triple-concentric nanowire. (c) The enlarged image showing the crystalline Si core, amorphous SiO_y interlayer and SiO_x outer sheath are separated by atomically sharp interfaces. (d) The atom-resolved crystalline Si core grows along the $[21\bar{1}]$ orientation.

4.2.4 Carbon layer thickness and annealing duration

Fig. 4-9 a and b show the structure of the nanowires after 1-min annealing of the 600-nm a-C/Ni film at 1100 °C under Ar atmosphere. The nanowires have a mean outer diameter of 57.2 ± 11.8 nm, a mean core diameter of 21.0 ± 5.1 nm and a mean sheath thickness of 18.0 ± 2.9 nm. The ratio of the core diameter over the sheath thickness is 1.2 ± 0.1 . After prolonging the annealing to 3 min, the nanowire's outer diameter increases to 84.8 ± 25.5 nm, and the core diameter reduces a lot, down to 8.6 ± 0.5 nm and the sheath thickness increased to 36.5 ± 14.4 nm (cf., **Fig. 4-9** c and d). The ratio of the core diameter over the sheath thickness is 0.3 ± 0.1 , which is dramatically decreased compared to the 1-min annealing. The end of the core is surrounded by a 12.1 nm thin sheath layer as shown in the inset of **Fig. 4-9d**. The details of the grown nanowires are summarized in **Table 4-1**.

Table 4-1 Details of the as-deposited a-C/Ni, Ni film and the grown nanowires

Film structure	Thickness of the a-C layer (nm)	Thickness of the Ni layer (nm)	Annealing duration (min)	Ratio of core diameter over sheath thickness
a-C/Ni	570	30	1	1.2 ± 0.1
a-C/Ni	570	30	3	0.3 ± 0.1
a-C/Ni	130	30	3	0
Ni	0	50	3	0

Fig. 4-9 TEM images of the grown nanowires via (a)-(b) 1-min annealing of the 600-nm a-C/Ni film, (c)-(d) 3-min annealing of the 600-nm a-C/Ni film, (e)-(f) 3-min annealing of the 160-nm a-C/Ni film, and (g)-(h) 3-min annealing of the 50-nm Ni film, at 1100 °C under Ar atmosphere.

Oxidation obviously takes place inward to consume the core. **Fig. 4-9** e and f show the nanowires via 3-min annealing of the 160-nm a-C/Ni film. The nanowire in **Fig. 4-9f** is of 70.1 nm in diameter showing a homogenous amorphous structure without the inside core. **Fig. 4-9** g and h show the structure of the nanowires after 3-min annealing of the 50-nm Ni film without sputtering the a-C film at 1100 °C under Ar atmosphere. Also, homogeneous amorphous nanowires are observed without the black core. The dark lines randomly entangled with the Si nanowires do not belong to Si nanowires. They are the residual carbon dissolved in the solution during the preparation of the TEM samples. In summary, with or without the a-C film on the top of the Ni layer, homogeneous or heterogeneous nanowires are able to form. It also confirms that Si in the nanowire is from Si wafer. However, the cover layer of a-C does provide the oxidation retardation. As shown in **Table 4-1**, within the same annealing duration of 3 min, the ratio of the core diameter over the sheath thickness decreases from 0.3 ± 0.1 to 0 as the a-C layer thickness reduces from 570 nm to 130 nm (cf., **Fig. 4-9** c-f). Besides, for the same a-C layer thickness of 570 nm, prolonging the annealing from 1 min to 3 min gives rise to reduced ratio of the core diameter over the sheath thickness from 1.2 ± 0.1 to 0.3 ± 0.1 (cf., **Fig. 4-9** a-d).

4.2.5 Summary

The structural evolution of the Si nanowires during rapid thermal annealing is summarized as follows:

- (1) Wire-like nanostructures are grown during thermal annealing of the a-C/Ni/Si-wafer and Ni/Si-wafer samples. The Ni particles don't appear at the tip of the nanowire (i.e., surface of the annealed films).
- (2) The heterogeneous coaxial nanostructure is confirmed to be Si/SiO_x ($x \approx 2$) nanowire, which is constructed with crystalline Si surrounded by amorphous SiO_x sheath. The triple-concentric nanostructure is Si/SiO_y/SiO_x ($y \approx 1$) nanowire with a crystalline Si core surrounded by the amorphous SiO_y interlayer, and followed by the amorphous SiO_x outer sheath. The homogeneous nanostructure is amorphous SiO_x nanowire.
- (3) Si in the nanowire is from the Si wafer. The a-C cover layer could reduce oxidation from the residual oxygen. In the case of the coaxial Si/SiO_x nanowires, within the same annealing duration of 3 min, the ratio of the Si core diameter over the SiO_x sheath thickness decreases from 0.3 ± 0.1 to 0 as the a-C layer thickness reduces from 570 nm to 130 nm. For the same a-C layer thickness of 570 nm, prolonging the annealing from 1 min to 3 min gives rise to reduced ratio of the core diameter over the sheath thickness from 1.2 ± 0.1 to 0.3 ± 0.1 .

4.3 Origin of the growth orientation

This section investigated the morphology, cross section, growth orientations of the grown Si nanowires, and the orientation relation with the seeding Ni particles. The origin of the growth orientations in metal-seeded semiconductor nanostructures is discussed.

4.3.1 Morphology

Upon 1-min thermal annealing under Ar atmosphere, various one-dimensional Si nanostructures with smooth surface profile (the dark arrow) and sinusoidal surface profile (the white arrow) extruded out of the cracked a-C layer (cf., **Fig. 4-10a**). A TEM image of a bundle of nanowires shows primarily filamentary nanowires entangling into each other with diameters on the order of around 80 nm, and lengths longer than 10 μm (cf., **Fig. 4-10b**). Note that, the diameter of the sinusoidal nanowires (not in a small mount) is larger than the smooth filamentary ones (cf., **Fig. 4-10** a and b, upper-right inset). All nanowires terminate at the root in dark ball-shaped nanoclusters with diameter 1.2 to 1.5 times that of the connected wires (cf., **Fig. 4-10c**), whereas no nanocluster is observed at the tip of the nanowire (cf., **Fig. 4-10d**). The EDX cross sectional element mapping analysis of a single smooth-surface nanowire shows that it consists of only Si in the core, and Si and O in the sheath, exhibiting a coaxial structure, i.e., dark Si core is surrounded by light grey SiO_x sheath, Si/SiO_x ($x \approx 2$) (cf., **Fig. 4-7a**). The observation of the dark nanoclusters at the root is suggestive of a Ni-seeded growth process similar to the vapor-liquid-solid growth, except for the opposite seeding

location of the nanoclusters. Si in the nanowire comes from the wafer, thus the nanocluster always seeds at the root till the end of the growth. These are typical features of the solid-liquid-solid growth of Si nanowires directly using the Si wafer, rather than any additional liquid or vapor as the source material.

Fig. 4-10 Solid-liquid-solid growth of the Ni-seeded Si nanowires. (a) Various smooth and sinusoidal Si nanowires extruding from the cracked a-C film. (b) A bundle of Si nanowires, where the root and tip are respectively highlighted by the dotted white rectangles. The upper-right corner shows a sinusoidal Si nanowire. (c) The dark nanoclusters locating at the root indicate the Ni-seeded growth. (d) The nanocluster-free nanowire tip.

4.3.2 Cross section

Fig. 4-11a shows a Si nanowire grows along $[\bar{1}\bar{3}1]$, inset shows the SAED patterns generated from Si zone axis of $[101]$. The Si core has a rectangle-shaped cross section (cf., **Fig. 4-11b**). **Fig. 4-11c** shows a Si nanowire grows along $[21\bar{1}]$, the bottom inset shows the SAED patterns generated from Si zone axis of $[102]$. The top inset shows the SAED patterns of the cross section (cf., **Fig. 4-11d**), which is indexed from Si $[102]$ zone axis. The cross section exhibits a hexagon shape, surrounded by plane (010) , $(21\bar{1})$, and $(\bar{2}11)$.

Fig. 4-11 Cross section of the Si nanowire. (a) A nanowire grows along $[\bar{1}\bar{3}1]$ orientation, (b) the rectangle-shaped cross section of the nanowire, (c) a Si

nanowire grows along $[2\bar{1}1]$ orientation, (d) the hexagonal cross section of the Si nanowire. Insets show the corresponding SAED patterns.

4.3.3 Growth orientation

To date, three categories of techniques have been applied to determine the growth orientation of single crystalline nanowires: (1) atom-resolved TEM image and the 2D FFT patterns;[9, 29] (2) normal TEM image and selected area electron diffraction (SAED) patterns;[17, 32] and (3) geometric relation to the substrate orientation by optical microscope, scanning electronic microscopy or TEM.[65, 148] Approaches (1) and (2) are the most accurate ways, and can completely eliminate the influence from the environment and instrument. Approach (3) might be the most convenient, but of the biggest error since the observed orientations are likely changed during sampling, especially for the long and slim nanowires with heavy nanoclusters seeding at the tip. In this study, the growth orientation was determined by atom-resolved TEM image and FFT patterns (cf., **Fig. 4-8**), in conjunction with the SAED patterns generated from different zone axis of the crystalline Si core.

HRTEM images captured on three individual Si nanowires along different growth orientations provide atomic insight into the structure of these Si nanowires (cf., **Fig. 4-12**). The nanowires consist of a uniform diameter crystalline Si core surrounded by an amorphous SiO_x sheath. The core and sheath are separated by an atomically sharp interface. The reciprocal lattice peaks obtained from the FFT of the atom-resolved image of the Si core (cf., **Fig. 4-12a**, right inset) are indexed for the $[102]$ zone axis of crystalline Si, suggesting that the nanowire grows along the $[2\bar{1}1]$ orientation. This orientation is again confirmed in the atom-resolved TEM image of

the crystalline Si core, which clearly shows the $(2\bar{1}\bar{1})$ atomic planes (spacing, 2.22 Å), the (020) atomic planes (spacing, 2.72 Å), and their dihedral angle 65.9°. Similarly, [111] and [112] zone axis of the crystalline Si are respectively indexed from the FFT patterns of the atom-resolved Si core (cf., **Fig. 4-12**, b and c). In conjunction with the atom-resolved TEM images of the Si core, the nanowires grow along $[0\bar{1}1]$ and $[1\bar{1}\bar{1}]$ orientations, respectively. **Fig. 4-12b** clearly shows the atomic planes of $(\bar{1}10)$ and $(0\bar{1}1)$ (spacing, 3.84 Å) and their dihedral angle 120.0°, where $(0\bar{1}1)$ plane is perpendicular to the nanowire axis. **Fig. 4-12c** reveals the $(2\bar{2}0)$ atomic planes (spacing, 1.92 Å), and the $(1\bar{1}\bar{1})$ (spacing, 3.14 Å), and their dihedral angle 90.0°, where $(1\bar{1}\bar{1})$ planes are perpendicular to the growth axis. The amorphous SiO_x sheath surrounding the crystalline Si core is formed through precipitation of the supersaturated Si oxide from the liquid Ni-Si-O eutectic droplet, and is easily removed by hydrofluoric acid.[29]

Fig. 4-12 HRTEM images of the Si nanowires growing along different orientations

(a) $[21\bar{1}]$ -oriented Si nanowire. (b) $[01\bar{1}]$ -oriented Si nanowire. (c) $[11\bar{1}]$ -oriented Si

nanowire. Insets show the respective FFT patterns of the atom-resolved Si core generated from the zone axis perpendicular to the growth axis.

As shown in the inset of **Fig. 4-13a**, the SAED patterns reveal the crystalline Si core and the amorphous SiO_x sheath, i.e., c-Si/a- SiO_x . A unit cell of face-centred-cubic structure of Si (5.43 Å in lattice parameter) is consistent with the diffraction patterns. The SAED patterns are indexed for the Si [001] zone axis, indicating the Si nanowire grows along the [110] orientation. Likewise, the insets in **Fig. 4-13 (b)-(f)** respectively show the SAED patterns generated from the zone axis of Si [101], [101], [315], [323], and [116], determining the Si nanowires grow along the $[\bar{1}\bar{1}1]$, [010], $[\bar{2}11]$, $[\bar{1}3\bar{1}]$, and $[\bar{3}31]$ orientations.

Fig. 4-13 TEM images of the grown Si nanowires along different orientations (A) [110], (B) $[\bar{1}\bar{1}1]$, (C) [010], (D) $[\bar{2}11]$, (E) $[\bar{1}3\bar{1}]$, and (F) $[\bar{3}31]$. Inset shows the respective SAED patterns generated from the different zone axis of Si.

4.3.4 Interfacial structure

Fig. 4-14a shows an elliptic Ni particle seeding the Si nanowire at the root. The particle is of around 47.0 nm in semi-major axis and 39.3 nm in semi-minor axis. It is surrounded by a 7.2-nm-thick amorphous SiO_x layer, forming the Ni-Si-O nanocluster. The EDX spectrum shown in the top-right inset is generated from the nanocluster, confirming the chemical composition of the core in the seeding nanocluster is Ni, where the signals of C and Cu are from the TEM grid, while Si and O are from the SiO_x layer surrounding the Ni core. The SAED spots, or systematic rows, generated by directing the electron beam on the area of both the seeding Ni particle and the connected grown Si nanowire provide the crystalline information of both the particle and the nanowire (cf., **Fig. 4-14b**). These spots are indexed for the zone axis of Ni [112]. The dotted white squares are respectively indexed for Ni ($\bar{3}11$), Ni ($\bar{1}\bar{1}1$) and Ni ($1\bar{1}\bar{1}$). Though the information in the SAED spots is not enough to determine the growth orientation of the Si nanowire, the dotted white circle near Ni ($\bar{1}\bar{1}1$) still could be indexed for Si (020) based on the measured lattice spacing of around 2.70 Å (cf., **Fig. 4-14c**), and the relation to the spot reflected by the Ni ($\bar{1}\bar{1}1$) plane. It is noted that the single crystalline Ni particle is surrounded by a layer of amorphous Si-oxide in the nanocluster. There is a small dihedral angle of around 3° between Si (020) and Ni ($\bar{1}\bar{1}1$) as observed in both the SAED systematic spots (cf., **Fig. 4-14b**), and at the Ni/Si interfacial structure (cf., **Fig. 4-14c**). There is around 20.6° drift in anti-clockwise during HRTEM observation. The interface between the Ni particle and the Si nanowire exhibits a spherical shape. From Ni ($\bar{1}\bar{1}1$) (spacing, 2.03 Å) to Si (020) (spacing, 2.72 Å) the

two planes are almost parallel (dihedral angle of 3°), though there is about 25.4% difference in lattice spacing ($((2.72-2.03)/2.72=25.4\%)$).

Fig. 4-14 Interfacial structure between a Si nanowire and the seeding Ni particle. (a) A Si nanowire is seeded by an elliptic Ni particle. Inset shows the EDX spectrum generated from the nanocluster. (b) The SAED patterns generated from the area covering both the ending nanocluster and the connected nanowire, which are indexed for the zone axis of Ni [112]. (c) The interfacial structure between the seeding Ni particle and grown Si nanowire.

4.3.5 Determinant factor on growth orientation

In this work, the Si nanowires are of many growth orientations instead of certain preferred ones such as $\langle 112 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ that are reported in literatures.[8, 17, 27] It was commonly believed that the preference of growth orientations was

dictated by the surface energy of the various Si nanocrystal planes. In this work, however, the Ni-seeded growth of Si nanowires involves mass transfer of Si from the Ni-Si-O droplet to a solid crystalline Si phase. It is an energy-releasing, rather than an energy-consuming process in forming the liquid droplet.[35] Therefore, surface energy may not be the key determining factor in nucleation and growth orientations. A structure-sensitive seeding principle is found at the Ni-particle/Si-wire spherical interface, i.e., Ni ($\bar{1}\bar{1}1$) is parallel to Si (020) with dihedral angle of only 3 degrees and 25.4% mismatch in lattice spacing. It indicates that the matching degree of the lattice planes in terms of lattice spacing and dihedral angle at the Si-wire/Ni-particle interface dictates the growth of Si nanowires. As such, we propose that the growth of Si nanowires follows certain structure-sensitive principle to achieve the most stable structure with the minimum mismatch in lattice spacing and dihedral angle at the wire/particle interface (in this work, Ni). Si nanowires maintain the principle to the metal catalyst particles.

In conjunction with the results in literatures,[6, 9, 17, 26, 149] the determinant factor of the growth orientation of nanowires could be inferred as follows. In this work, the nanowire growth could be regarded as an epitaxial growth with the eutectic Ni-Si-O droplet as the substrate. In this case, the ordered planes of the catalytic metal particle at the Si-wire/metal-particle interface determine the growth orientation of the nanowire. This could be proved in the Au-seeded Si nanowires. The growth orientation of the nanowires is controlled by the reaction pressure,[6, 9] or the size of the Au particle.[17] Actually, it is determined by the partially ordered Au planes at the wire/particle interface through the structure-sensitive seeding principle between Au and Si. This principle also works in other semiconductor nanowires. For instance, the nucleation and growth of the ZnO nanowires are

initiated by the ordered planes of the Sn particle at the ZnO-wire/Sn-particle interface (cf., **S_Figure 5**).^[149] Sn preserves the orientation as defined by the interface with the ZnO nanowire at the onset of the growth. In Au-seeded ZnSe nanowires,^[26] $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, and $(0\bar{2}0)$ planes of ZnSe and Au are parallel with each other in the $[\bar{1}21]$ oriented nanowire (cf., **S_Figure 6a**); $(\bar{1}\bar{1}\bar{1})$ and $(11\bar{1})$ planes of ZnSe and Au are parallel with each other in the $[\bar{1}01]$ oriented nanowire (cf., **S_Figure 6b**); $(11\bar{1})$ and $(\bar{1}11)$ planes of ZnSe and Au are almost parallel with each other or with a small dihedral angle in the $[0\bar{1}0]$ oriented ZnSe nanowire (cf., **S_Figure 6c**).

4.3.6 Summary

This section investigated the detailed growth mechanisms of the grown Si nanowires from Ni-coated Si wafer beneath sputtered carbon upon 1-min thermal annealing. It can be summarized as follows:

- (1) It exhibits a solid-liquid-solid growth process, where the Ni-Si-O droplet seeds the nanowire at the root. The Si nanowire along the $[\bar{1}\bar{3}1]$ orientation shows the rectangle-shaped cross section, while the $[2\bar{1}\bar{1}]$ oriented exhibits a hexagon shape, surrounded by the Si planes of (010), $(21\bar{1})$, and $(\bar{2}11)$.
- (2) The growth orientations of Ni-seeded Si nanowires is not dictated by surface energy of the various nanocrystal planes, but follows structure sensitive principle with the seeding Ni nanoparticles to minimize the mismatch in lattice spacing and dihedral angle at the wire/particle interface.
- (3) It is inferred that the growth orientation of Si nanowires is determined by the ordered planes of the Ni catalyst particle at the wire/particle interface.

4.4 Origin of the morphology

This section investigated the various morphologies of grown Si nanowires, and the morphological relation with the seeding Ni particles. The origin of the morphologies of Si nanowires is discussed.

4.4.1 Morphology

4.4.1.1 Coaxial nanowires

Fig. 4-15a shows a smooth Si/SiO_x coaxial nanowire constructed with a dark Si core surrounded by a grey SiO_x sheath (19.1 nm in core diameter, 23.1 nm in sheath thickness). A unit cell of face-centred-cubic structure (5.43 Å in lattice parameter) is consistent with the selected area electron diffraction (SAED) patterns shown in the inset. The patterns are indexed for Si [102] zone axis, suggesting the wire grows along the $[2\bar{1}1]$ orientation. **Fig. 4-15b** shows the cross section of a 65.0-nm-diameter ball-shaped Ni particle, which is connected to a Si/SiO_x coaxial nanowire (20.1 nm in core diameter, 8.6 nm in sheath thickness). The particle is surrounded by a 3.6-nm-thick SiO_x layer, thus the Ni/Si interface is obstructed. The SAED patterns of the Ni particle are indexed for Ni [315] zone axis. These patterns show the Ni {315} cross section is surrounded by $(\bar{3}12)$, $(12\bar{1})$, $(\bar{1}30)$, $(\bar{2}11)$, $(\bar{3}\bar{1}2)$, $(\bar{1}2\bar{1})$, $(\bar{1}30)$ and $(2\bar{1}\bar{1})$ planes, exhibiting a rhombic atomic planes with an equal length in the $[12\bar{1}]$ and $[\bar{2}11]$ orientations. The transition of the polycrystalline face-centred-cubic structure of the sputtered Ni layer to the single crystalline ball-shaped Ni nanoparticle also reveals the formation of the liquid Ni-Si phase does take place during the growth of nanowires.[61, 69]

Fig. 4-15 Coaxial Si/SiO_x nanowires. (a) A coaxial nanowire grows along the $[21\bar{1}]$ orientation. (b) Cross sectional view of a Ni particle connected to another coaxial nanowire.

4.4.1.2 Side-by-side biaxial nanowires

A side-by-side Si/SiO_x biaxial nanowire is shown in **Fig. 4-16a**, where the thickness of the upper Si side is 13.2 nm, and the lower SiO_x side is 15.3 nm thick (cf., **S_Figure 7**). The wire is seeded by a 52.0-nm-diameter Ni nanoparticle. Though the SAED patterns generated from the nanowire is unable to be indexed to any Si zone axis (cf., **Fig. 4-16b**, inset), they could still indicate the crystalline structure of the nanowire. It is noted that the line-shaped spots pointed out by the dotted circles imply the existence of the defects. They could be either micro-twin or stacking faults,[150] requiring further atom-resolved observation to confirm.

Fig. 4-16 A ball-shaped Ni nanoparticle seeds a side-by-side Si/SiO_x biaxial nanowire. The inset is the SAED patterns of the wire.

4.4.1.3 Triple-concentric nanowires

Fig. 4-17a shows a smooth Si/SiO_y/SiO_x triple-concentric nanowire constructed with a 31.8-nm-diameter Si core, a 15.7-nm-thick SiO_y interlayer, and a 17.8-nm-thick SiO_x outer sheath. The section in the white rectangle is examined in **Fig. 4-8c**, determining the nanowire grows along the $[2\bar{1}\bar{1}]$ orientation. **Fig. 4-17b** shows a 65.5-nm-period triple-concentric Si/SiO_y/SiO_x sinusoidal nanowire. At the valley, the 24.7-nm-diameter Si core is surrounded by the 13.3-nm-thick SiO_y interlayer and the 11.7-nm-thick SiO_x outer sheath. At the peak, the 29.6-nm-diameter Si core is surrounded in a 13.5-nm-thick SiO_y interlayer and a 19.2-nm-thick SiO_x outer sheath. The SAED patterns generated from the Si core are indexed for Si $[10\bar{2}]$

zone axis, revealing the highly crystalline Si core grows along the $[2\bar{1}\bar{1}]$ orientation.

Fig. 4-17c shows a fishbone-profiled Si/SiO_y/SiO_x nanowire is seeded by a Ni nanoparticle. As magnified in the bottom-left inset, the nanoparticle has a width of 95.5 nm, and a length of 128.3 nm, embedded in the 10.3-nm-thick SiO_x layer. The bottom-right SAED patterns are generated from the Si nanowire in the rectangle. They are indexed for Si $[11\bar{3}]$ zone axis, determining the wire is along the $[30\bar{1}]$ orientation. **Fig. 4-17d** magnifies the rectangle part of the fishbone-profiled nanowire in **Fig. 4-17c**. The wire is constructed with a sinusoidal Si core of 54.6 nm in valley diameter and 68.4 nm in peak diameter, surrounded by a sinusoidal SiO_x outer sheath of 119.4 nm in period, 160.0 nm in valley diameter and 199.8 nm in peak diameter. There is a 26.2-nm-thick SiO_y interlayer between the below SiO_x sinusoidal outer sheath (10.0 nm in valley thickness, 32.6 nm in peak thickness) and the Si core (cf., **Fig. 4-17d**, bottom-left inset). On the contrary, an 8.6-nm-thick SiO_y interlayer is observed between the SiO_x outer sheath (39.9 nm in valley thickness, 66.4 nm in peak thickness) and the Si core (cf., **Fig. 4-17**, bottom-right inset).

Fig. 4-17 Smooth and sinusoidal Si/SiO_y/SiO_x triple-concentric nanowires. (a) A smooth nanowire grows along the $[2\bar{1}1]$ orientation. (b) A sinusoidal nanowire grows along the $[2\bar{1}1]$ orientation. (c) A fishbone-profiled nanowire grows along the $[30\bar{1}]$ orientation. (d) The enlargement of the rectangle area in (c). Insets in (c) and (d) are the respective SAED patterns and the enlarged structure of the wire.

4.4.1.4 Ni-nanosphere entrapped nanowire

Fig. 4-18a shows that four Ni nanospheres are entrapped in a Si/SiO_y/SiO_x triple-concentric nanowire. The white dotted line is across the triple-concentric structure. The 14.0-nm-diameter Si core gradually disappears, and then the amorphous 53.6-nm-diameter SiO_y interlayer is shielded by a 17.8-nm-thick SiO_x sheath. Two nanospheres are completely entrapped in the amorphous SiO_y core, i.e., the 45.1-nm-diameter nanosphere 1, and the 48.0-nm-diameter nanosphere 2 (cf., **Fig. 4-18b**). The SAED patterns in **Fig. 4-18c** are generated from nanosphere 2 as highlighted by dotted white circle in **Fig. 4-18b**, indicating the crystalline structure of the nanosphere. The EDX spectrum generated from nanosphere 2 double confirms the nanosphere is Ni, where the signals of C and Cu are from the TEM grid, while Si and O are from the wire. Note that, the upper side of the 36.2-nm-diameter nanosphere 3 is connected to a 69.2-nm-length Si core, while the bottom side of the 30.6-nm-diameter nanosphere 4 is connected to the all-Si core in the wire. With the disappearance of the Si core, the diameter increases about 11.8 nm from nanosphere 3 to 2. Note that, all the Ni nanospheres are not entrapped in the all-Si core of the triple-concentric nanowire. This is consistent with the Au-nanosphere-entrapped Si oxide nanowire,[116] where one side of the nanosphere is connected to the crystalline Si core (cf., **FIG.4** in ref [116]), while the rest of the nanosphere is surrounded by Si oxides. The addition of oxygen could increase the amount of the nanospheres entrapped in the Si oxide nanowires due to the continuous oxidation of the Au-Si phase in the Au-Si-O droplet, accelerating the supersaturation of Au and the subsequent precipitation of the Au nanospheres from the droplet (cf., **FIG.6** in ref [116]). It is understandable that the amount of Ni in the Ni-Si-O droplet is also variable since the droplet always seeds at the interface

between the Ni layer and the Si wafer, where Ni could dissolve in the Ni-Si-O droplet from the Ni layer as the case of Si dissolving from the Si wafer.

Fig. 4-18 Entrapping of the Ni-nanospheres in the Si/SiO_y/SiO_x triple-concentric nanowire. (a) Entrapping of four Ni nanospheres in the amorphous SiO_y core, where the Si/SiO_y/SiO_x triple-concentric nanowire transits to SiO_y/SiO_x coaxial nanowire. (b) Zoom-in of the Ni-nanosphere-entrapped Si nanowire shows the gradual disappearance of the Si core (white arrow), till the complete entrapping of the Ni nanospheres (dark arrow) in the SiO_y core. (c) The SAED patterns and the EDX spectrum generated from nanosphere 2.

4.4.1.5 Transitional nanowires

Fig. 4-19a shows a Si/SiO_x nanowire transits the coaxial structure to the side-by-side biaxial structure. The Si core diameter decreases from 20.9 nm at the top to 18.7 nm at the bottom, meanwhile, the SiO_x sheath thickness at the right-side gradually increases from 5.1 nm to 8.3 nm (cf., **S_Figure 8**). The SAED patterns are indexed for Si [111] zone axis, implying the growth occurs in the $[\bar{1}10]$ orientation. The white line-shaped patterns also indicate defects of micro-twin or stacking faults,[150] which is also consistent with the white shining lines directly observed in the dark Si side. As shown in **Fig. 4-19b**, this wire is seeded by a Ni particle (44.6 nm in horizontal width, 51.4 nm in vertical height) surrounded by a 2.9-nm-thick SiO_x layer. The Si core offsets a little to the left, exhibiting a side-by-side biaxial structure. As it proceeds, the nanowire becomes coaxial at the nanowire tip (cf., **S_Figure 8**). The SAED patterns shown in the bottom-left inset are indexed for Ni [203] zone axis. The Ni {203} cross section is surrounded by (020), (0 $\bar{2}$ 0), ($\bar{3}$ 12), ($\bar{3}$ 02), ($\bar{3}$ 1 $\bar{2}$), (31 $\bar{2}$), (30 $\bar{2}$) and (31 $\bar{2}$) planes, exhibiting a rectangle-like shape with an aspect ratio of 3.6 in the $[30\bar{2}]$ and $[0\bar{2}0]$ orientations, which is possibly responsible for the side-by-side biaxial structure.

Fig. 4-19c shows another spherical 81.1-nm-diameter Ni particle seeded nanowire transits from the sinusoidal surface profile (85.8 nm in period, 87.7 nm in valley diameter, 112.8 nm in peak diameter) to the smooth coaxial one with a 21.3-nm-diameter Si core surrounded by a 15.6-nm-thick SiO_x sheath. The Ni particle is enlarged in the upper-right inset, exhibiting a spherical Ni/Si interface and a 3.0-nm-thick SiO_x layer surrounding the particle. The SAED patterns shown at the bottom-left corner are generated from the Ni particle and indexed for zone axis of

Ni [102], indicating that the single crystalline of the Ni nanoparticle. **Fig. 4-19d** enlarges the transition of the Si nanowire from sinusoidal surface profile to smooth profile, where the SAED patterns are indexed for the zone axis of Si [323], determining the growth is along the $[\bar{1}3\bar{1}]$ orientation.

Fig. 4-19 Nanowires with transitional structures. (a) Transition of a $[\bar{1}10]$ oriented Si/SiO_x nanowire from the coaxial structure (at the top) to the side-by-side biaxial structure (at the bottom). The SAED patterns in the inset are generated from the zone axis of Si [111]. (b) Cross sectional view of the Ni nanoparticle seeding the transition of the wire in (a). The SAED patterns in the inset are generated from the

zone axis of Ni [203]. (c) Transition of a nanowire from smooth profile at the bottom to sinusoidal surface profile morphology at the tip. The SAED patterns in the inset are generated from the zone axis of Ni [102]. (d) The wire grows along the $[\bar{1}\bar{3}\bar{1}]$ orientation. The SAED patterns in the inset are generated from the zone axis of Si [323].

4.4.2 Growth mechanism

4.4.2.1 Scrutiny of the existing mechanisms

Analyzing the mechanisms that have been used to explain the formation process of the various morphologies of Si/Si-oxide nanowires grown by different growth methods, in all due respect to the science and the authors who developed these mechanisms, it is found that none of them could perfectly explain the growth process taking place in the present work due to the flaws as discussed below.

Table 4-2 Key experimental conditions in the reported growth of the various Si nanowires

Ref	Growth process	Grown nanostructures
[61, 69]	Chemical vapor deposition of SiCl_4/H_2 on Au-covered Si wafers at 900-1250 °C	Coaxial and diameter-oscillating Si nanowires
[151, 152]	Thermal annealing of Au-coated Si wafers up to 1250 °C in a quartz ampoule	Coaxial and diameter-oscillating Si nanowires
[90]	Laser ablating the Si disk (made by pressing Si powder at 150 °C for 48 h under a hydraulic press) in a quartz tube under 50 sccm Ar atmosphere at 1200 °C	Coaxial, diameter-oscillating and nanosphere-entrapped Si nanowires
[114]	Thermal annealing of an Au/a-Si/Si wafer at 1030 °C in nitrogen ambient flowing at 50 sccm and under 1 atmosphere pressure	Au_2Si nanosphere entrapped Si oxide nanowires

[115]	Thermal annealing of the Au/SiN ₂ /Si wafer sandwiched with an Au-coated Si wafer at 530 °C in a gas mixture of H ₂ (200-250 sccm) and NH ₃ (300-350 sccm) atmosphere under 50-70 torr pressure in a microwave chamber	Au nanosphere entrapped Si oxide nanowires
[116]	Thermal evaporation of SiO powders at 1050 °C on an Au-coated Si wafer in a fused quartz tube at 25 mbar	Au/Si nanoparticle entrapped Si oxide nanowires
[153]	Thermal annealing of an Au/SiO ₂ /Si wafer in a quartz tube at 1200 °C in the presence of forming gas (95% N ₂ +5% H ₂) for 30 min	Au nanosphere entrapped Si oxide nanowires
[154]	Thermal evaporation of SiO powders at 1250 °C in an alumina tube in 50 sccm 5% H ₂ mixed with 95% Ar atmosphere at 400 torr	Coaxial and side-by-side biaxial Si/SiO ₂ nanowires
[155]	Thermal evaporation of SiO powders at 1250 °C on the carbon-nanotube-containing Si substrates in an alumina tube which was evacuated with 5% H ₂ and Ar at a flow rate of 50 sccm under 500 torr	Coaxial and side-by-side biaxial SiC/SiO ₂ nanowires
[156]	Laser ablation of the compressed powders of BN, C, SiO, and Li ₃ N under 300 sccm nitrogen atmosphere and 500 torr pressure at 1200 °C in a quartz tube	Coaxial SiC/SiO ₂ nanowires
[157]	Thermal evaporation of SiO/carbon/graphite powder mixture in an alumina tube at around 1500 °C for 12 h	Coaxial, side-by-side biaxial and the transitional SiC/SiO ₂ nanowires

(1) Growth mechanisms based on redox reactions

Growth of Si/Si-oxide nanowires requires freely mobile atoms or molecules in vapour,[30] or melt,[29] or solution,[6] therefore, the redox reaction of carbon and SiO, only involving the migration of electrons, but no physical movement of atoms or molecules, is unable to explain the growth process of the coaxial, or the side-by-side biaxial, or their transitional nanowires during laser ablation of the compressed powders of BN, C, SiO, and Li₃N in a quartz tube,[156] or thermal evaporation of SiO powders on the carbon-nanotube-containing Si substrates in an alumina tube,[155] or thermal evaporation of SiO/carbon/graphite powder mixture in an

alumina tube.[157] Moreover, the crystalline Si side in the coaxial or the side-by-side biaxial nanowires grown is misinterpreted as SiC,[155-157] because the SAED patterns are actually generated from the zone axis of Si [101], not SiC [101] (cf., **S_Figure 9, Fig.1** in ref [156] and **FIG.2.** in ref [157], External database Data 3 and Data 10).[156, 157] Additionally, the growth kinetics or surface energy is also unable to explain the transition between coaxial to biaxial nanostructures,[157] because the growth of one-dimensional nanostructures, i.e., phase transition from vapor to solid, or from liquid to solid, however, is an energy-releasing process,[35] different from building a tower with the solid bricks. For instance, 3.04×10^5 J is released when 1 mole Si vapor (at 1000 K, 1 atmosphere) transits into solid, and 5.0×10^4 J is released when 1 mole liquid Si (at 1693 K) becomes to solid state.

As discussed above, the disproportionation reaction of SiO, i.e., $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, [86] is also unable to explain the growth process of the Si/Si-oxide nanowires during laser ablating the Si disk in the quartz tube,[90] where the grown necklace-shaped or fishbone-shaped were wrongly explained either by the regular change of the diameter of the Si nanoparticles, or by the monocentric nucleation of the Si nuclei and periodic unstable growth. In fact, there is no SiO to start with in the growth since Si disk is made of Si powders. Si vapor pressure of around 0.837 torr can be produced during thermal evaporation of the bulk Si at 1200 °C,[97] under 500 torr, however, the mean free path of these vaporized atoms or molecules is only around 1.24 μm , i.e., a galaxy away from the location where the nanowire grew, i.e., 15 cm downstream.[89] The sublimated Si atoms couldn't reach the growth location to supply the growth of Si nanowires. Due to the dramatic size and mass difference with the Ar molecules, on the other hand, the ejected Si particles could reach the growth location, i.e., the wall of the quartz tube, where metallic

impurities including Al and Cu are already there.[105, 106] Al-Si eutectic droplet could form at only 577 °C (cf., **Fig. 4-20a**).[56] Cu-Si eutectic droplet could form at 802 °C (cf., **Fig. 4-20b**). The nanowire growth taking place at around 900 °C,[86, 89, 90] therefore, is actually seeded by the Al-Si or Cu-Si eutectic droplets.

Fig. 4-20 Binary alloy phase diagrams. (a) The Al-Si eutectic alloy melts at 577 °C, (b) the Cu-Si eutectic alloy melts at 802 °C, (c) the Ni-Si eutectic alloy melts at 993 °C.[56]

To summarize, the mechanisms based on the redox reactions are difficult to explain the growth process of the nanowires with various morphologies due to the lack of physical movement of atoms or molecules.[155-157] The crystalline side in the coaxial or side-by-side biaxial nanowire is Si. The growth kinetics or surface energy is unable to explain the transition between coaxial to biaxial nanostructures.[157] The nanowire growth taking place in quartz tube actually is seeded by Al-Si or Cu-Si droplet at the wall of the tube, not by the Si nanoparticle that is precipitated through the disproportionation of SiO.²[86, 89, 90]

(2) Entrapping mechanisms of the nanospheres

As discussed above, the disproportionation reaction of SiO can't explain the growth process of nanowires during laser ablating the Si disk in the quartz tube,[90] not to mention the formation of the frog-egg-entrapped nanowire. Serious doubts are put on the composition of the entrapped "eggs", since they have never been characterized. It is highly possible that the entrapped "eggs" are actually Al or Cu nanoparticles, rather than Si nanoparticles, since the growth is actually seeded by the Al-Si or Cu-Si eutectic droplet on the wall of the quartz tube.

Another two distinct entrapping mechanisms are developed by the same group to explain the entrapping of the periodic chains of Au/Si,[114] or Au nanospheres,[115] in the Si oxide nanowires during thermal annealing of an Au/a-Si/Si wafer,[114] or thermal annealing of the Au/SiN₂/Si wafer sandwiched with an Au-coated Si wafer,[115] The first mechanism believes the entrapped Au/Si nanospheres are formed by dislodging of the two necks of the supersaturated liquid Au-Si alloy during the extension of the alloy nanosphere,[114] and the oxide sheath is produced by the oxidation in the atmosphere. In that case, however, the nanowire should have the wavy sheath rather than the smooth one. Moreover, Si and Au are

believed to be precipitated together in the form of Au-Si/SiO_x coaxial structure from the Au-Si droplet, i.e., Au-Si core surrounded by SiO_x sheath. However, Au and Si can't be the solute in the Au-Si droplet at the same time to reach supersaturation. Only one of them could reach supersaturation at certain moment, when the other acts as the solvent. The second mechanism believes the growth of Au-nanopeapodded nanowires starts with the formation of a silica nanotube with a gold attachment at the end.[115] With increasing growth time, Au starts to flow into the hollow nanocavity due to the capillary force and shows a discrete wire-like morphology. With prolonged growth, the gold nanowires transform into a droplet-like chain owing to insufficient supply of gold, and finally evolve into a peapod. The source for the nanocavity filling is attributed to the continuing supply of Si-containing species from the top Si cover. However, the nanotube has never been observed. The spacing between the podded Au nanopeas is not hollow, but filled with silica. The dark core in the coaxial nanowire has never been characterized to be Au, and it is highly possible to be Si core surrounded by SiO₂ sheath through separating the supersaturated Si and SiO₂ phases in the Au-Si-O droplet.

Lastly, it is also proposed that the Si core of the grown coaxial nanowire is formed by the phase separation of Si in the Au-Si droplet during thermal evaporation of SiO powders,[116] or thermal annealing of an Au/SiO₂/Si wafer,[153] where Si originates from the disproportionation of SiO; the oxide sheath, however, is directly formed by the disproportionate SiO₂ without entering the Au-Si droplet. It is believed that the additional amount of oxygen changes the ratio of the disproportionate Si and SiO₂, i.e., the amount of SiO₂ increases, and thus that of Si decreases. Therefore, the oxide sheath could grow faster than the Si core, resulting in the deformation of the Au-Si droplet into a cylindrical shape. Till a certain length,

the liquid Au-Si droplet becomes unstable and pinches off periodically to entrap the Au/Si particles in the nanowire. However, it is reported that the commercially available SiO powders were not 100% SiO, but an inhomogeneous mixture of amorphous SiO₂ and amorphous Si with SiO phase at the interface.[121-124] Upon thermal evaporating the SiO powder at 1050 °C under 25 mbar (i.e., 18.75 torr) nitrogen atmosphere, Si atoms, SiO and SiO₂ molecules could be sublimated by conversion of thermal energy to kinetic energy, meanwhile, the SiO micro-particles could eject in space due to the volume expansion of the residual gas,[96] and then land on the tube wall. The vaporized atoms or molecules have a limited mean free path of around 18.3 μm,[96, 99, 100] thus couldn't reach the location where the nanowire grows. Si in the nanowire could only come from the Si portion in the ejected Si micro-particles. As discussed before, on one hand, the disproportionation of SiO, i.e., $2\text{SiO} \rightarrow \text{Si} + \text{SiO}_2$, takes place at around 900 °C through the migration of electrons.[122] However, no physical movement of Si atoms or SiO₂ molecules occurs in this reaction. After the redox reaction, therefore, the particle becomes a microscopic mixture of Si and SiO₂ clusters. These clusters are not separable, but still confined in the particle, not able to move freely and separately in space. On the other hand, though Si has a high melting point of 1410 °C,[97] Si and Au could form eutectic droplet at a low temperature of 363 °C to provide the mobile Si atoms (cf., the growth temperature is 850-900 °C).[56] While the disproportionate SiO₂ molecules are still in the particle due to the too high melting point (1703 °C [97]), thus unable to move around to form the oxide sheath. The growth takes place under nitrogen atmosphere (not a high vacuum ambient), therefore, the Au-Si droplet is easy to be oxidized into the Au-Si-O droplet. As such, the only source of the oxide sheath is the supersaturated Si oxides in the liquid Au-Si-O droplet, rather than the SiO₂ molecules that are directly produced through the disproportionation of SiO.

Upon the above scrutiny of the experimental details in these nanosphere-entrapped nanowires,[90, 114-116, 153], therefore, the entrapping mechanism is still mysterious. However, it is also found that these nanosphere-entrapped nanowires are only observed in the metal-seeded growth, where the metallic catalyst seeds the growth at the root of the nanowire, and the Si either comes from the Si-containing powder particles,[90, 116] or from the Si films.[114, 115, 153] The nanowires are grown in a protective gas ambient (e.g., Ar atmosphere) under certain pressure, rather than in a high vacuum atmosphere, therefore, the metal-Si droplet could be oxidized into metal-Si-O droplet. Since the metal-Si-O droplet seeds the nanowire at the metal-covered substrates, the metal could dissolve into the droplet from the surrounding metal layer as the case of Si to reach supersaturation at certain moment.

4.4.2.2 Ni-Si-O droplet seeded growth mechanism

In the present nanowire growth, though Si vapor pressure of around 0.3045 torr could be produced during thermal annealing the Si wafer at 1100 °C and under 1.08×10^5 Pa Ar atmosphere,[97] however, the mean free path of the vaporized Si atoms is only around 0.76 μm . [96, 99, 100] The Si wafer is covered with a Ni layer, on top of which a thick a-C layer is sputtered. The Ni-Si-O nanoclusters are located at the root of the grown nanowires. Therefore, Si atoms couldn't come from the vapor, but only from the Si wafer substrate through the eutectic melting of Ni and Si at 993 °C to form Ni-Si droplet at the interface (cf. **Fig. 4-20c**). [56] This liquid droplet serves as a preferred site for melting the surrounding solid-phase Si and Ni in. Ar surrounds the droplet and exchanges energy and momentum with the atoms in the droplet, giving rise to overcooling effect to the droplet, and seeding the preferential growth of the Si nanowire at the root, upon the supersaturation of Si in the Ni-Si droplet. During the growth, the droplet directs the growth orientation and

defines the diameter of the nanowire. Ultimately, the growth terminates when the temperature is below the eutectic melting point of the Ni-Si droplet or the reactants are run out. Though the residual oxygen could be partially retarded by the top carbon layer at the beginning of the growth, however, it could still oxidize the droplet into Ni-Si-O droplet when the a-C top layer becomes porous or cracked during annealing. Upon supersaturation of Si oxides in the Ni-Si-O droplet, Si oxides could be precipitated from the droplet to form the oxide sides of the Si nanowire. The rhombus-shaped Ni {315} cross section of the seeding Ni particle may be related to the Si/SiO_x coaxial nanowire. On the other hand, the rectangle-arranged Ni {203} cross section of the seeding Ni particle may be related to the side-by-side Si/SiO_x biaxial nanowire. The defects such as micro-twins or stacking faults found in the Si side of the side-by-side Si/SiO_x biaxial nanowires are possibly formed by the different precipitation rate of the supersaturated SiO_x and Si phases from the phase-decentred Ni-Si-O droplet (cf., **Fig. 4-16**, and **Fig. 4-19a**). The nonexistence of defects in coaxial or triple-concentric Si nanowires is possibly due to the central symmetric structure, where the interfacial force between the core and the sheath could be effectively balanced.

As summarized in **Table 4-3**, it is found that the morphologies of the grown Si nanowires are related to the size of the seeding Ni nanoparticles that are embedded in the Ni-Si-O nanoclusters, and the phase distribution in the Ni-Si-O droplet. They could be grouped into two categories: (1) double-phased coaxial or side-by-side biaxial Si/SiO_x nanowires are seeded by Ni particles with diameters smaller than 80 nm; (2) triple-phased smooth or sinusoidal Si/SiO_y/SiO_x nanowires are seeded by Ni particles with diameters bigger than 80 nm. Since the seeding Ni nanoparticles are directly originated from the sputtered Ni interlayer during thermal annealing, it

is hard to control the uniformity of the diameter. As such, the phase number in the nanowire is possibly related to the size of the Ni-Si-O eutectic droplet. The complete oxidation of the Ni-Si-O_y phase into Ni-Si-O_x phase in small Ni-Si-O droplet results in double-phased structure, i.e., Si and SiO_x. The partial oxidation of the Ni-Si-O_y phase into Ni-Si-O_x phase in big Ni-Si-O droplet results in triple-phased structure, i.e., Si, SiO_y and SiO_x.

Table 4-3 Size distribution of the seeding Ni nanoparticles and the grown Si/Si-oxide nanowires

Morphology and structure	Thickness of Si core (nm)	Thickness of SiO _y interlayer(nm)	Thickness of SiO _x sheath(nm)	Ni particle diameter (nm)	Ref
Coaxial smooth	19.1,20.1	0	23.1,8.6	65.0	Fig. 4-15a,b
Side-by-side biaxial smooth	13.2	0	15.3	52.0	Fig. 4-16
Side-by-side biaxial to coaxial smooth	18.7-20.9	0	5.1-8.3	44.6-51.4	Fig. 4-19a, b
Triple-concentric smooth	33.3, 31.8	14.1,15.7	17.6,17.8	-	Fig. 4-7b, Fig. 4-17a
Triple-concentric sinusoidal (valley)	24.7	13.3	11.7	-	Fig. 4-17b
Triple-concentric sinusoidal (peak)	29.6	13.5	19.2		
Fishbone- profiled (valley)	54.6	8.6-26.2	10.0 (bottom), 39.9 (top)	95.5-128.3	Fig. 4-17c,d
Fishbone- profiled (peak)	68.4		32.6 (bottom), 66.4 (top)		
Ni-nanosphere- entrapped	14.0	19.8-53.6	17.8	-	Fig. 4-18a, b
Sinusoidal to smooth	21.3	0	15.6	81.3	Fig. 4-19c,d

Fig. 4-21 schematically sketches the nanowires in relation to the seeding Ni-Si-O droplets to illustrate the growth mechanisms responsible for the various

morphologies of the grown nanowires. The diameter of the single crystalline Ni nanoparticles that are embedded within the resultant Ni-Si-O nanoclusters in **Fig. 4-21(a)** and **(b)** is smaller than 80 nm, while that in **Fig. 4-21(c)-(e)** is bigger than 80 nm. The Si/SiO_x coaxial nanowire is grown through precipitating the supersaturated Si and SiO_x phases from the Ni-Si-O droplet, where the Ni-Si inner phase is concentrically surrounded by the Ni-Si-O_x outer phase in the Ni-Si-O droplet (cf., **Fig. 4-21a**); while the side-by-side Si/SiO_x biaxial one is seeded by the droplet with decentred Ni-Si and Ni-Si-O_x phases in the Ni-Si-O droplet (cf., **Fig. 4-21b**). The coaxial nanowire could transit to side-by-side biaxial structure as the Ni-Si and Ni-Si-O phases in the Ni-Si-O droplet become decentred (c.f., **Fig. 4-19, a** and **b**). The smooth Si/SiO_y/SiO_x triple-concentric nanowire is precipitated from the Si, SiO_y and SiO_x supersaturated Ni-Si-O droplet, where the Ni-Si inner phase is concentrically surrounded by the Ni-Si-O_y inter phase, followed by the Ni-Si-O_x outer phase (cf., **Fig. 4-21c**). The periodic vibration of the Ni-Si-O triple-concentric droplet gives rise to the sinusoidal or even fishbone-profiled Si/SiO_y/SiO_x nanowire (cf., **Fig. 4-21d**). If the droplet stays central symmetrically ball-shaped throughout the growth process, the grown nanowire is of a smooth triple-concentric structure (cf., **Fig. 4-17a**). The periodically vibrating Ni nanoparticle is responsible for the sinusoidal triple-concentric ones (cf., **Fig. 4-17b**). The fishbone-profiled Si nanowire (with the highest curvature in the core, interlayer and sheath), is precipitated from the droplet with the most violent vibration (cf., **Fig. 4-17, c** and **d**). The oscillating diameter of the sinusoidal nanowire is possibly controlled by the factors related to the liquid Ni-Si-O eutectic droplet, including the supersaturation of Si, liquid-forming Ni impurity, diameter, temperature, interfacial energy, surface curvature, roughening transition at the liquid-solid interface, contact angle of the droplet, the onset and development of periodicity, and the subsequent oxidation of

the grown nanowire. The sinusoidal nanowire could become smooth, as the droplet stops the vibration and maintains the ball-shaped morphology (cf., **Fig. 4-19**, c and d). The Ni nanospheres are entrapped in the SiO_y core through the precipitation of the supersaturated Ni, SiO_y and SiO_x phases from the Ni-Si-O droplet (cf., **Fig. 4-18**, a and b), when the Si doesn't reach supersaturation due to the oxidation of the Ni-Si phase in the droplet (cf., **Fig. 4-21e**). The reason why the entrapped Ni is in the form of nanosphere is possibly due to the uniform force from the surrounding SiO_y phase, in conjunction with the limited amount of the supersaturated Ni in the droplet. The nanospheres disappear as Ni is not supersaturated, but Si becomes supersaturated again and is precipitated as the core.

Fig. 4-21 Schematic diagrams of the Ni-Si-O droplet seeding the nanowires of various morphologies. (a) The concentric Ni-Si-O droplet seeds the nanowire

constructed with Si core coaxially surrounded by SiO_x sheath; (b) The decentred Ni-Si-O droplet seeds the side-by-side Si/ SiO_x biaxial nanowire; (c) The triple-concentric Ni-Si-O droplet seeds the smooth Si/ $\text{SiO}_y/\text{SiO}_x$ triple-concentric nanowire. (d) The periodically vibrated Ni-Si-O droplet seeds the Si/ $\text{SiO}_y/\text{SiO}_x$ sinusoidal and sometimes even fishbone-profiled nanowires. (e) The Ni-Si-O droplet seeds the entrapping of Ni nanospheres in the Si/ $\text{SiO}_y/\text{SiO}_x$ nanowire as Ni, instead of Si, reaches supersaturation. The droplet is related to the Ni nanoparticle that is embedded in the resultant Ni-Si-O nanocluster. The diameter of the Ni nanoparticles in (a) and (b) is smaller than 80 nm, while that in (c)-(e) is bigger than 80 nm.

4.4.3 Summary

This section investigated the origin of the various morphologies of Si nanowires from Ni-coated Si wafer beneath sputtered carbon upon 1-min thermal annealing. It can be summarized as follows:

- (1) The coaxial or side-by-side biaxial Si/ SiO_x , smooth or sinusoidal triple-concentric, fishbone-shaped, Ni-nanosphere entrapped Si/ $\text{SiO}_y/\text{SiO}_x$ nanowires and their transitional nanostructures were grown through 1-min thermal annealing of a nickel (Ni) coated Si wafer beneath sputtered amorphous carbon. The Ni nanoparticles are embedded in the Ni-Si-O nanoclusters connecting with the grown Si nanowires, confirming the root growth of the Si nanowires from the Ni-Si-O droplets. The rhombus-shaped Ni {315} cross section of the seeding Ni particle is related to the Si/ SiO_x coaxial nanowire. The rectangle-

arranged Ni {203} cross section of the seeding Ni particle is related to the side-by-side Si/SiO_x biaxial nanowire.

- (2) The origin of the various morphologies of Si nanowires is discussed. It is found that the grown Si nanowire is controlled by the diameter and vibration of the seeding Ni-Si-O droplet, the distribution of the Ni-Si, Ni-Si-O_y and Ni-Si-O_x phases, and the supersaturated content in the Ni-Si-O droplet.

Chapter 5. **CONCLUSIONS AND RECOMMENDED WORK**

5.1 Conclusions

Crystalline silicon (Si) nanowires of various morphologies were grown via thermal annealing of nickel (Ni) coated Si wafer beneath sputtered amorphous carbon. Si nanowire is seeded by the Si-supersaturated Ni-Si-O droplet at the root of the nanowire. The structure of the surface coverings, structural evolution of the Si nanowires, and the corresponding growth mechanisms of Si nanowires in relation to the seeding Ni particles have been studied systematically. Conclusions are drawn in the following aspects:

1. Structural evolution of surface coverings

The sputtered Ni film exhibits a face-centered cubic polycrystalline structure. The oxygen contaminations exist on the top surface of the film (27.06 at.%) and at the interface between Ni film and Si wafer substrate (13.35 at.%) due to the exposure in the ambient environment. In the as-sputtered 600-nm a-C/Ni film, the amount of Si was very small, and no Si⁰ exist. 3-min thermal annealing of the film dramatically trailed off the content of carbon and boosted up that of the oxygen and silicon were greatly boosted up. Ni remained at the bottom. The annealed film has a close chemical composition to stoichiometry SiO₂. As a result of the growing carbon sp² clusters and the conversion from sp³ to sp² bonding configuration, I_D/I_G

increased from 0.98 to 1.77, G-band position upshifted from 1533 cm^{-1} to 1588 cm^{-1} , second-order bands appeared at 2643 cm^{-1} and 2908 cm^{-1} .

2. Oxidation retardation by the surface covering

Upon annealing of the a-C/Ni/Si-wafer and Ni/Si-wafer samples, wire-like nanostructures appeared on the film surface. The heterogeneous coaxial one was confirmed to be the Si nanowire constructed with crystalline Si surrounded by amorphous SiO_x ($x \approx 2$) sheath. The triple-concentric nanostructure was Si/ SiO_y / SiO_x ($y \approx 1$) nanowire with a crystalline Si core surrounded by the amorphous SiO_y interlayer, and followed by the amorphous SiO_x outer sheath. The homogeneous one was the amorphous SiO_x nanowires. Ni particle didn't appear at the tip of the nanowire. The Si source material came from the Si wafer rather than the film. The a-C covering layer reduced the oxidation. Within the same annealing duration of 3 min, the ratio of the core diameter over the sheath thickness decreased from 0.3 ± 0.1 to 0 as the a-C layer thickness reduces from 570 nm to 130 nm. For the 570 nm a-C covering layer, prolonging the annealing from 1 min to 3 min gave rise to reduced ratio of the core diameter over the sheath thickness from 1.2 ± 0.1 to 0.3 ± 0.1 .

3. Origin of the growth orientations

The origin of the growth orientations of Ni-seeded Si nanowires is not dictated by surface energy of the various nanocrystal planes, but follows a specific structure-sensitive principle in relation to the seeding Ni nanoparticles to minimize the mismatch in lattice spacing and dihedral angle at the wire/particle interface. It is

inferred that the growth orientation of Si nanowires is determined by the ordered planes of the Ni catalyst particle at the wire/particle interface.

4. Origin of the various morphologies

The morphologies of Si nanowires grown through thermal annealing of Ni covered Si wafers are controlled by the diameter, phase distribution, vibration, and the supersaturated content of the liquid Ni-Si-O droplet. The droplet solidifies into a Ni-Si-O nanocluster of a Ni particle surrounded by a layer of Si oxide at the end of the nanowire growth. Bigger droplet (e.g., Ni particle larger than 80 nm in this work) results in triple-phased or Si/SiO_y/SiO_x nanowires; smaller ones give rise to two-phased or Si/SiO_x nanowires. Vibration of the Ni-Si-O droplet results in nanowires of sinusoidal surface profile. Extreme vibration gives rise to the fishbone morphology. At no vibration, the smooth profile is obtained. If precipitation of supersaturated Ni from the droplet takes place, Ni nanosphere is entrapped within the Si nanowire. As Si becomes supersaturation again, precipitation of Si takes over, thus the Ni entrapment disappeared. The side-by-side biaxial structure appears when the droplet is off-centre.

5.2 Recommended work

This project has grown highly crystalline Si nanowires from Ni-coated Si wafers through rapid thermal annealing. The properties of the surface covering, the structural evolution of the grown Si nanowires as function of the thickness of the surface covering, the detailed growth mechanisms for the various Si nanowires

were elucidated in detail. From the schedule of this project, and the results obtained so far, it can be concluded that the following directions are very important and recommended future work should focus on these areas.

1. Growth of other semiconductor nanowires

Based on the feasible growth of Si nanowires from Ni-coated Si wafers in this project through thermal annealing, the growth of other semiconductor (Ge, GaN, GaP, and etc.) nanostructures may carry out by adopting alternative metallic surface covering (such as Au, Cu, Al, and etc.).

2. Orientation relationship

Though the structure-sensitive principle was discovered in the grown Si nanowires in relation to the seeding Ni particles, more theoretical analysis is needed to find out the exact principle. And also, more high resolution images are needed to confirm the principle.

3. Relationship between cross section and growth orientation

Only two kinds of cross section, i.e., hexagon and rectangle, are observed in this project, in the nanowires respectively growing along the $\langle 112 \rangle$ and $\langle 113 \rangle$ orientations. More work is needed to reveal the relationship between cross section and growth orientation.

4. Control of the growth rate, diameter and orientation

Preliminary work was carried out on the retardation of the oxidation of the nanowires by sputtering the amorphous carbon surface covering. Work on the control of the growth rate, distribution of the diameter and growth orientation is necessary.

5. Properties and applications of Si nanowires

The work in this project mainly focuses in the aspects of academy and scientific theory. More work should focus on the electronic, optical and mechanical properties. Also their application in the real device is still in the stage of laboratory.

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SUPPLEMENTARY MATERIALS

S_Figure 1

S_Figure 1 Thermal evaporation source.[96] (a) The Drumheller source. (b) Compartmentalized source. Powder source materials, such as SiO, would release large quantities of residual gases upon heating, thus causing the ejection of evaporant particles. In (a), a ring-shaped lid prevents the ejection of the particles, and in (b), a reflecting hood is placed on the top of the powder source to stop the ejected particles. (c) Chromium sublimation source, the electric current flows through the tantalum cylinder (heavy lines). Since the source is compact and well shielded, sublimation occurs from the entire surface area of the rod, which is uniformly heated by radiation. Therefore, the ejection of particles does not occur.

S_Figure 2

S_Figure 2 The surface morphology of the quartz tube. (I) Heat center, (II) 3 cm away from the heat center, and (III) unheated fused tube wall. The quartz tube wall is peeled off in (I), and cracked in (II), but still uncracked in (III).

S_Figure 3

S_Figure 3 (a) The fused quartz tube after heating up to 1150 °C and holding for 45 min, (b) the unheated fused quartz tube wall, (c) 7.5 cm away from the heat center, (d) 10.5 cm away from the heat center, (e) the magnified area in (d). The rectangle in (a) indicates the heat center. The white arrows point at the location of (c) and (d).

S_Figure 4

S_Figure 4 Nanosphere-entrapped Si nanowires grown through laser ablation of Si disk in a quartz tube under Ar atmosphere,[90] or thermal annealing of Au/amorphous-Si bilayers in a nitrogen ambient atmosphere,[114] or heating the Au/SiN_y/Si wafer sandwiched with an Au-coated Si wafer in a microwave chamber,[115] or thermal evaporation of Si monoxide powders on Au-coated Si wafer.[116, 117] (a) Frog-egg-shaped and fishbone-shaped Si nanowires, where the

eggs marked by the hollow arrow actually were the metallic Cu or Al nanoparticles, while the fishbone marked by the solid arrow was the wavy crystalline Si core. The wavy structure was resulted from the periodic vibration of the metal-Si droplet seeded at the quartz tube wall.[90] (b) Morphology of the Au₂Si nanopea-podded Si oxide nanowires.[114] (c) Nanostructure and analytical electron microscopic analysis of the nanowire and the peapodded nanosphere.[114] The inset shows the amorphous patterns corresponding to the nanowire. (d) TEM images of the gold nanopeapodded silica nanowire.[115] The inset shows an electron-diffraction pattern recorded along the [102] zone axis of Au. (e) HRTEM image of the gold core in a silica nanowire. (f) The periodic chains of Au/Si nanoparticles entrapped in the SiO₂ nanowire.[116] (g) The colored and overlayed element mappings (silicon: green; gold: red). Energy-dispersive X-ray spectroscopy element mappings of (h) the Si K α line and (i) the Au L α line. (j) High resolution TEM image of a nanoparticle. The two regions of the particle were identified as crystalline Si and Au.

S_Figure 5

S_Figure 5 (a-c) Schematics of atomic planes at the epitaxial interfaces between the Sn particle and the $[0001]$, $[01\bar{1}0]$, and $[2\bar{1}\bar{1}0]$ growth ZnO nanostructures, respectively.[149]

S_Figure 6

S_Figure 6 ZnSe nanowires grown along (a) $\langle 112 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 001 \rangle$ orientations adopted from ref [26]. Modification is conducted based on the FFT

patterns for the atom-resolved seeding Au particle and as-grown ZnSe nanowire. All the patterns are indexed to be from the [101] zone axis of Au and ZnSe. In image (a) the matching planes are $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(0\bar{2}0)$; in images (b), the matching planes are $(\bar{1}\bar{1}\bar{1})$ and $(1\bar{1}\bar{1})$; in images (c), the matching planes are $(1\bar{1}\bar{1})$ and $(\bar{1}11)$.

S_Figure 7

S_Figure 7 Side-by-side Si/SiO_x biaxial nanowire

S_Figure 8

S_Figure 8 Transition of Si/SiO_x nanowire from the coaxial to side-by-side biaxial structure

S_Figure 9

S_Figure 9 (a) High resolution TEM image of the biaxially structured Si/SiO_x nanocables, showing the crystallographic and defect structures of the nanowire. [157] The electron beam is along [101] perpendicular to the nanowire. A Fourier transform of the image from a defect-free area, given at the bottom shows that the growth direction of the nanowire is [311]. (b) and (c) Enlargements of the areas between the interfaces of SiO_x-Si at the contact area and near the surface of Si-SiO_x, respectively, showing the {111} faceted nanoareas at the interface. S and T stand for stacking fault and twin, respectively. (d) A magnified image shows the crystalline core and an amorphous layer of the Si/SiO_x coaxial nanocables.[156] The selected area diffraction pattern indicates that the crystalline core is with the [101] axis parallel to the electron beam. The asterisks represent twinning planes. (e) A high-resolution image of the nanocable structure. Top inset shows the magnified lattice

fringes of the outer layers. Bottom inset shows the A magnified lattice image of the Si core.

EXTERNAL DATABASE

Data 1 PDF#04-0850 Nickel

Downloaded from the database of software **MDI Jade 5**

PDF#04-0850: QM=Star/Calculated; d=Other/Unknown; l=(Unknown)													PDF Card				
Nickel, syn																	
Ni																	
Radiation=CuKa1								Lambda=1.5406				Filter=					
Calibration=								d-Cutoff=				l/lc(RIR)=					
Ref= Level-1 PDF																	
Cubic, Fm3m(225)												Z=4		mp=			
Cell=3.524x3.524x3.524<90x90x90>																	
Density(c)=8.907				Density(m)=				Mwt=				Vol=					
Pearson=																	
Ref= Ibid.																	
Strong Line: 2.03/X 1.76/4 1.25/2 1.06/2 0.79/2 0.81/1 1.02/1																	
8 Lines, Wavelength to Compute Theta = 1.54056A(Cu), l%-Type = (Unknown)																	
#	d(A)	l(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	l(f)	h	k	l	2-Theta	Theta	1/(2d)
1	2.0340	100.0	1	1	1	44.507	22.253	0.2458	5	1.0172	7.0	2	2	2	98.446	49.223	0.4915
2	1.7620	42.0	2	0	0	51.846	25.923	0.2838	6	0.8810	4.0	4	0	0	121.930	60.965	0.5675
3	1.2460	21.0	2	2	0	76.370	38.185	0.4013	7	0.8084	14.0	3	3	1	144.669	72.335	0.6185
4	1.0624	20.0	3	1	1	92.944	46.472	0.4706	8	0.7880	15.0	4	2	0	155.653	77.826	0.6345

Data 2 Si [001] zone axis

ICSD_29287 (44 reflections)
AV/kV:200.00, CL/mm:2000, ZA:[0, 0, 1], FN:[0, 0, 1]

Data 3 Si [101] zone axis

(-1, -5, 1), LZ : 0

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [1, 0, 1]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (94 reflections)
AV/kV:200.00, CL/mm:4000, ZA:[1, 0, 1], FN:[1, 0, 1]

Data 4 Si [102] zone axis

(2, 2, -4), LZ : 0

Center of Laue circle : (0.000,0.000,0.000)::Zone axis : [1, 0, 2]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (18 reflections)
AV/kV:200.00, CL/mm:2000, ZA:[1, 0, 2], FN:[1, 0, 2]

Data 5 Si [111] zone axis

(2, 2, -4), LZ : 0

Center of Laue circle : (0.000,0.000,0.000)::Zone axis : [1, 1, 1]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (54 reflections)
AV/kV:200.00, CL/mm:2000, ZA:[1, 1, 1], FN:[1, 1, 1]

$(2, 2, -4)$, LZ : 0

Center of Laue circle : (0.000,0.000,0.000)::Zone axis : [1, 1, 2]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (54 reflections)
AV/kV:200.00, CL/mm:2000, ZA:[1, 1, 2], FN:[1, 1, 2]

Data 7 Si [116] zone axis

(-6, -2, 4), LZ : 0
 Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [1, 1, 6]
 Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (20 reflections)
 AV/kV:200.00, CL/mm:4000, ZA:[1, 1, 6], FN:[1, 1, 6]

Data 8 Si [315] zone axis

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [3, 1, 5]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (16 reflections)
AV/kV:200.00, CL/mm:4000, ZA:[3, 1, 5], FN:[3, 1, 5]

Data 9 Si [323] zone axis

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [3, 2, 3]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_29287 (26 reflections)
AV/kV:200.00, CL/mm:4000, ZA:[3, 2, 3], FN:[3, 2, 3]

Data 10 SiC [101] zone axis

(-2, 3, -14), LZ : 0

Center of Laue circle : (0.000, -0.000, 0.000)::Zone axis : [2, -1, 48]=[5, -4, -1, 144]

Tilt angle / deg. : 0.00

Closest zone axis : [2, -1, 48]=[5, -4, -1, 144]

5 nm⁻¹

ICSD_156190 (34 reflections)

AV/kV:200.00, CL/mm:8000, ZA:[1, 0, 1]=[2, -1, -1, 3], FN:[1, 0, 1]=[2, -1, -1, 3]

Data 11 Ni [102] zone axis

(6, 4, 0), LZ : 0

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [1, 0, 2]
Tilt angle / deg. : 0.00

20 nm⁻¹

ICSD_162279 (22 reflections)
AV/kV:200.00, CL/mm:3000, ZA:[1, 0, 2], FN:[1, 0, 2]

Data 12 Ni [112] zone axis

(6, 4, 0), LZ : 0

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [1, 1, 2]
Tilt angle / deg. : 0.00

20 nm⁻¹

ICSD_162279 (40 reflections)
AV/kV:200.00, CL/mm:3000, ZA:[1, 1, 2], FN:[1, 1, 2]

Data 13 Ni [203] zone axis

(6, 4, 0), LZ : 0

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [2, 0, 3]
Tilt angle / deg. : 0.00

20 nm⁻¹

ICSD_162279 (14 reflections)
AV/kV:200.00, CL/mm:3000, ZA:[2, 0, 3], FN:[2, 0, 3]

Data 14 Au [101] zone axis

Center of Laue circle : (0.000,0.000,0.000)::Zone axis : [1, 0, 1]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_163723 (68 reflections)
AV/kV:200.00, CL/mm:2000, ZA:[1, 0, 1], FN:[1, 0, 1]

Data 15 ZnSe [101] zone axis

Center of Laue circle : (0.000, 0.000, 0.000)::Zone axis : [1, 0, 1]
Tilt angle / deg. : 0.00

10 nm⁻¹

ICSD_167830 (138 reflections)
AV/kV:200.00, CL/mm:4000, ZA:[1, 0, 1], FN:[1, 0, 1]