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Aaron Mao
San Jose State University

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VAPOR-LIQUID-SOLID APPROACH FOR THE GROWTH OF ORIENTED
SILICON NANOWIRE

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Aaron Mao

December 2004

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October 22, 2004

Dr. Stefanie Harvey

OCTOBER 22, 2004

Dr. Melanie McNeil

10/28/04

Dr. Meyya Meyyappan, NASA Ames Research Center

APPROVED FOR THE UNIVERSITY

ABSTRACT

VAPOR-LIQUID-SOLID APPROACH FOR THE GROWTH OF ORIENTED SILICON NANOWIRE

By Aaron Mao

Silicon nanowires are potential building blocks for the semiconductor industry. To realize potential applications, the nanowires must be vertically-aligned, crystalline, and less than 100 nm. These characteristics were achieved with the vapor-liquid-solid (VLS) mechanism. The vapor source is the reduction of silicon tetrachloride by hydrogen; the liquid catalyst is generated by a 5 nm gold film; and the solid is [111] silicon. For this study, the effect of temperature, reactor residence time, silicon tetrachloride concentration, and hydrogen concentration on silicon nanowire growth were evaluated. The results indicate that variable interactions are present and that growth is strongly affected by the silicon tetrachloride concentration and temperature. Inappropriate conditions lead to pitting, wire instability, homogeneous nucleation, or no growth. Vertically-aligned, crystalline wires, with average diameters less than 100 nm, are produced at 925°C by four different experimental conditions. For these conditions, silicon tetrachloride concentrations are extremely low, with a range of 0.04-0.10%.

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TABLE OF CONTENTS

LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
CHAPTER 1 INTRODUCTION.....	1
CHAPTER 2 LITERATURE REVIEW.....	3
2.1 VAPOR-LIQUID-SOLID MECHANISM BACKGROUND.....	3
2.2 CHARACTERISTICS OF SI NANOWIRES AND WHISKERS.....	4
2.3 MECHANISM.....	4
2.4 GROWTH PARAMETERS.....	5
2.4.1 PRESSURE.....	5
2.4.2 TEMPERATURE.....	6
2.4.3 SOURCE.....	9
2.4.4 CATALYST.....	12
2.4.5 SUBSTRATE.....	16
2.5 CHEMICAL VAPOR DEPOSITION.....	16
2.5.1 INTRODUCTION.....	16
2.5.2 THERMODYNAMICS.....	17
2.5.3 TEMPERATURE.....	17
2.5.4 INPUT CONCENTRATION.....	18
2.5.5 CHEMICAL REACTIONS.....	20
2.5.6 MASS TRANSFER.....	20
CHAPTER 3 BEST TEST CONDITIONS.....	23
CHAPTER 4 HYPOTHESIS.....	25
CHAPTER 5 PROBLEM STATEMENT.....	26

CHAPTER 6 EXPERIMENTAL EQUIPMENT AND METHODS.....	27
6.1 SETUP.....	27
6.1.1 PROCESS DELIVERY.....	28
6.1.2 REACTOR.....	29
6.2 SUBSTRATE PREPARATION.....	30
6.3 ANALYTICAL EQUIPMENT.....	30
6.4 WIRE PROCESSING STAGES.....	31
6.5 TEST PLAN.....	32
CHAPTER 7 RESULTS AND DISCUSSIONS.....	35
7.1 CATALYST BEAD GENERATION.....	35
7.2 LOCATING SiNW GROWTH CONDITIONS	38
7.2.1 CONDITIONS A1, A2, AND A3: HIGH SiCl ₄ CONCENTRATIONS (1.0-5.5%)	39
7.2.2 CONDITIONS B1, B2, B3, AND B4: LOW SiCl ₄ CONCENTRATION (0.013-0.125%).....	42
7.2.3 CONDITIONS C1 AND C2: TEMPERATURE EFFECTS.....	45
7.2.4 SUBSTRATE RELOCATION: BOUNDARY LAYER THICKENING.....	47
7.2.5 MISCELLANEOUS OBSERVATIONS.....	50
7.2.5.1 CONCENTRATION NON-UNIFORMITY ON SUBSTRATE	50
7.2.5.2 SURFACE CHARACTERISTICS EFFECT ON WIRE MORPHOLOGY.....	53
7.3 EXPERIMENTAL MATRIX.....	55
7.3.1 QUALITATIVE ANALYSIS.....	57
7.3.1.1 TYPE I WIRES.....	60
7.3.1.2 TYPE II WIRES.....	64
7.3.1.3 TYPE III WIRES.....	66

7.3.1.4 TYPE IV WIRES.....	69
7.3.1.5 TYPE V WIRES.....	69
7.3.2 PROCESS VARIABLE ANALYSIS.....	71
7.3.2.1 H ₂ CONCENTRATION.....	74
7.3.2.2 TEMPERATURE.....	80
7.3.2.3 SiCl ₄ CONCENTRATION.....	83
7.3.2.4 RESIDENCE TIME.....	90
CHAPTER 8 CONCLUSIONS.....	93
REFERENCES.....	95
APPENDIXES.....	100
A. EQUILIBRIUM REACTIONS.....	100
B. MASS TRANSFER THROUGH STAGNANT FILM.....	101
C. BOUNDARY LAYER CALCULATED WITH EQUATION 12.....	102
D. ERROR ANALYSIS FOR EQUATIONS 16-20.....	104

LIST OF TABLES

Table 1.	Effect of SiCl_4/H_2 on SiNW morphology [36].....	12
Table 2.	Summary of temperature effects on whiskers and nanowires.....	24
Table 3.	Summary of source effects on whiskers and nanowires morphology...	24
Table 4.	Chemical use for nanowire production.....	28
Table 5.	Conditions for locating nanowire growth.....	33
Table 6.	Variable ranges determined from locating matrix for experimental design.....	34
Table 7.	Calculated concentrations and residence times for locating conditions.	38
Table 8.	Observations for experimental matrix.....	39
Table 9.	Wire diameter distribution for growth within and outside of band.....	55
Table 10.	Calculated concentrations and residence times for experimental matrix.	56
Table 11.	Summary of wire type observed in Figure 22. Bolded values indicate characteristic growth variables for each wire type.....	59
Table 12.	Quantitative wire characteristics determined with Equations 16-20. Calculated uncertainties for D_{avg} , L_{avg} , Growth Rate, Deposition Rate and Wire Density are 8.7, 8.7, 8.7, 10, and 5% respectively.....	73
Table 13.	Summary of experimental matrix analysis.....	74
Table 14.	Conditions that generate ideal wires.....	93
Table C1.	Calculated δ for horizontal reactor at experimental condition for two total flow of 200 and 500 sccm.....	103

LIST OF FIGURES

Figure 1.	VLS process described by Givargizov [41, 44].	5
Figure 2.	Relation between Si whisker stability and SiCl_4/H_2 concentration [43].	7
Figure 3.	Si nanowires stability as a function of silane partial pressure [28].	8
Figure 4.	Deposition of Si on various substrates as a function of temperature [39].	13
Figure 5.	Phase diagram for Au-Si system [39].	14
Figure 6.	Growth rates for ~0.1 molar % SiCl_4 , SiH_4 , SiH_2Cl_2 , and SiHCl_3 [50].	18
Figure 7.	Experimental setup for wire growth.	27
Figure 8.	Temperature program for Si nanowire processing.	31
Figure 9.	Substrate locations use for experiment.	34
Figure 10.	SEM image of bare substrate with no gold film (scale=200 nm).	36
Figure 11.	SEM images of A) 5 nm Au film. B) 10 nm Au film at 925°C in 180 sccm of Ar and 20 sccm of H_2 for 15 minutes. Specimens are viewed with SEM at 45° with a scale of 200 nm.	37
Figure 12.	Diameter distributions for catalyst produced by 5 and 10 nm gold films.	37
Figure 13.	Specimen produced by conditions A1 (scale=200 nm), A2 (scale=1 μm), and A3 (scale=500 nm). Specimens are viewed with SEM at 45°.	40
Figure 14.	Specimen produced with SiCl_4 concentrations of 0.013, 0.025, 0.05, and 0.125% for conditions B1, B2, B3, and B4. Specimens are viewed with SEM at 45°. Specimens B1-B3 have a common scale of 200 nm, while specimen B4 has a scale of 500 nm. The circle indicates possible concealed wires.	43
Figure 15.	Comparison of specimens generated at 925°C by conditions B1 and B2 and at 1000°C by conditions C1 and C2. Specimens B1 and C1 are grown with SiCl_4 concentration of 0.013%, while specimens B2 and C2 are grown with 0.025%. Specimens are viewed with SEM at 45° and have a common scale of 200 nm.	46

Figure 16.	Specimen produced by condition B4. Specimen is viewed with SEM at 45° and at resolutions of 1 μm and 500 nm respectively.....	48
Figure 17.	Comparison of distribution for wires generated by condition B4 with beads generated by 5 nm Au substrate.....	49
Figure 18.	Specimen generated by condition D1, viewed with SEM at 0° and at different resolutions: D1a) scale=1 μm; and D1b) scale=200 nm.....	50
Figure 19.	Specimen produced by condition B2. Image with SEM at center (B2a); center-edge (B2b); and edge (B2c). Specimen is viewed at 45° with a scale of 200 nm.....	51
Figure 20.	Specimen generated by condition D1, viewed with SEM at 0° and at different resolutions. D1a) Center (scale=1 μm); D1b) edge (scale=1 μm); D1c) center (scale=200 nm); and D1d) edge (scale=200 nm).....	52
Figure 21.	Specimen produced by condition B4, viewed with SEM at 45° and at different resolutions. B4a) scale=50 μm; B4b) scale=5 μm; B4c) outside band (scale=500 nm); and B4d) within band (scale=500 nm).	54
Figure 22.	Specimens produced by experimental matrix (scale= 500 nm).....	58
Figure 23.	Type I wires produced by conditions E1, E3, F1, and F3. Circles indicate possible catalyst beads and ovals indicate screw-like patterns on wires. Wires are viewed with SEM at 45° and have a common scale of 200 nm.....	60
Figure 24.	TEM images for straight wire produced by condition E3. Crystal lattice of A) wire body, B) wire tip and C) wire body (circle indicates non-crystalline outer SiO _x sheath). D) Diffraction pattern of wire body.....	61
Figure 25.	Histogram for aligned wires. Bin interval is 5 nm.....	63
Figure 26.	Type II wire specimen generated by conditions E2, E4, F2, and F4. Specimens are viewed with SEM at 45° with a common scale of 500 nm.....	65
Figure 27.	Figure 27. Type III wire specimens produced by conditions G3, G4, H3, and H4. Specimens are viewed with SEM at 45° with a common scale of 2 μm.....	66
Figure 28.	Histogram for long unaligned wires produced by conditions G3, G4, H3, and H4. Bin interval is 5 nm.....	67

Figure 29.	Different tip morphologies observed on large wires specimen generated by condition G4. Specimen viewed with SEM at 45° and at different scales. G4a) scale=10 μm G4b) scale=2 μm. Circles indicate unstable wire tips.....	68
Figure 30.	Specimen generated by conditions G1 and H1. Specimens are viewed with SEM at 45° with a common scale of 2 μm.....	70
Figure 31.	Specimen generated by conditions G2 and H2. Specimens are viewed with SEM at 45° with a common scale of 2 μm.....	71
Figure 32.	Illustration of increasing misalignment with an increase of H ₂ concentration by 2.5 times for SiCl ₄ concentration of 0.04% (E1 and F1) and 0.10% (E3 and F3). Specimens are viewed with SEM at 45° and have a common scale of 500 nm.....	75
Figure 33.	Illustration of unaligned wire orderliness produced by conditions E3 and F3. Specimens are viewed at 0° and have a common scale of 2 μm.....	76
Figure 34.	Average diameter, length, deposition rate and density at 925°C as a function of H ₂ concentration. Residence times are 2.9 and 7.3 seconds for H ₂ concentration of 4-10% and 10-25% respectively. Error bars indicate uncertainties.....	78
Figure 35.	Average diameter, length, deposition rate and density at 1000°C as a function of H ₂ concentration. Residence times are 2.9 and 7.3 seconds for H ₂ concentration of 4-10% and 10-25% respectively. Error bars indicate uncertainties.....	79
Figure 36.	Average diameter, length, deposition rate, and density as a function of temperature for lower H ₂ concentration level. Error bars indicate uncertainties.....	81
Figure 37.	Average diameter, length, deposition rate, and density as a function of temperature for upper H ₂ concentration level. Error bars indicate uncertainties.....	82
Figure 38.	Illustration of wire morphology by increasing SiCl ₄ concentration from 0.04% (conditions E1 and F1) to 0.10% (conditions E2 and F2) at 925°C and τ=2.9 seconds. Specimens are viewed with SEM at 45° and have a common scale of 500 nm.....	85

Figure 39.	Illustration of wire morphology by increasing SiCl_4 concentration from 0.04% (conditions E3 and F3) to 0.10% (conditions E4 and F4) at 925°C and $\tau=7.3$ seconds. Specimens are viewed with SEM at 45° and have a common scale of 500 nm.....	86
Figure 40.	Illustration of wire morphology by increasing SiCl_4 concentration from 0.04% (G1 and H1) to 0.10% (G2 and H2) at 1000°C and $\tau=2.9$ seconds. Specimens are viewed with SEM at 45° and have a common scale of 2 μm	87
Figure 41.	Average diameter, length, deposition rate, and density as a function of SiCl_4 concentration for various temperature and H_2 concentration. For SiCl_4 concentration of 0.04-0.10% $\tau=2.9$ seconds and for 0.10-0.25% $\tau=2.9$ seconds. Error bars are for uncertainties.....	89
Figure 42.	Response at 925°C for residence time of 7.3 seconds (F2) and 2.9 seconds (E2) and at 1000°C for residence time of 6.9 seconds (H2) and 2.8 seconds (G3).....	91
Figure 43.	Diameter, length, deposition rate, and density as a function of SiCl_4 concentration. Error bars indicate uncertainties.....	92
Figure B1.	Calculations to determine mass transfer of SiCl_4 through stagnant Ar film.....	101
Figure B2.	Results of mass transfer calculation.....	102
Figure C1.	Calculated δ for experimental condition.....	102

CHAPTER 1

INTRODUCTION

Nanotechnology is expected to revolutionize major technology fields—semiconductor, pharmaceutical, energy, auto, etc. For example, in the semiconductor industry, nanoscale electronics can be assembled without costly and complex fabrication facilities [1]. Besides cost reduction, nanotechnology will generate new possibilities through the advancement of materials properties.

Bulk materials are considered three-dimensional. As the length scale is reduced to less than 100 nm the dimensionality is also reduced [2]. Hence a film, with a thickness less than 100 nm thick, is 2D; a wire, with a diameter less than 100 nm, is 1D; and a dot, with all three lengths less than 100 nm, is 0D. As a length scale shrinks to less 100 nm, it is comparable to the electron mean free path for some materials [2]. As a consequence of electron confinement, the energy is quantized, resembling that of molecules and atoms [3]. Novel materials properties—such as electron transport, photoemission, and electron emission—which are not present in bulk, emerge in nano-size materials and can be controlled as a function of size [4].

In the semiconductor industry, current processing technology is a top-down approach. It is encountering many obstacles and will not be able to keep pace with Moore's law, which correlate that the computing power of microprocessors would double every eighteen months [5]. Examples of current processing obstacles are the anisotropic etching of deep contact holes and the fabrication of defect-free structures [6].

Nanotechnology can circumvent these processing obstacles. For example, with nanotechnology, a bottom-up approach can be used to eliminate the need for high aspect ratio holes through the growth of nanowires [7-9].

In the semiconductor industry, crystalline silicon nanowires (c-SiNWs) are attracting much interest. It is an ideal system for device fabrication. To begin with, c-SiNWs retains its semiconducting property, even as its diameter is varied in the nano regime [7]. Secondly, doping with boron and phosphorous does not compromise the crystallinity of c-SiNWs [9]. Thirdly, c-SiNWs could function as interconnects [6, 10, 11], nanoelectronic components [11], optical devices [12], lasers [13], etc. This ability will add much flexibility for the construction of the integrated circuit and the development of novel devices. As an interconnect, c-SiNWs is an efficient conductor by confining and forcing electrons to move unimpeded in a more directed path [14], thus producing a faster computer [15]. Lastly silicon is the foundation of semiconductor industry. Therefore, fabrication knowledge already exists and is well known [5, 9, 15].

CHAPTER 2

LITERATURE REVIEW

2.1 Vapor-Liquid-Solid Mechanism Background

Research and development efforts are required for the growth of vertically-aligned c-SiNWs with diameters less than 100 nm. In 1964, Wagner developed the vapor-liquid-solid (VLS) mechanism for the growth of aligned, crystalline Si whiskers that are microns in diameter. Wagner used silicon tetrachloride (SiCl_4) and hydrogen (H_2) as the vapor source, gold as the liquid catalyst, and [111] Si substrate as the solid.

Today three major techniques, based on the VLS mechanism, are commonly used for the production of silicon nanowires (SiNWs): laser ablation [16-20], thermal evaporation [21-27], and CVD [28-38]. Laser ablation and thermal evaporation are similar. In both systems, a target, typically made of Si [16-19, 22-27], is combined with a catalyst [17-19, 22, 26]. As the target is heated or thermally ablated, nanometer diameter catalyst beads are formed and are carried to the deposition surface, which is at a lower temperature. After the catalyst bead is supersaturated with Si, solid Si precipitates from solution and provides a solid surface for the formation of SiNWs.

The main advantage of these two methods is the extremely small wire diameter, which ranges from 6-20 nm [16, 21-23]. However, these methods produce randomly-oriented wires, since the catalysts are not bound on a solid. The formation of randomly-oriented wires renders both methods unfeasible. Learning from both of these methods, however, could still provide valuable information for the growth of SiNW.

Chemical vapor deposition (CVD), in contrast, could grow oriented SiNWs. Unlike laser ablation and thermal evaporation, CVD uses a stationary substrate to anchor and to provide the initial directionality for oriented SiNW. This technique is similar to and complements the VLS mechanism used by Wagner in the 1960s for oriented Si whisker production.

2.2 Characteristics of Si Nanowires and Whiskers

Compared to Si whiskers, SiNW research is a relatively new field and has been intensely studied in the past ten years. Whiskers and nanowires are essentially the same systems with a difference in diameter. Both Si whisker and SiNW are dislocation free systems with preferable $\langle 111 \rangle$ growth directions [28, 29, 32, 36, 39]. Whiskers have diameters that are typically microns in size, but could be as small as 100 nm [39, 42]. In contrast, SiNWs are nanometers in diameter and could be as small as 3 nm [15, 21]. Even though the diameter regime is different, the whisker system will be able to provide valuable understandings for the growth SiNWs.

2.3 Mechanism

Givargizov et al. describe the mass transfer and crystallization processes for the VLS mechanism by four major steps [41, 44]. Figure 1 illustrates these four processes:

1. Silicon diffuses toward the catalyst bead [41, 44].
2. Silicon is incorporated through the vapor-liquid interface [41, 44].
3. Silicon diffuses in the liquid phase [41, 44]. For crystallization to occur the silicon source must supersaturate the liquid phase.

4. Once silicon supersaturates the liquid phase, silicon precipitates from the solution and is incorporated into the crystal lattice, according to the crystalline direction of the substrate [41, 44].

Givargizov et al. determine that step four is the limiting step by observing that growth rate increases with increasing wire diameter [41, 44]. Givargizov concludes that the larger wire diameter facilitate precipitation from the liquid catalyst bead [44].

Figure 1. VLS process described by Givargizov [41, 44].

2.4 Growth Variables

2.4.1 Pressure

Even though laser ablation is a different process, it could provide insights into the behavior observed for CVD growth. For instance, in a study of whisker growth, Zhang et

al. correlate that the resulting whisker diameter is proportional to $P^{0.4}$ for ambient pressures of 100 to 800 Torr [27]. Besides larger diameters, increasing system pressure could affect the wire composition. At high pressure, such as atmospheric pressure, more SiO_x nanowires are produced [36].

2.4.2 Temperature

Temperature is one of the more important process variables for controlling wire diameter, growth rate, and stability. To begin with, whisker diameter increases with increasing temperature [39, 44]. At high temperature, vapor-solid deposition is comparable to the vapor-liquid deposition [39, 44]. Consequently, radial growth is comparable to axial growth [39, 44]. Evidence of vapor-solid deposition is the larger diameter of the base compared to the tip [39, 44].

Secondly, for a given effective chemical potential, $\Delta\mu$, growth rate, as described by Equation 1, is inversely proportional to temperature [44].

$$V = b \left(\frac{\Delta\mu}{KT} \right)^n \quad \text{Equation 1}$$

The other variables in Equation 1 are the Boltzmann constant (K) the absolute temperature (T), the coefficient independent of supersaturation (b) and the power factor (n). From whiskers studies, Givargizov determined that $n=2$ [44]. According to Equation 1, growth rate is inversely proportional to T^2 [44]. Givargizov attributed this decrease to the increase in both solubility and vapor pressure with increasing temperature [44].

Wagner and Givargizov have reported a relationship between stability and temperature for whiskers. A stable system is required to produce whiskers that are free of defects such as kinks and branches. Instabilities are attributed to high temperature gradient, unstable temperature, or process temperature being too high or too low [39]. Instabilities associated with temperature are exasperated by high concentrations. Figure 2 illustrates the relationship between concentration and temperature on wire stability and reinforces Wagner's observations [43]. Hence, temperature and concentration are critical for the growth of straight whisker.

Figure 2. Relation between Si whisker stability and SiCl₄/H₂ concentration [43].

For growth with SiH₄, Figure 3 illustrates the relationship between wire stability and temperature, indicating that high temperature and low concentration are best. The result does not contradict the results for Figure 2, since there is no temperature overlap. Even though Figure 3 is for SiH₄, it is consistent with the whisker system. According to Figure 3, for a given SiH₄ partial pressure, temperature influences both wire diameter and

stability. Both wire diameter and stability is proportional to temperature [28].

Additionally, a lower concentration enhances the formation of a stable kink-free system.

Figure 3. Si nanowires stability as a function of silane partial pressure [28].

A narrow temperature range is reported for defect-free Si whisker growth. For Si whisker growth, Givargizov reported a range of 940-980°C [43]. Instabilities for whiskers are most evident for a range of 1060-1100°C. [43]. For temperature greater than 1100°C, vapor-solid deposition becomes more important [43]. Consequently, wire diameter increases and wire surface instabilities are mask [43].

Too low of a temperature generates unstable whiskers. The result is consistent with Ozaki et al., who observed structural defects for whiskers grown at 320-450°C with

silane (SiH_4) [29]. Zhang et al. report that even at temperature as high as 900°C , energy is inadequate for recrystallization of Si-O species within the core, resulting in formation of amorphous silica instead of crystalline wires with an amorphous SiO_x layer [36].

Whiskers and nanowires have a similar growth temperature range. A typical temperature range for whiskers is $950\text{-}1050^\circ\text{C}$ [39, 41]. For aligned nanowires grown with SiCl_4 and H_2 , Fan et al. recommend $900\text{-}950^\circ\text{C}$ [31], while Wu et al. recommend 1050°C [32]. The similar growth range suggests that temperature effects for whiskers could provide an understanding of temperature effect on SiNW morphologies.

2.4.3 Source

For whisker production, Wagner [39] and Givargizov et al. [40-44] utilize SiCl_4 , which is diluted in and reduced by H_2 . The main requirements for straight wire growth are source purity, concentration and flow stability, and appropriate concentrations of the various reactants [39, 40]. Undesirable impurities such as water or oxygen could be incorporated into the whisker matrix and could interrupt the crystal lattice, thus producing kinks and branches [41]. An abrupt change in source flow rate, too high of concentration, or inconsistent concentration could cause instabilities, which could lead to kinks and branches [39].

As expressed by Equation 1, the effective chemical potential, $\Delta\mu$, is the driving force for whisker growth and is related to the supersaturation of Si in the vapor phase. In crystallization, many expressions for supersaturation are possible [45]. Equations 2-4 define three of the most common forms for supersaturation in terms of concentration (c).

$$\Delta c = c - c_{eq} \quad \text{Equation 2}$$

$$S = c / c_{eq} \quad \text{Equation 3}$$

$$\sigma = \Delta c / c_{eq} = S - 1 \quad \text{Equation 4}$$

The variables for Equations 2-4 are the equilibrium concentration (c_{eq}), concentration driving force (Δc), supersaturation ratio (S) and relative saturation ratio (σ). For gas phase, pressure (P) is preferable and could be substituted for concentrations (c).

A relationship is observed between wire diameter and chemical potential (i.e. the supersaturation). For a given $\Delta\mu$, larger diameter whiskers have a greater growth rate than smaller ones, since a larger area would facilitate deposition [44]. The chemical potential is a function of the whisker diameter, as defined by Equation 5 [44].

$$\Delta\mu = \Delta\mu_0 - 4\Omega\alpha / d \quad \text{Equation 5}$$

The atomic volume of Si (Ω), the specific energy of the whisker (α), and the whisker diameter (d) account for this difference.

To grow Si whiskers, a low supersaturation is ideal. For $\text{SiCl}_4\text{-H}_2$ systems, typical molar ratios are low –1-10% [39], 0.1-0.2% [41], and 0.04-0.4% [43]. These different ranges could be due to the differences in system configuration. Too high of supersaturation causes the catalyst bead to destabilize, resulting in non-oriented and defective structures [43]. Low supersaturation stabilizes the system [43].

Concentrations for whiskers are similar to those for SiNW production. At appropriate operating conditions, Ozaki et al. produce straight wires using 1% SiCl_4 [29],

while Westwater et al. produce straight oriented wires using 0.0013-0.02% SiH₄ [28].

Wu et al. produce the best-oriented nanowires, with 2% SiCl₄ [30].

For SiNW production, Si containing sources such as SiH₄ and SiCl₄ are used. The choice of Si source gas and concentration could affect wire diameter. Silane could produce SiNW with diameter as small as 10 nm, while SiCl₄ could produce SiNW with radius of 50-100 nm [28, 29, 36]. Westwater attributed this difference to the significantly higher effective chemical potential of Si in silane than in SiCl₄, for similar pressure and temperature conditions [28]. But SiH₄ is much more dangerous and expensive [36].

The wire diameter reduction can also occur by increasing the supersaturation [35, 36]. This result is consistent with Figure 3, in which Westwater et al. observe that higher partial pressure of SiH₄ produces smaller and curvier wires, with diameters as small as 15 and 20 nm [28]. However, as discussed earlier, a higher supersaturation tends to produce curved wires. As will be discussed in the catalyst section, a higher supersaturation reduces the critical minimum radius.

In Table 1, Zhang et al. summarize the effect of different SiCl₄ concentration on morphology [36]. At relatively low molar ratio of 5-7% SiCl₄/H₂, whiskers are formed. Whiskers and particles are produced for molar ratio of 20-30%. No whiskers are formed for molar ratio greater than 40%. Additionally, too high of a SiCl₄/H₂ ratio could cover and deactivate the catalyst beads [36]. Lastly, the yield of whiskers decreases with increasing mole ratio of SiCl₄/H₂. For molar ratio of 5-7%, yield is “large”, while yields are “small” and “hardly found” for ~30 and >40%, respectively [36].

Table 1. Effect of SiCl_4/H_2 on SiNW morphology [36].

H_2 flow rate (sccm)	Water temperature (K)	Mole ratio of SiCl_4/H_2 (%)	Whisker?	Particle?	Average diameter (nm) of the whiskers	Yield
250	293	5–7	yes	yes	> 500 nm	Large
800	293	5–7	yes	no	~ 500 nm	Large
1400	293	5–7	yes	no	~ 300 nm	Large
1800	293	5–7	yes	no	< 200 nm	Large
1400	303	~ 20	yes	yes	500 nm	Middle
1400	313	~ 30	yes	yes	> 500 nm	Small
1400	323	> 40	no	yes	–	Hardly found

2.4.4 Catalyst

The key to oriented growth is the catalyst bead [39, 40]. Wagner has observed that the catalyst bead controls whisker quality, diameter, and placement [39]. Without a catalyst, the products are polycrystalline nodules or films, instead of silicon whiskers [39].

A good catalyst should form an alloy with the desired nanowire material. A variety of catalyst with different growth promoting properties could be used—gold, nickel, palladium, copper, gadolinium, magnesium, osmium, gallium, and gallium-gold alloy promote whisker growth [39, 43]. Zinc, carbon, manganese, tin, and germanium promote nodule or film growth [39].

Figure 4 illustrates the deposition rate on different substrates [39]. According to Figure 4, the deposition rate on gold (Au) is much greater than on Si substrate. For example, at 950°C, the deposition on Au is approximately forty times greater than on Si substrate [39]. The differences originate from the longer “lifetime” of adsorbed species on the liquid surface and the heterogeneous-reaction catalyzing property of the surface [39].

Figure 4. Deposition of Si on various substrates as a function of temperature [39].

Two important consequences arise from this phenomenon. To begin with, the rate of material incorporation into the catalyst is much greater than that of the bare Si substrate [39]. Consequently, whisker lengths could be hundreds times greater than its diameters; and controlled placement of whisker is possible [39, 43]. The catalyst bead remains on the growing tip [39]. Lastly, whisker diameter is related to the bead diameter [39]. Therefore, bead diameter determines if the growth is a whisker or nanowires.

The catalyst bead, a high interfacial energy system, is very unstable [39, 43]. These instabilities can lead to undesirable morphologies such as kinks and branches, and are related to the crystallization temperature, vapor phase supersaturation, and gaseous

impurities [39, 43]. For whiskers, sub micron wires are less stable than larger wires [43]. Therefore, it can be deduced that nanowires will be more difficult to produce.

Gold is studied most often and produces the best results. Most often Au catalyst bead, with either SiH_4 or SiCl_4 , produces aligned SiNWs [28, 31, 32]. According to the phase diagram for Au-Si system shown in Figure 5, Au-Si system has a relatively low eutectic temperature (363°C) and forms simple phases. In theory, growth occurs between the eutectic and the melting point of the nanowire [32]. More importantly the desired growth temperature range of $900\text{--}1050^\circ\text{C}$ is encompassed by the eutectic and melting point of Au-Si system. In addition, the low eutectic temperature of Au is desirable, since a lower reaction temperature is necessary for thinner whiskers [28-33, 35, 36, 44]. Lastly, Au is inert and capable of forming a protective barrier from the environment.

Figure 5. Phase diagram for Au-Si system [39].

The catalyst thickness determines whether the structure is a whisker or nanowire. For whisker growth, Givargizov et al. uses Au film that is approximately 100 nm [41]. For SiNW, Ozaki et al. use a 2 nm Au film [29], while Westwater et al. utilize 0.6 nm Au film [35].

Conversion from a film to beads occurs during the heating process. When heated above the eutectic point, the film melts and breaks into droplets as a result of surface tension [39, 41]. The beads are then alloyed with the substrate [43]. Alloying, a difficult and necessary step, ensures proper lattice matching [39, 43].

The catalyst bead diameter determines whether the formation is a whisker or a nanowire. The catalyst beads generated are not mono-disperse, with uniformity being dependent on the local properties of the substrate and the thickness of the initial Au film [41]. Thinner films tend to produce more uniform catalyst bead diameters [41].

For whiskers or nanowires formation, a minimum catalyst bead radius is required for a supersaturation level. Equation 6 determines the minimum wire radius (R_{min}) that can be formed [39].

$$R_{min} = \frac{2\sigma_{LV}V_L}{RT \ln \sigma} \quad \text{Equation 6}$$

As indicated by Equation 6, R_{min} is determined by the liquid-vapor interfacial energy (σ_{LV}), liquid molar volume (V_L), temperature (T), and supersaturation (σ). Lastly R is the universal gas constant. For a gas-phase system, supersaturation is defined by Equation 7.

$$\sigma = (P - P_{eq}) / P_{eq} \quad \text{Equation 7}$$

Supersaturation is the difference between the equilibrium vapor pressure, P_{eq} and the actual vapor pressure, P . For SiCl_4 , R_{min} is determined to be 50-100 nm [41]. According to Equation 6, a higher supersaturation produces wires with smaller diameters [44].

2.4.5 Substrate

Substrates provide the initial directionality and the subsequent anchoring for Si whiskers and SiNWs. With both Si whiskers and SiNWs growing along the $\langle 111 \rangle$ directions, the compatible substrate is [111] Si substrate, which provides the correct matrix matching [28, 29, 32, 36, 39]. Other Si surfaces, such as [100], produces three equivalent $\langle 111 \rangle$ directed SiNWs [32]. Surface properties are important for SiNW growth [36]. For example, an oxide on the surface is a diffusion barrier for Au, thus preventing Au from alloying with the Si substrate [36].

2.5 Chemical Vapor Deposition

2.5.1 Introduction

With the growth method being CVD, an understanding of this method is necessary. Concepts from CVD—such as chemical reduction of SiCl_4 , equilibrium, and diffusion and reaction limitation—could be applicable for the growth of SiNWs.

When using SiCl_4 as a Si source, CVD is a complex method that involves multi-component species, reaction intermediates, numerous independent variables, and many consecutive steps [46]. The different reactions are summarized in Appendix A [47]. The overall effect could range from deposition to etching. The major deposition and etching are defined Equations 8 and 9 [47]. Equation 8 is the overall reaction for Si deposition,

while Equation 9 is the overall reaction for Si etching through the formation of volatile species [47].

2.5.2 Thermodynamics

Thermodynamics provides important estimates of the extent of the departure from equilibrium and supersaturation. Similar to the growth of whiskers and SiNWs, supersaturation is an important and useful concept for CVD. For CVD using SiCl_4 , the reduction to Si involves many reactions. Equations A1-A13 in the Appendix A express possible reactions and its many equilibrium species [47, 48]. At equilibrium, Liaw recognizes H_2 , HCl , SiCl_2 , SiH_2Cl_2 , SiHCl_3 , and SiCl_4 as the important species [46]. In their equilibrium calculation, Putte et al. and Yoon et al. also include Si, SiCl , SiCl_3 , SiH , SiH_4 , SiH_3Cl , Cl , Cl_2 , and H [47, 48].

2.5.3 Temperature

Temperature affects the equilibrium concentration of each species and the formation of desirable morphologies. Equilibrium calculation indicates that for temperature less than 1000 K, no Si is deposited, and SiCl_4 and SiHCl_3 are predominant. At temperature greater than 1600 K, deposition is rapid, and SiCl_2 and SiCl_3 are predominant [46]. These results indicate that SiCl_2 and SiCl_3 are important intermediates for Si deposition and epitaxial growth [46].

Generally, epitaxial films are produced at or above the knee temperature. As shown by Figure 6, the knee temperature is approximately 1100°C for SiCl₄ [50]. For most CVD processes, a higher temperature increases the surface mobility of adsorbed species and improves the crystal perfection of the layers [49]. At lower temperature, less energy is available and polycrystalline films are formed [50]. Again, this is analogous to the growth of whiskers and SiNWs.

Figure 6. Growth rates for ~0.1 molar % SiCl₄, SiH₄, SiH₂Cl₂, and SiHCl₃ [50].

2.5.4 Input Concentration

Similar to the growth of SiNWs and Si whiskers, supersaturation is also critical for CVD. Supersaturation, as defined by Liaw, is the difference between the partial pressure of the input chlorosilane and the Si solubility in the gas phase [46]. Solubility of

Si is determined by summing the equilibrium partial pressures of Si containing species present at system temperature and pressure [46].

Knowledge of the supersaturation level provides insights into deposition kinetics and morphology [46]. Depending on the degree of supersaturation, deposition qualities could be epitaxial, polycrystalline or amorphous [49]. High supersaturation causes high deposition rate and generates polycrystalline deposits [46, 49]. Physically, the rate of reactant reaching the surface exceeds the heterogeneous and lattice incorporation rate, thus producing an imperfect crystal [49]. Additionally, a high supersaturation increases the probability of misoriented saturations, which could lead to three-dimensional catalyst particle in the gas phase, with the resultant nuclei falling on the substrate surface to produce misoriented regions [49]. Similar to SiNWs and Si whiskers, a low supersaturation is preferred. Epitaxial film is formed with low gas-phase supersaturation [49].

Unlike with other Si source gases, the SiCl_4 deposition rate does not increase with increasing concentration. After a maximum value is achieved, deposition rate decreases with increasing concentration [47, 48, 50]. Beyond a critical concentration, etching occurs [47, 48]. Putte and Yoon characterize the transition from deposition to etching as function of $[\text{Cl}]/[\text{H}]$ for Si-Cl-H system [47, 48]. Etching, as indicated by Equation 8, is due to reaction of HCl with Si to produce volatile SiCl_2 [47]. In addition to SiCl_2 , Liaw notes that HCl could also react with the Si substrate to form other volatile species— SiH_2Cl_2 and SiHCl_3 [46].

2.5.5 Chemical Reactions

With CVD, gas phase and surface reactions are possible [46]. Gas phase reactions are homogenous reactions, while surface reactions are heterogeneous reactions. Heterogeneous reaction may include surface reactions in which the incoming gas species and the intermediate products are adsorbed on the surface and diffuse to energetically favorable sites for the incorporation of Si atoms into the crystal lattice [46]. To produce high quality layers, a high temperature is required, typically ranging from 1150-1300°C [46]. Homogeneous reactions are more likely when the supersaturation is high. As a result, Si clusters, which interfere with epitaxial growth, are generated [46]. Clusters interfere with the formation of a single-crystal Si [46]. For clusters to form homogeneously, a critical nucleus is required. The critical nucleus for homogeneous nucleation (r^*) can be determined by Equation 10 [46].

$$r^* = \frac{2uv}{KT \ln(P/P_{eq})} \quad \text{Equation 10}$$

This equation is similar to Equation 6 for minimum wire diameter, with slight differences in notation. Equation 10 states that the critical nucleus is a function of the specific surface free energy (u), the atomic volume (v), temperature (T), and supersaturation (P/P_{eq}). The Boltzmann constant is K . As expressed by Equation 10, for high supersaturation, a smaller nucleus is required for homogeneous nucleation.

2.5.6 Mass Transfer

Growth kinetics involves two steps: 1) mass transport from bulk gas to the surface and 2) surface reaction [46]. A majority of the resistance to mass transport is in the boundary layer (δ). For diffusion-controlled process, mass flux by diffusion through the boundary layer (J_d) is expressed by Equation 11 [46].

$$J_d = \frac{D}{RT} \left(\frac{P_b - P_s}{\delta} \right) \quad \text{Equation 11}$$

According to Equation 11, $(P_b - P_s)$, the difference in partial pressure between the bulk and surface, is the driving force for mass flux. Diffusion is accounted by the diffusion coefficient, D . For horizontal reactors with laminar flow, δ can be calculated by Equation 12 [46].

$$\delta = 5 * L \left(\frac{1}{Re} \right)^{1/2} \quad \text{Equation 12}$$

In Equation 12, Re is the local Reynolds number, based on distance L from leading edge.

When surface reaction is rate controlling, Equation 13 is used [46].

$$J_s = \frac{K_d}{RT} (P_s - P_{eq}) \quad \text{Equation 13}$$

In Equation 13, K_d is the mass transfer coefficient and P_{eq} is the equilibrium partial pressure.

At steady state, equating Equations 11 and 13 provides the useful dimensionless CVD reactor design number, N_{cvd} [46].

$$\frac{P_b - P_s}{P_s - P_{eq}} = \frac{K_d \delta}{D} = N_{cvd} \quad \text{Equation 14}$$

According to Equation 14, a large N_{cvd} indicates that diffusion limits mass transfer, while a smaller N_{cvd} indicates that reaction is rate limiting. Equation 14 can be solved for P_s , which can be substituted into either Equation 11 or 13 to arrive at Equation 15. This equation encompasses both diffusion and reaction rate limited regimes.

$$J = \frac{P_b - P_{eq}}{RT(\delta / D + 1 / K_d)} \quad \text{Equation 15}$$

For reduction of SiCl_4 at low temperature, reaction is rate limiting [50]. At higher temperature, mass transfer is rate limiting [50].

CHAPTER 3

BEST TEST CONDITIONS

Even though Si whiskers have a larger diameter, previous Si whiskers investigations provide important clues for SiNW fabrication, filling in the gaps of current nanowire research. According to the literature review, substrate, catalyst, temperature and source concentrations are critical for the controlled growth of oriented SiNWs.

The commonly reported substrate and catalyst are [111] Si and Au, respectively. The [111] Si substrate provides the proper lattice matching with the SiNWs and anchors the SiNWs to maintain alignment. Requirements for the substrate are cleanliness and oxide-free. Cleanliness minimizes impurities incorporation and ensures proper alloying. The surface must be oxide-free to facilitate alloying of Au with the Si substrate. Gold is the catalyst of choice, since the low eutectic temperature allows the formation of thin SiNWs over a broader range of operating temperature. To generate smaller and more uniformly-distributed catalyst beads, a typical film thickness is less than 10 nm.

Temperature controls the growth rate, diameter, and morphology. In Table 2, the influence of temperature on whisker and wire growth are summarized in Table 2. According to Table 2, the temperature should be at least 900°C, where energy for atomic arrangement is available for the formation of crystalline structures [36]. However, it should not be above 1050°C, since higher temperature would destabilize the system to generate undesirable morphologies [43]. Also at higher temperature, vapor-solid deposition, which contributes to wire thickening, becomes more important.

Table 2. Summary of temperature effects on whiskers and nanowires.

Si Wire Type	Investigators	T (°C)	Observations
Whiskers	Givargizov [43]	940-980	Aligned whisker growth
	Wagner [39], Givargizov et al. [41]	950-1050	Aligned whisker growth
	Givargizov [43]	1060-1100	Instabilities observed
	Givargizov [43]	>1100	Vapor-solid depositions important
	Ozaki et al. [29]	320-450	Structural defect observed
	Zhang et al. [36]	900	Inadequate energy for recrystallization of Si-O
Wires	Fan et al. [31]	900-950	Aligned nanowires
	Wu et al. [32]	1050	Aligned nanowires

Source concentration determines growth morphology and whether growth will occur. A range of SiCl_4 concentrations for both whisker and wire growth, evaluated by various investigators, are summarized in Table 3. Based on the work of these investigators, with the assumption that whiskers and wires are similar systems, the expected SiCl_4 concentration is expected to be very low, since higher concentrations tend to cause instabilities [28, 39, 41, 43] and catalyst bead coverage and deactivation [36]. A low supersaturation is desired and encourages the formation of aligned wires. A molar ratio less than 10% is a good starting point.

Table 3. Summary of source effects on whiskers and nanowires morphology.

Si Wire Type	Investigators	Source	Conc. (%)	Observations
Whiskers	Wagner [39]	SiCl_4	1-10	Whisker growth
	Givargizov et al. [41]	SiCl_4	0.1-0.2	Whisker growth
	Givargizov [43]	SiCl_4	0.04-0.4	Whisker growth
	Zhang et al. [36]	SiCl_4	5-7	Whisker growth
	Zhang et al. [36]	SiCl_4	20	Whiskers and particles
Wires	Ozaki et al. [29]	SiCl_4	1	Straight wires
	Westwater et al. [28]	SiH_4	0.0013-0.02	Straight oriented wires. SiH_4 produces thinner wires than SiCl_4 . Higher partial pressure of SiH_4 produces thinner wires.
	Wu et al. [30]	SiCl_4	2	Best oriented nanowires

CHAPTER 4

HYPOTHESIS

Uniform-diameter, vertically-aligned, and crystalline Si nanowires with diameters less than 100 nm and length greater than 1 μm can be fabricated through the proper selection of temperature, SiCl_4 concentration, H_2 concentration, reactor residence time, substrate, and catalyst.

CHAPTER 5

PROBLEM STATEMENT

Uniform-diameter, vertically-aligned, and crystalline SiNWs facilitate the fabrication of nano devices. Not much is reported on the fabrication of SiNWs with these characteristics. From the literature review, only Wu et al. report such SiNWs using SiCl_4 . Wu et al., however, do not provide specifics about the experimental setup and reactor geometry. Therefore, the information provided has limited applicability. As mentioned, inappropriate temperature and SiCl_4 concentration ratio can lead to undesirable morphologies, such as kinks, bends, and particles formation. These morphologies complicate the processing of the nanowires into useful structures for industrial application.

CHAPTER 6

EXPERIMENTAL EQUIPMENT AND METHODS

The methods and equipment were selected to produce nanowires that meet the thesis objectives, and to confirm wire characteristics. As a minimum, the test setup must be able to reproduce conditions found in the literature review, maintain flow and temperature stabilities, and minimize contamination. Experimental methodologies ensured the most efficient and expedient method of achieving desirable catalyst bead generation, growth condition location, and variables study.

6.1 Setup

The growth system, as illustrated by Figure 7, was composed of two main components—the process delivery and the reactor. The process delivery system independently controlled the SiCl_4 concentration, H_2 concentration, and reactor residence time (τ), while the reactor provided the energy for SiCl_4 reduction.

Figure 7. Experimental setup for wire growth.

6.1.1 Process Delivery

The process gas delivery line introduced the source gas and purged the system to remove gaseous impurities. As illustrated in Figure 7, it was composed of the carrier gas and dilution gas line. For accurate flow control, MKS Mass-Flo controllers delivered all process gases. Specifications for the process gases are summarized in Table 4.

Table 4. Chemical use for nanowire production.

Chemical	Manufacturer	Purity (%)
SiCl ₄	Aldrich	99.998
Ar	Scott Specialty Gas	99.999
H ₂	Airgas	99.99

The SiCl₄ vapor was introduced into the system by flowing carrier gas (Q_{carrier}) through the liquid SiCl₄ reservoir. Transport of SiCl₄ vapor source occurred by the saturation of the Ar carrier gas, as it bubbled through the sparger. The amount of SiCl₄ depended on the amount of carrier gas and bath temperature. Raoult's Law was used to determine the amount of SiCl₄ delivered.

The introduction of SiCl₄ must be precisely controlled and under isothermal condition. Since the SiCl₄ concentration was expected to be low, the lowest capacity mass flow controller (MFC), with a capacity 50 sccm, introduced carrier gas into the sparger. The MFCs, which were factory calibrated, was assumed to be accurate. Additionally, an ice bath maintained the liquid SiCl₄ at 0°C to minimize the vapor pressure for a finer control. Isothermal operation was necessary, since a varying vapor pressure caused by temperature instabilities would affect the amount of SiCl₄ delivered.

As depicted in Figure 7, before entering the heated quartz tube, the saturated carrier gas was diluted by the dilution flow, which transported the diluent, Ar, and the reducing agent, H₂. The premixing length for the carrier and dilution gas mixture was 20" of 1/4" tube. According to Sakiadis, this length should provide the satisfactory mixing before the mixture enters the quartz tube [53]. The premixed process gas entered the quartz tube and flowed toward the substrate, which was held by a quartz boat in the middle of the heater. As it traveled downstream, the gas was heated by flowing through seven inches of heated quartz reactor tube before arriving at the boat. The dilution line purged the system to minimize impurities such as water and oxygen before SiCl₄ was introduced.

Gaseous and solid impurities were minimized through the application of a suitable material and isolation valves. Perfluoroalkoxy (PFA), an acid-resistant plastic, was the material of choice for the valves and tubing. Valves isolated the liquid source from water and air.

6.1.2 Reactor

The reactor chamber was a quartz tube (1" x 25") that was heated by a four-zone, programmable Lindberg Blue heater. The heater could heat up to 1100°C and could maintain the temperature within $\pm 1^\circ\text{C}$. The quartz tube wall temperature was measured by a thermocouple that was located in the middle of the reactor. For accurate temperature measurement, the substrates were situated at the thermocouple.

6.2 Substrate Preparation

The substrate was n-type [111] Si that is 4° off normal. The specified resistivity for the substrate was 0.001-0.005 Ω -cm. Surface treatment involved removing impurities that could be incorporated into the nanowires, and eliminating the outer oxide layer that could be a barrier against Au alloying with Si. The cleaning processes were as followed:

1. Sonicate wafers in double distilled water for fifteen minutes.
2. Rinse with double distilled water.
3. Sonicate with acetone.
4. Rinse with double distilled water.
5. Soak wafer in 10% HF for two minutes to remove SiO₂ surface layer.
6. Rinse with double distilled water and dry with Ar.
7. Sputter a thin film of Au with ion beam sputter.
8. Cleave substrates into 10±5 mm² pieces.

6.3 Analytical Equipment

Two analytical tools were used for the analysis of wire growth. The Hitachi S-4000 scanning electronic microscopy (SEM) was the primary tool, which provided analysis of surface topologies and wire morphologies. Because of limited accessibility, the transmission electronic microscopy (TEM) was reserved for crystal analysis of high quality samples.

6.4 Wire Processing Stages

The wire growth processes, as shown in Figure 8, were composed of five stages (A-E). Each processing stage served a purpose. In stage A, the temperature was ramped up, and the system was purged with Ar and H₂ to remove oxygen and moisture. Hydrogen reduced residual the oxygen that was not removed by purging. With the Ar and H₂ still flowing, the temperature was stabilized in zone B. In this zone, Au was alloyed with the Si substrate for 5 more minutes at the operating temperature. In stage C, SiCl₄ was introduced for 15 minutes to supply material for wire growth. In stage D, the carrier flow was stopped, while the temperature was maintained and the dilution gases—Ar and H₂—continued flowing for five more minutes. With Ar still flowing in zone E, the system was slowly cooled over 15 minutes to minimize instabilities, which could be caused by a steep temperature gradient and an unstable temperature.

Figure 8. Temperature program for Si nanowire processing.

6.5 Test Plan

The overall study included catalyst bead generation, initial growth conditions location and experimental matrix to evaluate process variables effects. The first stage determined an appropriate film thickness to generate uniformly-distributed catalysts beads that were less than 100 nm in diameter, since these characteristics would ensure the production of uniform-size wires with diameter less than 100 nm. The initial growth conditions location established suitable growth baseline and provided the process variables ranges for experimental matrix. After the determination of wire growth conditions, the experimental matrix evaluated the temperature, SiCl_4 concentration, H_2 concentration, and reactor residence time (τ) on growth morphology and determined growth conditions for wire with desirable characteristics.

Before any meaningful data was collected, all system instabilities were identified, and their effects were minimized or eliminated. To identify instabilities, conditions with characteristic growth were identified, repeated, and reproduced. After instabilities were minimized or eliminated, system stability was confirmed daily, by reproducing known results at the beginning and at the end of each day.

To locate growth conditions, wide ranges for each process variable were run and evaluated. The objective was to locate conditions that promote wire growth by controlling temperature, total flow (Q_{tot}), carrier flow (Q_{carrier}), and H_2 flow (Q_{H_2}). As depicted by Figure 7, the total flow, which was the combined dilution and carrier flow, determined τ . Based on the literature review, temperature and SiCl_4 concentration were

considered to be the most important variables. Each preceding experiment provided directions for the next set of experiments.

The locating growth conditions are tabulated in Table 5. For all conditions, H₂ concentration was maintained at 10% to minimize explosion danger. Two different substrate locations, as depicted by Figure 9, were evaluated. The first set of conditions—A1, A2, and A3—evaluated the influence of temperature for a relatively high and broad range of SiCl₄ concentrations (1-5.5%). The second set of conditions—B1, B2, B3, and B4—assessed SiCl₄ concentration effects at a lower range (0.013-0.125%). With concentration being similar to conditions B1 and B2, the third set of conditions—C1 and C2—evaluated elevated temperature effects. To determine substrate location effects, substrates were located in Location B for conditions B4 and D1, with condition D1 having a SiCl₄ concentration of 0.15%.

Table 5. Conditions for locating nanowire growth.

			Q _{carrier} (sccm)						
T	Q _{tot}	Q _{H2}	0 ^A	0.5	1.0	2.5	3.0	10.0	55.0
°C	sccm	sccm							
925	100	10						A1	A2
925	200	10	B1	B2	B3	B4 ^B	D1 ^B		
1000	100	10						A3	
1000	200	10	C1	C2					

A) No carrier flow with exit valve open. B) Substrate evaluated in location B in Figure 9

Figure 9. Substrate locations use for experiment.

After the location of acceptable growth conditions, the effect of temperature, SiCl_4 concentration, H_2 concentration, and τ on wire alignment, diameter, and length were evaluated. The ranges for each variable were determined from locating experiments, with the highs and lows for each variable being summarized in Table 6. These ranges provided an understanding of the different variable effects and of the optimal growth condition.

Table 6. Variable ranges determined from locating matrix for experimental design.

Variable	Low	High
T ($^{\circ}\text{C}$)	925	1000
Q_{tot} (sccm)	200	500
Q_{carrier} (sccm)	2	5
Q_{H_2} (sccm)	20	50

CHAPTER 7

RESULTS AND DISCUSSIONS

The growth of aligned SiNW was successful. From the sixteen experimental test conditions, four conditions generated wires with the desired qualities. These wires were grown on 5 nm Au substrates, since it generated very uniform catalyst beads that are less than 100 nm in diameter. The operating temperature range was very similar to the literature review, with the best temperature being 925°C. The SiCl₄ concentration, which was critical for the formation of wires, was much lower than found in the literature review. Particles and curvy growth were observed at high concentrations, while successful wire growth occurred at the low concentration of 0.04 to 0.10%. Additionally, wire growth was strongly dependent on the substrate location. Successful growth occurred only when the substrate was situated in the boat compartment, which is depicted as location B in Figure 9.

7.1 Catalyst Bead Generation

The bare [111] Si used for the fabrication of wires, shown in Figure 10, was relatively smooth. To create catalyst beads, 5 and 10 nm Au films were deposited on [111] Si substrates. After heating at 925°C with 180 sccm of Ar and 20 sccm of H₂ for 15 minutes, catalyst beads with distinctive characteristics for the two film thicknesses were created. Figures 11A and 11B illustrate the catalyst bead distributions and characteristics produced by 5 and 10 nm Au films, respectively. Figure 12 provides the numerical

distributions for these two films. These distributions are found by visually counting the bright spots in the SEM images. The minimum sample size for the distribution is thirty.

Figure 10. SEM image of bare substrate with no gold film (scale=200 nm).

As depicted by SEM images in Figures 11, different film thicknesses produced different catalyst bead qualities. The 5 nm Au substrate, depicted by Figure 11A, produced very uniform catalyst beads with an average diameter of 48.4 nm and standard deviation of 24.5 nm; the 10 nm Au substrate, depicted by Figure 11B, generated a wider range of catalyst bead diameters, ranging from 10 to 1400 nm. These results suggest that a thinner film generates catalyst beads with more uniform diameters and are consistent with the observation of Givargizov et al. [41]. For wire growth, the 5 nm Au substrates were more ideal and were used for all subsequent experiments.

Figure 11. SEM images of A) 5 nm Au film. B) 10 nm Au film at 925°C in 180 sccm of Ar and 20 sccm of H₂ for 15 minutes. Specimens are viewed with SEM at 45° with a scale of 200 nm.

Figure 12. Diameter distributions for catalyst beads produced by 5 and 10 nm gold films.

7.2 Locating SiNW Growth Conditions

Growth occurred within the expected temperature range but at a lower SiCl_4 concentration range than those reported in the literature review. The conditions to locate growth, summarized in Table 7, evaluated temperature and SiCl_4 concentration effects, since the literature review indicated that these were the most important variables. The observations for each experimental set are summarized in Table 8. The results for temperature and SiCl_4 concentration indicate that temperature and SiCl_4 concentration cannot be too high. A high SiCl_4 concentration generated deposits and uniform coating, and could cover and deactivate the catalyst bead [36]. At 1000°C , catalyst bead coverage and deactivation occurred at a lower SiCl_4 concentration. Lastly the results indicate that the physical location of the substrate in the boat was critical for wire growth, with the boat compartment being preferred over the top of the platform.

Table 7. Calculated concentrations and residence times for locating conditions.

Test	T	Q_{H_2}	Q_{tot}	Q_{carrier}	$[\text{SiCl}_4]$	$[\text{H}_2]$	τ
	$^\circ\text{C}$	sccm	sccm	sccm	mol %	mol %	sec
A1	925	10	100	10	1	10	14.6
A2	925	10	100	55	5.5	10	14.6
A3	1000	10	100	10	1	10	13.8 ^C
B1	925	20	200	0	0.013 ^A	10	7.3
B2	925	20	200	0.5	0.025	10	7.3
B3	925	20	200	1	0.05	10	7.3
B4 ^B	925	20	200	2.5	0.125	10	7.3
C1	1000	20	200	0	0.013 ^A	10	6.9 ^C
C2	1000	20	200	0.5	0.025	10	6.9 ^C
D1 ^B	925	20	200	3	0.15	10	7.3

A) SiCl_4 concentrations are calculated by assuming diffusion through stagnant film. B) Evaluated in location B (condition B4 was evaluated for both location A and B). C) Lower residence time is attributed to the temperature difference.

Table 8. Observations for experimental matrix.

Condition					
	[SiCl ₄] (%)	T (°C)	Loc.	Observations	Conclusions
A1, A2	1.0-5.5	925	A	--At 1%, hemispherical particles; fluffy clusters at 5.5%.	--High supersaturation resulted in particulate deposition.
A1	1.0	1000		--Smooth uniform coating.	--High temperature generates more uniform coating.
B1-B4	0.013-0.125	925	A	--Curvy worm-like growth at 0.025%. Smooth uniform coating at 0.05 and 0.125%.	--Wire-like growth occurs at lower supersaturation. Coating covers and deactivates the catalyst beads.
C1, C2	0.013-0.025	1000	A	--At 0.013%, curvy worm-like growth along surface. Smooth uniform coating at 0.025%.	--Higher temperature resulted increase growth and coating at lower concentrations.
B4, D1	0.125-0.15	925	B	--Wire-like growth. Aligned growth at 0.125%. Long unaligned growth at 0.15%.	--Placement is conducive to wire growth.

7.2.1 Conditions A1, A2, and A3: High SiCl₄ Concentrations (1.0-5.5%)

High SiCl₄ concentrations were unfavorable for wire growth. Figure 13 summarizes the results for conditions A1, A2, and A3. Images in Figure 13 are labeled with the corresponding test condition. Figure 13 indicates that the SiCl₄ concentrations of 1.0 to 5.5% are sufficient in providing material for wire growth, since wires, particles and films are observed. At the same time, catalyst beads are not observed. The results of Figure 13 suggest that the possibility of generating desired morphologies is very low, probably due to high SiCl₄ concentrations that could cause catalyst bead coverage and deactivation [36].

Figure 13. Specimen produced by conditions A1 (scale=200 nm), A2 (scale=1 μm), and A3 (scale=500 nm). Specimens are viewed with SEM at 45° .

As illustrated by Figure 13A1, with temperature at 925°C and SiCl_4 concentration of 1%, condition A1 produced a surface that is blanketed by hemispherical particles, on top of which are 60 nm diameter curvy growth and spherical particles. The density of the top growth is a fraction of catalyst beads generated by the 5 nm Au substrates. These

products indicate that the reactant is transported to the substrate for 1% SiCl_4 concentration. It cannot be determined if the top growth was catalyzed by the Au catalyst bead as described by the VLS mechanism [39, 44] or was a product of homogeneous nucleation caused by very high supersaturation [46]. The presence of particles and wires are similar to that of Zhang et al. who observed particle formation but at a higher SiCl_4 concentration of 20% [36]. For $\text{SiCl}_4\text{-H}_2$ system, Zhang et al. mention that particle formation for high supersaturation could cover and deactivate the catalyst bead [36].

When the SiCl_4 concentration was increased to 5.5% at 925°C for condition A2, clusters and buried curvy wires were generated, as illustrated by Figure 13A2. Compared with condition A1, the higher SiCl_4 concentration of condition A2 produced fluffier, higher quantity, and less organized deposits. This result is consistent with Zhang et al. who observed increase particle deposition at high SiCl_4 concentration [36]. Similar results are observed for CVD processes, when high supersaturation could lead to increase deposition rate and the formation polycrystalline deposits [46, 49]. Shaw also observed that a high supersaturation increases the probability of misoriented saturations and three-dimensional catalyst particles in the gas phase [49]. Consequently, misoriented deposits are formed on the substrate [49].

Condition A3, with a SiCl_4 concentration of 1% and at 1000°C , generated a uniform coating along with sparse deposits of 200 nm spherical agglomerates, as shown by Figure 13A3. Wires are absent. The coating conceals much of the catalyst beads. These results are consistent with Zhang et al.'s observation that high SiCl_4 concentration

would result in catalyst bead coverage and deactivation [36]. Unlike the surface quality for conditions A1 and A2, the surface is film-like, having fewer particles. This result is similar to CVD, in which the surface quality is improved at higher temperature [49]. As mentioned by Shaw, higher temperature causes a greater mobility of adsorbed species, thus improving surface perfection [49]. However, it cannot be determined if the film is amorphous, polycrystalline or crystalline.

7.2.2 Conditions B1, B2, B3, and B4: Low SiCl₄ Concentration (0.013-0.125%)

The results from conditions A1, A2, and A3 establish that high SiCl₄ concentration could cause catalyst bead deactivation and coverage, and the formation of undesirable depositions. A reduction in concentration was necessary. For this study, extremely low SiCl₄ concentrations of 0.013, 0.025, 0.05, and 0.125%, obtained with carrier flows of 0, 0.5, 1, and 2.5 sccm, respectively, were evaluated. The total process flow and temperature were maintained at 200 sccm and 925°C. The higher total process flow of 200 sccm was necessary for diluting SiCl₄ to a lower concentration.

For condition B1, SiCl₄ transport occurred by diffusion. To generate this low SiCl₄ concentration, only the source exit valve was opened and dilution gas flowed perpendicular to the exit valve. According to the calculation for diffusion through a stagnant film in Appendix B, an extremely low SiCl₄ concentration of 0.013% was obtained. This process was necessary, since the MFC has a lower accuracy limit of 0.5 sccm.

Spherical particles, with a diameter distribution that is similar to the 5 nm Au substrate, were generated by condition B1. As shown in Figure 14B1, these elongated particles appear to be wire precursors, providing evidence for material incorporation. However, growth rate is low, $< 6\text{nm/min}$.

Figure 14. Specimen produced with SiCl_4 concentrations of 0.013, 0.025, 0.05 and 0.125% for conditions B1, B2, B3, and B4. Specimens are viewed with SEM at 45° . Specimens B1-B3 have a common scale of 200 nm, while specimen B4 has a scale of 500 nm. The circle indicates possible concealed wires.

In condition B2, the SiCl_4 concentration was increased to 0.025 %. The increase in SiCl_4 concentration produced the expected effect, by producing worm-like growth shown in Figure 14B2. These uniformly-sized wires are approximately 75 nm in diameter. This increase in wire growth is in accordance with Equation 1, since at constant temperature, the larger $\Delta\mu$ should increase the driving force for growth and should increase the growth rate, V [44].

Morphological features suggest that the VLS mechanism was operative. The large length to diameter ratio (>10) implies that material is incorporated through the tip. The smoothness of the wires and the constant diameter imply that homogeneous nucleation is not a problem. However, these worm-like growths are unaligned and curvy, with a constant diameter of approximately 75 nm. Instead of being normally directed, these structures grew randomly along the surface.

When the SiCl_4 concentrations were increased to 0.05 and 0.125% for conditions B3 and B4, respectively, the surface was uniformly coated. As illustrated by Figures 14B3 and 14B4, the surface appears bumpy. For condition B3, the lumps, circled in Figure 14B3, resemble buried wires, like those in Figure 14B2. Wires and catalyst beads are not observed. These observations are consistent with Zhang et al.'s observation that too high of a SiCl_4 concentration could result in catalyst bead deactivation and coverage [36]. This result is alarming, since the SiCl_4 concentration is only 0.05%.

7.2.3 Conditions C1 and C2: Temperature Effects

A higher temperature intensified the effect of SiCl_4 concentration. Temperature effects were evaluated for SiCl_4 concentrations of 0.013 and 0.025%, which were already evaluated by condition B1 and B2 at 925°C. For SiCl_4 concentration of 0.013%, when the temperature was increased from 925 to 1000°C for conditions B1 and C1 respectively, growth was transformed from elongated, upright beads to a monolayer of curvy wires growing along the surface. The growth rate increased with increasing temperature. This result is illustrated by comparison of Figure 15B1 and 15C1, for process temperature of 925 and 1000°C, respectively.

These observations contradict Equation 1, in which growth rate, V , is inversely proportional to T^2 [44]. A possible explanation is that the supersaturation level was augmented at the elevated temperature. Equations A1-A10 in Appendix A—reactions which generates Si—are all endothermic reactions, for which the conversions increase with increasing temperature [54]. The increased conversion increases the formation of Si, which increases the supersaturation.

When the temperature was increased from 925 to 1000°C at the higher SiCl_4 concentration of 0.025%, curvy wires were transformed to a uniform coating, as illustrated by comparison of Figure 15B2 and 15C2. Again this observation is consistent with an increase in supersaturation. The coating is very similar to coatings produced by conditions B3 and B4 at higher SiCl_4 concentration of 0.05 and 0.125%.

Figure 15. Comparison of specimens generated at 925°C by conditions B1 and B2 and at 1000°C by conditions C1 and C2. Specimens B1 and C1 are grown with SiCl_4 concentration of 0.013%, while specimens B2 and C2 are grown with 0.025%. Specimens are viewed with SEM at 45° and have a common scale of 200 nm.

7.2.4 Substrate Relocation: Boundary Layer Thickening

Straight wires were produced when the substrate was relocated from the top of the platform to the center of the boat. These locations are identified as location A and B in Figure 9. For all subsequent experiments, location B was used.

As discussed earlier, when the substrate was situated in location A, condition B4 generated specimens that show evidence of catalyst bead deactivation and coverage. When the substrate was relocated to location B, nearly aligned wires are formed with the same condition. As illustrated by Figure 16, most of the wires generated are extremely straight and more than half of the wires are randomly directed, approximately 15° from substrate normal. With a length of approximately $4\text{ }\mu\text{m}$, the growth rate is approximately $0.26\text{ }\mu\text{m}/\text{min}$. The length to diameter aspect ratio is estimated to be as high as 80. Homogeneous nucleation is not significant, as indicated by the constant diameter along the wire length and by the absence of particles. These observations suggest that material was incorporated through the tip. These morphologies, with the exception of missing catalyst bead, are consistent with wires produced by the VLS mechanism [39, 44].

The difference between location A and B is in the boundary thickness. According to Table C1 in the Appendix C, location A has a calculated boundary layer (δ) greater than 2 cm, exceeding the 1 cm gap between the platform and the quartz tube. With the quartz tube being a no-slip surface also, it should have a boundary layer. Therefore, δ for both should be 0.5 cm, which was half the distance between the platform and the quartz tube. When the substrate was relocated to location B, the new δ is 1.5 cm, with the

additional 1 cm contributed by the boat depth. The observed differences with changing δ suggest that the process must be diffusion limited, not reaction limited. By increasing δ , the resistance to mass transfer by diffusion is increased and limits the material arriving to the substrate surface.

Figure 16. Specimen produced by condition B4. Specimen is viewed with SEM at 45° and at resolutions of 1 μm and 500 nm respectively.

As summarized by Figure 17, the wire diameter is widely distributed. This distribution is very similar to the unprocessed 5 nm Au substrate but at a lower density. The average wire diameter is 55.7 nm, with a standard deviation of 17.6 nm, and is consistent with catalyst beads generated by the 5 nm substrate. According to Figure 17, the wire density is only 10% of the catalyst beads produced by 5 nm Au substrates. Only the smallest diameter (23 nm) is curly. This observation is similar to Givargizov's observations that instability is greater for smaller wires [43].

Figure 17. Comparison of distribution for wires generated by condition B4 with beads generated by 5 nm Au substrate.

When SiCl_4 concentration was increased from 0.0125% to 0.015% for condition D1, curved wires, an indication of instability, were produced instead of aligned wires. Comparison of Figure 17 and Figure 18 also indicates that these wires are longer ($>10 \mu\text{m}$) and have smaller diameters (30-40 nm) than those wires formed at 0.0125%. The longer, thinner, and less aligned wires at higher concentrations are consistent with previous investigators. Firstly, in agreement with Equation 1, the higher SiCl_4 concentration increases the growth rate [44]. Secondly, the wire thinning with increasing concentration is consistent with those observed by Westwater et al., Zhang et al., Wagner and Givargizov [28, 35, 36, 39, 43]. Lastly, smaller wires and higher concentration increases the instability, causing the formation of curved wires instead of aligned wires [39, 43].

Figure 18. Specimen generated by condition D1, viewed with SEM at 0° and at different resolutions: D1a) scale=1 μm ; and D1b) scale=200 nm.

7.2.5 Miscellaneous Observations

7.2.5.1 Concentration Non-uniformity on Substrate

Localized concentration, defined as spatial concentration variation on the substrate, reinforces the detrimental effects of source overloading on morphology. Condition B2, with worm-like wires, and condition D1, with long thin wires, illustrate localized concentration effect on wire growth.

For condition B2, Figures 19B2a, 19B2b, and 19B2c are images for the same specimen taken at the center, between the center and edge, and at the edge, respectively. The edge is defined as the 100- μm band along the perimeter. With the catalyst bead acting as a sink, the center of substrate, being surrounded by catalyst beads, should be at a lower concentration than the edge, which was surrounded by half the catalyst beads. Consequently, the concentration should increase from the center to the edge. Between

the center and the edge, the concentration was intermediate between the center and edge. At this location, the growth, as illustrated by Figure 19B2b, is along the surface and dense. Compared to the center, as illustrated by Figure 19B2a, these wires are less distinguishable and curvier. At the edge where the concentration was highest, the wires are least distinct, comprising of particles and fused wires, as shown by Figure 19B2c.

Figure 19. Specimen produced by condition B2. Image with SEM at center (B2a), center-edge (B2b); and edge (B2c). Specimen is viewed at 45° with a scale of 200 nm.

For wire-like features produced by condition D1, the results are consistent with the higher concentration at the edge. As depicted by Figures 18D1b and 18D1d, the higher concentration at the edge generated curvier and thinner wires [28, 35, 36, 39, 43]. These wires have diameters as small as 30 nm. Consequently, the probability of ideal wire morphology is lower than the center.

Figure 20. Specimen generated by condition D1, viewed with SEM at 0° and at different resolutions. D1a) Center (scale=1 μm); D1b) edge (scale=1 μm); D1c) center (scale=200 nm); and D1d) edge (scale=200 nm).

7.2.5.2 Surface Characteristics Effect on Wire Morphology

Surface characteristics strongly influenced wire alignment. Again condition B4 was evaluated with the 5 nm Au substrate. As depicted by Figures 21, different characteristic growth bands are observed on the substrate. The growth within the band has distinctively different characteristics from the growth outside the band. This distinctiveness of the band suggests that difference was likely to be mechanically-scratched bands. These bands were likely to occur during the substrate processing.

Though both surfaces produced straight wire growth, only the band contains wires that are aligned with the substrate normal. As tabulated in Table 9, the differences between the wires within and outside the bands are the larger wire diameter of 123 nm, which are found only within the band. For both growths within and outside the band, the thinner wires are curvier, which is consistent with Givargizov's observation that instability is greater for smaller wires [43]. Aligned growth within the band could be attributed to several causes. The mechanical damages could create surfaces that promote aligned growth or destroy oxide films to improve the alloying process. These postulates cannot be substantiated since the mechanical scratch is not a controlled and repeatable process.

Figure 21. Specimen produced by condition B4, viewed with SEM at 45° and at different resolutions. B4a) scale=50 μm; B4b) scale=5 μm; B4c) outside band (scale=500 nm); and B4d) within band (scale=500 nm).

Table 9. Wire diameter distribution for growth within and outside of band.

Outside Band		Inside Band	
D (nm)	Characteristics	D (nm)	Characteristics
88	Straight, Unaligned	123	Straight, Aligned
66	Straight, Unaligned	96	Straight, Aligned
54	Straight, Unaligned	69	Straight, Aligned
38	Curvy	50	Straight, Aligned
		38	Curvy

7.3 Experimental Matrix

After possible growth conditions were determined, an experimental matrix was designed to understand the effects of temperature (T), residence time (τ), H_2 concentration, and $SiCl_4$ concentration effects on wire morphologies and to locate optimal wire growth conditions. To assess these effects, highs and lows for temperature (925 and 1000°C), total flow (200 and 500 sccm), H_2 flow (20 and 50 sccm), and $SiCl_4$ flow (2 and 5 sccm) were evaluated. The variable ranges were based on previous growth locating conditions. The resulting 16 conditions are tabulated in Table 10, which also provides calculated H_2 concentration, $SiCl_4$ concentration, and τ for each condition. For the same total flow, a 75°C difference in temperature causes a slight residence time difference of 6%. In the data analysis, this difference is assumed negligible.

In hindsight, instead of flows, H_2 and $SiCl_4$ concentrations should be used. To begin with, concentrations are used for the data analysis, since reactions depends directly on concentrations, not flows. Additionally, conversion from flows to concentrations

resulted in three different calculated H_2 and $SiCl_4$ concentrations, not satisfying a two-level, four-variable, full-factorial experiment design, which provides eight data pairs for the analysis of each variable. Consequently, only H_2 and $SiCl_4$ concentrations and temperature are analyzed with eight data pairs, while τ is analyzed with only two data pairs—a net loss of six data pairs.

To assist with condition identification, each condition is identified with a letter—E, F, G, and H—and number—1, 2, 3, and 4—combination. According to this nomenclature, as shown in Table 10, each number is assigned to a particular $SiCl_4$ concentration and τ combination, both of which increase with increasing number. Each letter corresponds to a particular temperature. Identification of H_2 concentrations requires a number and letter combination.

Table 10. Calculated concentrations and residence times for experimental matrix.

Test	T	Q_{H_2}	Q_{tot}	$Q_{carrier}$	$[SiCl_4]$	$[H_2]$	τ
	°C	sccm	sccm	sccm	mol %	mol %	sec
E1	925	20	500	2	0.04	4	2.9
E2				5	0.10	4	2.9
E3		200	200	2	0.10	10	7.3
E4				5	0.25	10	7.3
F1		50	500	2	0.04	10	2.9
F2				5	0.10	10	2.9
F3		200	200	2	0.10	25	7.3
F4				5	0.25	25	7.3
G1	1000	20	500	2	0.04	4	2.8
G2				5	0.10	4	2.8
G3		200	200	2	0.10	10	6.9
G4				5	0.25	10	6.9
H1		50	500	2	0.04	10	2.8
H2				5	0.10	10	2.8
H3		200	200	2	0.10	25	6.9
H4				5	0.25	25	6.9

Analysis of experimental matrix results is divided into two parts. The first part is the description and discussion of five characteristic wire types and its characteristic growth conditions. For each wire type, morphologies are analyzed to find consistency with the VLS mechanism. The second part is the correlation between the quantitative responses—diameter, length, deposition rate, and growth density—and process variables— H_2 concentration, $SiCl_4$ concentration, τ , and temperature.

7.3.1 Qualitative Analysis

The representative SEM images for each condition are summarized by Figure 22. Several distinct wire types can be identified. Observations for Figure 22 are summarized in Table 11 and show that five different wire types are produced. Each of wire type has a characteristic set of process variables, which are bolded in Table 11.

To facilitate the understanding of the different effects, images in Figure 22 are labeled with the corresponding condition labels and are arranged in such a way that each row is associated with a letter—E, F, G or H—and that each column is associated with a number—1, 2, 3 or 4. The meaning of each letter and number are described as before. In addition, each quadrant has a characteristic τ and temperature: top left (2.9, 925), top right (7.3, 925), bottom left (2.8, 1000), and bottom right (6.9, 1000). The first value in the bracket is the residence time, while the second value is the temperature. As mentioned before, the difference in residence time is assumed negligible.

Analysis of Figure 22 and Table 11 shows several trends for the characteristic conditions. To begin with, five different wire types are identified in Table 11.

Comparison of Type I and Type II wire conditions, for a given temperature, τ , and H_2 concentration (i.e., E1 with E2, E3 with E4, F1 with F2, and F3 with F4), indicates that these differences were caused by the $SiCl_4$ concentration, which is 2.5 times higher for Type II wires. This result suggests that a lower $SiCl_4$ concentration is required for the generation of aligned wires and that H_2 concentration is less critical.

Figure 22. Specimens produced by experimental matrix (scale= 500 nm).

Table 11. Summary of wire type observed in Figure 22. Bolded values indicate characteristic growth variables for each wire type.

Wire Type	Cond.	T (°C)	[SiCl ₄] (%)	τ (sec.)	[H ₂] (%)	Wires Characteristics & Surface Morphology	
I	E1	925	0.04	2.9	4	-Most ideal wires.	
	F1				10	-Straight and aligned.	
	E3		0.10		7.3	10	-Average diameter <100 nm.
	F3					25	-Greater than 3 μm long.
II	E2	925	0.10	2.9	4	-Thin and curvy.	
	F2				10	-Densest of all growth.	
	E4		0.25		7.3	10	
	F4					25	
III	G3	1000	0.10	6.9	10	-Straight, long but unaligned wires.	
	G4				25	-Large than that of Type I wires.	
	H3		0.25			10	
	H4					25	
IV	G1	1000	0.04	2.8	4	-Thin, long, curvy wires.	
	H1				10	-Pitted surfaces.	
V	G2	1000	0.10	2.8	4	-Combination of Type III & IV wires	
	H2				10		

When the temperature was increased to 1000°C, the trends are different. As illustrated by the lower right quadrant of Figure 22, Type III wires, generated by conditions G3, G4, H3, and H4, were unaffected by H₂ concentration and SiCl₄ concentration, since the wire morphologies are very similar for the different conditions. This morphology alteration by elevating the temperature from 925 to 1000°C is an indication of the importance of temperature and changing importance of other variables.

Conditions G1, G2, H1, and H2, as illustrated by left quadrant of Figure 22, generated both Type IV and V wires. Comparison of Type IV and V indicates that SiCl₄ concentration is again significant, but the effect of SiCl₄ concentration is opposite to that of Type I and II wires. At the lower SiCl₄ concentration, Type IV wires are characterized by thin wires and surface pits. At higher SiCl₄ concentration, more growth is observed.

7.3.1.1 Type I Wires

Type I wires, as shown by Figure 23, are the only wires, which satisfy all of the thesis requirements. The wires are aligned and crystalline, and have average diameters less than 100 nm. These aligned wires have average wire diameters of 68.3 to 96.4 nm.

Figure 23. Type I wires produced by conditions E1, E3, F1, and F3. Circles indicate possible catalyst beads and ovals indicate screw-like patterns on wires. Wires are viewed with SEM at 45° and have a common scale of 200 nm.

The wire crystallinity is confirmed by the TEM images. According to Figure 24A and 24C, regular crystal lattices, which are indication of crystallinity, are observed on the wire body. The thin outer layer, indicated by the oval in Figure 24C, lacks these orderly lattices.

Figure 24. TEM images for straight wire produced by condition E3. Crystal lattice of A) wire body, B) wire tip, and C) wire body (circle indicates non-crystalline outer SiO_x sheath). D) Diffraction pattern of wire body.

The outer sheath is likely to be amorphous silicon dioxide (SiO_x), which formed when the samples were exposed to oxygen. Crystallinity is also confirmed by the diffraction pattern on Figure 24D. The tip, however, is non-crystalline, as indicated by the absence of crystal lattice in Figure 24B. The non-crystallinity could be attributed to the change in temperature and concentration, which occur after growth stoppage. Also not found in Figure 24B is the catalyst bead.

The average diameters of the wires produced by the four conditions are larger than the average catalyst beads diameter of 48.4 nm generated by 5 nm Au substrates. As indicated by the histogram of the diameter distribution in Figure 25, wires smaller than 50 nm are not observed. This result suggests that the effective chemical potential was insufficient for formation of wires smaller than 50 nm and that wires were selectively formed on catalyst beads with a diameter that was larger than the minimum radius (R_{min}) determined by the process conditions. This result is consistent with the R_{min} of 50-100 nm estimated by Givargizov et al. [41].

Though the growth densities are high (38.6-46.9 per $10 \mu\text{m}^2$), it is less than 8% of the catalyst beads created by 5 nm Au substrates. The lower density could be explained in part by R_{min} , which is determined to be approximately 50 nm for the four different process conditions. According to Figure 12 for the 5 nm Au substrate, approximately 40% of the catalyst beads are less than 30 nm. The catalyst beads, however, cannot be substantiated on the SEM images.

Analysis of Figure 23 reveals two interesting wire features—shiny beads and screw-like features on wire side. The shiny beads, indicated by circles, are observed on the side of the wire. These beads could be the missing catalyst beads, but its composition is undetermined. A screw-like pattern, as marked by ovals in Figure 23, is also observed on approximately 10% of the wires. This pattern is independent of the wire diameter, length, and alignment. According to the right-hand rule, the screw directions are either into or out of the substrate. It cannot be determined whether the screw-like pattern originates from the substrate or catalyst bead instability. Several researchers provide support for catalyst bead instability. Both Wagner and Givargizov describe the catalyst bead as a high interfacial energy system that is very unstable [39, 43]. These instabilities can lead to undesirable morphologies [39, 43].

Figure 25. Histogram for aligned wires. Bin interval is 5 nm.

Type I wires are consistent with the VLS mechanism, even though no catalyst bead on the tip can be confirmed in the SEM images. To begin with, the wire diameter distributions are similar to the catalyst bead diameters distribution for the 5 nm Au substrate, as indicated by the overlap in distributions. This result suggest that a correlation between catalyst bead and wire diameters. Secondly, the relatively long wires suggest that the material incorporation rate into the wires is much greater than that of the bare Si substrate. This is possible only if the catalyst bead is present to increase the deposition rate, otherwise nodules or films would be produced [39, 43]. Lastly, the wire cross-sectional areas remain constant, suggesting that the catalyst bead remains on the growing tip during wire growth, as described by Wagner [39].

7.3.1.2 Type II Wires

Type II wire are curvy and unaligned. As illustrated by Figure 26, Type II wires are extremely dense ($\sim 170/10 \mu\text{m}^2$), thin ($\sim 30 \text{ nm}$), and short ($\sim 1.5 \mu\text{m}$). These wires are very uniform in diameter and length. Additionally, bright spots are observed at the tip and within the wires. These bright spots could be the catalyst beads, but without analysis, the composition is undetermined. If these bright spots were catalyst beads, it would contradict Wagner's observation that the catalyst bead remains on the growing tip [39].

The Type II wire curviness could be contributed by two sources. To begin with, the bright spots within the wires could be the catalyst or a foreign material. Incorporation of a foreign material could cause a mismatch in the crystal lattice, as described by Givargizov et al. [41]. Secondly, as observed in locating growth stage, thinner wires are

less stable. These are thinnest wires formed. Instability of thinner wires is consistent with Givargizov's observation that stability decreases with decreasing wire size [43].

Figure 26. Type II wire specimen generated by conditions E2, E4, F2, and F4. Specimens are viewed with SEM at 45° with a common scale of 500 nm.

These wires have features that are consistent with the VLS mechanism. The high length to diameter ratio suggests that material is incorporated through the growing tip.

Without the catalyst beads, polycrystalline nodules or film would be formed instead [39].

The wires, however, are curvy and unaligned.

7.3.1.3 Type III Wires

Long, straight, unaligned wires were formed at 1000°C, as depicted by Figure 27.

Figure 27. Type III wire specimens produced by conditions G3, G4, H3, and H4. Specimens are viewed with SEM at 45° with a common scale of 2 μm .

These wires are very similar to Type I wires in straightness. However, these wires are less densely grown (2.2-14.8 per $10 \mu\text{m}^2$), longer (12.9-43.8 μm), and larger (163.7-278.9 nm). The extremely long lengths, which are indications of the rapid growth rates, are estimated to be between 0.86 to 2.92 $\mu\text{m}/\text{min}$. Even at these rapid growth rates, most of the wires remain straight, with constant cross-sectional areas.

Both the wire densities and distributions have very important implications. As illustrated by Figure 28, these wires have wide diameter distributions, ranging from 50 to 960 nm, and have densities as low as 0.5% of the 5 nm substrates. To generate larger

Figure 28. Histogram for long unaligned wires produced by conditions G3, G4, H3, and H4. Bin interval is 5 nm.

wire, the catalyst beads must be larger [29, 35, 41]. The lower densities, larger wires, and unaccounted catalyst beads suggest that smaller catalyst beads could agglomerate to

form larger catalyst beads. Consequently, the catalyst bead distribution is fluid, and is affected by the process condition.

The shiny tips, circled in Figure 29, could provide important relation between wire diameter and stability. These shiny tips, which are not substantiated, could be the catalyst beads. As depicted by Figure 29G4a and 29G4b, larger wires tend to have more hemispherical tips, while wires smaller than 300 nm tend to have unstable tips. For the small wires, these unstable tips manifest as reduced diameters, undulations, and bends, and do not resemble the wires in diameter or straightness. These results are consistent with Givargizov's observation that larger wires are more stable than sub micron wires [43]. Additionally, tip instabilities suggest that destabilization occurred after the stoppage of SiCl_4 flow (i.e., concentration inconsistency [39, 40]) or after the cool down stage (i.e., temperature instability [39]). It cannot be determined which is the true cause.

Figure 29. Different tip morphologies observed on large wires specimen generated by condition G4. Specimen viewed with SEM at 45° and at different scales. G4a) scale=10 μm G4b) scale=2 μm. Circles indicate unstable wire tips.

Like the Type I wires, Type III wires have characteristics that are consistent with wires grown by the VLS mechanism. In addition to the reasons mentioned for the Type I and Type II wires, the shiny tips are observed on some of the wires, and are consistent with Wagner's observation that the catalyst bead remains on the growing tip [39].

7.3.1.4 Type IV Wires

This wire type illustrates the detrimental effect of high temperature and low SiCl_4 concentration. As observed in Figure 30, the few Type IV wires, generated by conditions G1 and H1, are long, thin, and curvy. Additionally, the surfaces are marked by triangular pits that are 3 μm long and 500 nm deep. These pits are apparent in Figure 30G1b and 30H1b. Within some of these pits are straight and large wires approximately 200 nm in diameter and 2 μm in length. Unlike the long, thin, curvy unaligned wires found outside the pit, these wires are larger, shorter, and aligned. The larger wires within the pits could be caused by the pits, which can act as wells to accumulate and enlarge the catalyst beads. The improved alignment of the larger wires is likely attributed to stability of larger wires, as described by Givargizov and Westwater [28, 43]. The combination of low wire densities and pits indicates etching is predominant.

7.3.1.5 Type V Wires

Comparison of Type IV with Type V wires confirms the necessity of increasing SiCl_4 concentration. Instead of pits, Type V wires, with a SiCl_4 concentration that is 2.5 times of Type IV wires, are characterized by an abundant growth. As illustrated by Figure 31, this wire type has a bimodal distribution, resembling both Type III and IV

wire characteristics. The thinner wires tend to be long and curvy, while the larger wire, specimen H2 in particular, confirms that larger wires are more stable.

Figure 30. Specimen generated by conditions G1 and H1. Specimens are viewed with SEM at 45° with a common scale of 2 μm.

Figure 31. Specimen generated by conditions G2 and H2. Specimens are viewed with SEM at 45° with a common scale of 2 μm .

7.3.2 Process Variable Analysis

The qualitative responses are useful for determining the contributions for the different test variables. Five different qualitative responses—average diameter (D_{avg}), average length (L_{avg}), growth rate ($\dot{L}$), deposition rate ($\dot{M}$), and growth density (f)—are determined for each specimen. These responses are calculated using Equations 16-20, and are summarized in the Table 12. For Equations 16-20, f_i is the frequency for wire i , t is SiCl_4 flow time, A is the area, and ρ is Si density. In estimating each response, SEM images with different resolutions are used and sample sizes are greater than thirty. For the deposition rate, it is assumed that the deposition is contributed only by wire growth. The calculated uncertainties for each response are shown in the Appendix D. Difficulties in the estimation process for wire length and density increases when wires are unaligned and curvy.

$$D_{avg} = \frac{\sum_1^i f_i D_i}{\sum_1^i f_i} \quad \text{Equation 16}$$

$$L_{avg} = \frac{\sum_1^i f_i L_i}{\sum_1^i f_i} \quad \text{Equation 17}$$

$$\dot{L} = \frac{L_{avg}}{t} \quad \text{Equation 18}$$

$$M = \frac{\rho \sum_1^i f_i \pi D_i^2 L_i}{4tA} \quad \text{Equation 19}$$

$$f = \sum_1^i f_i \quad \text{Equation 20}$$

A correlation is observed between the calculated values in Table 12 and the different wire characteristics. Each wire type has a characteristic wire diameter, wire length, deposition rate, and growth density. Since growth rate is wire length per time and the time being same for all conditions, it would provide the same trend as length. Therefore the growth rate is not discussed in the variable analysis. Wire length is used instead. The deposition rate, being a product of diameter, length, and density, is discussed selectively. The diameter, length, and density, which are less mathematically manipulated, are the primary responses discussed.

The trends for each variable are provided in Table 13. The observations for each analysis pair are based on maintaining three of the variables and varying one variable. For any comparison pair, temperature differs by 75°C; SiCl₄ concentration differs by 2.5

times; H_2 concentrations differs by 2.5 times; or τ differ by 2.5 times. Evidences for these conclusions are provided in the discussion for each variable. The observations in Table 13 suggest that low $SiCl_4$ concentration and low temperature are paramount.

Table 12. Quantitative wire characteristics determined with Equations 16-20. Calculated uncertainties for D_{avg} , L_{avg} , Growth Rate, Deposition Rate and Wire Density are 8.7, 8.7, 8.7, 10, and 5% respectively.

Condition	Wire Type	D_{avg}	L_{avg}	Growth Rate	Deposition Rate	Wire Density	Alignment
		nm	μm	$\mu m/min$	$\mu g/cm^2-min$	$\#/10 \mu m^2$	%
E1	I	71.6	1.3	0.08	4.5	43.3	80
E2	II	15.0	1.5	0.10	7.2	172.4	No
E3	I	80.6	3.3	0.22	10.9	42.3	90
E4	II	15.0	1.5	0.10	7.2	172.4	No
F1	I	68.3	1.2	0.08	6.6	46.9	80
F2	II	15.0	1.5	0.10	7.2	172.4	No
F3	I	96.4	3.8	0.26	15.5	38.6	90
F4	II	15.8	1.5	0.10	8.0	173.0	No
G1	IV	15.0	10.0	0.67	0 ^B	0.5	No
G2	V	180 ^A	2.0	0.13	17.2	2.2	No
G3	III	231.0	15.0	1.00	33.0	2.2	<5
G4	III	179.8	12.9	0.86	41.1	5.8	~5
H1	IV	15.0	10.0	0.67	0 ^B	0.5	No
H2	V	154 ^A	5.8	0.38	95.5	5.2	40
H3	III	278.9	43.8	2.92	274.2	14.8	No
H4	III	163.7	24.2	1.61	126.3	7.8	No

A) Gauzy thin growth not included in calculation. B) Etching, as indicated by pits, is present.

Table 13. Summary of experimental matrix analysis.

Variable	Analysis Pairs	# of Pairs	Δ for Each Pair	Observations for Increase in Variable
[H ₂]	E/F & G/H	8	2.5 times	--At 925°C, no strong correlation between variables and responses. Most responses increase at 1000°C. Wire length, deposition, and density increases for most cases. --Aligned wires become more misaligned. Misaligned is observed to be ordered.
T	E/G & F/H	8	75°C	--Wires longer, larger, and unaligned. --Surface pitted and marked by triangular pits for some cases.
[SiCl ₄]	1/2 & 3/4	8	2.5 times	--At 925°C, wires are curvier and thinner. --At 1000°C, deposition rate and wire density is increased.
τ	E3/F2 & G3/H2	2	2.5 times	--At 925°C (condition E3/F2), lower residence time produces curvier and thinner wires. --No difference at 1000°C (G3/H2).

7.3.2.1 H₂ Concentration

Hydrogen concentration effects are temperature dependent. At 925°C, no noticeable change is observed in wire morphology, diameter, and density. Hydrogen concentration effects, however, are more noticeable at higher temperature.

At 925°C, the most noticeable effect of H₂ concentration is in the wire alignment and is best illustrated for Type I wires in Figure 32. In the analysis of Figure 32, conditions E1 and E3 are compared with conditions F1 and F3. For the two cases, H₂ concentrations for conditions E3 and F3 are 2.5 times of conditions E1 and F1 respectively. Increasing the H₂ concentration by 2.5 times for the two cases correlates to an increase in misalignment.

Figure 32. Illustration of increasing misalignment with an increase of H_2 concentration by 2.5 times for $SiCl_4$ concentration of 0.04% (E1 and F1) and 0.10% (E3 and F3). Specimens are viewed with SEM at 45° and have a common scale of 500 nm.

Though unaligned, top view images of conditions E3 and F3 in Figure 33 indicate that these non-normally oriented wires are not randomly directed. Arrows in Figure 33 show that a majority of these non-oriented wires have three major directions that are approximately 60° from each other.

Figure 33. Illustration of unaligned wire orderliness produced by conditions E3 and F3. Specimens are viewed with SEM at 0° and have a common scale of $2\ \mu\text{m}$.

The unaligned wires orderliness is rationalized by the preferred SiNW growth directions. According to the literature review, SiNWs tend to grow along the $\langle 111 \rangle$ directions [28, 29, 32, 36]. The directionality of the unaligned wires and the preferred $\langle 111 \rangle$ growth directions suggest that the wires were likely to originate from other $\{111\}$ surfaces that are not uniformly and not normally directed.

These new surface are likely to be caused by surface etching. From the literature review, a possible etchant is hydrogen chloride (HCl), a common Si etchant and a by-product of SiCl_4 reduction by H_2 (Equation 9) [46]. The etching is slight, since the wire tip and base have similar thickness. If etching were aggressive, the wire base should be thinner than the top.

The correlations for H_2 concentration, as illustrated by Figure 34 and 35, indicate that these responses are strongly dependent on the temperature. At 925°C , the responses

are minimal or insignificant. Significant increases in responses are observed at 1000°C. The results for the different temperature suggest temperature and H₂ interaction.

For each plot, each trend line is composed of data pair having a common τ , SiCl₄ concentration and temperature. Two letters and a number identify these trend lines. The first letter corresponds to the lower H₂ concentration condition, while the second letter corresponds to the condition having a H₂ concentration that is 2.5 times of the former. The number corresponds to a particular τ and SiCl₄ concentration. For instance, 1EF denotes condition pair E1 and F1, with F1 having a SiCl₄ concentration that is 2.5 times of E1. For both plots, τ is 2.9 seconds for H₂ concentration of 4 to 10%, and τ is 7.3 seconds for H₂ concentration of 10 to 25%.

At 925°C, deposition rate, as illustrated by Figure 34, is the only observable response caused by a change in H₂ concentration. For deposition rate, a significant response is observed for trend lines 1EF and 3EF. For diameter, length, and density, the difference caused by H₂ concentration is not significantly different from the measurement uncertainties. Overall, H₂ concentration has a weak effect at 925°C.

At 1000°C, all responses to H₂ concentration, except diameter, are significant, as illustrated by Figure 35. For diameter, when the uncertainties are accounted, no significant changes are observed for the different H₂ concentration. Differences are observed for the wire length, deposition rate, and density. With increasing H₂ concentration, the length is longer, and the deposition rate and density are higher. This relationship is true for all comparison pair except 1GH, which is significantly etched.

The H_2 concentration contribution to wire length is significant. As mentioned earlier, the length is an equivalent measure for growth rate. According to Figure 35, length is proportional to H_2 concentration. For H_2 concentration to impact growth rate, it must influence the supersaturation, which Givargizov has determined in Equation 1 to cause an increase in growth rate [44].

Figure 34. Average diameter, length, deposition rate, and density at 925°C as a function of H_2 concentration. Residence times are 2.9 and 7.3 seconds for H_2 concentration of 4-10% and 10-25% respectively. Error bars indicate uncertainties.

Figure 35. Average diameter, length, deposition rate, and density at 1000°C as a function of H₂ concentration. Residence times are 2.9 and 7.3 seconds for H₂ concentration of 4-10% and 10-25% respectively. Error bars indicate uncertainties.

This inferred increase in supersaturation could also explain the increase in wire density with increasing H₂ concentration. According to Equation 6, the minimum wire radius (R_{min}) decreases with a higher supersaturation level [39]. Consequently, smaller wires could be formed in addition to the larger wires, resulting in high densities.

7.3.2.2 Temperature

In increasing the temperature from 925 to 1000°C, the wire morphologies and surfaces are significantly different. These differences are observed by comparing the first and third row and second and fourth row of Figure 22. Some surfaces are pitted, as described earlier for Type IV wires. Wires generated do not have desired morphologies generated. Again morphologies are described earlier for Type III and IV wires. Wires are unaligned, bigger, and longer. The deposition rates are higher. But the wire growth densities decrease. These results are consistent for the two different H₂ concentrations.

The quantitative responses to temperature are plotted in Figure 36 and 37. For conditions having the same τ , temperature, and SiCl₄ concentration, Figure 36 represents a H₂ concentration that is 2.5 times of Figure 37. The trend lines for each graph are composed of data pairs having the same τ , H₂ concentration, and SiCl₄ concentration. The legends for each trend line are similar to that described in the H₂ concentration analysis. When Figures 36 and 37 are compared, both plots have very similar trends. Therefore, the same analysis will be used for both Figures 36 and 37.

With exception of growth density, the responses are generally proportional to temperature. The exceptions are conditions 1EG and 1FH, in which aggressive etching is observed. Consistent results are observed for the two different H₂ concentrations, represented by Figures 36 and 37.

Wire diameter increases with increasing temperature. From the literature review, both Wagner and Givargizov observe that the wire diameter increases with increasing

temperature because of the increasing importance of vapor-solid deposition compared to the vapor-liquid deposition [39, 44]. Evidence for vapor-solid deposition is the larger diameter of the base compared to the tip [39, 44]. Examination of the Figures 22, 28-31 indicates that wire cross-sectional areas remain constant over the lengths of the wires. Therefore, contribution by vapor-solid deposition is insignificant.

Figure 36. Average diameter, length, deposition rate, and density as a function of temperature for lower H_2 concentration level. Error bars indicate uncertainties.

Figure 37. Average diameter, length, deposition rate, and density as a function of temperature for upper H₂ concentration level. Error bars indicate uncertainties.

Indirect evidences suggest that catalyst bead enlargement is more probable. As indicated by Figures 36 and 37, wire density decreases with increasing temperature. From the decreasing wire growth density and the larger wires, it can be inferred that the catalyst beads agglomerate into larger diameter catalyst beads. A larger catalyst bead correlates to a larger wire, since wire diameter is related to the catalyst bead [39]. From these results, wire diameter and density have an inversed relationship.

The wire length is significantly longer as the temperature was increased. This observation appears to contradict Equation 1, which correlates that growth is inversely proportional to T^2 . However, according to Equation 1, the growth rate is also proportional to $\Delta\mu$. To maintain consistency with Equation 1, $\Delta\mu$ must increase. Though the input concentrations for reactants were unchanged, increasing the temperature could increase the supersaturation by increasing the equilibrium Si concentration. As explained earlier in the locating growth condition section, Si is generated by endothermic reactions, for which conversion increases with temperature. Additionally, the temperature increase could increase the reaction rate, thus increasing the extent of reaction. A larger extent of reaction corresponds to concentration being nearer to equilibrium concentration. Because of the complexity of the reactions, the increase in supersaturation cannot be determined.

Additionally, Givargizov observes that the growth rate is proportional to the diameter [44]. This increase is contributed by two factors. The first factor is the increase in $\Delta\mu$ with increasing diameter, as expressed by Equation 5 [44]. As the diameter increases, the second term of Equation 5, $4\Omega\alpha/d$, becomes less important. The second factor is the increase in liquid-solid precipitation efficiency with increasing diameter [44].

7.3.2.3 SiCl₄ Concentration

Silicon tetrachloride concentration significantly affected wire morphologies and surface topologies. The analysis of SEM images indicates that SiCl₄ concentration effects are strongly dependent on the temperature level. These quantitative responses are

complicated and depend on the particular τ , temperature, and H_2 concentration. Unlike other variables, $SiCl_4$ concentration causes a noticeable decline in diameter.

The SEM images indicate that the most noticeable effect of $SiCl_4$ concentration is the wire morphology and surface topology. Its effect is dependent on the temperature level. At the lower temperature, increasing $SiCl_4$ concentration is detrimental to the creation of desired morphologies. Figures 38 and 39, with a τ of 2.9 and 7.3 seconds respectively, best illustrate these results. Each column in Figure 38 and 39 corresponds to a particular $SiCl_4$ concentration, with the second column being 2.5 times of the first; each row corresponds to a particular H_2 concentration, with the second row being 2.5 times of the first.

Comparison of the first column and the second column of Figures 38 and 39 indicates that increasing $SiCl_4$ concentration by 2.5 times causes a reduction in wire diameters and an increase in wire misalignment. These results are consistent with that of Westwater and Givargizov, who observed that wires are thinner and curvier with increasing $SiCl_4$ concentration [28, 35, 36, 43, 44]. Wagner provides the explanation for wire thinning in Equation 6, in which higher supersaturation decreases the minimum wire radius (R_{min}) required for wire growth [39].

At 1000°C, the diameter response to $SiCl_4$ concentration is opposite to that of the 925°C. This observation is provided by conditions on the lower left quadrant of Figure 22. As illustrated by Figures 40G1, 40G1a, 40H1, and 40H1a, for the lower $SiCl_4$ concentration of 0.04%, the wires are thin, and the surfaces are pitted. As mentioned

earlier, etching appears to dominate over deposition for these conditions. In increasing SiCl_4 concentration to 0.10% for conditions G2 and H2, growth is abundant, as illustrated by Figures 40G2 and 40H2. The change observed suggests that a small concentration change of 0.06% has a great effect on the growth, shifting from etching to deposition.

Figure 38. Illustration of wire morphology by increasing SiCl_4 concentration from 0.04% (conditions E1 and F1) to 0.10% (conditions E2 and F2) at 925°C and $\tau=2.9$ seconds. Specimens are viewed with SEM at 45° and have a common scale of 500 nm.

Figure 39. Illustration of wire morphology by increasing SiCl_4 concentration from 0.04% (conditions E3 and F3) to 0.10% (conditions E4 and F4) at 925°C and $\tau=7.3$ seconds. Specimens are viewed with SEM at 45° and have a common scale of 500 nm.

Figure 40. Illustration of wire morphology by increasing SiCl_4 concentration from 0.04% (G1 and H1) to 0.10% (G2 and H2) at 1000°C and $\tau=2.9$ seconds. Specimens are viewed with SEM at 45° and have a common scale of $2\text{ }\mu\text{m}$.

The quantitative responses as a function of SiCl_4 concentration are presented in Figure 41. Each trend line represents data pairs having common temperature, τ , and H_2 concentration. Trend lines for SiCl_4 concentration of 0.04 to 0.10% have a residence time of 2.9 seconds, while trend lines for SiCl_4 concentration of 0.10 to 0.25% have a residence time of 7.3 seconds.

According to Figure 41, the wire diameter response, as expected, is similar to the observation above. Six different trend lines indicate that diameter show a significant decrease for the various τ , temperature, and H_2 concentration. The explanation for the increase in diameter is provided above. Only conditions G and H with SiCl_4 concentration of 0.04 to 0.10% show a significantly different trend, in which the diameters are proportional to SiCl_4 concentration for the range of 0.04 to 0.10%. This result suggests an interaction between temperature and SiCl_4 concentration.

The lengths, as presented in Figure 41, show no change or a decrease with increasing SiCl_4 concentration. However, according to Equation 1, at constant temperature, the growth rate should be proportional to SiCl_4 concentration, since the supersaturation should also increase. This inconsistency could be mitigated by Equation 6, which correlates a decrease in supersaturation with decreasing wire diameter [44]. As discussed above, wire diameter decreases with increasing SiCl_4 concentration, thus compensating for the increase in supersaturation. Discrepancies are observed for G and H. For these two cases, growth rate decreases with increasing wire diameter. This is likely contributed to the increase in uncertainties for the random and curvy growth.

Figure 41. Average diameter, length, deposition rate, and density as a function of SiCl_4 concentration for various temperature and H_2 concentration. For SiCl_4 concentration of 0.04-0.10% $\tau=2.9$ seconds and for 0.10-0.25% $\tau=2.9$ seconds. Error bars are for uncertainties.

7.3.2.4 Residence Time

Residence time effect is contingent on the temperature level. Morphological changes are particularly significant at 925°C. For the two residence trend lines available, quantitative responses produced by residence time have very similar characteristics as the response produced by temperature change. Density is decreased with increasing residence time.

The results are presented in Figure 42. All images have common H₂ and SiCl₄ concentrations. The differences are in the temperature and τ . Figure 42 is organized with each row corresponding to a temperature and each column corresponding to a particular τ . The first and second rows correspond to 925 and 1000°C respectively, and the first and second columns correspond to residence times of 2.9 and 7.3 seconds.

According to Figure 42, the differences in morphology are observed only at 925°C. As illustrated by Figures 42F2 and 42E3, increasing τ from 2.9 to 7.3 seconds transforms curvy thin curvy wires into aligned wires at 925°C. Morphologies are unchanged at 1000°C, as shown by Figure 42H2 and 42G3. The importance of τ at 925°C suggests that equilibrium has not been reached. The increase in τ increases the extent of reaction (i.e. closer to equilibrium) by increasing the reaction time. At 1000°C where the reaction rate is more rapid, the change in τ does not have much effect, suggesting that the reaction has reached or is very close to equilibrium.

Figure 42. Response at 925°C for residence time of 7.3 seconds (F2) and 2.9 seconds (E2) and at 1000°C for residence time of 6.9 seconds (H2) and 2.8 seconds (G3).

The quantitative responses caused by τ have similar characteristics as those responses caused by temperature, as illustrated by comparison of Figure 36 and 37 with Figure 43. The diameter and length increases with increasing τ , while density decreases with increasing τ . The difference is in the deposition rate. It increases for increasing temperature, but it decreases for increasing τ .

The analogous responses for both τ and temperature suggest that the same discussion for temperature could provide insight for τ . As discussed above, τ affects the extent of reaction by influencing the reaction time, while temperature affects the reaction rate and equilibrium concentration. At higher τ , the approach to equilibrium is closer, resulting in higher level of supersaturation.

Figure 43. Diameter, length, deposition rate, and density as a function of SiCl_4 concentration. Error bars indicate uncertainties.

CHAPTER 8

CONCLUSIONS

Aligned, crystalline silicon nanowires with diameters less than 100 nm are produced within a narrow growth window. These wires are produced only at 925°C by the four sets of conditions summarized in Table 14.

Table 14. Conditions that generate ideal wires.

Condition	T	[SiCl ₄]	[H ₂]	τ
	°C	mol %	mol %	sec
E1	925	0.04	4	2.9
E3	925	0.10	10	7.3
F1	925	0.04	10	2.9
F3	925	0.10	25	7.3

The most significant effect of H₂ concentration is in wire alignment. The results indicate that a wide range of H₂ concentration of 4-25% could produce vertically-aligned wires. For a given temperature, SiCl₄ concentration, and τ, increasing the H₂ concentration elevates the formation of wire misalignment. These results suggest lowering the H₂ concentration below 4%.

Residence time effects are observed only at the lower temperature of 925°C. Significant effect of τ on morphology is observed when τ was increased from increased from 2.9 to 7.3 seconds. The longer τ of 7.3 seconds leads to a desirable morphology.

Temperature and SiCl₄ concentration are particularly critical for vertically-aligned growth. At the higher temperature of 1000°C undesirable wire morphologies and

aggressive etching are observed. For the conditions evaluated, higher temperature discourages wire alignment and the formation of thinner wires. Wires generated are thick and extremely long, and have wide size distributions. The few thin wires found are long and curved. The curviness is an indication of instability associated with thinner wires. Additionally, substrate surfaces are pitted.

High SiCl_4 concentration can also lead to unwanted effects, such as particles and clusters, film, or curved wires. Particles and clusters are attributed to homogeneous nucleation, when the gas phase is highly supersaturated. For this thesis, homogeneous nucleation occurs at a SiCl_4 concentration of 5.5%. For SiCl_4 concentration as low as 0.05%, substrate is coated, causing catalyst bead coverage and deactivation. Wire growth is achieved, when the substrate was relocated from the top of the platform to the middle of the boat, where the boundary layer was increased three times. With the new setup and SiCl_4 concentration as high as 0.10%, aligned, crystalline, with diameter less than 100 nm, are generated. Higher concentrations generate thinner and curvier wires.

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APPENDIXES

A Equilibrium Reactions

Reactions A1-A13 are like that from Putte and Yoon [46-47].

B Mass Transfer Through Stagnant Film

Es Equations Window

"For diffusion through a stagnant film (Ar) [51]."

$$N_{az} = c \cdot D_{ab} \cdot (x_{a1} - x_{a2}) / L \cdot (1 + 1/2 \cdot (x_{a1} + x_{a2}) + 1/3 \cdot (x_{a1}^2 + x_{a1} \cdot x_{a2} + x_{a2}^2)) / 1000$$

"System conditions"

P=1[atm]
T=273[K]
R=0.082057[L-atm/mol-K]
c=P/(R*T)

"Molar concentration at liquid interaface (1) and exit (2)"

Pa=0.1[atm] "Partial pressure of a=SiCl4"
x_{a1}=Pa/P "Assuming Raoult's law"
x_{a2}=0 "Assuming concentration is negligible at exit"

L=15[cm] "Length from liquid SiCl4 to dilution gas"

Ma=169.9[g/mol] "M=molecular wieght"
Mb=39.9[g/mol] "b=Ar"

V_a=V_{Si}+4*V_{Cl} "V=atomic diffusion volume. For SiCl4 the individual volume
is summed using Kopp's rule []."
V_b=16.2 "From Reid [52]"
V_{Si}=32 "From Yoon [47]"
V_{Cl}=21.6 "From Yoon [47]"

"Binary diffusion coefficient is determined by equations proposed by Fuller et al. [52]."

$$D_{ab} = 1.43 \times 10^{-3} \cdot (T^{1.75} \cdot (1/M_a + 1/M_b)^{0.5}) / (P \cdot (V_a^{0.33} + V_b^{0.33})^2)$$

W_a=N_{az}*pi*D^2*60 "Mass flux thru tube cross section"
D=0.48[cm]

Q=200[cm^2/min] "Dilution flow"
n_{dot}=P*Q/(R*T*1000) "Moles of dilution gas"

x_a=W_a/n_{dot}*100 "Mole % of SiCl4"

Figure B1. Calculations to determine mass transfer of SiCl₄ through stagnant Ar film.

Figure B2. Results of mass transfer calculation.

C Boundary Layer Calculated With Equation 12

Figure C1. Calculated δ for experimental condition.

Table C1. Calculated δ for horizontal reactor at experimental condition for two total flow of 200 and 500 sccm.

		200 sccm		500 sccm	
T	L	Re _t	δ	Re _t	δ
°C	cm		cm		cm
925	0.01	0.019	0.36	0.047	0.23
	0.1	0.188	1.15	0.471	0.73
	0.2	0.377	1.63	0.942	1.03
	0.3	0.565	2.00	1.412	1.26
	0.4	0.753	2.30	1.883	1.46
	0.5	0.942	2.58	2.354	1.63
	0.6	1.130	2.82	2.825	1.78
	0.7	1.318	3.05	3.296	1.93
	0.8	1.507	3.26	3.766	2.06
	0.9	1.695	3.46	4.237	2.19
	1	1.883	3.64	4.708	2.30
1000	0.01	0.018	0.37	0.045	0.24
	0.1	0.179	1.18	0.447	0.75
	0.2	0.357	1.67	0.894	1.06
	0.3	0.536	2.05	1.340	1.30
	0.4	0.715	2.37	1.787	1.50
	0.5	0.894	2.64	2.234	1.67
	0.6	1.072	2.90	2.681	1.83
	0.7	1.251	3.13	3.127	1.98
	0.8	1.430	3.35	3.574	2.12
	0.9	1.608	3.55	4.021	2.24
	1	1.787	3.74	4.468	2.37

D Error Analysis for Equations 16-20

The uncertainties in estimating $\delta f_i / f_i$, $\delta D_i / D_i$ and $\delta L_i / L_i$ are 5%. For random and independent, Equations D1-A5 are derived. The calculated uncertainties for Equations D1-D5 are 8.7, 8.7, 8.7, 10 and 5% respectively.

$$\frac{\delta D_{avg}}{|D_{avg}|} = \sqrt{\left(\frac{\delta f_i}{f_i}\right)^2 + \left(\frac{\delta D_i}{D_i}\right)^2 + \left(\frac{\delta f_i}{f_i}\right)^2} \quad \text{Equation D1}$$

$$\frac{\delta L_{avg}}{|L_{avg}|} = \sqrt{\left(\frac{\delta f_i}{f_i}\right)^2 + \left(\frac{\delta L_i}{L_i}\right)^2 + \left(\frac{\delta f_i}{f_i}\right)^2} \quad \text{Equation D2}$$

$$\frac{\delta \dot{L}}{|L|} = \sqrt{\left(\frac{\delta L_{avg}}{L_{avg}}\right)^2} \quad \text{Equation D3}$$

$$\frac{\delta M}{|M|} = \sqrt{2\left(\frac{\delta D_i}{D_i}\right)^2 + \left(\frac{\delta L_i}{L_i}\right)^2 + \left(\frac{\delta f_i}{f_i}\right)^2} \quad \text{Equation D4}$$

$$\frac{\delta f}{|f|} = \sqrt{\left(\frac{\delta f_i}{f_i}\right)^2} \quad \text{Equation D5}$$