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VAPOR-LIQUID-SOLID GROWTH OF GROUP IV (Si, Ge, Si$_{1-x}$Ge$_x$)

SINGLE AND HETEROSTRUCTURED NANOWIRES

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ABSTRACT

Several potential applications of semiconducting nanowires (NWs) from nanoscale electronic and photonic devices to biosensors have made them interesting materials and have motivated a vast amount of studies on the synthesis of nanowires and their electrical characterization. Group IV single and heterostructured nanowires, in particular, have received increasing attention due to their compatibility with the current microelectronic industry and numerous research has been going on to optimize their growth process. For this purpose, the majority of reports have primarily used silane (SiH₄) and germane (GeH₄) as their Si and Ge containing gas sources.

In this thesis, an alternative Si source, disilane (Si₂H₆) has been investigated which is of interest since it is more reactive than SiH₄ and therefore may enable higher growth rates at lower temperature and lower partial pressures. The lower thermal stability of Si₂H₆ could also be an advantage to enable the growth of Si₁₋ₓGeₓ nanowires over the entire composition range at lower temperatures which are more compatible with the range of conditions typically used for Ge nanowire growth and in turn may enable the fabrication of different types of heterostructures. To fulfill the objective of this research, a systematic study has been developed to explore the growth of group IV (Si, Ge, and Si₁₋ₓGeₓ alloy) single and heterostructured nanowires from Si₂H₆ and GeH₄ precursors.

First, the growth kinetics of individual SiNWs from Si₂H₆ was investigated by examining the effects of growth parameters on their growth rate. The results were compared to that obtained with SiH₄. In addition, to gain a better insight into the SiNW growth process, the results were also compared with Si films deposited under similar
conditions inside the same reactor. Overall compared to SiH₄, the use of Si₂H₆ enabled higher growth rates for both SiNWs and Si films. For both gases, a nonlinearity was observed in the growth rate of nanowire as a function of gas partial pressure which was explained by a simple decomposition mechanism including the adsorption, desorption and incorporation of precursor molecule on the Au droplet surface. The apparent activation energy of the process was found to be identical for both gases under the conditions examined in the present study, suggesting similar rate-determining step in the nanowire growth process from the two precursors.

Upon completion of studies on SiNW growth, the synthesis parameter space was then determined for undoped GeNWs and the influence of growth conditions on their morphology as well as their growth rate was examined. It was found that the fabrication of GeNWs strongly depends on the growth temperature and is achievable only for a very narrow range. To get nanowires with uniform diameter, growth temperature should be kept low otherwise, uncatalyzed radial growth on nanowire sidewalls results in tapered nanowires. The growth rate as a function of temperature revealed an Arrhenius behavior with a small apparent activation energy and was observed to increase linearly with germane partial pressure in the range examined here. Besides the undoped GeNWs, the fabrication of radial p-n junction GeNWs, which are of interest for photovoltaic cells, was also studied and it was found that the morphology of both the p-type core and the n-type shell is influenced by temperature and dopant ratios.

The outcomes of the studies on undoped GeNWs combined with the results on SiNWs were next used to explore the growth of Si₁₋ₓGeₓ nanowires from Si₂H₆ and GeH₄ gases. The variations in Ge fraction as well as growth rate of Si₁₋ₓGeₓ nanowires with
growth parameters were studied. In general, the higher reactivity of Si$_2$H$_6$ compared to SiH$_4$ enabled the growth of Si$_{1-x}$Ge$_x$ nanowires with Ge composition over a wide range from $x \sim 20 – 80\%$ which was controllable by varying the inlet GeH$_4$/Si$_2$H$_6$ ratio at a constant temperature. It was observed that at a given inlet gas ratio, the growth rate increases exponentially with increasing temperature and the apparent activation energy of the process reduces as the Ge content of the nanowire is enhanced indicating a change in the rate-limiting step of the process. For different growth temperatures, the growth rate of Si$_{1-x}$Ge$_x$ nanowire was found to have a non-linear dependence on variations in either GeH$_4$ or Si$_2$H$_6$ partial pressures which increases with both parameters when the other is fixed. The observed results were explained through a kinetic model that describes the reactions of precursors on the Au droplet surface.

Finally, the information gathered from single nanowire synthesis was used to fabricate Ge/SiGe and SiGe/Si axial heterostructures. The SiGe/Si nanowires were further processed as a possible approach to form SiNWs with more uniform length by selectively etching the SiGe segment away and releasing the SiNW segment. Producing monodisperse silicon nanowires (SiNWs) with uniform length has been a critical difficulty in the bottom-up assembly of nanowire devices. Currently, ultra-sonic agitation is frequently used to break the wires off of the substrate; however, they break at differing lengths, degrading the yield of successful wire integration and device fabrication. It was shown here that this problem can be mitigated through the use of SiGe/Si axial-heterostructure nanowire. After the fabrication of these structures, the SiGe segment can be selectively removed using NH$_4$OH:H$_2$O$_2$:H$_2$O solution. The process releases the SiNW segments with narrower length distribution.
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1.1 Motivation

The field of nanotechnology represents an exciting and rapidly expanding research area that could enable new functions and/or greatly enhanced performance in diverse applications ranging from electronics, optoelectronics, and energy to healthcare. As being an important class of one-dimensional (1D) nanostructures, nanowires have attracted considerable attention and have been the focus of extensive recent research that may open up substantial opportunities for novel nanoscale devices and/or may improve the performance of conventional devices. Unique properties of these materials such as quantum confinement effects and surface sensitivity have made them attractive as building blocks for future functional nanosystems. The interest in this research field is well reflected in the number of publications growing exponentially over the past two decades illustrated in Figure 1-1.1

The advantages of semiconductor nanowires have been demonstrated in a wide range of high performance devices, a few examples of which are shown in Figure 1-2. A typical model of such devices with broad potential applications is nanowire field-effect transistor (FET) that exhibits properties comparable or better than their planar counterparts. Vertically grown SiNWs have been employed to fabricate wrap-around-gate FETs2 (Figure 1-2(a)) which allow better electrostatic gate control of the conducting
channel and offer the potential to drive more current per device area than is possible in a conventional planar architecture.

![Graph showing the number of nanowire papers published each year since 1991.](image)

**Figure 1-1:** Number of papers on nanowires published each year since 1991.¹

The high performance characteristics of nanowire FETs, such as high surface to volume ratio and specially designed surface structures, have additionally made them great candidates as ultrasensitive nanosensors for detecting a wide range of gases, chemicals, and biomedical species. By modifying the nanowire surface through the attachment of receptor groups, nanowire FETs can be configured as highly selective and highly sensitive detectors (Figure 1-2(b)).³ As an example, linking monoclonal antibodies (mAbs) on SiNW surface converts the nanowire FET into a biosensor for cancer
detection. Selective binding of cancer marker proteins to surface linked mAbs produces a conductance change in the corresponding receptor-modified silicon nanowire and enables multiplexed detection of three cancer marker proteins, prostate specific antigen, carcinoembryonic antigen, and mucin-1.²

Figure 1-2: Examples of nanowires as (a) wrap-around-gate FET,² (b) multiplexed detector of cancer marker proteins,³ (c) tricolor nanoLED array⁴ and (d) solar cell⁵.
Apart from electronics and optoelectronics, nanowires represent attractive building blocks for active nanophotonic devices, including light emitting diodes (LEDs), lasers, and detectors. The ability to assemble nanowires in different structures allows for fully integrated nanophotonic systems. For instance, a crossed architecture enables the fabrication of single and multicolor nanoLED devices (Figure 1-2(c)).\(^4\) Using a solution-based approach, emissive n-doped direct band gap III-V and II-VI nanowires are assembled with nonemissive p-doped silicon nanowires in a crossed nanowire architecture to form nanoscale p-n diodes which show emission at the cross points. This concept has facilitated the assembly of a wide range of nanoLEDs on a single chip, with emission ranging from ultraviolet through near infrared in a manner not possible with conventional planar technology.

Finally, nanowires formed as a radial p-n junction (Figure 1-2(d)) have attracted great interest in recent years for their potential application as photovoltaic and solar cell devices since they have been proposed to improve the efficiency of the device relative to a conventional planar geometry.\(^5\) With the wires parallel to the incident light direction, their high aspect ratio (length/diameter) allows the use of a sufficient thickness of material to obtain good optical absorption while simultaneously it provides short collection lengths for excited carriers in a direction normal to the light absorption.

The rational design and development of such attractive nanowire based devices brings in the need to better understand the synthesis process and the mechanism of nanowire growth in order to gain control over the key parameters such as size, structure, morphology, chemical composition and doping. To date, a wide variety of nanowire materials from group IV, III-V and II-VI semiconductors have been grown successfully.
To generate these nanowires many methods such as vapor-solid and self-catalytic growth, oxide-assisted growth, solution-liquid-solid growth as well as vapor-liquid-solid (VLS) and vapor-solid-solid (VSS) mechanism have been developed and different techniques such as thermal evaporation, molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), laser-assisted and chemical vapor deposition (CVD) have been employed to provide the growth species. In this thesis, the focus is concentrated on group IV single nanowires (Si, Ge, and Si$_{1-x}$Ge$_x$ alloy) and their heterostructures which are of significant interest because of their compatibility with current microelectronic industry. The VLS mechanism, which is the most commonly used method for nanowire growth, is employed to grow Si and Ge nanowires and their alloys in a CVD system. Key points regarding this mechanism and the related theoretical models are summarized below. For more information on other methods and techniques the interested reader is referred to recent reviews of nanowire growth in references 7 and 8.

1.2 Background

1.2.1 Nanowire growth mechanism

Semiconductor nanowires are most commonly grown through a vapor-liquid-solid mechanism, first put forward by Wagner and Ellis in 1964. In VLS growth, a substrate coated with a metal particle which serves as a catalyst is heated above the eutectic point of the metal-semiconductor to form a liquid alloy. The gas precursor of semiconductor material flowing over the substrate, e.g. silane (SiH$_4$) in case of SiNW, adsorbs
preferentially on the catalyst droplet and diffuses into the liquid alloy. Eventually when the alloy becomes supersaturated, nucleation and crystallization occurs. The semiconductor precipitates out at the metal-semiconductor interface and the nanowire growth starts leaving the metal on top of the wires. The diameter of the nanowire is determined by the droplet size, while its length depends on the growth time and conditions. A schematic of VLS growth and the corresponding stages on a phase diagram are shown in Figures 1-3(a)-(e).

Figure 1-3: Schematic diagrams of the nanowire growth process: (a) metal is deposited on substrate and (b) forms the liquid alloy upon heating above eutectic point. (c) Exposure to a source gas such as SiH₄ supersaturates the droplet and (d) nanowire precipitates out. (e) Phase diagram for the Au-Si binary system.⁹
To fabricate group IV nanowires through the widely used VLS mechanism which is the focus of this study, different metals such as Al and Cu have been investigated, however, the majority of work on SiNWs and Ge nanowires (GeNWs) has employed Au catalysts due to its low eutectic temperature that is well matched to the decomposition temperatures of the hydride precursors typically employed in CVD. Nonetheless, additional catalysts such as Al, Cu, Mn, Pt, Ni, Fe, and Pd have also been investigated\cite{10} which provide growth at sub-eutectic temperatures through a catalyst that is in the solid rather than liquid state, leading to a vapor–solid–solid (VSS) growth mode.

Recently, by using in situ Transmission Electron Microscopy (TEM) of GeNWs Kodambaka et al.\cite{11} showed that the catalyst state depends not only on temperature but also on growth pressure and thus both VLS and VSS processes can occur below the eutectic temperature. The influence of temperature is examined on a single GeNW at a constant pressure, as shown in Figures 1-4 (a)-(d), where the growth starts with a liquid droplet at T=335ºC; upon cooling to T=225ºC the droplet solidifies but wires continue to grow via VSS process; although at rates much slower than the VLS. On heating, the catalyst remains solid until 435ºC and following reformation of the liquid droplet, the VLS growth persists even after the temperature is reduced again to 335ºC. The role of precursor pressure at a constant temperature below the eutectic point that is represented in Figures 1-4 (e)-(g) becomes apparent when reducing the source gas pressure (Ge$_2$H$_6$) causes the nanowires to solidify with larger wires solidifying later. Consequently, the existence of a liquid catalyst at sub-eutectic temperature can be attributed to the large Ge supersaturation which inhibits the nucleation of solid gold and stabilizes the droplet against solidification. If sufficient supersaturation is not maintained, the particle
solidifies and VSS growth proceeds.

Figure 1-4: (a-c) Bright field TEM images showing the solid-to-liquid (a to b) and liquid-to-solid (b to c) transitions in a Au-Ge catalyst particle with variation in temperature. The corresponding temperatures are marked in Fig. (d). (e-g) Representative TEM image series showing the solidification of Au-Ge catalysts on top of two Ge wires (29 and 39 nm in diameter) (f) 106 s and (g) 283 s after the Ge₂H₆ pressure is reduced from 4.8×10⁻⁶ to 8.6×10⁻⁷ Torr during growth at constant temperature (350°C).¹¹

Both VLS and VSS mechanisms facilitate the formation of modulated nanostructures in which the composition or doping can be varied. Once the nanowire begins to grow, two surfaces are exposed to the gas source: the surface of the liquid alloy and the surface of the nanowire. If the adsorption of the precursor continues on the
surface of the liquid alloy, the axial nanowire growth will resume. Under this situation, addition of a new precursor or dopant during the growth will form axial heterostructures or axial p-n junctions, as schematically depicted in Figure 1-5. However, if the growth condition is changed in a way that adsorption/decomposition of vapor phase occurs on the wire sidewall, a shell will coat the original nanowire by a vapor-solid growth mode. Hence by changing the gas sources or using different dopants, core-shell heterostructure nanowires can be synthesized.

Figure 1-5: Schematic illustration of nanowire heterostructure synthesis. (a) One-dimensional axial growth resumes by preferential reactant adsorption on the catalyst surface. (b) A change in the reactant leads to either (c) axial heterostructure growth if the reactant is incorporated at the catalyst surface or (d) radial heterostructure growth when the precursor adsorbs uniformly on the wire surface. Alternating reactants will produce (e) axial superlattices or (f) core-multi-shell structures.\textsuperscript{12}
The abovementioned approach has been employed in this thesis to form different axial heterostructures. By introducing a Si-containing source such as disilane \((\text{Si}_2\text{H}_6)\) during GeNW growth or terminating the Ge-containing source such as germane \((\text{GeH}_4)\) from SiGe nanowire growth, Ge/SiGe or SiGe/Si axial heterostructures are fabricated, both of which are of interest for fundamental studies of nanowire heteroepitaxy as well as device development. In case of GeNWs, by flowing trimethylboron (TMB) or diborane \((\text{B}_2\text{H}_6)\) simultaneously with germane \((\text{GeH}_4)\) at conditions favorable for axial growth, a p-type core is formed. Switching the dopant source to phosphine \((\text{PH}_3)\) and changing the growth condition to promote vapor-solid growth on the nanowire surface coats the wire with an n-type shell and generates a radial p-n junction which, as mentioned earlier, is of interest for potential photovoltaic applications.

1.2.2 Mathematical models of nanowire growth process

In both VLS and VSS growth, the interface between the semiconductor and the catalyst provides a preferential interface for the incorporation of adatoms into the growing crystal. As mentioned earlier, dissociation of the precursor gas that directly impinges on the seed particle initiates the nanowire growth. Upon formation of the nanowire, two additional surfaces can also influence the growth process: the surface of the substrate and that of the nanowire that are exposed to the gas source as well. Due to a concentration gradient, atoms can diffuse on these surfaces towards the liquid metal to get incorporated into the nanowire at the liquid-solid interface. Therefore, the nanowire growth may occur not only due to the flux directly impinging on the liquid metal, but also
from the surface diffusion of adatoms on the substrate and the nanowire sidewalls to the metal drop. The overall growth process, shown in Figure 1-6, consists of the following steps:

1. Diffusion in the gas phase
2. Reaction on the vapor-liquid interface
3. Diffusion in the liquid phase
4. Crystallization on the liquid-solid interface
5. Diffusion from the sidewalls to the drop
6. Diffusion from the substrate along the sidewalls to the drop

Over the past years, several researchers\textsuperscript{13-18} have modeled the nanowire growth process to better understand the competing mechanisms which determine the nanowire growth properties.

Particular attention has been paid to the effect of the nanowire diameter on the growth rate in order to explain the contradictory results experimentally observed for SiNW growth, represented in Figure 1-7, where the growth rate has been shown to increase,\textsuperscript{19,20} decrease\textsuperscript{21} or remain independent\textsuperscript{22} with wire diameter. For micron sized Si whiskers grown in CVD system using SiCl\textsubscript{4}/H\textsubscript{2}, the experiments done by Givargizov showed an increase in growth rate (V) with increasing diameter.\textsuperscript{19} Later on, Kikkawa investigated
Figure 1-7: Nanowire length/growth rate as a function of diameter indicating an increasing dependence for (a) micron sized\textsuperscript{19} and (b) nanoscale wires\textsuperscript{20}, (c) independent relation\textsuperscript{22} and (d) decreasing function\textsuperscript{21}.

the dependency of SiNW length on diameter for smaller size nanowires using SiH\textsubscript{4} as the gas source and found a similar trend, smaller nanowires grow slower than the larger ones.\textsuperscript{20} However, surprisingly diameter independent growth of SiNWs from Si\textsubscript{2}H\textsubscript{6} precursor was reported by Kodambaka \textit{et al.}\textsuperscript{22} using real-time in situ ultrahigh vacuum TEM system. They discussed that in their system the dissociative adsorption of disilane
is rate controlling step in which case the growth rate is independent of the Si chemical potential in the droplet and consequently independent of diameter. Using molecular beam epitaxy (MBE) as the synthesis method, Schubert et al. reported a growth rate increase with decrease of diameter.\textsuperscript{21} Time independent growth rate was also observed. They attributed this behavior to the surface diffusion of Si adatoms on the nanowire and their incorporation into the droplet. Considering that the former occurs so fast that the flux of Si is limited by the latter, a diameter dependence and time independence of the growth rate is expected.

To reconcile the discrepancies in the growth rate dependence on wire diameter, Schmidt et al.\textsuperscript{13} has approached the problem by discussing the rate-determining step of the process. Usually steps (2) and (4) in Figure 1-6 are debated as the rate-limiting step since steps (1) and (3) are fast and don’t impede the growth process. Kodambaka et al.,\textsuperscript{22} Bootsma et al.,\textsuperscript{23} and Lew et al.\textsuperscript{24} proposed that the precursor gas decomposition at the vapor-liquid interface (step 1 in Figure 1-6) is the rate-limiting step since the Si nanowire growth rate was found to linearly increase with the precursor gas partial pressure. In contrast, based on the dependence of growth rate on the crystallographic orientation of the wires, Givargizov suggested that the crystallization step (step 4 in Figure 1-6) controls the growth.\textsuperscript{19} The model developed by Schmidt argues both cases to examine whether the observed complex behavior in Figure 1-7 can be explained through different rate-limiting steps. In this model, the growth rate is given as:\textsuperscript{13}

\begin{equation}
  v = v_0 + \frac{\omega_1 \alpha_1}{\omega_1 - \alpha_1} \frac{2\Omega^s \gamma^s}{r} \tag{1-1}
\end{equation}

in which \(v_0\) is the growth rate as \(r \to \infty\), \(\Omega^s\) and \(\gamma^s\) are respectively the molar volume and
surface tension of solid silicon. $\omega_1$ and $\alpha_1$ are the slopes of crystallization and incorporation velocities as a function of droplet supersaturation, respectively. In both limits when the crystallization step governs the growth (corresponding to $\alpha_1 \to \infty$) or the incorporation step limits the process (corresponding to $\omega_1 \to \infty$), the growth rate exhibits an increase with wire diameter for $\omega_1 > 0$ and $\alpha_1 < 0$. Negative $\alpha_1$ corresponds to the usual situation where the incorporation rate increases with increasing pressure. This suggests that the rate-determining step could be the interplay of both incorporation and crystallization steps and the assumption of a single rate-limiting step may not be valid. Thus, a discussion on which step is the rate-determining one cannot account for the observed differences in growth rate-diameter dependence. The decrease in growth rate with diameter can be explained if $\alpha_1 > 0$. $\alpha_1$ can be positive if the incorporation velocity exhibits a maximum which was shown to be possible. When $\alpha_1 \to 0$, the growth rate is independent of diameter and in agreement with results by Kodambaka et al.

To develop the model, Schmidt et al. only considered the incorporation, diffusion and crystallization steps and neglected the incorporation through the substrate and nanowire sidewalls. Consequently, as stated by the authors, their model cannot be applied for MBE systems.

Some other reports have been published in which the diffusion of surface adatoms from the substrate is included but the kinetic processes on the sidewalls are completely neglected. Some studies have taken into account the contribution of adatoms impinging and diffusing on the nanowire sidewalls, but have not considered the substrate adatoms or have ignored the influence of the Gibb-Thomson effect in the drop on the resulting diffusion flux. Recently, Dubrovskii et al. presented a general model for the
vertical growth rate of a nanowire which considers the overall contributions of diffusion flux from the substrate and the nanowire sidewalls as well as direct impingement onto the drop, taking into account the influence of the Gibbs-Thomson effect in the liquid drop caused by its curvature. Under steady state conditions, the adatom concentrations on the substrate surface \( n_s \) and on the nanowire sidewalls \( n_f \) are described by:\textsuperscript{18}

\[
D_s \Delta n_s + J \cos \alpha - \frac{n_s}{\tau_s} = 0 \tag{1-2}
\]

\[
D_f \frac{d^2 n_f}{dz^2} + J \sin \alpha - \frac{n_f}{\tau_f} = 0 \tag{1-3}
\]

with \( \Delta \) being the two-dimensional Laplace operator in the substrate plane, \( r \) and \( z \) being the radial and vertical coordinate, \( D_s, D_f \) being the diffusion coefficients, and \( \tau_s, \tau_f \) being the effective lifetimes on the substrate and the sidewalls, respectively.

Four boundary conditions required to solve Eqs. (1-2) and (1-3) can be written as:\textsuperscript{18}

\[
\left. \frac{dn_s}{dr} \right|_{r \to \infty} = 0 \tag{1-4}
\]

\[
D_s \left. \frac{dn_s}{dr} \right|_{r=R_{NW}} = -D_f \left. \frac{dn_f}{dz} \right|_{z=0} \tag{1-5}
\]

\[
\sigma_s n_s(R_{NW}) = \sigma_f n_f(0) \tag{1-6}
\]

\[
k_B T \ln[\sigma_f n_f(L)] = \mu_L^\infty + \frac{2\gamma \Omega_L}{R_{NW}} \tag{1-7}
\]

The first boundary condition states the adatom concentration far away from the NW assuming that the interwire separation is large. The second condition is simply the continuity equation at the NW foot. The third condition indicates the continuity of chemical potential at the NW foot, with \( \sigma_s \) and \( \sigma_f \) being the areas of elementary adsorption sites at the surface and the sidewalls, respectively. Finally, the fourth condition is the
continuity of chemical potential at the NW top which considers the Gibbs-Thomson effect of elevation of chemical potential in the drop with radius $R_{NW}$ caused by its curvature. $\Omega_l$ is the volume per atom in the liquid drop. The adatom concentrations are assumed as being dilute ($\sigma n << 1$) so that their chemical potentials equal $k_B T \ln(\sigma n)$.

By solving Eqs. (1-2) and (1-3), the diffusion flux from the substrate and the nanowire sidewalls to the metal particle can be obtained as $j_{diff}(L) = -D_f 2\pi R d\sigma_f(L)/dz$, which in turn when added to the flux directly impinging the liquid droplet and multiplied by the factor $\Omega_s/\pi R_{NW}^2$ results in the overall nanowire growth rate. Typically the substrate contribution into the NW growth becomes prevalent in the molecular beam epitaxy with shorter nanowire lengths and it can be neglected for CVD growth where NWs are typically much longer than the adatom diffusion length (normally of order of 100 nm).\(^{18}\) Since the focus of this study is on the CVD growth of nanowires, only the simplified form of Dubrovskii’s model is therefore represented here where the direct impingement and the sidewall diffusion mainly account for the NW growth rate $(dL/dt)$.

$$GR_{NW} = \frac{1}{\theta_\infty} \Omega_s 2J \left[ 1 - \frac{\exp \left( \frac{R_{GT}}{R_{NW}} \right)}{\theta_{sl}} \right] + \Omega_s J \left[ 1 - \frac{\exp \left( \frac{R_{GT}}{R_{NW}} \right)}{\theta_{fl}} \right] \frac{2\lambda_f}{R_{NW}} \quad (1-8)$$

$\theta_{vs}, \theta_{sl},$ and $\theta_{fl}$ are the effective supersaturation of the vapor with respect to the surface adatoms, the effective supersaturation of the surface adatoms with respect to the liquid phase and the effective supersaturation of sidewalls with respect to the drop. The quantities $R_{NW}$ and $R_{GT} = (2\gamma \Omega_t)/(k_B T)$ respectively denote the nanowire and the
characteristic Gibbs-Thompson radius with \( k_B \) being the Boltzmann constant, and \( T \) being the growth temperature. \( \lambda_f \) indicates the diffusion length on the nanowire sidewalls and is equal to \( \lambda_f = \sqrt{D_f \tau_f} \), where \( D_f \) is the diffusion coefficient of the adatoms and \( \tau_f \) is their effective lifetime on the nanowire sidewalls. \( J \) is the impingement flux of a molecule from kinetic theory of gases described as 
\[
J = P / \sqrt{2 \pi MRT}
\]
with \( P \) and \( M \) being the partial pressure and molar mass of the precursor, respectively.

Eq. (1-8) implies that the length-diameter dependence at typical values of diffusion length (more than few tens of nanometers) and Gibbs-Thomson radius (few nanometers) is a function that has one maximum. Thus, the thick nanowires for which the growth is dominated by surface diffusion exhibit a decreasing behavior; whereas, the growth of thin nanowires is mainly controlled by the Gibbs-Thomson effect, due to which the net flux of atoms incorporated into the catalyst decreases as the wire diameter decreases reducing the supersaturation in the catalyst. Since the supersaturation in the catalyst drives the nanowire growth, the wire growth rate decreases at smaller wire diameter.

1.3 Research objectives

Investigation on the growth kinetics of group IV nanowires as well as their structural and physical properties has not been only limited to the impact of nanowire diameter, but the influence of other parameters such as growth temperature and precursor partial pressures have also been examined over the past years. Detailed reviews of
previous work on Si, Ge, and Si$_{1-x}$Ge$_x$ individual and heterostructured nanowires in CVD systems are accordingly given in chapters 3 to 6. An interesting point of these studies is that the majority of them have primarily used SiH$_4$ and GeH$_4$ as their Si and Ge containing gas sources for low temperature CVD. However, as an alternative Si source, Si$_2$H$_6$ is of interest since it is more reactive than silane and therefore may enable higher growth rates at lower temperature and lower partial pressures. The lower thermal stability of disilane could also be an advantage to enable the growth of Si$_{1-x}$Ge$_x$ nanowires over the entire composition range at lower temperatures (275°C to 375°C) which are more compatible with the range of conditions typically used for Ge nanowire growth and in turn may enable the fabrication of different types of heterostructures.

Consequently, a systematic study has been developed in this thesis to explore the growth of group IV single and heterostructured nanowires from Si$_2$H$_6$ and GeH$_4$ precursors. Chapter 2 describes the nanowire low pressure chemical vapor deposition (LPCVD) reactor used for the studies. A description of experimental procedure including the substrate preparation and the nanowire growth process along with details concerning the characterization methods is included.

The growth kinetics of individual SiNWs from Si$_2$H$_6$ is represented in chapter 3. The effects of growth parameters, namely growth temperature and precursor partial pressure, on the growth rate of SiNWs using disilane are investigated and the results are compared to that obtained with silane. In addition, to gain a better insight into the SiNW growth process, the results are also compared with Si films deposited under similar conditions inside the same reactor. Moreover, a numerical model is developed to simulate the gas phase above the substrate as well as to predict the deposition rate of
silicon films from both silane and disilane gas sources. The importance of contributing species into the growth process and their differences in Si film deposition vs. nanowire growth is discussed.

In chapter 4, the synthesis parameter space is first determined for undoped GeNWs and the influence of growth conditions on their morphology is examined. The outcome of this study combined with the results on SiNWs helps to better select the growth parameters to synthesize Si$_{1-x}$Ge$_x$ nanowires from disilane gas. Besides the undoped GeNWs, an additional interesting but as yet not explored structure is the radial p-n junction GeNW. The advantages that such structures offer for photovoltaic cells compared to planar geometry, discussed earlier, make radial p-n junction GeNW a great candidate for thermophotovoltaic (TPV) applications. This has motivated the studies of chapter 4 to investigate the influence of growth parameters on the fabrication of radial p-n junction GeNWs. Once the most favorable growth condition for undoped GeNWs is determined, the viability of the formation of p-type GeNWs and the effect of dopant on their structure is investigated. Then, the deposition of n-type Ge thin films are initially investigated on sapphire substrates as calibration runs in order to find the uniformity and dopant concentration of n-type Ge shell for GeNW coating and eventually the optimum conditions are transferred to GeNWs to regrow a smooth n-type shell on their sidewalls.

Considering the higher reactivity and higher adsorption probability of Si$_2$H$_6$ compared to SiH$_4$, the use of this precursor to grow Si$_{1-x}$Ge$_x$ nanowires is examined in chapter 5, with the aim to tune the chemical composition of nanowires over a wide range at a constant temperature, which is technologically attractive but has not been achieved through SiH$_4$ and GeH$_4$ gases due to differences in the thermal stabilities of these two
sources. The variations in Ge fraction as well as growth rate of $\text{Si}_{1-x}\text{Ge}_x$ nanowires with growth parameters such as temperature and precursor partial pressures are studied and a kinetic model is developed to explain the observed results.

Finally, the information gathered from single nanowire synthesis in chapters 3-5 is used to fabricate Ge/SiGe and SiGe/Si axial heterostructures described in chapter 6. Both of these structures are of interest for fundamental studies of nanowire heteroepitaxy as well as device development. Moreover, producing monodisperse silicon nanowires (SiNWs) with uniform length has been a critical difficulty in the bottom-up assembly of nanowire devices. SiNWs grown by the VLS method attach firmly to the growth substrate, making it difficult to remove them for single nanowire device assembly. Currently, ultra-sonic agitation is frequently used to break the wires off of the substrate; however, they break at differing lengths, degrading the yield of successful wire integration and device fabrication. SiGe/Si axial-heterostructure nanowires are investigated as a possible approach to overcome this problem by selectively etching the SiGe segment away and releasing the SiNW segment with more uniform length required for high-yield assembly.

1.4 References


Chapter 2

Experimental Procedure and Characterization Techniques

In order to synthesize group IV single and heterostructured nanowires examined in this thesis, a low-pressure chemical vapor deposition (LPCVD) system was used. While the main focus here is the fabrication of nanowires, in some cases thin film depositions are also investigated for comparison and calibration purposes. Both nanowire and film growths were carried out in the same reactor. The LPCVD system consists of five sections: gas delivery system, gas manifold, reactor, exhaust and safety panel (as shown in Figure 2-1). The first part of this chapter describes the reactor of the system and the furnace temperature profile that will be used later on in chapters 3 and 4 for modeling purposes. For more information on the remaining parts of the system, interested readers should refer to Dr. Kok-Keong Lew’s thesis.\(^1\) The second part of this chapter discusses the materials studied in both nanowire and thin film geometries, the substrates used for the fabrications and their preparation methods, and the procedure of the growths. Finally, the characterization techniques involved in the study of nanowires as well as those used for thin film examination will be stated in the last section.

2.1 Reactor configuration

The hot wall reactor of the system is a horizontal quartz tube with a diameter and length of 1 and 32 inch, respectively, which is located inside a Linberg Blue M single
zone tube furnace (HTF55322A) (part (3) in Fig. 2-1). To perform the growths, the substrates were placed horizontally on a quartz boat and were pushed into the center of the reactor (schematically represented in Fig. 2-3(b)), where the temperature was constant over a 6-inch length. The temperature controller of the furnace at the center of the reactor was calibrated by Dr. Robert Burke, a former Materials Science and Engineering graduate student in our group, and it was found that the actual temperature in the center of the reactor is approximately 20°C higher than the set point on the furnace controller (Fig. 2-2). Therefore, during the growths, a set point of 20°C lower than the desired temperature was chosen to correct for the difference.

Figure 2-1: (a) The LPCVD system illustrating the (1) gas delivery system, (2) system gas manifold, (3) reactor, (4) exhaust and (5) safety panel.
The furnace temperature was also measured at different positions along the reactor to obtain the temperature profile, as shown in Figure 2-3 (b). Three temperature zones with linear dependencies on position were specified, as follows:

\[ T(z) = (0.15T_a - 43.28)z - 0.35T_a + 300 \]

\[ T(z) = 14.83z + 1.01T_a - 207 \]

\[ T(z) = T_a \]

where, \( z \) denotes the position inside the tube in inch and \( T_a \) denotes the actual temperature at the center of the furnace in Kelvin.

![Figure 2-2: Temperature calibration of the furnace controller](image)

Throughout this thesis, the reported temperatures refer to the actual temperature at the center of the reactor. However, for model calculations (discussed in chapters 3 and...
4), in order to obtain the time evolution of the precursor as it traverses along the tube and to simulate the gas phase above the substrate, the measured axial temperature gradients were taken into account.

![Schematic diagram](image)

Figure 2-3: (a) Schematic representation of the reactor tube inside the furnace (b) Axial temperature profile of the reactor. 

![Temperature profile graph](image)
2.2 Nanowire growth process

2.2.1 Semiconductor materials investigated

The LPCVD system was equipped with two Si sources – silane (10% SiH$_4$ in H$_2$, Air Products Inc.) and disilane (1% Si$_2$H$_6$ in H$_2$, Voltaix Inc.) – and a Ge precursor (2% GeH$_4$ in H$_2$, Voltaix Inc.), which were used as the semiconductor source gases during the growths. For in-situ doping purposes, phosphine (500 ppm PH$_3$ in H$_2$) and diborane (2% B$_2$H$_6$ in H$_2$), both from Voltaix Inc., were also available as n-type and p-type dopants, respectively.

Different growth conditions were first investigated for undoped Si, Ge, and Si$_{1-x}$Ge$_x$ single nanowires and the influence of the growth parameters on the structure and the growth rates were examined. To grow SiNWs, both Si$_2$H$_6$ and SiH$_4$ sources were utilized and the results were compared. Synthesis of SiGe nanowires were solely conducted by Si$_2$H$_6$ precursor. In case of Si and Ge nanowires, the growth rates of nanowires and the activation energy of the processes were also compared with that of the thin films deposited under similar conditions to obtain more information on the VLS process.

Once the growth conditions were optimized for single nanowires, different kinds of axial heterostructures such as Ge/Si$_{1-x}$Ge$_x$ and Si$_{1-x}$Ge$_x$/Si were fabricated and their properties were studied. In addition, the formation of radial p-n junction was investigated for GeNWs by growing a p-type GeNW core and coating it with an n-type shell. The optimum condition for the deposition of n-type Ge shell was obtained through studies on undoped and n-type Ge thin films served as calibration runs.
2.2.2 Substrate Preparation

Si and Si$_{1-x}$Ge$_x$ single nanowires as well as Ge/SiGe and SiGe/Si heterostructured nanowires were all grown on oxidized silicon wafers. A 3 nm thick layer of Au was sputter deposited on the oxide-coated Si substrates and served as the catalyst for the VLS growth.

To grow GeNWs, both Si(111) and Ge(111) substrates were used. The Si wafers were coated with 3 nm Au thin films. Prior to deposition, the oxide was removed from the silicon substrates using 10:1 buffered oxide etch (BOE) to assist the epitaxial growth. In the case of Ge substrates, either undoped or p-type (Ω-cm) wafers were used and were covered with 50 nm Au nanoparticles. For nanoparticle application, the substrates were first rinsed with ethanol and then shaken in a solution of 10% APTMS (3-aminopropyltrimethoxysilane) in ethanol for 5 min. The substrates were then rinsed four times with ethanol and DI water, consecutively and were transferred into the Au colloid solution (200 µL Au in 3000 µL DI water) and were shaken for 5 min. The negatively charged citrate stabilized Au nanoparticles attach to the positively charged amine groups on the substrate surface resulting in Au monolayer. Finally, the substrates were rinsed with DI water three times, were blow dried with N$_2$ and were immediately loaded into the reactor.

Growth of GeNWs was also examined using the low cost anodized aluminum oxide (AAO) coated glass substrates which are of interest to reduce the cost of device fabrication. The substrates were provided by Illuminex Corporation. Figure 2-4 schematically illustrates the process used to fabricate these substrates. A thin layer of
Figure 2-4: Schematic of the fabrication process of AAO-coated glass substrate indicating (a) anodic oxidation of Al thin film and (b) formation of AAO membrane pores through anodization and etching in which (c) Au is electrodeposited.\textsuperscript{3}

Indium tin oxide (ITO) of about 100-150 nm thick is deposited onto the glass substrate followed by an aluminum film approximately 1 μm thick deposited by e-beam evaporation. To form the AAO membrane, the aluminum films are anodized using oxalic acid. To ensure a clear opening through the AAO pores, anodization is carried out at a
constant voltage 20-200 V to form a base array of ~30-60 nm diameter nanopores until
the pores reach the desired depth. Al₂O₃ is then etched in a 10 wt % phosphoric acid
solution to widen the pores and open them at the bottom to fully expose the ITO layer.
The average pore size in these samples was around 98 ± 23 nm in diameter. Finally,
approximately 25 nm of Au, which serves as the catalyst for VLS growth, is electrolessly
deposited into the pores. During the growth, the gas precursor diffuses into the pores,
supersaturates the alloy and initiates the growth forming the nanowires. By growing the
wires outside the pore and coating them with a shell, radial p-n junctions can also be
formed.

For thin film deposition experiments, the growths were carried out on sapphire
substrates. Prior to deposition, wafers were subsequently cleaned by ultrasonication in
acetone and isopropanol alcohol (IPA) for 10 min followed by a rinse in DI water. The
wafers were then dried with nitrogen and loaded into the reactor.

2.2.3 Nanowire synthesis

After preparing the samples, they were transferred into the reactor on a quartz boat.
For all the growths, the boat was pushed to the center of the tube inside the hot zone,
except for the n-type coating of GeNWs when the boat was shifted 3 cm closer to the gas
inlet to reduce the gas depletion. The system was then pumped down to a pressure of
about 5×10⁻⁴ Torr. To check the possibility of any leak, the system was isolated from the
pump by closing the appropriate valve and the increase in the reactor pressure due to
outgassing was monitored. A pressure rise at a rate faster than ~ 8e⁻⁵ Torr/min would
indicate a possible leak in the reactor or system gas manifold, upon which the run would be aborted to find the source of the leak. Once the leak check was passed, the nitrogen gas was introduced into the system at the maximum value of MFCs for about 5 minutes. It was drained from the run line afterwards and was replaced with H₂ gas. The furnace was turned on and the temperature was increased to the growth temperature at a rate of 15°C/min. If the precursor lines had not been used in over a week, they were flushed with N₂ at this time. The sample was annealed at the growth temperature for approximately 20 min, during which the reactor pressure was set to the growth pressure using a throttle valve. The growth was initiated by flowing the required precursors through the reactor at the appropriate flow rate in the range of 5-90 sccm. Additional H₂ was provided to the reactor to keep the total flow rate constant at 100 sccm. After the growth was complete, the precursors were switched to vent and the system was cooled down at a rate of 60°C/min. The throttle valve pressure controller was opened, and the H₂ was drained from the lines along with the precursors. Once the gases were drained, N₂ was reintroduced into the reactor, the throttle valve was closed, and the reactor was brought up to atmospheric pressure to unload the sample.

2.3 Characterization

After the growths, the as-grown nanowires were analyzed by a FEI-Philips XL-20 scanning electron microscope (SEM) to verify the success of the growth. Cross-sectional images were taken and the lengths of individual nanowires were measured using ImageJ software. The length was measured from the substrate edge to the catalyst at three
different sections of the sample and was averaged for 20-50 wires. The growth rate was obtained by dividing the length of the nanowire by the growth time defined by the time gas precursors containing growth species were flown through the reactor. To obtain the relation between the length of the nanowires and their diameter, field emission SEM (FE-SEM, Leo 1530) with higher resolution of 2.5 nm at 5 kV was used.

The structural properties of the nanowires as well as their growth directions were assessed using Philips 420 and JEOL 2010F field emission transmission electron microscopes (TEM). The nanowires were released from the substrate by ultrasonication and suspended in isopropanol. The suspension was then dropped on a lacy carbon-coated copper grid and examined in the microscope. The JEOL 2010F TEM is equipped with an x-ray energy dispersive spectrometer (XEDS) for elemental analysis in scanning TEM mode, which was used to probe the composition of individual Si$_{1-x}$Ge$_x$ nanowires for a few batches of nanowire samples. The characterizations on JEOL TEM were entirely performed by Dr. Xiaojun Wang, a research associate at the Materials Research Institute and TEM images on Philips 420 were taken by the author.

The composition of the as-grown Si$_{1-x}$Ge$_x$ nanowires was also determined from grazing incidence x-ray diffraction (GIXRD, PANalytical X’pert PRO with Cu tube) performed on array of as-grown nanowires. This method is less expensive and less time consuming than TEM analysis yet it has shown to produce reliable results comparable to that obtained from TEM.\textsuperscript{4} The small angle of the incidence beam to the sample (2 degree) in GIXRD enables a surface sensitive diffraction to extract the lattice parameter of the SiGe nanowires as a bulk. The lattice parameters ($a$) were determined from peak locations using Jade software by MDI, Inc. of Livermore, Ca. (version 8). The Si$_{1-x}$Ge$_x$
nanowire compositions were then estimated using Vegard’s law given in Eq. (2-1) that linearly relates the lattice parameter of the alloy in bulk materials with the fraction and lattice parameter of its constituents and has been shown to be effective for nanowires as well.\

\[
a_{Si_{1-x}Ge_x} = (1 - x)a_{Si} + xa_{Ge}
\]  

(2-1)

In case of thin films, the thickness was determined by a Tencor P-10 profilometer. To perform a profilometry test on Ge and Si samples for determining the thickness, half of the layer was masked off by black wax and the other half was etched using 3% hydrogen peroxide (etch rate of about 1 μm/hr) at room temperature for Ge films and 30% potassium hydroxide (KOH) at about 80°C for Si films. This forms the required step for profilometry measurements. The wax was then removed using a standard opticlear.

To study the electrical properties of the films, Hall measurements were carried out on squared samples. Indium dots were placed in each corner of the sample and heated on a hot plate to form ohmic contacts. The contacts were examined on a curve tracer to confirm that they exhibit the ohmic linear I-V characteristics.

Finally, for Ge p-n diodes fabricated both in planar and nanowire geometry, the current-voltage characteristics were measured in the dark using a 4155A HP semiconductor parameter analyzer. These experiments were performed by Dr. Chito Kendrick, a current postdoc in our group. Square pieces of the samples were cleaned in acetone, isopropanol and DI water and were blown dry with N₂. A square area in the center of the sample was then masked using photoresist and the n-type Ge layer outside this region was etched away by reactive ion etching using an SF₆ plasma for 3 minutes.
The photoresist was then stripped away and indium contacts were placed on the n-type Ge layer and the p-type Ge substrate.

2.4 References

Chapter 3

Comparison of Silane and Disilane as Source Gases in the Growth of Si Nanowires

3.1 Introduction

Over the course of intensive research on SiNW growth, different techniques have been employed to fabricate these wires with chemical vapor deposition (CVD) being one of them. In this method, depending on the growth conditions, namely the temperature and the operation pressure, different gaseous silicon sources can be used to fabricate the nanowires such as silicon tetrachloride (SiCl₄), silane (SiH₄) and disilane (Si₂H₆).

Being more stable than nonchlorinated silanes, SiCl₄ requires higher temperatures to thermally crack. Hence, it is typically chosen as the silicon precursor for high temperature (ranging from about 800°C to 1200°C), atmospheric pressure CVD.¹⁻⁶ If used in combination with H₂, SiCl₄ facilitates the homoepitaxial growth of SiNWs on a Si substrate by producing hydrochloric acid (HCl) which etches the unwanted oxide from the substrate surface.⁵ The high temperature growth of SiNWs with SiCl₄ gives the advantage of a broader choice of catalyst materials such as Cu; however, the diffusion of catalyst droplets due to Ostwald ripening at elevated temperatures, which causes the larger catalysts to grow at the expense of smaller ones, yields a wide diameter distribution.⁶

In contrast to SiCl₄, SiH₄ and Si₂H₆ decompose at lower temperature and enable fabrication of SiNWs at temperature ranges typically between 400°C to 650°C.⁷⁻¹³ Using
these precursors additionally allows for growths at lower pressures. \( \text{SiH}_4 \) with partial pressures in the range of 0.075-7 Torr has been mainly used as the Si source gas in LPCVD systems to investigate the SiNW growth kinetics in the low pressure regime. The influences of temperature, \( \text{SiH}_4 \) partial pressure and reactor total pressure on the growth rate have been examined. An exponential dependence of growth velocity on inverse temperature was observed and apparent activation energies in the range of 11-55 kcal/mol depending on the growth conditions were deduced.\(^{8,10,11,13-15}\) An approximately linear increase in growth rate with increasing \( P_{\text{SiH}_4} \) between 0.13-0.65 Torr was reported at \( T = 500^\circ \text{C} \).\(^8\) Examining the effect of total pressure on the growth rate showed a Langmuir-type behavior with a second-order dependence at lower pressures followed by a slower change in growth rate at higher pressures which eventually approached a maximum.\(^{16}\)

In contrast to \( \text{SiH}_4 \), disilane has been less frequently applied particularly in LPCVD systems to study the growth kinetics of SiNWs. As an alternative precursor for low temperature CVD, however, \( \text{Si}_2\text{H}_6 \) is of interest since it is more reactive than silane and therefore enables higher growth rates at lower temperature and lower partial pressures. In the past, the advantages of disilane precursor in enhancing the growth rate and/or lowering the growth temperature have been exploited to deposit silicon films for microelectronic device fabrication. Both effects have been shown to be beneficial for amorphous silicon (a-Si) deposition, where recrystallization of the a-Si films grown by \( \text{Si}_2\text{H}_6 \) leads to higher quality polycrystalline films with larger grain sizes,\(^{17-21}\) suitable for device applications.\(^{22,23}\) The capability of \( \text{Si}_2\text{H}_6 \) in increasing the deposition rate has also been advantageous for in-situ phosphorous doping of silicon films. It is well known that
the deposition rate for the SiH₄ system drops dramatically with the addition of phosphine (PH₃) as it blocks surface sites for silane adsorption.²⁴,²⁵ Several reports demonstrated that replacing silane with disilane could reduce this negative effect significantly, due to the formation of silylene (SiH₂), a highly reactive species that can compete very effectively for surface sites with phosphine.²⁶-²⁸

With recent emerging interest in nanowires, Si₂H₆ has once again become an attractive gas source for SiNW growth specifically in ultra high vacuum chemical vapor deposition (UHV-CVD) systems with partial pressures as low as 2×10⁻⁸ Torr. By using an in-situ transmission electron microscope (TEM) for real-time observations, some aspects of the SiNW growth process have been examined in these systems over the past years. For example, it was found that during nanowire growth at very low disilane pressure and high temperature, Au diffuses on the nanowire surface and migrates from the smaller droplets to the larger ones due to Ostwald ripening which changes the length, shape, and sidewall properties of the nanowires.²⁹ Continued coarsening eventually consumes the Au droplet and terminates the VLS growth. It was shown that by introducing oxygen, the diffusion of Au reduces and this enables the growth of long untapered SiNWs.³⁰ Sawtooth faceting was also observed on the SiNW sidewalls whenever no stable orientations parallel to the growth direction existed.³¹

By using disilane in a UHV-TEM system, Kodambaka et al. explored the relation between the growth rate and the nanowire diameter (as described in chapter 1) and observed an independent behavior that was explained assuming the dissociative adsorption of disilane on the Au catalyst is the rate-limiting step.³²

In addition, disilane was utilized in UHV systems to investigate the growth
kinetics of SiNWs from solid catalysts such as Cu\textsuperscript{33} and Pd\textsuperscript{34} through the vapor-solid-solid (VSS) mechanism when the growth occurs by ledge propagation at the solid silicide/silicon interface.

While the majority of reports on using Si\textsubscript{2}H\textsubscript{6} for SiNW growth are under UHV conditions, there are few studies that have applied disilane as their Si source in LPCVD systems. Kawashima and his coworkers used it in a cold wall reactor to illustrate the correlation between the shape of the Au catalysts and those of SiNWs in the VLS mechanism.\textsuperscript{35} Rod-like SiNWs were grown from Au metals with relatively small aspect ratio (the ratio of long to short axis of Au), whereas polycrystalline catalysts with high aspect ratio resulted in branched nanowires. They also showed that insufficient supply of Si source to the liquid catalyst at lower total or disilane partial pressures induces instability in the Au-Si liquid and causes kinking in the nanowire as well as diffusion and formation of Au particles on the nanowire sidewalls.\textsuperscript{36} Upon examining the morphology of SiNWs grown by Si\textsubscript{2}H\textsubscript{6}, Akhtar \textit{et al.} observed a size dependence where smaller nanowires with diameters below 16 nm grew defect free, while larger wires grown in the [111] and [110] directions exhibited periodic and multiple twins, respectively.\textsuperscript{37,38} Further studies of SiNW growth from Si\textsubscript{2}H\textsubscript{6} to investigate the effect of substrate on the growth process revealed that additional annealing at certain conditions were required prior to the growth to form SiNWs on amorphous Si substrate while the growth on crystalline Si(100) substrate occurred without annealing.\textsuperscript{39,40}

Moreover, applying the reactive Si\textsubscript{2}H\textsubscript{6} precursor in a hot wall LPCVD system enabled the fabrication of millimeter-long SiNWs (Figures 3-1(a) and (b)) with growth rates of approximately 130 times larger than that obtained from SiH\textsubscript{4} at T= 400°C, as
shown in Figure 3-1(c). The importance of reactant decomposition kinetics was suggested in determining the observed growth rates; however, the gas phase chemistry and the species involved in the growth mechanism have not been examined in detail.

Figure 3-1: (a) SEM image of millimeter long SiNWs grown at 400°C and $P_{\text{SiH}_6} = 2.3$ Torr for 30 min. (b) A series of 20 SEM images of a 2.3 mm-long SiNW transferred on SiO$_2$/Si substrate. (c) SiNW length vs. growth time for Si$_2$H$_6$ at 400°C (black), SiH$_4$ at 400°C (red) and SiH$_4$ at 450°C (blue).

Hence, this chapter represents a systematic study of the growth kinetics of SiNWs using Si$_2$H$_6$ in a hot wall LPCVD system. First, the effects of growth parameters on the
growth rate of SiNWs using disilane are investigated and the results are compared to that obtained with silane. In addition, to gain a better insight into the SiNW growth process, the results are also compared with Si films deposited under similar conditions inside the same reactor. Next, a numerical model is developed to simulate the gas phase above the substrate as well as to predict the deposition rate of silicon films from both silane and disilane gas sources. The importance of contributing species into the growth process and their differences in Si film deposition vs. nanowire growth is discussed.

3.2 Growth conditions

The entire growths of Si nanowires and Si thin films were conducted at constant total reactor pressure and total flow rate of 13 Torr and 100 sccm, respectively, with the exception of some Si thin films which were deposited at \( P_t = 3 \) Torr. 3 nm Au thin films deposited on oxidized Si wafers and sapphire substrates were used to grow SiNWs and Si films, respectively. By using 10 sccm of \( \text{Si}_2\text{H}_6 \) at 450°C as well as 500°C, the lengths of SiNWs were measured at three different times to examine the dependency of the growth rate on growth duration. The effect of precursor partial pressure on the growth velocity was investigated at \( T = 450^\circ\text{C} \) by changing the flow rate of \( \text{Si}_2\text{H}_6 \) from 5 to 90 sccm and that of silane from 9-50 sccm. At the same temperature, the relation between the growth rate and the nanowire diameter was obtained by choosing \( P_{\text{Si}_2\text{H}_6} = 0.013 \) Torr and \( P_{\text{SiH}_4} = 0.65 \) Torr. The consequence of growth temperature variations on the nanowire growth rate was studied at two \( \text{Si}_2\text{H}_6 \) partial pressures of 0.013 Torr as well as a \( \text{SiH}_4 \) partial pressure of 0.65 Torr and temperatures over a range of 450°C to 525°C were examined.
The influence of temperature was also investigated for Si thin films deposited using both SiH$_4$ and Si$_2$H$_6$ under the same growth conditions applied for SiNWs, except for longer growth durations. In case of Si films deposited from disilane, a wider range of deposition temperatures from 450°C to 725°C was examined at two total reactor pressures of 13 and 3 Torr. Due to the slow growth rates of Si films from SiH$_4$, higher temperatures than those used for nanowire growth were examined (above 550°C) and the results were extrapolated to the corresponding condition applied for nanowire growth.

### 3.3 Results

In general, as expected, larger growth rates were observed from Si$_2$H$_6$ than SiH$_4$. Cross sectional SEM images in Figures 3-2(a) and 3-2(b) illustrate the comparison at 475°C. Applying an order of magnitude lower disilane partial pressure than silane ($P_{\text{Si}_2\text{H}_6} = 0.065$ Torr and $P_{\text{SiH}_4} = 0.65$ Torr) lead to a growth rate of $2.4 \pm 0.25$ µm/min, which was about eight-fold higher than that obtained with silane ($0.31 \pm 0.04$ µm/min).

In both cases, the nanowires were mainly grown straight with uniform diameters along their length. The wires had smooth surfaces, as shown in the TEM images of Figure 3-3 for SiNWs grown by Si$_2$H$_6$. Au particles were found in a small region near the tip which may have occurred due to Au diffusion from the catalyst on the sidewalls either during growth or after growth while cooling the reactor down to room temperature. As can be seen, the length of Au covered surface of NW sidewall increased from ~50 nm at 450°C to ~140 nm at 500°C, which can be explained considering enhanced mobility of the gold at higher temperatures as well as longer times required to cool down the sample.
As mentioned earlier, the gold diffusion on the nanowire surface has been previously observed and is of more concern in UHV systems when the growth rate could be affected. However, as Hertog et al. showed, this phenomenon is reduced at higher precursor partial pressures ($P_{SiH_4} \geq 1\text{ mbar}$). They have reported Au diffusion on the wire surfaces both during and after growth and discussed that the presence of Au clusters near the catalyst more likely occurs after the growth which is believed to be the case in our studies. Otherwise, a continuous loss of catalyst material during the growth would
have resulted in tapered nanowires. In addition, the presence of Au during growth could have induced faceting of the NW sidewalls,\textsuperscript{41} neither of which was observed here.

![Figure 3-3: TEM images of SiNWs grown from Si$_2$H$_6$ using a partial pressure of 0.013 Torr at (a) 450°C and (b) 500°C. The arrows indicate the length of Au covered sidewalls to be \~50 nm in (a) and \~140 nm in (b).](image)

Whether Au diffusion occurs during growth or upon subsequent cooling, the amount of gold loss is so small that it would not have any impact on the growth rate. However, there are indeed two other important factors that may present larger effects on the growth velocity and may contribute to nanowire length variation; \textit{i.e.} the growth incubation time and the nanowire diameter. Therefore, for accuracy and reliability of the length measurements, it is important to understand the consequence of these two parameters under the growth conditions examined which will be considered in the next two sections.
3.3.1 The variation of the length of SiNWs with growth time

Figure 3-4 represents the influence of growth duration on the nanowire length for SiNWs grown from disilane at 450°C and \( P_{Si2H6} = 0.013 \) Torr. A linear proportionality was found with an intercept at zero, suggesting a negligible incubation time for the onset of nanowire growth. Similar conclusion can be made for nanowires grown at higher temperatures under the same disilane partial pressure, as it was shown by Kalache et al. that the incubation time reduces with temperature.\(^{42}\) The authors have observed a reduction in incubation time from 180 s at 450°C to 15 s at 650°C for SiNWs grown by SiH\(_4\).

Figure 3-4: Plot of SiNW length vs. growth time for Si\(_2\)H\(_6\) at (●) 450°C and (■) 500°C with a partial pressure of 0.013 Torr.

It was demonstrated later on that not only the growth temperature but also the precursor pressure affects the incubation time. By using Si\(_2\)H\(_6\) at 400°C, Clement
obtained incubation times of 68, 47, and 30 s for 0.3, 1, and 3 mTorr disilane pressures. An order of magnitude increase in pressure lowered the incubation time by more than half. Considering that the lowest partial pressure examined in this study is at least twice larger than those applied by Clement, further reduction in incubation time (less than 30 s) would not be surprising.

In case of SiH₄, the lengths of SiNWs as a function of growth duration were examined in the past by Dr. Nimmaatoori using the same LPCVD reactor employed in this study (Fig. 3-5). Similar behavior to that of disilane was observed with estimated incubation time as small as 10 s for nanowires with diameter of 10 nm.

![Figure 3-5](image)

Figure 3-5: Length dependence of SiNWs grown using SiH₄ on the growth time.

Based on the results observed here as well as prior literature, the assumption of negligible incubation time for growth rate calculations seems to be reasonable. Thus, the
growth rates were calculated by dividing the nanowire length by the overall growth time.

### 3.3.2 The influence of nanowire diameter on the growth rate

SiNWs with a wide range of diameters from as small as 14 nm to as large as 100 nm were observed for both SiH$_4$ and Si$_2$H$_6$ grown nanowires. A typical size histogram for each case is shown in Figure 3-6. The majority of the nanowires were in the diameter range between 30-50 nm. For nanowires with diameter below ~ 30 nm, the growth rate increased with increasing diameter, while it remained almost constant for thicker nanowires, as illustrated in Figure 3-7. The observed behavior is consistent with the Gibbs-Thomson effect (discussed in chapter 1) that results in reduction of the growth rate of SiNWs as the diameter is decreased until the diameter reaches a critical value.

The observed growth rate dependency on wire diameter is similar to that reported by Kikkawa et al.$^{10}$ and Dubrovskii et al.$^{44}$ for SiNWs grown from SiH$_4$. In the former work, the Gibbs-Thomson effect was observed for small nanowires in diameter ranges of 3-40 nm grown at 430°C and P$_{\text{SiH}_4}$=0.75 Torr, whereas the latter reported similar effect for larger wires of 90-310 nm in diameter grown at 500°C using a silane partial pressure of 5.5 mTorr.

For disilane grown SiNWs, the independent growth rate-diameter behavior observed by Kodambaka et al. does not contradict the results in the present study, as only nanowires with diameters of 50-150 nm were investigated there.$^{32}$ In that diameter range, it was also observed in this study that the growth rate remained almost unchanged.
For further studies on the dependency of growth rate on partial pressure and temperature, wires larger than ~ 30 nm in diameter, whose length stayed almost the same, were chosen to calculate the growth rate. The average growth rates were obtained with
the corresponding standard deviations to account for the slight dispersion in length.

Figure 3-7: Dependence of growth rate on diameter of SiNWs grown from (a) disilane at $P_{\text{Si}_{2}\text{H}_{6}} = 0.013$ Torr and (b) silane at $P_{\text{SiH}_{4}} = 0.65$ Torr. The growth temperature for both cases was 450°C.
3.3.3 Growth rate as a function of partial pressure

For SiNWs grown from Si$_2$H$_6$ at a constant temperature of 450°C, the nanowire growth rate clearly exhibited a nonlinear dependence on partial pressures between 0.0065-0.117 Torr (Figure 3-8). This is different than the linear behavior reported by Kodambaka et al.\textsuperscript{32} However, careful attention should be given to the range of pressures investigated in each study. Prior work only focused on very low Si$_2$H$_6$ partial pressures in the range of $10^{-8}$-$10^{-5}$ Torr, for which a linear relation could be expected, as will be discussed in section 3.4.3.

Similar to disilane, a nonlinear form can be proposed for growth rate of SiNWs grown from SiH$_4$ as a function of partial pressure, even though it was not possible to examine smaller partial pressures due to the higher concentration of the available silane tank. Further reduction of $P_{\text{SiH}_4}$ below 0.12 Torr would have required changes in either total flow rate or total reactor pressure, both of which would have changed the residence time of the gas that may affect the growth. Moreover, a linear function predicts a growth rate larger than zero for a zero partial pressure which is not reasonable. This argument seems to hold for data found by Lew et al., shown in Figure 3-9, who also examined the influence of similar partial pressures used in the present study (0.13-0.65 Torr) on the growth rate, only at higher temperature (500°C).\textsuperscript{8} Their data seem to indicate a nonlinear dependence rather than the linear relation proposed by the author.

Section 3.4.3 debates two possible phenomena that may yield a nonlinear behavior of SiNW growth rate when the partial pressure is changed.
Figure 3-8: Correlation between SiNW growth rate and partial pressure of disilane and silane gas sources at a constant temperature of 450°C.
Figure 3-9: Dependence of SiH$_4$ partial pressure on Si nanowire growth rate at a constant temperature of 500°C and a constant total pressure of 13 Torr.$^8$

3.3.4 Temperature dependence of growth rate

The variations in growth rate with temperature for Si thin films have extensively been investigated in the past for both silane and disilane gases. Based on the chosen temperature range as well as the pressure, which determines the rate-limiting step of the growth process, a wide range of activation energies has been reported. Thus, for meaningful comparison between SiNW and Si thin film processes it is important that both samples are grown under the same conditions. This section summarizes the results of such studies performed in this thesis.

3.3.4.1 The effect of temperature on deposition rate of Si thin films

The Si films deposited under the growth conditions examined in this study
showed the features of amorphous silicon. Examples of Raman spectra for the films grown from Si$_2$H$_6$ at temperatures and total reactor pressures of 550°C and 13 Torr as well as 600°C and 3 Torr are depicted in Figure 3-10. If the films were polycrystalline Si, only one peak would be visible which is centered approximately at 520 cm$^{-1}$. The three peaks observed around 480 cm$^{-1}$, 340 cm$^{-1}$ and 170 cm$^{-1}$ indicate the common peaks for a-Si.$^{45}$

![Raman Spectra of amorphous Si films deposited at different temperatures and total reactor pressures.](image)

**Figure 3-10:** Raman Spectra of amorphous Si films deposited at different temperatures and total reactor pressures.

When the temperature-deposition rate dependency of Si films from SiH$_4$ was investigated at a total pressure of 13 Torr (Figure 3-11(a)), the common Arrhenius behavior with an apparent activation energy ($E_a$) of 43 ± 1 kcal/mol was observed, in very good agreement with values reported in ref. 46 and references therein.
Figure 3-11: Deposition rate as a function of temperature for Si films grown using (a) SiH$_4$ at partial and total pressures of 0.65 Torr and 13 Torr, respectively and (b) Si$_2$H$_6$ at different total pressures of (▲) 13 Torr and (■) 3 Torr, but the same P$_{Si2H6} = 0.013$ Torr.
In case of Si$_2$H$_6$, when the precursor with an inlet partial pressure of 0.013 Torr was flown through the reactor at $P_t = 3$ Torr, a similar trend to what has previously been reported in the literature$^{18,19,21,47-50}$ was observed; the deposition rate increased sharply as the temperature was increased up to 550°C; while, above that temperature it showed a tendency to saturate (Figure 3-11(b)). However, using the same inlet $P_{Si_2H_6} = 0.013$ Torr at higher total pressure of 13 Torr resulted in an unusual behavior where the deposition rate increased from 0.2 nm/min at 450°C to 1.6 nm/min at 550°C, followed by a decrease to 0.8 nm/min at 600°C and an additional increase up to 3 nm/min upon further raising the temperature to 725°C.

At $P_t = 3$ Torr, $E_a = 42 \pm 2$ kcal/mol extracted for Si films deposited from disilane at lower temperatures was similar to that of silane, but it reduced to 31 ± 5 kcal/mol at $P_t = 13$ Torr. Activation energies ranging from about 30 to 55 kcal/mol, depending on the deposition condition, have been previously measured for Si film growth by disilane pyrolysis. The results can be explained considering the surface reactions and the precursor flux which controls the rate of deposition. This will be discussed in detail in section 3.4.2.

### 3.3.4.2 The effect of temperature on growth rate of SiNWs

Studies on the growth rate of SiNWs from Si$_2$H$_6$ as a function of temperature revealed a change in the slope of the graph at about 485°C (Fig. 3-12), below which the exponential increase in growth rate with increasing temperature is more pronounced, while it slows down above that point. Assuming an Arrhenius behavior, an apparent
activation energy of 31 ± 3 kcal/mol was calculated for temperatures from 425 to 485°C. The obtained $E_a$ is larger than the available values of 12.2 kcal/mol$^{32}$ and 14.8 kcal/mol$^{51}$ for Si$_2$H$_6$ at temperatures between 500 and 650°C extracted in UHV systems, suggesting that a different rate-determining step may be controlling the growth process due to the differences in growth conditions. To the best of our knowledge, there is no activation energy reported for SiNWs related to the use of this precursor at lower temperatures and pressures examined in the present study.

![Graph](image)

Figure 3-12: Temperature dependency of the growth rate of SiNWs of 30-80 nm in diameter grown from (●) Si$_2$H$_6$ and (■) SiH$_4$ gases at $P_{Si2H6} = 0.013$ Torr and $P_{SiH4} = 0.65$ Torr. The total reactor pressure is 13 Torr in both cases.

Interestingly, the obtained $E_a$ in the lower temperature range is similar to that obtained for the Si thin films deposited using Si$_2$H$_6$ gas under the same conditions.
(31 ± 5 kcal/mol in Figure 3-11), even though the growth rates of SiNWs are about 3 orders of magnitude higher.

The observed result for disilane at lower temperatures differed from SiH₄ in that for the latter the \( E_a \) of NW growth (32 ± 1 kcal/mol) was smaller than the one found for Si thin film (43 ± 1 kcal/mol). This is in agreement with Schmid’s observation who also found a lower \( E_a \) for axial SiNW growth (19 kcal/mol) compared to that of non-catalyzed radial growth on nanowire sidewalls (29 kcal/mol).¹¹ This behavior is typically attributed to the catalytic activity of the Au droplet which reduces the activation energy of the SiH₄ decomposition upon its impingement on the Au surface.

It should be mentioned that among the literature data for Si nanowire growth using SiH₄, there are large differences in reported apparent activation energies. Table 3-1 summarizes those values. The activation energy obtained in the present study falls between the values reported previously. The variation in \( E_a \) may have been caused by different growth conditions used in various studies. This effect becomes more significant in hot wall CVD reactors where gas phase reactions could play an important role. It may also be an effect of nanowire diameter; the smaller the nanowire diameter, the greater the activation energy. It was demonstrated by Chen⁵² that the activation energy of crystallization step at the liquid-solid interface depends on the nanowire diameter and is reduced with increasing diameter. If the rate determining step in the VLS mechanism is assumed to be the crystallization step, the observed changes in activation energy may be explained. However, such conclusion would be valid only if the growths are all carried out under the same conditions; since the changes in growth parameters may impact the rate-determining step of the process similar to the Si thin film deposition. In addition, as
discussed in chapter 1, it is difficult to determine whether the adsorption on the vapor-liquid interface is the rate limiting step or the crystallization at the liquid-solid interface and this is still an open question among researchers.

Table 3-1: Activation energies of SiNW growth using SiH₄ in CVD systems

<table>
<thead>
<tr>
<th>Growth conditions</th>
<th>( E_a ) (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_1 ) (Torr)</td>
<td>( P_{SiH_4} ) (Torr)</td>
<td>( T ) (°C)</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>600-800</td>
</tr>
<tr>
<td>4</td>
<td>0.08</td>
<td>450-600</td>
</tr>
<tr>
<td>2.25</td>
<td>0.045</td>
<td>560-650</td>
</tr>
<tr>
<td>13</td>
<td>0.65</td>
<td>400-500</td>
</tr>
<tr>
<td>13</td>
<td>0.65</td>
<td>425-500</td>
</tr>
<tr>
<td>13</td>
<td>0.65</td>
<td>450-500</td>
</tr>
<tr>
<td>735</td>
<td>7.35</td>
<td>365-495</td>
</tr>
</tbody>
</table>

3.4 Discussion

In order to interpret the observed results, a model was developed to examine the gas phase chemistry and the impact of different species formed due to the pyrolysis of disilane and silane precursors during their residence time in the reactor. The contributions of both homogenous and heterogeneous decompositions were taken into account to simulate the silicon growth and to predict the deposition rate of silicon films.
3.4.1 Reactor modeling

Under the growth conditions examined in this study, the reactant mixture flows through the tube reactor in the laminar flow regime (29 < Re < 148). With a steady state assumption and in terms of dimensionless variables, the governing two dimensional mole balance equation for each species can be written as:\(^5^3\)

\[
\frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial X_i}{\partial \xi} \right) = p \left[ \frac{\partial}{\partial \psi} \left( X_i \right) - \frac{1}{Pe} \frac{\partial}{\partial \psi} \left( \frac{\partial X_i}{\partial \psi} \right) + Da_i \left( X \right) \right] \tag{3-1}
\]

where, \( p = \frac{t_D}{\tau_c} \), \( Pe = \frac{t_z}{\tau_c} \), \( Da = \frac{\tau_c}{t_R} \) denote the transverse Peclet number, the axial Peclet number and the Damköhler number, respectively. The characteristic times for transverse diffusion \((t_D)\), axial diffusion \((t_z)\), chemical reaction \((t_R)\) and convection \((\tau_c)\) are defined as follows:

\[
t_D = \frac{r^2}{D_{im}}, \quad t_z = \frac{L^2}{D_{im}}, \quad t_R = \frac{C}{R(C)}, \quad \tau_c = \frac{L}{u} \tag{3-2}
\]

It should be mentioned that equation (3-1) is valid only for constant \( C \cdot D_{im} \) (total molar concentration \(\times\) multicomponent diffusion coefficient of the mixture). Since the system is dilute in the reactants, the physical properties such as \( \rho \) and \( \mu \) would approximately equal to that of H\(_2\) and \( D_{im} \) can be replaced by the effective diffusion coefficient for the diffusion of species \(i\) in H\(_2\) \((D_{H2})\) whose value can be calculated using Chapman-Enskog expression:\(^5^4\)

\[
D_{ij} = 0.001858 \sqrt{\frac{T^3 \left( \frac{1}{M_i} + \frac{1}{M_j} \right)}{(P/760)\sigma_{ij}^2\Omega_D}} \tag{3-3}
\]
\[
\Omega_D = \left( 44.54 \tilde{T}^{-4.909} + 1.911 \tilde{T}^{-1.575} \right)^{0.1}
\]
(3-4)

\[
\dot{T} = \frac{kT}{\varepsilon_{ij}} \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} = \frac{1}{2} \left( \sigma_i + \sigma_j \right)
\]
(3-5)

For the temperatures used in the present study, the increase in \( C_i D_{im} \) between the tube inlet and the position of the substrate due to the furnace temperature gradient is only \(~1.5\) times and therefore, it would be a reasonable approximation to assume it is constant.

In the limit of \( t_D \) being very small compared to \( t_z \), \( t_R \), and \( \tau_c \), radial gradients become negligible and equation (3-1) reduces to a one dimensional model. Furthermore, when \( Pe \to \infty \), the axial diffusion would be small and the equation can be simplified to a plug flow model.

Table 3-2 compares the values of these parameters for two extreme temperatures at which the growths were carried out. As can be seen, for both \( \text{SiH}_4 \) and \( \text{Si}_2\text{H}_6 \) precursors, \( Pe \) numbers are sufficiently large so that the axial diffusion can be ignored. Over the entire temperature range, the time required for radial diffusion of \( \text{SiH}_4 \) is much shorter than \( t_z \), \( t_R \), and \( \tau_c \) and accordingly, the first condition applies and it can be considered that the concentration of silane is radially homogenous. Similar approximation is applicable for disilane except only at higher temperatures and higher total pressure. However, as will be discussed, at these conditions, disilane quickly decomposes into silane and hence neglecting the radial gradients would not result in large errors in view of the uncertainty in heterogeneous rate constants.

For the species with high reactive sticking coefficients (\( \text{SiH}_2 \), \( \text{H}_3\text{SiSiH} \), etc.) the rates of volume reactions are so high that they are consumed quickly upon production and only those in the layer adjacent to the wall contribute to surface reactions. This step,
itself, also occurs fast due to the high reactivity of these species on surfaces. Therefore, radial and axial gradients would be negligible for these molecules as well.

Table 3-2: Physical properties and characteristic time scales of SiH₄ and Si₂H₆ sources

<table>
<thead>
<tr>
<th></th>
<th>T=450°C &amp; Pₜ=13 Torr</th>
<th>T=725°C &amp; Pₜ=13 Torr</th>
<th>T=725°C &amp; Pₜ=3 Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_{avg} ) (cm/s)</td>
<td>41</td>
<td>57</td>
<td>248</td>
</tr>
<tr>
<td>( \tau_c ) (s)</td>
<td>1.4</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>SiH₄</td>
<td>131</td>
<td>228</td>
<td>987</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>103</td>
<td>178</td>
<td>771</td>
</tr>
<tr>
<td>( D_{H2} ) (cm²/s)</td>
<td>0.012</td>
<td>0.007</td>
<td>0.0016</td>
</tr>
<tr>
<td>( t_D ) (s)</td>
<td>24</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>( t_z ) (s)</td>
<td>24</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>( t_{R,g} ) (s)*</td>
<td>8400</td>
<td>0.4</td>
<td>0.002</td>
</tr>
<tr>
<td>( t_{R,w} ) (s)*</td>
<td>3192</td>
<td>0.6</td>
<td>0.004</td>
</tr>
<tr>
<td>Pe</td>
<td>17</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

* \( t_{R,g} \) and \( t_{R,w} \) represent the characteristic time scales of homogenous reactions in the gas phase and heterogeneous reactions on the tube wall, respectively. To calculate the latter, a rate constant is defined as \( k_{R,w} = v_{th}S^g/2r \). Section 3.4.1.6 describes how to find \( v_{th} \) and \( S^g \). Based on the foregoing discussion, concentration profiles were obtained using the mole balance equation with a plug flow approximation:

\[
\frac{d(uCX_i)}{dz} = \sum_j v_j r_j - \frac{S}{V} r_i^g
\]  

(3-6)

The gas phase net production of a species \( i (\sum v_j r_j) \) and its depletion on the tube wall \( (r_i^g) \) determines the concentration profile of that species as the gas traverses along
the reactor. The following sections describe the mechanism of gas phase reactions and the surface decompositions included in this study and illustrate how the related reaction rates were obtained.

3.4.1.1 Homogeneous reaction mechanism

As the gas precursor traverses through the reactor, complex multiple reactions happen in the gas phase which lead to the formation of large number of reactive intermediates that can take part in the silicon deposition process. Homogenous decomposition in the Si-H system can involve as many as 31 reaction steps, of which listed in Table 3-3 have been considered in the present study. It will be shown later on that among different species, SiH₄, SiH₂, and Si₂H₆ have the main contributions to the deposition rate under the growth conditions examined here and the influence of other species is negligible. Therefore, the simplified mechanism is sufficient to describe the deposition process.

The unimolecular reactions proceed through collisional excitation as represented qualitatively in Eqs. (3-7) and (3-8):56

\[
M + R \rightleftharpoons M + R^* \quad (3-7)
\]
\[
R^* \rightarrow \text{Products} \quad (3-8)
\]

Here, R is the reactant molecule, \( R^* \) is the collisionally activated reactant molecule with sufficient internal energy for unimolecular reaction and \( M \) represents any gas phase molecule including another \( R \) molecule itself. Considering the production and consumption of \( R^* \) under a steady state condition gives an expression for the overall
Table 3-3: Gas phase reactions and related Arrhenius parameters for the forward reactions.\textsuperscript{55}

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>log(_{10} A_i^*)</th>
<th>(B_i)</th>
<th>(C_i)</th>
<th>(E_{a,i}) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>(\text{Si}_2\text{H}_6 \leftrightarrow \text{SiH}_4 + \text{SiH}_2)</td>
<td>52.88</td>
<td>0.5513</td>
<td>-12.743</td>
<td>62.14</td>
</tr>
<tr>
<td>G2</td>
<td>(\text{SiH}_4 \leftrightarrow \text{SiH}_2 + \text{H}_2)</td>
<td>23.33</td>
<td>0.9615</td>
<td>-4.383</td>
<td>58.77</td>
</tr>
<tr>
<td>G3</td>
<td>(\text{SiH}_2 + \text{Si}_2\text{H}_6 \leftrightarrow \text{Si}_3\text{H}_8)</td>
<td>11.45</td>
<td>1/3</td>
<td>0</td>
<td>0.40</td>
</tr>
<tr>
<td>G4</td>
<td>(\text{Si}_2\text{H}_6 \leftrightarrow \text{H}_3\text{SiSiH} + \text{H}_2)</td>
<td>31.63</td>
<td>0.5513</td>
<td>-6.060</td>
<td>59.32</td>
</tr>
<tr>
<td>G5</td>
<td>(\text{SiH}_4 + \text{H}_3\text{SiSiH} \leftrightarrow \text{Si}_3\text{H}_8)</td>
<td>11.14</td>
<td>1/3</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>G6</td>
<td>(\text{H}_3\text{SiSiH} \leftrightarrow \text{H}_2\text{SiSiH}_2)</td>
<td>6.44</td>
<td>1.0</td>
<td>0</td>
<td>5.30</td>
</tr>
<tr>
<td>G7</td>
<td>(\text{H}_2\text{SiSiH}_2 \leftrightarrow \text{Si}_2\text{H}_2 + \text{H}_2)</td>
<td>30.83</td>
<td>0.5513</td>
<td>-6.060</td>
<td>57.03</td>
</tr>
<tr>
<td>G8</td>
<td>(\text{SiH}_2 + \text{Si}_3\text{H}_8 \leftrightarrow \text{Si}<em>4\text{H}</em>{10})</td>
<td>13.04</td>
<td>0</td>
<td>0</td>
<td>0.41</td>
</tr>
</tbody>
</table>

The units of A depend on the reaction order, but are given in terms of moles, cubic centimeters, and seconds.

The unimolecular rate constant, \(k_{uni} = k_1 k_3 [M] / (k_3 + k_2[M])\), which shows a complicated dependency on the total pressure. At low enough \(P_t\), \(k_3 >> k_2[M]\), the rate constant becomes proportional to the total pressure; whereas, at high total pressure, \(k_2[M] >> k_3\), the rate constant is independent of \(P_t\). The region between these two extremes would be the so-called falloff region. At the total pressures examined in this study (3 and 13 Torr), the unimolecular reactions would be either in the low pressure limit or in the falloff region where the activation energy and the \(A\)-factor of the Arrhenius relation changes as a function of pressure. Thus, the following approximation with the related parameters also listed in Table 3-3 can be used for the forward reactions when small ranges of pressure are investigated:

\[
k_i = A_i P^B T^C \exp(-E_{a,i} / RT)
\]  (3-9)
with $P$ being the total reactor pressure in Pa.

A pressure dependency of $1/3$ was assumed for bimolecular reactions G3 and G5 based on the experimental evidence.

For the reverse reactions, the rate constants can be calculated from the pressure independent equilibrium constants as:

$$k_{-i} = \frac{(9.869 \times 10^{-6} \, RT)^{\Delta n_i}}{K_{P,i}} \, k_i$$  (3-10)

Here, $\Delta n_i$ is the summation of the stoichiometric coefficient of species involved in reaction $i$, $R$ is the ideal gas constant in J/(mol.K) and $K_{P,i}$ represents the equilibrium constant of reaction $i$ in partial pressure of species which can be obtained from the Gibbs free energy of the reactions, as follows:

$$\ln K_{P,i} = -\Delta G_i / RT$$  (3-11)

$$G / RT = a_1 (1 - \ln T) - 1/2 a_2 T - 1/6 a_3 T^2$$
$$- 1/12 a_4 T^3 - 1/20 a_5 T^4 + a_6 / T - a_7$$  (3-12)

The polynomial coefficients used in Eq. (3-12) to obtain Gibbs free energy can be found in ref. 55.

### 3.4.1.2 Heterogeneous surface decomposition

In general, the heterogeneous reaction steps of Si containing precursors include adsorption, surface decomposition (conversion of surface species), surface diffusion, lattice incorporation, and H$_2$ desorption. By means of different techniques such as temperature programmed desorption (TPD), secondary ion mass spectroscopy (SIMS),
and optical second-harmonic generation (SHG), several groups have investigated the chemisorption of SiH₄, Si₂H₆ as well as H₂ on different surfaces like Si(111)⁵⁷-⁵⁹ and Si(100)⁶⁰-⁶⁴, with the latter being the most common. Hence, data on Si(100) were used to extract the reaction rate constants for modeling purposes. For SiH₄ and Si₂H₆, there are also reports on kinetic parameters extracted for the CVD of polycrystalline Si films deposited in hot⁴⁶,⁶⁵ and cold⁶⁶ wall reactors, which also will be considered here.

3.4.1.2.1 Silane surface decomposition chemistry

Silane is believed to adsorb dissociatively on Si(100) through a dual site mechanism. A six-step reaction scheme presented below was proposed to illustrate the heterogeneous reaction steps of silane on Si(100) surface.⁶⁴

\[
\begin{align*}
\text{SiH}_4(g) + 2* & \to \text{SiH}_3^* + H^* \\
\text{SiH}_3^* + * & \to \text{SiH}_2^* + H^* \\
2\text{SiH}_2^* & \to 2\text{SiH}^* + H_2(g) \\
2\text{SiH}^* & \to 2\text{Si}^* + H_2(g) \\
2H^* & \to H_2(g) + 2* \\
\text{Si}^* & \to \text{Film} + *
\end{align*}
\]

(S1)  
(S2)  
(S3)  
(S4)  
(S5)  
(S6)

The symbol * indicates a free surface site. The dangling bonds are consumed in the adsorption and decomposition steps and are regenerated by desorption of H₂ in reactions S4 and S5. In practice, there is no difference between species H* and SiH* except that in SiH* the H is bonded to the silicon atom which originates from the gas phase precursor. Therefore these reactions have the same rate parameters.

Reactions S2 and S3 are believed to be fast and the decomposition of the monohydride – a first order surface reaction - is known to be the rate limiting surface step
of Si deposition at lower temperatures (roughly below 900 K) that controls the deposition rate considering that reaction S6 is a fast surface diffusion step.\textsuperscript{64}

It should be noted that the surface reaction rate of silane may be manipulated in the presence of H\textsubscript{2}. Indeed, there is some experimental evidence that hydrogen suppresses the growth rate under certain conditions.\textsuperscript{46} By adsorbing on silicon surfaces and saturating the dangling bonds through the following reaction path, H\textsubscript{2} may inhibit silane adsorption and therefore, its effect should be included in the model:

\[
H_2 + 2* \leftrightarrow 2H^* \tag{S7}
\]

### 3.4.1.2.2 Disilane surface decomposition chemistry

It has been proposed that the adsorption/decomposition of disilane on a silicon surface forms two trihydride (SiH\textsubscript{3}) fragments through the following step:\textsuperscript{67}

\[
Si_2H_6(g) + 2* \rightarrow 2SiH_3^* \tag{S8}
\]

Similar to the case of silane, the formed SiH\textsubscript{3} species decompose to monohydride species by reactions S2 and S3 and the consecutive recombinative desorption of hydrogen opens up surface sites for further disilane adsorption, which has been assumed to be second order in free surface sites as implied by Eq. S8.

Recently, Ferguson demonstrated that two distinct pathways exist for disilane adsorption: direct and trapping-mediated chemisorption.\textsuperscript{61} In the direct chemisorption mechanism, the incident molecules have enough energy to react immediately with the surface sites on their impact. However, in the trapping-mediated channel, the precursor to chemisorption is the physisorbed disilane molecule. An incident molecule gets trapped
on the surface by losing some energy upon its collision with the surface. Once physisorbed, the molecule can then either chemisorb or desorb depending on the surface temperature. Since the activation energy of disilane chemisorption ($E_c$) is lower than that for desorption ($E_d$), $E_c - E_d = -6.57 \pm 0.16 \text{ kcal/mol}$, molecules tend to desorb rather than chemisorb as the temperature is increased. Therefore, the chemisorption probability drops as the temperature is raised (Figure 3-13).

![Figure 3-13: Initial chemisorption probability vs. temperature for $T_{\text{gas}}=T_{\text{surface}}$.]

It can be seen that the trapping-mediated pathway dominates adsorption at lower temperatures and the contribution of direct chemisorption to the adsorption probability becomes significant at $T > 600$K. To calculate the initial adsorption probability of Si$_2$H$_6$ at zero hydrogen surface coverage, a third order polynomial that considers the contribution of both direct and trapping-mediated channels can be employed.$^{67}$ For the case when the gas temperature equals the temperature of the surface, disilane initial
adsorption probability within the temperature range of 700 K < T < 1200 K would be as follows:

\[
S_0 = 1.6 - 4.215 \times 10^{-3} T + 3.812 \times 10^{-6} T^2 - 1.163 \times 10^{-9} T^3
\]  
(3-13)

3.4.1.2.3 Surface decomposition chemistry of highly reactive species

Apart from SiH\textsubscript{4} and Si\textsubscript{2}H\textsubscript{6}, other species are highly reactive molecules that can adsorb and decompose along different paths. For these species, it is suggested that interaction with surface occurs not only through direct chemisorption on free surface sites but also by insertion into surface Si-H bonds\textsuperscript{46}. The species adsorbed on Si-H bonds may then decompose either by interaction with remaining free surface sites or without any further interaction with surface sites. The following mechanism represents both pathways:

\[
\begin{align*}
\text{Si}_{\alpha_i}H_{\beta_i} + m_i* & \rightarrow (\text{Si}_{\alpha_i}H_{\beta_i})^* \\
\text{Si}_{\alpha_i}H_{\beta_i} + H^* & \rightarrow (H\text{Si}_{\alpha_i}H_{\beta_i})^* \\
(H\text{Si}_{\alpha_i}H_{\beta_i})^* & \rightarrow x\text{Si} + H^* + \frac{y}{2}H_2 \\
(H\text{Si}_{\alpha_i}H_{\beta_i})^* + m_i* & \rightarrow H^* + (\text{Si}_{\alpha_i}H_{\beta_i})^* \\
(\text{Si}_{\alpha_i}H_{\beta_i}) + (y - z - m_i)* & \rightarrow x\text{SiH}^* + (y - x - z)H^* + \frac{z}{2}H_2
\end{align*}
\]

(S9) (S10) (S11) (S12) (S13)

\(m_i\) is the number of sites required for the chemisorption of species \(i\) upon impingement (first step of chemisorption).

3.4.1.3 Coverage of free surface sites

When etching or evaporation of Si atom does not occur during the deposition
(below \(\sim 1100\ \text{K}\)), the contribution of different species to the growth process equals their adsorption rates. The surface decomposition rate of a species \(i\) can be then expressed as:

\[
r_i' = k_i,\ C_iC_* + k_{i,H}C_i(N_{Si} - C_*)
\]

(3-14)

or identically as:

\[
r_i' = S_{iR}J_i
\]

(3-15)

\(k_i,\) and \(k_{i,H}\) are respectively the adsorption rate constants on free and occupied surface sites of species \(i\), which correlate to the reactive sticking probability of a molecule \(S_{iR}\) as follows:

\[
k_{i,*} = \frac{1}{4} \frac{v_{th,i}}{NT} \frac{S_0}{(N_{Si})_{iR}} \quad \text{(3-16)}
\]

\[
S_{iR} = \begin{cases} S_{0,i} \theta_*^2 & \text{for SiH}_4 \text{ and Si}_2\text{H}_6 \\ S_{0,i} & \text{for other species} \end{cases}
\]

(3-17)

For SiH\(_4\) and Si\(_2\)H\(_6\), \(k_{i,H}\) equals zero and for the rest of the species, it is assumed to be the same as \(k_{i,*}\). \(C_*\) and \(\theta_* = \frac{C_*}{N_{Si}}\) respectively denote the concentration and the fraction of free surface sites and \(S_{0,i}\) is the initial adsorption probability of a molecule at zero hydrogen surface coverage \((\theta_* = 1)\). \(v_{th,i} = \sqrt{8RT/\pi M_i}\) represents the thermal velocity of species \(i\) with \(M_i\) being the molar mass.

In Eq. (3-15), \(J_i\) denotes the impingement flux of a molecule and can be described by the kinetic theory of gases, \(J_i = P_i/\sqrt{2\pi M_iRT}\). Careful attention should be given to the partial pressure of the reactant molecule, \(P_i\), which drops from \(P_{i,g}\) in the bulk gas to \(P_{i,s}\) at the substrate surface due to the diffusion of gas through the stagnant boundary.
layer of thickness $\delta$ formed adjacent to the substrate.

Based on Fick’s law, the corresponding diffusion flux across the boundary layer is given by
\[ J_{i,gs} = \frac{D_{im} (P_{i,g} - P_{i,s})}{\delta RT} \]
assuming a linear concentration profile for the laminar boundary layer. From Eq. (3-14), the flux consumed by the reactions taking place at the surface of the growing film is
\[ J_{i,s} = \frac{k_{i,s} P_{i,s}}{RT}, \]
where
\[ k_{i,s} = k_{i,*} C_s^m + k_{i,H} (N_{Si} - C_s) = \frac{1}{4V_{th}S^R}. \]

At steady state, $J_{i,gs} = J_{i,s}$ and therefore,
\[ P_{i,s} = \frac{P_{i,g}}{1 + k_{i,s}\delta/D_{im}}. \]

Now, if $k_{i,s} >> D_{im}/\delta$, the film growth will be dominated by the mass transfer of molecules to the surface and
\[ P_{i,s} = \frac{P_{i,g}}{k_{i,s}\delta/D_{im}}. \]
On the other hand, when $k_{i,s} << D_{im}/\delta$, surface reactions will control the growth, in which case $P_{i,s} = P_{i,g}$.68

For the temperature range examined in the present study at total reactor pressure of 13 Torr, the surface rate constants ($k_{i,s}$) of SiH$_4$ and Si$_2$H$_6$ sources, respectively, are 0.0002 and 0.0027 cm/s at 450°C and 1.06 and 139 cm/s at 725°C. Under these conditions, even if it is assumed that the boundary layer above the substrate is entirely extended in radial direction, meaning that $\delta$ takes its maximum value and equals the diameter of the reactor (1 in), $D_{im}/\delta_{max}$ of SiH$_4$ and Si$_2$H$_6$ will respectively equal to 51 and 40 cm/s at 450°C and 90 and 70 cm/s at 725°C. It can be seen that for SiH$_4$ precursor the condition of $k_{i,s} << D_{im}/\delta$ holds over the entire temperature range indicating that the growth is restricted by surface reactions and therefore $P_{i,s}$.
approaches $P_{i,g}$. Similar argument is valid for Si$_2$H$_6$, particularly at lower temperatures at which Si$_2$H$_6$ molecule takes part into the growth process. For higher temperatures, as will be discussed, disilane quickly decomposes into silane before the gas arrives at the substrate and thus, its mass transport through a boundary layer is of no importance.

Concerning highly reactive species, as mentioned earlier, they are consumed quickly upon production due to their high rates of volume reactions and therefore, only those in the layer next to the substrate contribute to film growth.

Returning to Eq (3-14), $C_*$ and consequently $\theta_*$ can be calculated from the surface hydrogen coverage of all H* and SiH* species ($\theta_{H^*}$) involved in the decomposition mechanisms discussed above by making a steady state approximation and assuming that they are the most abundant species on the surface. Summation of surface hydrogen coverage and surface free sites equals the total number of surface sites per cm$^{-2}$, $N_{Si}$. As shown by Holleman et al., the following equation can be used in cases when the contribution of multiple species coexists:\textsuperscript{46}

$$\theta_* = \left(1 + N_{Si}^{m_*-1} \sum n_i K_i [A_{\alpha}, H_{\beta_*}](\theta_*)^{(m_*-1)} \right)^{-1}$$ (3-18)

Equation (3-18) considers the fact that different species formed due to gas phase reactions compete for the same surface sites and hence their effect should be taken into account. $A$ in $[A_{\alpha}, H_{\beta_*}]$ generally denotes the Si atom in Si containing species except for H$_2$ that $A$ is no element and can be modeled by setting $\alpha = 0$. The contribution of H$_2$ has been included since as discussed earlier, it can also chemisorb on free surface sites and depending on the condition may suppress the deposition rate, especially in case of SiH$_4$. $K_i = k_{i,*} / k_d$, where $k_d$ is the desorption rate constant of H$_2$. $n_i$ indicates the total number
of \( H^* \) and \( SiH^* \) produced during the overall decomposition of species \( i \). For those molecules that adsorb and decompose along the path of reactions S9-S13 (all species except \( SiH_4 \) and \( Si_2H_6 \)), \( n_i \) should be calculated as:

\[
n_i = n_i'(1 + k_{S11} / k_{S12})/(\theta_e^{ni} + k_{S11} / k_{S12})
\]

(3-19)

where, \( n_i' \) is the number of \( H^* \) sites formed along the path that surface sites are involved. The ratio \( k_{S11} / k_{S12} \) is taken to be 0.05. Table 3-4 lists the initial adsorption probability of each species to calculate the related rate constants as well as parameters \( m_i \) and \( n_i \) used in this study to obtain \( \theta_e \).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>( S_0 ) or ( k_d )</th>
<th>( n_i ) or ( n_i' )</th>
<th>( m_i )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( SiH_4 )</td>
<td>( S_0 = 0.0023\exp(-3000/RT) )</td>
<td>3</td>
<td>2</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>( k_d = 8 \times 10^{11}\exp(-47000/RT) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 = 0.006\exp(-3590/RT) )</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( k_d = 1.02 \times 10^{12}\exp(-46610/RT) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Si_2H_6 )</td>
<td>( S_0 = 1.6-4.215 \times 10^{-3} T + 3.812 \times 10^{-6} T^2 - 1.163 \times 10^{-9} T^3 )</td>
<td>6</td>
<td>2</td>
<td>67</td>
</tr>
<tr>
<td>( SiH_2 )</td>
<td>( S_0 = 1 )</td>
<td>1</td>
<td>1</td>
<td>( a )</td>
</tr>
<tr>
<td>( H_3SiSiH )</td>
<td>( S_0 = 1 )</td>
<td>5</td>
<td>2</td>
<td>( a )</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>( Si(100): S_0 = 10^{(-12\pm0.5)}\exp(-17300\pm2300/RT) )</td>
<td>2</td>
<td>2</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>( Si(111): S_0 = 7 \times 10^{(-12\pm0.5)}\exp(-20000\pm2300/RT) )</td>
<td></td>
<td></td>
<td>59</td>
</tr>
</tbody>
</table>

\( a \): assumed \( n_i' \) and \( m_i \) in this study based on the decomposition mechanism of such species along the path of reactions S9-S13.
Among the Si containing species included in Table 3-3, only the interaction of disilane, silane and silylenes (SiH₂ and H₃SiSiH) with free surface sites were considered to calculate θ, and the influence of other species have been neglected due to their very low concentrations.

The data adopted for the initial adsorption probability of Si₂H₆ on Si(100) surfaces taken from Ferguson et al., to the best of our knowledge, is the only inclusive quantity available that considers the variation in S₀ with temperature. Other reports have assumed a constant value. The reactive sticking coefficient of Si₂H₆ has also been extracted from polycrystalline Si data. To do so, one study assumed the dissociative adsorption of disilane on three free surface sites to form three SiH₂ groups and the other considered a simple one-site chemisorption model. However, a dual site mechanism is proposed to be more plausible for disilane chemisorption. Therefore, the values of S₀ on polycrystalline Si films were not examined here.

Regarding the dual site mechanism of SiH₄ adsorption, both Gates and Holleman examined the kinetic parameters. Holleman fitted the reactive sticking coefficient to the growth rate-partial pressure measurements of polycrystalline Si films at 625°C, while Gates obtained the adsorption rate constant from growth rate-temperature experiments of mostly epitaxial films. Their predicted deposition rates for polycrystalline Si films were also comparable to the experimental values. The initial sticking probability reported by Holleman et al. is about twice larger than that obtained by Gates et al. Hence, both values have been examined here. For each case, the related reported values for hydrogen desorption rate constant were employed.

In view of H₂ dissociative adsorption on Si, the small values of its sticking
coefficient makes the accurate measurement difficult and consequently, large disagreement exists in the literature to define its initial adsorption probability. The data given by Bratu et al. on both Si(100) and Si(111) have been chosen here to examine the influence of H₂. The reported S₀ on these two surfaces differ from each other by an order of magnitude. As it will be shown in section 3.4.2, a value of initial sticking coefficient similar to that reported on Si(111) fits better to the experimental results at P₁ = 13 Torr.

3.4.2 Deposition rate of Si films

Using the mole balance equation and considering the formation and consumption of each species as well as its surface decomposition (Eq. 3-6), a set of differential equations of reaction rates is formed, the integration of which yields the concentration transformation along the reactor. The numerical solver, ode15s, in MATLAB software is used to perform the numerical integration through the backward differentiation formulas. From the relative concentrations, the contribution of each species and ultimately the overall deposition rates can then be calculated at the center of the tube (where the substrate was located), as follows:

\[
GR_{film} = \frac{M_{Si}}{\rho_{Si}} \sum_i \alpha_i r_i^s
\]  

(3-20)

where, \(M_{Si}\) and \(\rho_{Si}\) are the molar mass and the density of silicon, respectively, and \(\alpha_i\) is the number of Si in the molecule under consideration.

The calculated deposition rate profiles and their comparison with experimental
data for both silane and disilane precursors at $P_t = 13$ Torr are plotted in Figure 3-14. It should be noted that the data of growth rate from SiH$_4$ should not be directly compared to that of Si$_2$H$_6$ because of the difference in their partial pressures as detailed in the figure caption. The results represent the evaluation of growth rates choosing different data sets of initial sticking probabilities of SiH$_4$ and H$_2$, those given by Gates$^{64}$ and Holleman$^{46}$ for SiH$_4$ and those reported for H$_2$ on Si(100)$^{63}$ and Si(111)$^{59}$ surfaces. An additional case was also examined when the influence of H$_2$ in saturating the dangling bonds was ignored and $k_{H_2}$ was set to zero to calculate the free surface coverage.

As can be seen, applying different values of initial sticking probability had little impact on the predicted deposition rates of Si films under the conditions when SiH$_4$ gas source was used ($P_{SiH_4} = 0.65$ Torr) and the results were in good agreement with experiments. The SiH$_4$ molecule itself is the main species contributing to the deposition below about 525°C, as it is depicted in Figure 3-15(a), and the contribution of SiH$_2$ becomes important only above that point.

In contrast to silane, the choice of $S_0$ made a significant difference in case of Si$_2$H$_6$ precursor mainly above $T = 525$°C. The Si growth from disilane can be divided into three regions:

- **Region 1**: growth temperatures below 525°C, when the decomposition of disilane precursor is less than ~55% and the growth is mainly due to SiH$_2$ with a small contribution from Si$_2$H$_6$ and H$_3$SiSiH. As Figure 3-15(b) illustrates the participation of different species into the growth, the role of the SiH$_4$ molecule in this region is negligible and hence the choice of $S_0$ for SiH$_4$ and H$_2$ does not alter the calculations.
Figure 3-14: Predictions of Si deposition rate from (a) silane at $P_{SiH_4} = 0.65$ Torr and (b) disilane at $P_{Si_2H_6} = 0.013$ Torr. The total pressure is 13 Torr for both cases. The calculated profiles compare the impact of $S_0$ when data of (1) Gates and (2) Holleman are used for SiH$_4$ in combination with the H$_2$ adsorption value on Si (100) surface. For two additional cases, the value of Gates for silane is examined when $S_0$ of H$_2$ equals (3) to that on Si(111) surface and (4) zero. Solid points represent the experimental results.
• Region 2: growth temperatures between 550-600°C. The contribution of Si₂H₆ and SiH₂ species drops and the influence of SiH₄ molecule becomes more significant such that at 600°C - the minimum point observed - it comprises ~92% of the growth rate. At this point, disilane totally decomposes (conversion = 100%) in the reactor before it reaches the substrate and produces silane with a partial pressure less than 0.014 Torr. This is well within the pressure range at which Holleman demonstrated⁴⁶ that H₂ inhibits the adsorption of silane and suppresses the growth rate (ₚ₆₄ < 0.075 Torr at 625°C). Thus, it is expected that an inappropriate selection of sticking coefficient for H₂ would result in significant error in growth rate estimations. A bigger value of $S_{H_2}^R$ would reduce the fraction of free surface sites for silane adsorption and would underestimate the deposition rate from SiH₄, while elimination of H₂ would result in larger growth rates by exposing more surface sites to silane. In addition, temperature is also in a range for which deposition rate depends on the initial sticking probability of SiH₄. Gates showed that for 0.001 < ₚ₆₄ < 0.05 Torr the growth rate of the Si film is independent of the sticking coefficient of SiH₄ only for temperatures below ~500°C.⁶⁴ Taken as a whole, the correct estimation of the deposition rates under these conditions will strongly depend on the proper choice of $S_0$ for SiH₄ and H₂.

• Region 3: growth temperatures above 600°C. At this high temperature
limit, with the depletion of Si$_2$H$_6$ from the gas phase, SiH$_4$ becomes the key component responsible for the growth. In this region, the deposition rate would be the same as if silane precursor were used as the silicon source. A result that was also suggested by Meyerson et al. who found that the difference between the Si deposition rates from Si$_2$H$_6$ and SiH$_4$ gas sources decreased as the temperature was increased such that with similar precursor partial pressures of 0.1 Torr, the deposition rate from Si$_2$H$_6$ gas at 625°C was only 1.75 times higher than that of SiH$_4$.\(^{70}\)

The main difference between Meyerson’s work and this study, however, is that no decrease in the deposition rate was observed in the former. A possible reason could be the shorter residence time used by Meyerson (0.1 s). In fact, by reducing the residence time of the gas from \(~0.6\) s at $P_t = 13$ Torr to \(~0.1\) s at $P_t = 3$ Torr under the same disilane partial pressure, the drop in deposition rate in region 2 disappears, as shown in Figure 3-11(b). Even though the decomposition of the Si$_2$H$_6$ precursor decreases at reduced residence times (e.g. from 100% to \(~56\)% at 600°C) which in turn increases its contribution to the growth rate particularly at higher temperatures, the larger impact is due to the changes in SiH$_2$ which is the main species responsible for the growth, similar to the case of $P_t = 13$ Torr. This indicates the importance of the gas phase reactions at different growth conditions.

To achieve a more comprehensive understanding of the influence of homogenous reactions, the variations of the flux of different species with temperature over the substrate surface were examined assuming no surface decomposition occurs on the reactor wall. Figures 3-16 (a)-(c) illustrate the comparison. As can be seen, the larger
Figure 3-15: Contribution of Si-carrier species to deposition rate as a function of temperature for (a) SiH₄ and (b) Si₂H₆ precursors. The corresponding values of initial sticking coefficients employed in profile (3) of Figure 3-14 is used in the calculations.

concentration of H₂ employed at P₁ = 13 Torr (~ 4 times) enhances the disilane pyrolysis and particularly, the consumption of silylene reactive species through its insertion into
hydrogen molecules (reverse reaction of G2). This gives rise to the dissimilarities in the behavior of SiH2 species whose flux reduces with increasing temperature above 550°C at $P_i = 13$ Torr before the disilane is entirely converted into monosilane, which consequently results in a drop in the deposition rate. Therefore, under a similar residence time, a lower concentration of H2 will reduce the consumption of SiH2 species and the decrease in its flux at higher temperatures. This is demonstrated in Figure 3-16(c) for the conditions that the H2 partial pressure was reduced to 23% of that in Figure 3-16(b) by reducing the total flow rate to 23 sccm and the total reactor pressure to 3 Torr to keep the residence time the same.

Based on the above mentioned discussions, one can realize the importance of SiH2 species and the role that it can play in controlling the Si film deposition when disilane is used in hot wall reactors. More explicitly, if the growth conditions are chosen such that the depletion of SiH2 does not occur in the gas phase and sufficient amount of this molecule impinges on the substrate, then the deposition rate will be controlled by the desorption of H2 from the surface to open up free sites for further adsorption of SiH2. This explains the observed $E_a$ of 42 kcal/mol at $P_i = 3$ Torr, which is close to the SiH decomposition activation energy of 47 kcal/mol listed in Table 3-4. On the other hand, when SiH2 is in short supply, the growth will be regulated by its flux, the situation occurring at $P_i = 13$ Torr because of the reduction in silylene flux due to gas phase reactions. Such condition results in the apparent activation energy of 31 kcal/mol obtained for Si film deposition from a disilane source.

It is worthy to mention that the rate-determining step of the growth process is independent of the Si-containing source and a similar conclusion can be reached for the
Figure 3-16: The gas phase simulation for the temperature dependence of the flux of different species at different residence time and H$_2$ concentrations. An inlet disilane partial pressure of 0.013 Torr was used in all cases. The total flow rate and the total reactor pressure were (a) 3 Torr and 100 sccm, (b) 13 Torr and 100 sccm, and (c) 3 Torr and 23 sccm, respectively.
SiH₄ precursor, as demonstrated in Figure 3-17. With adequate supply of silane at a partial pressure of 0.65 Torr, the growth becomes limited by monohydride decomposition and hydrogen desorption from the surface, resulting in $E_a = 47$ kcal/mol. A reduction in the partial pressure by two orders of magnitude changes the rate-limiting step and the deposition becomes restricted by the precursor flux designated by $E_a = 33$ kcal/mol.

Thus, regardless of the gas source, it is the chosen growth condition that determines the rate-limiting step, being either desorption of H₂ or precursor flux for the conditions examined in the present study.

Figure 3-17: Calculated deposition rate of Si film from SiH₄ gas at a partial pressure of 0.65 Torr (solid line) and 6.5mTorr (dash-dotted line).
3.4.3 Growth rate of SiNWs

Given the VLS mechanism, two pathways exist for the incorporation of Si atoms to the growth process: direct impingement of the source gas on the liquid metal as well as the surface diffusion of Si adatoms on the substrate and the nanowire sidewalls to the droplet (depicted in Figure 1-6). The growth rate of a nanowire is due to the overall contribution of both fluxes. While the substrate involvement into the NW growth becomes prevalent in the molecular beam epitaxy\(^\text{71}\) with shorter nanowire lengths and reduced densities, it can be neglected in CVD processes when NWs are typically much longer than the adatom diffusion length (normally of order of 100 nm\(^\text{44}\)). This is the case for the SiNWs grown in this study with lengths of several microns. Therefore, the modified form of Dubrovskii’s model,\(^\text{44}\) described in chapter 1, is used to illustrate the nanowire growth rate. The proposed expression considers the direct impingement (the first term of Eq. 3-21) and the sidewall diffusion (the second term of Eq. 3-21), taking into account the influence of the Gibbs-Thomson effect in the liquid droplet caused by its curvature.

\[
GR_{NW} = \frac{1}{\theta_{vr}} \Omega_s 2J_{\text{top}} \left[ \exp \left( \frac{R_{GT}}{R_{NW}} \right) \right] \left[ 1 - \frac{\exp \left( \frac{R_{GT}}{R_{NW}} \right)}{\exp \left( \frac{2\lambda_f}{R_{NW}} \right)} \right] + \Omega_s J_f \left[ 1 - \frac{\exp \left( \frac{R_{GT}}{R_{NW}} \right)}{\exp \left( \frac{2\lambda_f}{R_{NW}} \right)} \right] \frac{2\lambda_f}{R_{NW}} \quad (3-21)
\]

While the detailed mechanism of the decomposition of SiH\(_4\) and Si\(_2\)H\(_6\) precursors is known on Si surfaces (implying the nanowire sidewalls), no clear information is available for their adsorption mechanism on the liquid catalysts. Nevertheless, considering the larger growth rates of SiNWs compared to Si films, the adsorption rate on
the liquid droplet is expected to be higher than that on the solid surface. Thus, to obtain the effective supply of the material, different effective adsorption coefficients from the vapor phase to the surface of the liquid droplet \( S_{vl}^R \) and the nanowire sidewalls \( S_{vf}^R \) have been taken into account to get \( J_{\text{top}} = S_{vl}^R J \) and \( J_f = S_{vf}^R J \). \( J \) is the impingement flux of a molecule from kinetic theory of gases as described earlier.

By the dissociative adsorption of precursors on the nanowire sidewalls and formation of SiH\(^*\) surface species through intermediate steps (reactions S1–S3), the surface Si adatoms are created which can then diffuse on the surface before getting trapped by the liquid catalysts. The diffusion length of Si adatoms on the nanowire sidewalls is given by \( \lambda_f = \sqrt{D_f \tau_f} \),\(^{44}\) where \( D_f \) is the diffusion coefficient of the adatoms and \( \tau_f \) is their effective lifetime on the nanowire sidewalls before they are either desorbed from the surface or incorporated into the lattice. With the low growth temperatures used in the present study, the evaporation of adatoms can be neglected and \( \tau_f \) can be interpreted as the interarrival time of Si adatoms from the precursor, determined by \( \tau_f = \frac{N_s}{J_f} \), with \( N_s \) being the density of surface sites.\(^{72}\)

Furthermore, when the surface growth rate is negligible, the chemical potential of the adatoms is similar to that of the vapor, resulting in \( \theta_{vs} = 1 \) and \( \theta_{sl} = \theta_{vl} \). These assumptions can be well applied to our experiments; since as mentioned earlier, the thin film growth from both SiH\(_4\) and Si\(_2\)H\(_6\) gases is significantly slower than that of the nanowire.

Applying the above assumptions, Eq. 3-21 shrinks to:
indicating the dependence of growth rate on the nanowire radius as well as the impinging flux.

For the evaluation of the characteristic Gibbs-Thomson radius \((R_{GT} = 2\gamma_{l}/k_{B}T)\), the surface energy and molar volume of the liquid alloy particle were calculated from the bulk properties of individual Au and Si elements (listed in Table 3-5), under the assumption that they are independent of the size, which is valid for the diameter range in the present study.\(^{73}\) For the investigated growth temperature of 450°C, the quantity of \(R_{GT}\) varies in the range of 3.33 - 4.56 nm for pure Si to pure Au. A value of \(R_{GT} = 4.26\) nm was taken in calculations for both SiH\(_{4}\) and Si\(_{2}H_{6}\) gases, assuming an atomic concentration of 25% Si in the Au-Si alloy, following the work of Dhalluin\(^{74}\) who showed that a silane partial pressure of 0.65 Torr at T=500°C yielded in nanowires with critical radius of ~3 nm and a Si fraction of ~ 0.25 in the liquid droplet.

Table 3-5: Surface energy and molar volume of elemental Au and Si atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>Surface energy (J/m(^2))(^{44})</th>
<th>Molar volume (m(^3)/mol)(^{45})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>(\gamma_{l,Si} = 0.775-0.000145(T-1683))</td>
<td>(\Omega_{l,Si} = 11.1\times10^{-6}[1+0.000014(T-1687)])</td>
</tr>
<tr>
<td>Au</td>
<td>(\gamma_{l,Au} = 1.145-0.0002(T-1338))</td>
<td>(\Omega_{l,Au} = 11.3\times10^{-6}[1+0.000069(T-1336)])</td>
</tr>
</tbody>
</table>

The effective impingement rates of precursors on the nanowire sidewalls \((J_f)\) are extracted on the basis of previous data on planar film growth (Eqs. 3-15 and 3-17). As
discussed in section 3.4.2, at the growth temperature of 450°C for which the variation in growth rate with precursor flux is examined, the depletion of silane gas during its residence time in the reactor is negligible (conversion = 0.004 %) and thus, SiH₄ is the only species attaching on the nanowire sidewalls as well as the Au droplet. Consequently, \( J_{\text{top}} \) and \( J_f \) are the impingement flux of the same molecule only with different coefficients.

In the case of Si₂H₆, however, as illustrated earlier in Figure 3-15(b), homogeneous conversion of disilane produces enough of highly reactive SiH₂ in the gas phase to take over the planar growth process. At such condition, the effective impingement rate of SiH₂ on the Si surface is much higher than that of Si₂H₆ so that the flux of diffusing Si atoms on the nanowire sidewalls to the droplet will be mainly due to the adsorption of silylene molecules. As an example, for an inlet disilane pressure of 0.013 Torr, with ~ 4.6% conversion of disilane, the produced SiH₂ with an effective impingement rate of \( 2.97 \times 10^{-7} \text{ mol/(m}^2\text{.s)} \), which is about forty times higher than that of Si₂H₆ (\( 7.7 \times 10^{-9} \text{ mol/(m}^2\text{.s)} \)), controls the sidewalls contribution into the nanowire growth. It should be noted that with the same amount of SiH₂ impinging on the liquid Au particle, its contribution to the nanowire growth rate from direct impingement is at most 0.43 nm/min, not sufficient to explain the observed growth rate of 0.32 μm/min. This indicates that in contrast to thin film deposition, the incorporation of silylene to the nanowire growth through direct impingement at low temperatures is less pronounced than that of disilane. The foregoing argument also holds for larger fluxes investigated. Thus, for disilane precursor, \( J_{\text{top}} \) is taken to be the effective impingement flux of Si₂H₆ molecule and \( J_f \) is taken to be the flux of SiH₂ species.
Returning to Eq. 3-22, one of the factors that may lead to the observed nonlinearity in growth rate as a function of flux is a significant amount of adatoms diffusing on the nanowire sidewalls. As set by the definition of $\lambda_f$, the growth rate will be a function of $J^{1/2}$ for this situation, resulting in a nonlinear dependence (shown explicitly for $\text{Si}_2\text{H}_6$ in Eq. 3-23).

\[
GR_{NW} = \Omega_x \left[ 1 - \frac{\exp \left( \frac{R_{GT}}{\tau_f} \right)}{\theta_f} \right] \left( 2 \times 2S_{vl}^R J_{\text{Si}_2\text{H}_6} + \frac{2}{R} \sqrt{D_f N_s J_{\text{Si}_2\text{H}_6}^{1/2}} \right) \tag{3-23}
\]

A prefactor of 2 has been added into the first term of Eq. (2-23) to take into account the number of Si atoms that each $\text{Si}_2\text{H}_6$ molecule introduces into the growth upon its direct impingement on the Au liquid drop. The designation of $\tau_f$ also puts the maximum coverage of the sidewall adatoms ($\theta_f = J_f \tau_f / N_s$) equal to 1. Now, if it is assumed that $S_{vl}^R$ of $\text{Si}_2\text{H}_6$ is constant similar to what was suggested by Kodambaka et al.,$^{32}$ then Eq. 3-23 can be fitted to the growth rate-flux experimental data to extract $\theta_f$, $S_{vl}^R$ and $D_f$ (under further assumption that the changes in liquid drop with flux is negligible). Note that for the entire range of investigated fluxes, $J_{\text{SiH}_2}$ was about $8.3 \times 10^{-6}$ times of $J_{\text{Si}_2\text{H}_6}$. Figure 3-18(a) represents the fit for $\theta_f = 2.3$, $S_{vl}^R = 0.0022$ and $D_f = 6 \times 10^{-8}$ cm$^2$/s. Calculation is made for nanowires with an average diameter of 40 nm.

The obtained $D_f$ is much larger than the diffusion coefficient values in the range of about $10^{-13}$-$10^{-10}$ cm$^2$/s typically reported for Si adatom diffusion on Si(100)$^{75-77}$ and Si(111)$^{78}$ surfaces. In addition, even though by such a large value of $D_f$, a dominant sidewall diffusion seems to explain the observed growth rate-flux relation, if the fitting
Figure 3-18: Calculated SiNW growth rate (solid line) as a function of (a) flux and (b) nanowire radius obtained from Eq. (3-23) at $\theta_f = 2.3$, $S_{vl}^R = 0.0022$ and $D_f = 6 \times 10^{-8}$ cm$^2$/s.

A value of 4.26 and 20 nm is set for $R_{GT}$ and $R$, respectively. Circle points in (a) are the experimental growth rates measured at 450°C using Si$_2$H$_6$.

parameters are used to evaluate the variation in growth rate with nanowire diameter for $J_{Si2H6} = 0.034$ mol/(m$^2$.s) (corresponding to $P_{Si2H6} = 0.013$ Torr), they predict a drop in the
growth rate, as shown in Figure 3-18(b), that was not observed experimentally.

A possible explanation for this inconsistency could be that the assumption of a constant $S_n^g$ is not valid. Indeed, this can be illustrated by a simple mechanism for Si$_2$H$_6$ decomposition upon direct impingement on Au droplet surface. A similar mechanism that was examined by Boles et al. for SiH$_4$ decomposition is adopted here. The processes that lead to the nanowire growth, namely the adsorption, desorption and incorporation of the precursor molecule as well as the desorption of produced H$_2$, can be generally described through four steps:

\[
\text{Si}_{i_{1}}H_{\beta_{i}}(g) \xrightarrow{k_{a,Si_{i}H_{\beta_{i}}}} \text{Si}_{i_{1}}H_{\beta_{i}}^* \\
\text{Si}_{i_{1}}H_{\beta_{i}}^* \xrightarrow{k_{d,Si_{i}H_{j}^*}} \text{Si}_{i_{1}}H_{\beta_{i}}(g) \\
\text{Si}_{i_{1}}H_{\beta_{i}}^* \xrightarrow{k_{i,Si_{i}H_{j}^*}} \alpha_{i}Si(s) + \frac{\beta_{l}}{2}H_{2}^* \\
H_{2}^* \xrightarrow{k_{a_{1}H_{2}^*}} H_{2}(g)
\]

$\text{Si}_{i_{1}}H_{\beta_{i}}$ denotes a precursor molecule being either SiH$_4$ or Si$_2$H$_6$. $k$'s are the reaction rate constants and the asterisk indicates a surface-adsorbed species. With the assumption of first order reaction, the reaction rates of Eqs. S14-S17 will be:

\[
r_{S14} = k_{a,Si_{i}H_{\beta_{i}}} \theta_{\text{empt}} J_{Si_{i}H_{\beta_{i}}} \\
r_{S15} = k_{d,Si_{i}H_{j}^*} \theta_{Si_{i}H_{\beta_{i}}^*} \\
r_{S16} = k_{i,Si_{i}H_{j}^*} \theta_{Si_{i}H_{\beta_{i}}^*} \\
r_{S17} = k_{a_{1}H_{2}^*} \theta_{H_{2}^*}
\]

At steady state, there is no accumulation of H$_2$ and its production rate ($r_{S16}$) should equal its desorption rate ($r_{S17}$). Furthermore, the adsorption rate of precursor ($r_{S14}$) equates the sum of incorporation ($r_{S16}$) and desorption rates ($r_{S15}$). Additionally, the
overall fraction of adsorbed species and empty sites should equal to one.

\[ \theta_{\text{empty}} + \theta_{\text{Si}_{i}H_{j}^{*}} + \theta_{H_{k}^{*}} = 1 \] (3-28)

Applying the above conditions result in the steady state nanowire growth rate (from the direct impingement of precursor on Au droplet surface), as follows:

\[ r_{S16} = \frac{k_{a,\text{Si}_{i}H_{j}^{*}} k_{I,\text{Si}_{i}H_{j}^{*}} J_{\text{Si}_{i}H_{j}^{*}}}{k_{d,\text{Si}_{i}H_{j}^{*}} + k_{I,\text{Si}_{i}H_{j}^{*}} + \left( 1 + \frac{k_{I,\text{Si}_{i}H_{j}^{*}}}{k_{H_{k}^{*}}} \right) k_{a,\text{Si}_{i}H_{j}^{*}} J_{\text{Si}_{i}H_{j}^{*}}} \] (3-29)

Eq. (3-29) explains the nonlinear dependence of growth rate on flux found in experiments, even in the absence of diffusion on the nanowire sidewalls. It illustrates that the effective adsorption coefficient of the precursor is indeed a function of flux:

\[ S_{vl}^{R} = k_{a,\text{Si}_{i}H_{j}^{*}} \theta_{\text{empty}} = \frac{1}{1 + \left( 1 + \frac{k_{I,\text{Si}_{i}H_{j}^{*}}}{k_{H_{k}^{*}}} \right) k_{d,\text{Si}_{i}H_{j}^{*}} + k_{I,\text{Si}_{i}H_{j}^{*}}} \] (3-30)

Dependency of \( S^{R} \) on flux proposed here does not contradict the results given by Kodambaka et al.\textsuperscript{32} in UHV systems. In fact, it supports their findings since for very small pressures, \( S_{vl}^{R} \) becomes independent of flux and the growth rate increases linearly with pressure.

To further examine the contribution of Si adatoms through direct impingement and sidewall diffusion pathways into the nanowire growth process, Eq. (3-22) is fitted to the experimental data of growth rate-diameter curve obtained at 450°C for \( P_{\text{SiH6}} = 0.013 \) Torr and \( P_{\text{SiH4}} = 0.65 \) Torr. The outcome is represented in Figures 3-19(a) and (b) with the corresponding fitting parameters given in Table 3-6. Similar to Figure 3-18, when disilane precursor is used, \( J_{f} \) is taken to be the flux of SiH\(_{2}\) molecule.
Figure 3-19: Theoretical SiNW growth rate (solid lines) calculated for (a) SiH₄ and (b) Si₂H₆ precursors by using Eq. (3-22) with the corresponding parameters given in Table 3-6. Circle points are the experimental growth rates measured at 450°C.

(2.97×10⁻⁷ mol/(m².s)), while for silane gas, it is extracted from the results on Si thin film deposition by extrapolating the experimental data of deposition rates to a temperature of
450°C (Figure 3-11(a)) to get a reactive sticking coefficient of $S_{ij}^R = 2.11 \times 10^{-8}$.

The fit to data from SiH$_4$ suggests a critical radius of ~ 5 nm, slightly larger than $r_c = 3$ nm found by Dhalluin et al.\textsuperscript{74} at 500°C for the same silane partial pressure of 0.65 Torr. This could be due to lower temperature used in the present study (450°C), as the critical radius is not only a function of partial pressure but also a function of temperature.

Table 3-6: Fitting parameters of Eq. (3-22) to obtain SiNW growth rate as a function of radius from SiH$_4$ and Si$_2$H$_6$ gases at T = 450°C

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Partial Pressure (Torr)</th>
<th>J (mol/m$^2$.sec)</th>
<th>$\theta_{ij}$</th>
<th>$S_{ij}^R$</th>
<th>$\lambda_f$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$</td>
<td>0.65</td>
<td>2.49</td>
<td>2.17</td>
<td>1.09 $\times$ 10$^{-4}$</td>
<td>418</td>
</tr>
<tr>
<td>Si$_2$H$_6$</td>
<td>0.013</td>
<td>0.034</td>
<td>2.3</td>
<td>6.2 $\times$ 10$^{-3}$</td>
<td>176</td>
</tr>
</tbody>
</table>

The diffusion length of 418 nm obtained from SiH$_4$ data compares well with the value of 90 nm found by Dubrovskii et al.,\textsuperscript{44} taking into account that the effective impingement rate in the present study is lower. Also $\lambda_f = 418$ nm corresponds to a diffusion coefficient of $D_f = 5.5 \times 10^{-12}$ cm$^2$/s, which in contrast to Figure 3-18 is well within the range of previous reports for Si adatom diffusion. The same value of $D_f$ results in a diffusion length of 176 nm for SiH$_2$ species used in Figure 3-19(b).

With such diffusion lengths, the flux of adatoms from the nanowire sidewalls into the Au droplet becomes negligible for both SiH$_4$ and Si$_2$H$_6$ precursors and thus, the direct impingement of source gases on liquid Au takes the main role in the growth process.

The effective adsorption coefficient of 6.2 $\times$ 10$^{-3}$ gained for direct impingement of
Si$_2$H$_6$ molecule on Au is consistent with prior values reported at higher temperatures and lower pressures. A reactive sticking coefficient of 0.01 found at 590°C and $P_{Si_2H_6} = 9.75 \times 10^{-5}$ Torr$^{34}$ and a value of 0.1 extracted at 575°C for disilane partial pressures in the range of $2 \times 10^{-8}$-$3 \times 10^{-6}$ Torr$^{32}$ in conjunction with the present results indicate the influence of temperature and pressure on the reactive sticking coefficient and suggest that the lower the temperature and the higher the partial pressure, the lower the adsorption coefficient.

An interesting outcome of the comparison between SiH$_4$ and Si$_2$H$_6$ gases in Table 3-6 is that despite the differences in their impinging flux under the chosen partial pressures, their effective adsorption rate on the Au droplet ($S_{vl}^pJ$) is about the same. Consequently, by introducing two silicon atoms into the growth, disilane precursor results in growth rates twice larger than that of silane. The ratio stays the same for the entire investigated temperature range of 450-485°C (Figure 3-12), suggesting similar effective impingement rates on Au droplet irrespective of the precursor type. This explains the observed similarity in the apparent activation energies of SiNW growth from silane and disilane gases, given the fact that the rate-determining step of the growth process will be identical under the same effective impingement flux and the same temperature.

In addition, the obtained $E_a$ of ~ 30 kcal/mol for SiNW growth is comparable to that of Si film deposition for the situations when deposition is regulated by the precursor flux, as discussed in section 3.4.2. The resemblance of this quantity between the nanowire growth and the planar film suggests that the adsorption of source gas restricted by its flux may similarly be controlling the nanowire growth process. In this case, the
role of Au as a catalyst would be to enhance the incorporation rate of Si atoms and consequently, the desorption rate of H₂ that provides abundant empty sites for precursor adsorption.

As a final remark concerning the variation in SiNW growth rate with temperature, it should be pointed out that the saturation in growth velocity with temperature above ~ 485°C observed for Si₂H₆ gas (Figure 3-12) occurs due to the depletion of this precursor during its residence time in the reactor. As demonstrated in Figure 3-16(b), because of the gas phase reactions happening upstream of the substrate, the impinging flux of Si₂H₆ molecule at 525°C is reduced to 0.015 mol/(m².s), about 45% of the corresponding flux for Pₜₐₚ₉ = 0.013 Torr. This explains the drop in growth rate by half of the amount that would have been expected if the exponential trend would have continued.

3.5 Conclusions

Overall compared to SiH₄, the use of disilane gas as the Si-containing precursor enables higher growth rates for both SiNWs and Si films. The difference between the planar and the nanowire growth processes lies in the different species responsible for the growth. Under the conditions examined in the present study, the Si film deposition from Si₂H₆ precursor is carried out mainly due to the SiH₂ reactive species. Thus, it is of importance to avoid the reduction in its flux due to long residence time of the gas in the reactor or the high concentration of H₂ carrier gas. Otherwise, a drop in the deposition rate with temperature will occur. The SiNW growth, on the other hand, arises mainly
from Si₂H₆ molecule directly impinging on the Au droplet surface as the dominant pathway for the incorporation of Si atoms and the contribution of adatoms diffusing on the nanowire sidewalls as an additional route to the growth velocity is negligible. Similarly for SiNWs grown from silane, the direct adsorption of SiH₄ species on the Au surface carries on the growth.

For both gases, a simple decomposition mechanism including the adsorption, desorption and incorporation of precursor molecule on the Au droplet surface explains the observed nonlinearity in the growth rate as a function of gas partial pressure and suggests that the effective adsorption coefficient of the precursor on the catalyst depends on its flux.

When a disilane partial pressure of 0.013 Torr and a silane partial pressure of 0.65 Torr is chosen at 450°C, the effective impingement flux of gases on the catalyst surface becomes the same and results in identical rate-determining step for both gases, which justifies the obtained similar apparent activation energies. Furthermore, the obtained apparent activation energies for nanowire growth compares to that of the film whenever the growth is restricted by the flux of precursor adsorbing on the surface.

3.6 References

B. Meyerson, B. Scott, and R. Tsui, Chemtronics 1, 150 (1986).
Chapter 4

Fabrication of Undoped and Radial p-n Junction Germanium Nanowires

4.1 Introduction

As a semiconducting material, germanium offers great potential to enhance the functionality of future electronic devices and to compete with Si in CMOS transistors.\textsuperscript{1-3} The higher carrier mobility of germanium compared to that of silicon (\(\mu_n=3900\ \text{cm}^2/\text{Vs}\) and \(\mu_p=1900\ \text{cm}^2/\text{Vs}\) for bulk Ge versus \(\mu_n=1500\ \text{cm}^2/\text{Vs}\) and \(\mu_p=450\ \text{cm}^2/\text{Vs}\) for bulk Si at 300K), makes it an attractive material to grow nanowires for high speed and higher frequency electrical devices.\textsuperscript{1} In addition, the larger excitonic Bohr radius of Ge (24.3 nm) than that of Si (4.9 nm for Si), yields a more pronounced quantum confinement effect in germanium nanowires.\textsuperscript{4,5}

Considering the advantages of Ge over Si, the investigation on the growth kinetics and morphology of germanium whiskers was initiated at the microscale back in the 1970’s\textsuperscript{5,6} and has continued to date with significant reduction in the size of wires down to diameters of about 12 nm, well below the Bohr radius.\textsuperscript{7} Various methods such as chemical vapor deposition (CVD),\textsuperscript{8-14} solovothermal,\textsuperscript{15-17} thermal evaporation,\textsuperscript{1,18-22} and laser ablation\textsuperscript{23,24} have been used to fabricate GeNWs. Using the common VLS mechanism, the feasibility of GeNW growth through alternative catalysts than the frequently used Au metal - such as indium,\textsuperscript{21,25,26} bismuth,\textsuperscript{20,27} and antimony\textsuperscript{21} – has been demonstrated. By employing manganese germanide seeds in CVD\textsuperscript{28} or MBE\textsuperscript{29} systems,
the VSS synthesis of GeNWs has also been accomplished at a growth temperature of 350°C that is 370 °C below the lowest eutectic point on the Mn-Ge binary phase diagram. Moreover, catalyst-free fabrication of GeNWs has been reported, where nucleation of nanocrystalline seeds induced on a reactive silicon-rich oxide (SiOₓ) surface initiated the nanowire growth via a vapor-solid mechanism without a metal catalyst. The reactive oxide surface was formed by etching a piece of hydrogen-terminated silicon wafer with ultrapure water. The precursors adsorbed on the reactive thin oxide surface and decomposed to form nanocrystalline seeds, thus promoting anisotropic nanowire growth.

In view of the influence of growth parameters on GeNW morphology and growth rate using Au metal in CVD systems, Wang et al. found that there exists a dependency of the optimum growth temperature on the size of the gold nanoparticle, namely, 295°C and 310°C for gold seeds of respectively 20 and 50 nm in diameter, indicating that smaller gold seeds can nucleate and grow nanowires at lower temperatures. They also observed that when GeH₄ is used as the precursor, the desired nanowire growth is obtainable by controlling the GeH₄ decomposition through H₂ addition. At a constant germane flow, low H₂ flow rate results in excessive GeH₄ pyrolysis and germanium deposition on the substrate, while the increase of H₂ concentration leads to insufficient germanium feed to grow wires. Using a different gas source, digermane, Dailey et al. investigated the effect of pressure at 400°C and observed a linear dependence of nanowire growth rate on digermane pressure. In this study, two types of nanowires were detected, straight wires having uniform diameters along the length and tapered ones which was suggested to occur due to lateral growth and Ge deposition on wire surface. Using nanoporous anodic aluminum oxide (AAO) membrane as a template, Lew et al. examined the temperature
and growth rate dependency and by observing the Arrhenius behavior, reported an apparent activation energy (Ea) of 11.4 kcal/mol for GeNWs.\textsuperscript{11}

The use of AAO template with branched channels has additionally enabled the growth of GeNWs with variable morphologies.\textsuperscript{31} As an example, a template with Y-shaped nanochannels resulted in Y-shaped GeNWs with two branches growing from the same stem. Additionally, GeNWs with multiple branches on the surface of a single stem - named as ‘nanotrees’ due to their tree-like morphologies – have also been fabricated by sequential seeding of Au nanoparticles on as-grown GeNW sidewalls.\textsuperscript{32} Furthermore, by taking advantage of uncatalyzed growth on nanowire sidewalls, Ge nanocones of controlled taper morphology were obtained.\textsuperscript{33} Within a single CVD process run and using the same catalyst particle, control over the taper was achieved in situ by changing the growth temperature to form nanocones of different types such as faceted obelisk-like pillars consisting of a base segment of largely uniform diameter and a conical tapered tip or nanocones having a base with a wider taper and tips with a smaller taper.

As an important factor to determine the growth direction of nanowires, the role of substrate has been investigated both for homoepitaxial growth\textsuperscript{4,14} of GeNWs on Ge(111) substrates and their heteroepitaxial growth\textsuperscript{12,13,32} on Si(111) surfaces. In both cases, most of the nanowires grow vertically up from the substrate and a few align themselves to the other <111> directions. Growth of vertical nanowires is more readily achieved on Ge substrates, especially when Au colloid solution is used due to solubility of germanium oxide in water. For Si substrates, when a thin Au layer is used to form the growth catalyst, a complete removal of any native oxide present on the surface by etching the
substrate in HF is required prior to deposition of the Au in a UHV chamber to obtain GeNWs normal to the surface.\textsuperscript{12} In case of using Au colloid, vertical growth can be achieved if the oxidation of the Si substrate due to wet chemistry is prevented by employing a thin Ge buffer layer.\textsuperscript{32}

Besides the undoped GeNWs, the synthesis of doped wires in the form of individual p-type\textsuperscript{34} and n-type\textsuperscript{35} nanowires as well as axial p-n junction\textsuperscript{36} has been demonstrated and the influence of dopants on the morphology and structure of these nanowires has been investigated. An additional interesting but as yet not explored structure is the radial p-n junction GeNW. The advantages that such structures offer for photovoltaic cells compared to planar geometry, discussed in section 4.2.2, make radial p-n junction GeNW a great candidate for thermophotovoltaic (TPV) applications. This has motivated the studies of this chapter to investigate the influence of growth parameters on the fabrication of radial p-n junction GeNWs.

First the synthesis parameter space is determined for undoped GeNWs and the influence of growth conditions on their morphology is examined. The outcome of this study not only helps to better select the growth parameters to dope GeNWs, but combined with the results on SiNWs, it also becomes useful to synthesize SiGe nanowires from disilane gas, as will be discussed in chapter 5. Once the most favorable growth condition for undoped GeNWs is determined, the viability of the formation of p-type GeNWs and the effect of dopant on their structure is investigated. Then, the deposition of n-type Ge thin films are initially investigated on sapphire substrates as calibration runs in order to find the uniformity and dopant concentration of n-type Ge shell for GeNW coating and eventually the optimum conditions are transferred to GeNWs.
to regrow a smooth n-type shell on their sidewalls.

Before presenting the experimental results, in order to better realize the importance of studies on the fabrication of radial p-n junction GeNWs for potential application in TPV systems, it will be advantageous to consider briefly the fundamentals of a TPV system, the role of PV cell and the suitable materials for its fabrication as well as the benefits of nanowire geometry over the conventional planar cells.

4.2 Basics of thermophotovoltaic energy conversion

The interest in generating electricity using a light-weight, quiet, low-maintenance device has motivated the development of thermophotovoltaic devices. The concept of TPV energy conversion is to convert thermal energy produced by solar and combustion sources into electrical energy. The ability to use heat storage in a solar TPV gives it the capability of 24-hour operation and makes it advantageous compared to conventional photovoltaic cells. Stand-alone domestic gas furnaces for the cogeneration of electricity and heat, power systems for navigation of sailing boats, silent power supplies on recreational vehicles, low weight battery charger for military missions and recovery of the waste heat from industrial processes such as glass manufacture can be some of the potential applications of combustion driven TPV.

Whether a TPV system would be feasible or not will depend upon its efficiency and cost. Several advantages and multiple applications of TPV systems have attracted a lot of attention and a significant amount of research has been focused on the optimization of individual components to increase the system efficiencies while keeping the cost low.
4.2.1 TPV system

A basic TPV system consists of a source of heat, an emitter and a photovoltaic semiconductor cell. Figure 4-1 illustrates the concept.\(^44\)

For good performance, the efficiency of a TPV cell needs to be optimized. Considering a simple model assuming an ideal PV cell and no leakage of radiation out of the system, maximum efficiency ($\eta_{\text{max}}$) can be calculated by determining the ratio of the electrical power output to the total thermal power input in the TPV system. It can be shown that $\eta_{\text{max}}$ is a function of a dimensionless band gap energy ($u_g$) and spectral control ($R$), defined as follows:\(^44\)

$$u_g = \frac{E_g}{kT_E} \quad (4-1)$$

$$R = \frac{\varepsilon_{E_L} (1 - \rho_{cl}) (1 - \varepsilon_{E_L})}{\varepsilon_{E_b} (1 - \rho_{cb}) (1 - \varepsilon_{E_b})} \quad (4-2)$$

where, $E_g$ is the PV cell band gap energy, $T_E$ is the emitter temperature, and $k$ is the Boltzmann constant. $\varepsilon_{E}$ and $\rho_{E}$ are the spectral emittance of the emitter and spectral reflectance of the PV cell, respectively, which have been assumed to be different but constant in two regions of the spectrum, out-of-band ($0 \leq E < E_g$) denoted with subscript $l$ and in-band ($E_g \leq E < \infty$) denoted with subscript $b$.\(^44\)

Considering a typical TPV system where $T_E = 1700\text{K}$ and $E_g = 0.66\text{eV}-0.72\text{eV}$ (Ge and GaSb), the PV cell dimensionless band gap energy, $u_g$, would approximately be 4.5. If there is no spectral control and optical properties of the emitter and the PV cell are constant over the entire spectrum, $R=1$, then as shown in Figure 4-2 efficiency greater than 20% is not expected. However, if $R$ is reduced to 0.1, $\eta_{\text{max}}$ will increase to about
0.6, near its maximum value. Hence, proper variation of $\varepsilon_E$ and $\rho_c$ is required to increase the in-band emittance and out-of-band reflectance. In other words, to have an efficient system, above band gap photons which are converted to electrical energy should be directed to the PV cell and below band gap photons should be redirected back towards the radiator where their energy can be recovered.

There are different approaches to spectral control depending on the individual component being used. Selective emitters with a variable spectral emittance provide the option to produce band gap-matched radiation with a large emittance for photon energies greater than the PV cell band gap energy, and a low emittance for sub-band gap photons. In the case of a broad band emitter with a constant spectral emittance, a front surface filter can be placed between the emitter and cell to pass the above-band gap photons and
to reflect photon energies less than the band gap. With this method, the useful in-band photons are also reflected to some extent which reduces the power density. An alternative approach is to use a back surface reflector placed behind the PV cells to reflect long wavelength photons. Here the PV cells should be fabricated on non-absorbing substrates so that sub-band gap photons can pass through the substrate without being significantly absorbed and wasted as heat.

![Figure 4-2: Maximum TPV efficiency as a function of R and $u_g = E_g/kT$.](image)

Since individual components play an important role in the TPV system efficiency, research has mainly been focused on improving their performance by developing new materials and integration techniques. Being the major part of the system to convert
thermal energy into electrical energy, photovoltaic cells have specifically attracted a lot of attention and significant efforts have been going on to increase their conversion efficiency.

4.2.2 Photovoltaic cells

In the traditional planar geometry of PV cells, in order to have sufficient light absorption, relatively thick layers of semiconducting materials are typically used. For example, in case of Si, the thickness should be $\geq 100 \, \mu m$ to absorb the majority of radiation. However, for effective collection of generated charge carriers, the diffusion length should be long enough for the carriers to reach the junction without recombination. In fact, the difference in light absorption depth and minority diffusion length can cause either insufficient absorption or carrier collection loss. As a result, fabrication of efficient PV cells requires pure and therefore relatively expensive materials.

Recently, Kayes et al. proposed that using nanowire structures can resolve this issue by collecting charge carriers in a direction perpendicular to that of light absorption. As shown in Figure 4-3, by aligning the wire arrays parallel to the incident light, their large aspect ratio would provide sufficient optical absorption while charge carriers could be collected radially over a short distance and hence reduce their loss. Theoretical analysis of the device has shown that such nanowire structures can improve cell efficiency compared to traditional PV cells. The highest efficiency improvements occur for materials where the minority carrier collection length ($L$) is on the order of the wire radius.
Besides the carrier collection loss in a planar geometry, the reflection of a large portion of incident light from the surface can reduce the absorption and consequently the efficiency of the system. Hence, anti-reflection coatings (ARCs) such as vacuum multilayer dielectric films (e.g., ZnS/MgF$_2$) are often used. However, these coatings can only reflect a narrow range of wavelengths and their fabrication is quite expensive.

Figure 4-4: Effective refractive index profile between air (a) a-Si:H thin film, (b) a-SiNW arrays, and (c) a-Si:H NC arrays calculated by averaging the refractive indices of air and a-Si:H weighted by volume at the interface.
Experiments on nanowire structures have interestingly shown that the reflectance can be reduced without any ARC. In general, the effective refractive index (RI) changes sharply from the RI of the semiconductor material to that of air causing the reflection of light from the surface. However, for nanowire arrays, the change in RI occurs through an intermediate step and causes a decrease in reflection. The behavior of RI change has been depicted in Figure 4-4 for a-Si:H semiconducting material.\textsuperscript{46}

![Graph](image1.png)

**Figure 4-5:** (a) Absorption measurement for a-Si:H thin film, nanowire arrays, and nanocone structures.\textsuperscript{46} (b) Reflectivity measurements on bare GaSb wafer (black line) and templated nipple arrays for 1.5 min (blue line) and 2.5 min (red line).\textsuperscript{49}
Interestingly, the decrease in effective RI happens more gradually if the shape of wires is changed to a nanocone structure due to gradual decrease of the diameter from the base to the tip. Hence, lower reflectivity and higher absorption would be expected for nanocone structures. In fact, measurements on thin film and nanowire structures for two semiconducting materials, a-Si:H and gallium antimonide (GaSb) - which is one of the common materials studied for TPV applications - have confirmed the anticipated behavior (Figure 4-5).

4.2.3 Semiconductor materials for TPV application

It was mentioned earlier that the maximum efficiency of a TPV system depends on spectral control and dimensionless band gap energy and as shown in Figure 4-2, the maximum value of $\eta_{\text{max}}$ increases with decreasing $R$ which in turn increases the optimum value of $u_g$ for maximum efficiency. The maximum value of $\eta_{\text{max}}$ would be reached if $u_g<5$. This indicates that for reasonable emitter temperatures ($1200<T_E<2000K$) the semiconductor band gap ($E_g$) should be less than 0.8 eV.

Thus, Ge with $E_g = 0.66$ eV was initially suggested to be used as the semiconductor in PV cells. Nonetheless, despite a reasonable band gap, the low efficiency of Ge cells prompted researchers to investigate the use of new materials such as GaSb ($E_g=0.72$ eV) and In$_x$Ga$_{1-x}$As ($0.36\leq E_g \leq 1.42$ eV depending on value of $x$). In work done by Sulima et al., it was shown that for a simple TPV cell consisting of a p-n junction and front and backside contacts, GaSb has higher efficiency and higher output power density compared to Ge. Pure GaSb is intrinsically p-type and in order to be used...
in TPV applications needs to be doped with elements such as Te, Se. However, doping generally reduces the quality and monocristallinity of the material.\textsuperscript{51} High native defect concentrations of GaSb and related alloys which are electrically and optically active can cause problems in device fabrication.\textsuperscript{52}

As the substrates play a key role in a TPV device, growing crystals with better quality and larger sizes is important. But the main goal is to keep the cost of fabrication low. More available and less expensive substrates would significantly reduce the overall cost of the final device.

Taking advantage of germanium substrates available in larger sizes and lower prices, fabrication of cost effective TPV cells can be realized. This has motivated researchers to improve the performance of planar Ge PV cells by different methods such as passivating the front surface to reduce surface recombination velocity, using an ARC on the PV cell surface to reduce the reflection loss of incident photons, and using a back surface reflector which returns the sub-band gap energy radiation back to the emitter and increases the overall efficiency.\textsuperscript{53-56} In fact, reflectance measurements for Ge and GaSb based planar samples has shown higher reflectance for Ge.\textsuperscript{57} Hence the lower cost of Ge based cells and the high sub-band gap photon reflection makes germanium a promising material for TPV applications.

To date, the studies on Ge as an important substance for TPV cells has been limited to the planar geometry. The attractive potential of nanowire structures in increasing the efficiency and photon absorption of PV cells are being mainly explored for silicon as the semiconductor in solar cell applications.\textsuperscript{58-64} However, as mentioned above, Si is not appropriate for combustion driven TPV applications due to its large band
gap and semiconductors with smaller band gaps are required for this purpose. To the best of our knowledge there is no report on nanowire radial junction PV cells suitable for TPV applications. It is the aim of this study to investigate the growth of radial germanium nanowire p-n junction for their potential applications in TPV cells.

4.3 Growth conditions

Undoped GeNWs were grown on three different substrates, Si(111), Ge(111) and AAO-coated glass. The Si wafers were coated with 3 nm Au thin films. The Ge substrates were covered with 50 nm Au nanoparticles, and the anodized aluminum oxide membranes had approximately 25 nm thick Au deposited into their pores. Using these substrates, the structural properties of the nanowires were examined over the temperature range from 275-425°C and total pressures ranging from 8-63 Torr. During these growths, GeH₄ at a flow rate of 50 sccm was flown through the reactor and the total flow rate was held constant at 100 sccm by supplementary H₂ carrier gas. In addition, the influence of the growth parameters on the growth rate of GeNWs was investigated for wires grown on Si substrates. First, a temperature of 300°C and a total pressure of 38 Torr were used to study the variation in the length of nanowires with time. Then, the effect of temperature on the growth velocity was examined at two total pressures of 13 and 38 Torr and at P₁ = 13 Torr, the growth rate of GeNW was compared to the deposition rate of Ge film. Next, by fixing the temperature at 300°C or 350°C, the changes in growth rate with total pressure were studied. Finally, the GeH₄ flow rate was varied in the range of 15 to 90 sccm to investigate the influence of partial pressure at T = 375°C and P₁ = 13 Torr.
Growth of radial p-n junction GeNWs was initiated by investigating the formation of p-type GeNWs using diborane as the dopant source and the influence of dopant on the structure of nanowires was examined at $T = 300^\circ$C, $P_t = 13$ Torr, $v_{\text{GeH}_4} = 50$ sccm and for $\text{B}_2\text{H}_6/\text{GeH}_4$ ratios in the range of $3.3\times10^{-5}$ - $5\times10^{-3}$. Radial deposition on the GeNW sidewalls to coat the nanowires with an n-type shell was investigated for temperatures ranging from 425 to 600°C and $\text{PH}_3/\text{GeH}_4$ ratios between $2\times10^{-5}$ and $2\times10^{-2}$. The optimum growth conditions to obtain uniform and highly doped n-type Ge shells was first gained from calibration runs of Ge films deposited on sapphire substrates and was then transferred to GeNWs to regrow a smooth n-type shell on their sidewalls.

4.4 Results and discussion

4.4.1 Growth properties of undoped Ge nanowires

To synthesize the undoped GeNWs, three types of substrates were used: Ge(111) covered with 50 nm Au nanoparticles, Si(111) coated with a 3 nm Au thin layer and anodized aluminum oxide (AAO) template. Each substrate offers its own advantages and disadvantages that will be further discussed in the following sections.

4.4.1.1 GeNWs grown on (111) Ge substrate coated with 50 nm Au nanoparticles

The cross-sectional SEM images in Figure 4-6 illustrate that for a total reactor pressure of 38 Torr, the growth of undoped GeNWs is practical when a growth temperature as low as $300^\circ$C is chosen which is about $60^\circ$C below the eutectic point of
the bulk Ge-Au phase diagram and it can continue to temperatures as high as 375°C. The possibility of GeNW growth below the eutectic temperature has already been discussed in chapter 1.

Figure 4-6: Cross-sectional SEM images of GeNWs grown at (a) 300°C, (b) 325°C, (c) 350°C, and (d) 375°C. For all these growths, the total reactor and germane partial pressures are chosen to be 38 and 0.38 Torr, respectively and a solution of 100 μL of Au nanoparticles in 3000 μL DI water is used to cover the Ge substrates.

For temperatures below ~350°C, nanowires grow with a uniform diameter along their length; whereas, at 350°C and higher temperatures, they start to exhibit a tapered
structure with a wider diameter at the base which narrows down towards the tip. Increase in temperature enhances the un-catalyzed radial growth on the nanowire sidewalls via the vapor-solid mechanism and leads to the observed tapering. Figure 4-7 exhibits the TEM image of a tapered GeNW grown at 375°C with non-uniform diameter and tapering of about $55 \pm 5$ nm/μm. The diameter of the wire is about $50 \pm 6$ nm at the tip, close to the size of gold nanoparticles. The nanowire is single crystalline with smooth surface and no defects and it is coated with a thin amorphous layer believed to be germanium oxide.

Figure 4-7: (a) TEM image of a tapered GeNW grown at $T = 375^\circ$C (corresponding to image (d) in Figure 4-6). The image is taken after removal of gold from nanowire tip. (b) Diffraction pattern indicating $<111>$ growth direction. (c) HRTEM of the nanowire tip.
Apart from the tapering effect, the increase in temperature improves the density of nanowires and increases it at higher temperatures. For lower temperatures, in order to enlarge the number of GeNWs, a possible approach is to perform a two-step growth\textsuperscript{12} as shown in Figure 4-8. Here, the synthesis of nanowires is conducted at an initial temperature of 350°C for 5 min and then the temperature is ramped down to 300°C at which the growth continues for 55 min. During the cooling process, the GeH\textsubscript{4} source is turned off.

![SEM image of GeNWs grown by a two-step technique](image)

**Figure 4-8:** SEM image of GeNWs grown by a two-step technique where the growth initiates at 350°C for 5 min and continues at 300°C for 55 min. P\textsubscript{r}, P\textsubscript{GeH\textsubscript{4}} and Au colloid concentration are the same as that in Figure 4-6.

Figures 4-6 and 4-8 clearly show the advantage of Ge substrates in epitaxially growing vertical nanowires when Au nanoparticles are used. However, due to the reduced densities of nanowires at lower temperatures as well as their poor reproducibility under these conditions (below 350°C), the Ge substrates are replaced by Si wafers
covered with 3 nm Au layer to investigate the influence of growth conditions on the growth rate of GeNWs.

4.4.1.2 GeNWs grown on (111) Si substrate covered with 3 nm Au thin film

As can be seen in SEM images of Figure 4-9, temperature exhibits a similar effect on the morphology as that for GeNWs grown on Ge substrates. Nanowires with uniform diameter can be obtained if the temperature is kept below 350°C. For these temperatures, higher densities are obtained on Si substrates covered with 3 nm Au film as opposed to Ge substrates coated with Au nanoparticles. However, if the temperature is further reduced to 275°C, despite the formation of nanowires their density drops dramatically. Above 350°C, the Ge deposition on nanowire sidewalls results in tapered structure. The tapering effect increases and the nanowires change to nanocone structures as the temperature increases up to 425°C. At this point, nanowire growth fails and thin film deposition is observed instead of nanowire formation. This is believed to be due to the high GeH₄ decomposition rate which leads to a Ge deposition faster than diffusion of Ge atoms into the catalyst droplet, blocking the possible formation of GeNWs.

The morphology and the density of the nanowires remain unaffected with the changes in total pressure except for the lowest pressure examined, Pₜ = 8 Torr, where the number of nanowires falls significantly. This is illustrated in Figure 4-10 for the growth temperature of 300°C.

At this temperature for which nanowires with uniform diameter are obtained, the variation in the length of nanowires with time is investigated for Pₜ = 38 Torr and similar
Figure 4-9: GeNWs grown on (111) Si substrate covered with 3 nm Au thin film. The growth temperatures are (a and b) 275°C, (c) 300°C, (d) 325°C, (e) 350°C, (f) 375°C, (g) 400°C and (h) 425°C. $P_t = 38$ Torr and $P_{GeH_4} = 0.38$ Torr are used in all cases.
to SiNWs, a linear dependency is observed with an intercept at zero (Figure 4-11), suggesting a negligible incubation time for the onset of nanowire growth. Consequently, it is reasonable to obtain the growth rate of GeNWs by dividing their length to the overall growth time.

Figure 4-10: GeNWs grown at different total pressures of (a) 8 Torr, (b) 13 Torr, (c) 38 Torr, and (d) 63 Torr. Growths are carried out on (111) Si substrate covered with 3 nm Au thin film when 50 sccm of GeH₄ is flown at the growth temperatures of 300°C.

For the total pressures of 13 and 38 Torr, the growth rate of GeNWs as a function of temperature reveals an Arrhenius behavior for temperatures below 375°C from which apparent activation energies of 7.4 ± 0.8 kcal/mol and 6.5 ± 0.7 kcal/mol can be extracted, respectively. Figure 4-12 displays the temperature dependence of the growth
rate at both pressures. At the total pressure of 13 Torr, the growth rate of GeNWs is also compared to the deposition rate of Ge films. As can be seen, the temperature influence is more pronounced during the deposition process of Ge film that proceeds with an apparent activation energy of $23.6 \pm 0.5$ kcal/mol at lower temperatures. The obtained activation energies are in agreement with previously reported values of 11 kcal/mol for GeNW growth$^{11,65}$ and 22 kcal/mol for Ge film deposition.$^{66,67}$

![Graph](image)

**Figure 4-11**: Variation in GeNW length with time for a growth temperature of 300°C. The total reactor and germane partial pressures are 38 and 0.38 Torr, respectively.

The connection between the growth and the species responsible for it can be understood from the kinetic model developed to predict the deposition rate of Ge films. By applying a similar approach to that used in chapter 3 for Si films, concentration profiles of Ge-containing species can be obtained using Eq. (3-6) provided the
homogeneous reactions of source gas and heterogeneous deposition of produced species on the reactor wall are considered. Table 4-1 summarizes the gas phase reactions and their related rate constants taken for the calculations. As will be discussed shortly, GeH₄ exhibits negligible homogeneous decomposition in the gas phase for temperatures examined here. Thus, only the contributions of GeH₄, Ge₂H₆ and GeH₂ molecules to the deposition rate are considered in calculations.

Figure 4-12: Growth rate as a function of temperature for GeNWs grown at total reactor pressures of (■) 38 and (●) 13 Torr, as well as (♦) Ge films deposited at P₁ = 13 Torr. The growths are entirely carried out when 50 sccm of GeH₄ is flown through the reactor.
Table 4-1: Gas phase forward and reverse reactions and their related rate constants in the form of $k_i = A_i \exp(-E_{a,i}/RT)$. The units of $A_i$ are given in terms of moles, cubic centimeters, and seconds, depending on the order of reaction.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Forward reactions</th>
<th>Reverse reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_i$</td>
<td>$E_{a,i}$</td>
</tr>
<tr>
<td>GeH$_4$ ↔ GeH$_2$ + H$_2$</td>
<td>$5.6 \times 10^8$</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH$_2$ + GeH$_4$ ↔ Ge$_2$H$_6$</td>
<td>$4.07 \times 10^{12}$</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge$_2$H$_6$ ↔ H$_3$GeGeH + H$_2$</td>
<td>$3.6 \times 10^{10}$</td>
<td>48.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_3$GeGeH ↔ H$_2$GeGeH$_2$</td>
<td>$2.1 \times 10^8$</td>
<td>9.4</td>
</tr>
</tbody>
</table>

* To account for the pressure dependency of rate constants in the fall-off region, the pre-exponential factor is extracted for the pressure of 10 Torr in Ref.68, close to $P_t = 13$ Torr used in the present study.

To account for the surface decompositions, similar to silane, the surface reaction mechanism of these species are presented by their chemisorption on free surface sites followed by the hydrogen desorption to regenerate the surface sites,$^{72,73}$ as follows:

\[
Ge_{\alpha}H_{\beta} + m_i \ast \rightarrow \alpha_i Ge^\ast + \beta_i H^\ast
\]  
\[
2H^\ast \rightarrow H_2 + 2^\ast
\]  

For the highly reactive species of GeH$_2$, its interaction with both free surface sites and surface monohydride bonds are included through similar paths as those in steps (S9-S13) presented in chapter 3. Table 4-2 lists the required parameters of each species to calculate the coverage of free surface sites using Eq. (3-18) and to eventually predict the deposition rate for Ge-containing species through Eq. (3-14). The chemisorption of both germane and digermene gases as well as the hydrogen desorption are believed to be first
order.\textsuperscript{73,74} It should be noted that the kinetic parameters of germane adsorption have been taken from the data on Si(100) surface,\textsuperscript{73} as to the best of our knowledge, there is no report for its adsorption on Ge surfaces.

Table 4-2: Kinetic parameters of GeH\textsubscript{4} and Ge\textsubscript{2}H\textsubscript{6} chemisorption as well as hydrogen desorption from Si and Ge surfaces.\textsuperscript{73}

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Substrate</th>
<th>(A)</th>
<th>(E_a)</th>
<th>(S_0)</th>
<th>(A)</th>
<th>(E_a)</th>
<th>(n_i)</th>
<th>(m_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH\textsubscript{4}</td>
<td>Si (100)</td>
<td>0.23</td>
<td>0</td>
<td>(2\times10^{-4})</td>
<td>2.5(\times10^{10})</td>
<td>33</td>
<td>4*</td>
<td>1</td>
</tr>
<tr>
<td>Ge\textsubscript{2}H\textsubscript{6}</td>
<td>Ge (100)</td>
<td>500</td>
<td>0</td>
<td>0.8</td>
<td>2(\times10^{13})</td>
<td>39</td>
<td>6*</td>
<td>1</td>
</tr>
<tr>
<td>GeH\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

After Ref. 72, it is assumed that all 4 hydrogen on a GeH\textsubscript{4} molecule eventually desorbs from the monohydride state. Analogously for Ge\textsubscript{2}H\textsubscript{6}, 6 surface monohydrides are considered. The assumptions on GeH\textsubscript{2} are similar to that of SiH\textsubscript{2} in chapter 3, except that \(k_{S11}/k_{S12}\) is taken to be zero.

As depicted in Figure 4-13, when the hydrogen desorption parameters given for GeH\textsubscript{4} on Si substrate are used, the calculated deposition rates are largely underestimated. However, when the corresponding values given for Ge\textsubscript{2}H\textsubscript{6} on Ge substrate are used, excellent agreement between calculated and experimental deposition rates is obtained. The calculations (Figure 4-14) show that under the conditions examined, the deposition process of Ge film mainly proceeds through the GeH\textsubscript{4} molecule and the contributions of Ge\textsubscript{2}H\textsubscript{6} and GeH\textsubscript{2} species are extremely small. Correspondingly, a similar conclusion can be made for GeNW growth as the amount of produced Ge\textsubscript{2}H\textsubscript{6} and GeH\textsubscript{2} molecules will not be sufficient to take part in the nanowire growth process.
Figure 4-13: Deposition rate of Ge films as a function of temperature at $P_t = 13$ Torr and $P_{GeH_4} = 0.13$ Torr. Solid points represent the experimental results and the lines are the calculated profiles that compare the impact of kinetic parameters of $H_2$ desorption when the reported data on (1) Si and (2) Ge substrates are used.

In the case of Ge film, the reduced dependency on temperature above 425°C can be explained considering that the hydrogen desorption rate from the surface in this region is large and the growth is controlled by chemisorption of GeH$_4$, the rate of which is weakly dependent on temperature ($E_a = 0$ given in Table 4-2). However, as the growth temperature is reduced below 425°C, the hydrogen desorption decreases and becomes the rate limiting step explaining the larger slope of the growth curve approaching the activation energy of the hydrogen desorption step.

It should be noted that the foregoing discussion is valid only if the mass transport of GeH$_4$ molecule through the boundary layer adjacent to the substrate is fast so that the
Figure 4-14: Contribution of Ge-carrier species to deposition rate of Ge films as a function of temperature. The corresponding values of kinetic parameters employed in profile (2) of Figure 4-13 are used in the calculations.

film growth is controlled by the surface reaction. It has been discussed in chapter 3 that this condition occurs when $k_{GeH_4,s} < D_{GeH_4,H_2} / \delta$. For the total reactor pressure of 13 Torr examined here, the surface rate constant of GeH$_4$ ($k_{GeH_4,s}$) equals to 0.15 and 2.2 cm/s, respectively, at the lowest and highest temperatures of 375°C and 500°C investigated. Under these temperatures, the diffusion coefficient of GeH$_4$ in H$_2$ is in the range of 99 to 134 cm$^2$/s. Assuming a maximum value of 1 in (equal to the diameter of the tube) for the thickness of the boundary layer, $D_{GeH_4,H_2} / \delta$ will be 39 cm/s at 375°C and 53 cm/s at 500°C. This value is much larger than the surface rate constant at the corresponding temperature. This indicates that the growth of Ge film is indeed limited by the surface reactions; i.e. the hydrogen desorption at lower temperatures and
GeH₄ chemisorption at higher temperatures.

Consequently, the very small apparent activation energies obtained for GeNW growth at lower temperatures (≤375°C) may also suggest that the process is restricted by chemisorption of GeH₄ and the role of liquid Au as a catalyst is to reduce the barrier for hydrogen desorption.

In this low temperature range, the growth rate of GeNWs increases linearly with increasing germane partial pressure when either the germane flow rate is varied between 15-90 sccm at a constant total reactor pressure of 13 Torr or the total pressure is increased from 13 to 63 Torr by keeping the germane flow rate constant at 50 sccm (Figure 4-15).

Figure 4-15: The variation in growth rate of GeNWs with germane partial pressure. At (●) 300°C and (■) 350°C, the reactor total pressure is changed between 13 and 63 Torr at a constant germane flow rate of 50 sccm. For (▲) T = 375°C the germane flow rate is increased from 15 to 90 sccm at constant Pᵣ = 13 Torr.
Similar to disilane, a simple mechanism can be proposed for GeH₄ decomposition on Au droplet surface indicating the adsorption, desorption and incorporation steps of germane molecule as well as H₂ desorption from the surface:

\[
\begin{align*}
GeH_4(g) & \rightarrow GeH_4^* \\
GeH_4^* & \xrightarrow{k_{d, GeH_4}} GeH_4(g) \\
GeH_4^* & \xrightarrow{k_{I, GeH_4}} Ge(s) + 2H_2^* \\
H_2^* & \rightarrow H_2(g)
\end{align*}
\]

For the steady state condition when the concentrations of surface-adsorbed species remain constant, the fraction of empty surface sites and accordingly the growth rate of GeNW are given by:

\[
\begin{align*}
\theta_e & = \frac{1}{1 + (1 + \frac{2k_{I, GeH_4}}{k_{H_2^*}}) \frac{k_{a, GeH_4}}{k_{d, GeH_4} + k_{I, GeH_4}} P_{GeH_4}} \\
r_{Ge} & = \frac{k_{I, GeH_4} P_{GeH_4}}{k_{d, GeH_4} + k_{I, GeH_4}} \theta_e P_{GeH_4}
\end{align*}
\]

The observed linearity in the growth rate for GeH₄ partial pressures over the range of 0.039-0.5 Torr suggests that the fraction of empty surface sites is near unity. The hydrogen desorption as well as Ge incorporation into the nanowire occurs fast such that almost all surface sites remain open for the adsorption of GeH₄.

### 4.4.1.3 GeNWs grown in AAO template

As mentioned earlier, the feasibility of a TPV system depends not only on its efficiency but its cost. Thus, it is important to reduce the cost of fabrication for example
by using a low cost substrate. The objective of this section, therefore, is to investigate the possibility of GeNW growth on a low cost substrate such as AAO-coated glass. As mentioned in chapter 2, when AAO membrane is used, the gas precursor diffuses into the pores, supersaturates the alloy and initiates the growth. By growing the wires outside the pore and coating them with a shell, radial p-n junctions can be formed.

The studies of GeNW growth on Si substrates, presented in the previous section, showed that temperatures ranging from 275ºC to 400ºC would lead to the synthesis of wires. However, increasing the temperature above 350ºC would cause tapered wires, indicating gas phase decomposition and radial growth on the surface of the nanowire. For the case where AAO membranes are used, the thin film deposition on the surface would cover the pores and block the diffusion of GeH₄ to the metal. Hence, low temperatures and pressures are required to grow nanowires inside the pores.

Using the lowest temperature limit of 275ºC and 50 sccm of GeH₄, 5 hour-long growths of GeNWs on glass substrate are carried out at total reactor pressures of 20 and 30 Torr. The SEM images in Figures 4-16 (a) and (b) show that at Pₑ = 20 Torr, the wires density coming out of the pore is low. Increasing the total pressure increased the wire density. However, in both cases the wires tend to crawl on the surface rather than stick out of the substrate.

This issue was improved by increasing the temperature to 300ºC. As can be seen from the cross sectional images in Figure 4-16(c), more wires are standing straight out of the pores. The length of the wires is 1-2 µm and their diameter is about 100 nm close to the diameter of AAO membrane which suggests that the Ge nanowires are growing out of the AAO pores rather than growing on the surface of the membrane.
Figure 4-16: (a,b) Plan view SEM images of GeNWs grown on AAO-coated glass substrate at 275°C and $P_t=20$ Torr and $P_t=30$ Torr, respectively. (c) Cross sectional SEM image of GeNWs grown at $T=300°C$ and $P_t=13$ Torr.
Although growth of GeNWs on AAO-coated glass substrates is achieved, the change of quality of the surface of the substrates in different batches of substrates caused non-uniformity in density and yield. Hence, in the second part of this study which focuses on the growth of radial p-n junction GeNWs, either Si or Ge substrates are used to investigate suitable conditions for the formation of a p-type core and an n-type shell.

4.4.2 Growth properties of radial p-n germanium nanowires

As discussed in chapter 1, the radial heterostructures can be formed if the growth condition is changed in a way that adsorption/decomposition of vapor phase occurs on the nanowire sidewall as opposed to the liquid droplet surface. By changing the gas sources or using different dopants, core-shell heterostructure nanowires can be synthesized. In the case of GeNWs, by flowing trimethylboron (TMB) or diborane (B₂H₆) simultaneously with germane (GeH₄) at conditions favorable for axial growth, a p-type core can be formed. Switching the dopant source to phosphine (PH₃) and changing the growth condition to promote vapor-solid growth on the nanowire surface will coat the wire with an n-type shell and a radial p-n junction will form.

Hence, to fabricate the radial p-n junction GeNW arrays, first it would be necessary to find appropriate conditions for the growth of both p-type core and n-type shell and to study the effect of intentional doping on the structural properties of wires. To accomplish this goal, the growth of GeNWs in the presence of diborane for synthesizing p-type nanowires is investigated. Since the n-type shell on the nanowire surface forms via a vapor-solid mechanism, first n-type Ge thin film calibration runs are
carried out to develop the necessary conditions for nanowire coating. By gathering the information from both steps, attempts are made to synthesize core-shell GeNW arrays.

4.4.2.1 P-type Ge nanowires

To investigate the incorporation of diborane as the p-type dopant in the GeNW, the growths are carried out at 300°C, P\textsubscript{i}=13 Torr, v_{GeH4}=50 sccm on silicon substrate coated with 3 nm Au thin film. Three dopant ratios of B\textsubscript{2}H\textsubscript{6}/GeH\textsubscript{4}, 3.3×10\textsuperscript{-5}, 1×10\textsuperscript{-4}, 5×10\textsuperscript{-3}, are examined. Results are depicted in Figure 4-17.

It is observed that increasing the dopant ratio up to 1×10\textsuperscript{-4} does not alter the diameter of the wires significantly and they are similar to that of undoped GeNWs (Figure 4-10 (b)). However, at the highest dopant ratio, the wires are dramatically tapered indicating the B-enhanced thin film deposition on the nanowire sidewall. Tutuc et al.\textsuperscript{34} reported similar results when growing a B-doped GeNW with a dopant ratio of 3.3×10\textsuperscript{-3}. Also their attempt to grow a segment of undoped GeNW followed by a segment of p-doped GeNW resulted in coating the undoped GeNWs with a p-type shell. These observations imply that boron mainly gets incorporated through the nanowire surface rather than the Au metal. The same mechanism of dopant incorporation has been suggested for n-type doping of GeNWs in the presence of phosphine.\textsuperscript{35} In addition, atom probe tomography has revealed that the distribution of phosphorus is radially inhomogenous and the dopant concentration increases monotonically with increasing distance from the wire tip owing to longer exposure to phosphine at the base.\textsuperscript{75} This can cause variation in the resistivity of a GeNW both in the radial and axial direction. Hence,
Figure 4-17: SEM images of p-type GeNWs grown at 300°C with dopant ratios of (a) $\text{B}_2\text{H}_6/\text{GeH}_4 = 3.3 \times 10^{-5}$ (b) $\text{B}_2\text{H}_6/\text{GeH}_4 = 10^{-4}$, and (c) $\text{B}_2\text{H}_6/\text{GeH}_4 = 5 \times 10^{-3}$. 
the dopant incorporation through the surface should be suppressed to get more uniformly doped wires.

4.4.2.2 N-type Ge deposition

To find the desired growth rate, uniformity and dopant concentration of the n-type Ge shell for GeNWs coating, calibration runs were initially carried out by growing n-type Ge thin films on sapphire substrates and then the optimum condition was transferred onto GeNWs to regrow n-type shell on their sidewalls.

4.4.2.2.1 Thin film calibration experiments

In section 4.4.1.2, for comparison purposes with GeNW growth, the deposition rate of undoped Ge films on sapphire substrate as a function of temperature was obtained for a germane partial pressure of 0.13 Torr. It was observed that the deposition rate of Ge film increases with increasing the temperature only up to about 425°C and above that point it remains constant. Therefore, to further enhance the growth rate at these high temperatures, higher germane partial pressures should be used. Consequently, for calibration runs, undoped Ge films are deposited by flowing 80 sccm of GeH$_4$ (corresponding to $P_{\text{GeH}_4} = 0.21$ Torr) through the reactor during the growth. The total pressure and the total flow rate are kept constant at 13 Torr and 100 sccm, respectively. Thickness uniformity and the growth rate of the Ge films are investigated by changing the reactor temperature from 425°C to 500°C. For this set of experiments, the substrates
are positioned approximately at the center of the tube, commonly used throughout this study for nanowire growth.

Figure 4-18 shows the result of thickness measurements along the sapphire substrate where the growth rate of the film is plotted against different positions on the sample. It can be seen that in all cases, the growth rate decreases from the leading edge to the trailing edge of the substrate due to the gas phase depletion, mainly by heterogeneous reactions on the reactor wall which commonly occurs in hot wall CVD reactors. Indeed a coating on the tube wall is observed when temperatures above 375°C are used which is believed to be Ge film. Depletion of GeH₄ from the gas phase reduces the partial pressure along the tube and decreases the growth rate. Accordingly, when the substrate is located at the center of the tube, the maximum temperature at which more uniform film with less change in thickness along the substrate can be obtained is 450°C. However, if the depletion effect is reduced by simply pushing the boat 3 cm closer to the gas inlet (while the substrate is still in the hot zone), higher temperatures can be functional to grow uniform films. This is demonstrated in Figure 4-18 for a deposition temperature of 600°C.

Therefore, in the following studies in order to determine the dopant concentration of n-type Ge films deposited on sapphire as well as to regrow Ge layer on GeNWs, the boat has been moved forward towards the gas inlet (about 3 cm from the tube center).

By choosing two temperatures of 450°C and 600°C, doping of Ge films is studied by changing the inlet PH₃ to GeH₄ ratios from 2×10⁻⁵ to 2×10⁻², as shown in Tables 4-3 and 4-4. For the entire PH₃/GeH₄ ratios examined at 600°C and those below 2×10⁻³ at 450°C, the growth rate of doped Ge films is comparable to that of the undoped film.
Figure 4-18: Growth rate as a function of position on the substrate for undoped Ge thin films grown at $P_t = 13$ Torr. Solid symbols are when the substrate is approximately located at the center of the tube and open symbols indicate that the boat is pushed 3 cm closer to the gas inlet.

Based on the Hall measurement results at $450^\circ C$, the lightly doped thin films are actually p-type. Two factors may have caused this discrepancy: localized shallow electronic states near the edge of the valance band, particularly in the grain boundaries or some contamination in the CVD system. In order to get enough phosphine incorporated into the film, the dopant ratio needs to be increased to $2\times10^{-3}$. Attempt to reach higher dopant levels by increasing the $PH_3/GeH_4$ ratio to $2\times10^{-2}$ results in a significant decrease in growth rate as well as carrier density.

Although lowering the $GeH_4$ flow rate to 40 sccm - to keep the total flow rate constant - could reduce the growth rate, the decrease is more than half fold corresponding
to the common linear dependency of growth rate on partial pressure. This is considered to be an effect of phosphine. Introducing the dopant precursor into the reactor causes competition between GeH$_4$ and PH$_3$ for adsorption sites.$^{76}$ At higher phosphine concentrations, more phosphorus covers the surface reducing the free sites for germane adsorption and hence decreases the growth rate. Higher P coverage also enhances the chance for adsorbed monoatoms to interact and form electrically inactive P$_2$ dimmers$^{77,78}$ which in turn may cause a decrease in carrier density. The formed dimmers may change the structure of the layer as well, since they do not directly get incorporated into the film.

Table 4-3: Average growth rate and electrical properties of Ge thin films deposited on sapphire at 450°C and a total pressure of 13 Torr.

<table>
<thead>
<tr>
<th>PH$_3$/GeH$_4$ ratio</th>
<th>$v_{\text{GeH}_4}$ (sccm)</th>
<th>$v_{\text{total}}$ (sccm)</th>
<th>Growth rate (nm/min)</th>
<th>Resistivity ($\Omega .\text{cm}$)</th>
<th>Carrier Type</th>
<th>Carrier Density (cm$^{-3}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-3}$</td>
<td>80</td>
<td>100</td>
<td>32.7</td>
<td>0.0505</td>
<td>p-type</td>
<td>$2.405 \times 10^{18}$</td>
<td>51.3</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>80</td>
<td>100</td>
<td>31.7</td>
<td>0.0885</td>
<td>p-type</td>
<td>$2.343 \times 10^{18}$</td>
<td>30.1</td>
</tr>
<tr>
<td>$2 \times 10^{-3}$</td>
<td>80</td>
<td>100</td>
<td>39.7</td>
<td>0.0345</td>
<td>n-type</td>
<td>$1.77 \times 10^{19}$</td>
<td>10.2</td>
</tr>
<tr>
<td>$2 \times 10^{-2}$</td>
<td>40</td>
<td>100</td>
<td>2.4</td>
<td>0.37</td>
<td>n-type</td>
<td>$3.33 \times 10^{18}$</td>
<td>5.0</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>80</td>
<td>120</td>
<td>11.7</td>
<td>0.12</td>
<td>n-type</td>
<td>$3.1 \times 10^{19}$</td>
<td>1.6</td>
</tr>
</tbody>
</table>

To get higher carrier densities with reasonable film thicknesses at 450°C, the inlet dopant ratio is reduced to $1 \times 10^{-2}$ by using 80 sccm of germane gas source and increasing the total flow rate to 120 sccm. The growth rate is improved and higher electron density is obtained which is desirable for coating of GeNWs.

Interestingly, when the inlet dopant ratio is set to $1 \times 10^{-2}$ at 600°C (for GeH$_4$ and
total flow rates of 80 and 120 sccm, respectively), the electron concentration is lowered compared to that of 450°C. In order to get the maximum electron concentration at 600°C, the PH₃/GeH₄ ratio should be reduced to 1×10⁻³. One possibility is the interaction of PH₃ with GeH₄ precursor in the gas phase which will be more significant at higher temperatures. Another reason is the depletion of GeH₄ on the reactor wall which decreases the germane concentration along the reactor particularly at higher temperatures. For example, based on the kinetic model developed in section 4.4.1.2, the decomposition of GeH₄ at the lower temperature of 450°C is about 29%, but it doubles when the temperature is increased to 600°C and thus, reduces the concentration of GeH₄ above the substrate to 0.37 of its initial flux.

Table 4-4: Average growth rate and electrical properties of Ge thin films deposited on sapphire at 600°C and a total pressure of 13 Torr.

<table>
<thead>
<tr>
<th>PH₃/GeH₄ ratio</th>
<th>ν₃ (sccm)</th>
<th>νtotal (sccm)</th>
<th>Growth rate (nm/min)</th>
<th>Resistivity (Ω.cm)</th>
<th>Carrier Type</th>
<th>Carrier Density (cm⁻³)</th>
<th>Mobility (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6×10⁻⁴</td>
<td>80</td>
<td>120</td>
<td>34.7</td>
<td>0.0104</td>
<td>n-type</td>
<td>1.04×10¹⁹</td>
<td>51.3</td>
</tr>
<tr>
<td>1×10⁻³</td>
<td>80</td>
<td>120</td>
<td>34.1</td>
<td>0.0056</td>
<td>n-type</td>
<td>2.62×10¹⁹</td>
<td>30.1</td>
</tr>
<tr>
<td>2×10⁻³</td>
<td>80</td>
<td>120</td>
<td>36.7</td>
<td>0.0149</td>
<td>n-type</td>
<td>1×10¹⁹</td>
<td>10.2</td>
</tr>
<tr>
<td>6×10⁻³</td>
<td>80</td>
<td>120</td>
<td>33.4</td>
<td>0.0452</td>
<td>n-type</td>
<td>6.88×10¹⁸</td>
<td>5.0</td>
</tr>
<tr>
<td>1×10⁻²</td>
<td>80</td>
<td>120</td>
<td>33.6</td>
<td>0.0297</td>
<td>n-type</td>
<td>8.6×10¹⁸</td>
<td>1.6</td>
</tr>
<tr>
<td>2×10⁻²</td>
<td>80</td>
<td>120</td>
<td>34</td>
<td>0.0409</td>
<td>n-type</td>
<td>6.3×10¹⁸</td>
<td></td>
</tr>
</tbody>
</table>

Both these factors, gas phase reactions and germane depletion, can change the actual concentration of PH₃ and GeH₄ above the substrate. Thus, different initial dopant
ratios should be used at different temperatures in order to obtain the maximum carrier density.

4.4.2.2 Shell deposition on Ge nanowires

Unintentional p-type doping in the system on one hand and using a highly p-doped Ge substrate ($\rho \sim 0.05 \ \Omega \cdot \text{cm}$) on the other hand would most likely cause the GeNWs to be p-type. Hence to avoid inhomogeneous dopant distribution along the wires, initial studies of p-n radial junctions are carried out by coating undoped GeNWs with an n-type shell. Among previously examined growth conditions described in 4.4.1.1, the temperature of 375°C was chosen to grow undoped GeNWs on (111) p-type Ge substrate using 50 nm Au nanoparticles at total reactor and germane partial pressures of 38 and 0.38 Torr. This condition is deliberately selected to get tapered structures since as mentioned earlier, they have shown lower photon reflectivity and higher absorption compared to nanowires with uniform diameter, which could be beneficial in increasing the efficiency of the TPV system.

Before coating, gold is removed from the wires tip using a wet etching process and submerging the sample in a 9:1 ratio of TFA (a commercial gold etchant) and HCl (36%) mixture for about 25 seconds followed by rinsing in 1M HCl, DI water and isopropanol. The gold concentration analyzed by X-ray energy dispersive spectroscopy is below the detection limit indicating successful removal of the majority of Au from the wires (Figure 4-7 (c)).

Based on thin film calibration results in Table 4-3, deposition of n-type shell on
GeNWs is first investigated at the lower temperature of 450°C by choosing the optimum PH$_3$/GeH$_4$ ratio of $1 \times 10^{-2}$, for which maximum electron concentration is obtained. For comparison purposes, a piece of Ge substrate is also loaded in the reactor during the growth to make planar p-n diodes.

At this condition, a thickness of about 120 nm is expected for 10 min growth. Coating of GeNWs increases the average diameter of the wires near the tip to 191±11 nm (Figure 4-19 (a)), which compared to that of wires prior to coating (~50 nm) results in n-type layer of about 71 nm thick. The tapering rate is 54.8 ± 5.7 nm/μm which is similar to that of uncoated wires indicating uniformity in thickness along the length of the nanowires. TEM images in Figure 4-19 (b)-(d) reveals a rough surface for these wires. The shell has planar defects and is consisted of crystalline grains misoriented with respect to the surface of the core.

To investigate the electrical characteristic of the samples grown at this lower temperature, NW as well as planar diodes are fabricated. The fabrication method of diodes has previously been discussed in chapter 2.

The I-V characteristics of the planar diode in Figure 4-20 shows clear current rectification. However, a more linear behavior is observed in the case of NWs indicating a leaky diode.

There are several factors that may contribute to the observed I-V characteristics for the GeNW samples. While the gold etch was successful at removing the majority of the gold from the surface of the NW samples, it is possible that residual amounts are still present and serve to short out the device when the p-n junction is formed. In addition, while the n-type Ge thin film appears to coat the NWs conformally over their entire
Figure 4-19: (a) Cross sectional SEM and (b) TEM images of GeNWs coated with n-type Ge shell at 450°C and dopant ratio of $1 \times 10^{-2}$. The inset in (a) is the lower magnification SEM image. (c) Diffraction pattern indicating crystalline grains of Ge. (d) HRTEM of the n-type shell.

length, it is possible that the layer is very thin at the base of the wires and may short out the devices when the indium contact is made.

In addition, the polycrystalline coating of the n-type shell on GeNWs could have
lead to carrier recombination at the grain boundaries at the p-n junction interface which would reduce the device efficiency. Thus, it is important to improve the structural quality of the coating and to obtain a single crystalline shell. Prior studies on SiNWs have shown that when the deposition temperature of n-type shell on SiNW sidewalls is increased, the coating changes from rough polycrystalline surface to smooth single crystalline shell.79

Figure 4-20: Current-voltage characteristic of Ge p-n (a) planar and (b) radial nanowire diodes fabricated from the samples grown at 450°C and PH3/GeH4 = 1×10⁻².

Following this result, it is suitable to investigate the higher deposition temperature of 600°C in the present study in order to get a better n-type coating for GeNW. PH3/GeH4 ratio of 1×10⁻³ in Table 4-4 is selected to dope the shell as highly as possible. However, as shown in Figure 4-21, no improvement is achieved and the shell still remains rough.

Since not only the temperature but also the dopant may cause the roughness of the coating, a systematic examination of the former is undertaken to clarify its effect by
eliminating the phosphine dopant in the system. For this purpose, undoped shells are regrown on GeNWs and the influence of temperature on the morphology of coating is studied in the range of 450 - 600°C. Other growth conditions are held the same as those used for the n-type coating; *i.e.* total reactor pressure of 13 Torr, total flow rate of 120 sccm and germane flow rate of 80 sccm. For all temperatures, deposition of the undoped shell is carried out for 10 min except $T = 600^\circ$C for which a 3 min growth is used.

![Figure 4-21](image)

**Figure 4-21:** SEM image of a GeNW coated with n-type Ge shell at 600°C and dopant ratio of $1\times10^{-3}$ for 3 min growth. The inset shows the lower magnification cross-sectional image of wire arrays indicating a rough surface for all the nanowires.

The FESEM images in Figure 4-22 illustrate the results. It can be seen that even in the absence of PH$_3$, smooth coatings cannot be obtained when either temperatures of 450 or 600°C are used. The surface roughness of the coating can be removed and a
smooth undoped shell can be regrown on GeNWs only if the intermediate temperatures of 500 - 550°C are chosen.

Although the appropriate choice of temperature assures a smooth undoped coating, it cannot produce the same result for n-type shells if any dopant ratios are used since phosphine can also influence the morphology of the surface. This is shown in Figure 4-23 when n-type shells are deposited at optimized temperatures of 500 and 550°C and an arbitrary PH3/GeH4 ratio of 5×10^{-2}. Introducing the dopant at such high ratio indeed affects the surface, causing roughness and suggests that lower dopant ratios should be applied.

Figure 4-22: SEM images of GeNWs coated with undoped Ge shell at different temperatures of (a) 450°C, (b) 500°C, (c) 550°C and (d) 600°C.
Consequently, deposition of n-type shells on GeNWs would not be possible if both the growth temperature and the dopant ratio are not optimized. Based on the experiments one can conclude that the former should be in the range of 500-550°C, while further investigations are required to find the optimum dopant ratio at these temperatures to coat GeNWs with n-type shells that are smooth and have electron concentrations as high as possible.

Figure 4-23: SEM images of GeNWs coated with n-type Ge shell at temperatures of (a) 500°C and (b) 550°C and PH₃/GeH₄ ratio of 5×10⁻².
4.5 Conclusions

In general, the fabrication of GeNWs strongly depends on the growth temperature and is achievable only for very narrow range of about 300-400°C. The choice of temperature is further restricted depending on the type of structure needed. If nanowires with uniform diameter are desired, growth temperatures lower than 350°C have to be chosen as above this point uncatalyzed radial growth on nanowire sidewall results in tapered nanowires. For the same reason, lower temperatures should be used to grow GeNWs on AAO-coated glass substrates since the simultaneous thin film deposition along with nanowire growth can cover the pores and block the diffusion of GeH₄ to the metal.

The uncatalyzed radial growth on nanowire sidewall at temperatures above 350°C can be taken advantage of to form nanocone structures which are of interest for PV applications due to their capability to lower the photon reflectivity and to increase the absorption. These structures can be further modified in the form of radial p-n junction GeNWs to be explored as PV cells. The morphology of both the p-type core and the n-type shell is influenced by temperature and dopant ratios.

p-type GeNWs with uniform diameter can be obtained if the diborane to germane ratio is kept low as the B-enhanced thin film deposition on the nanowire sidewall at higher dopant ratios (B₂H₆/GeH₄ = 1×10⁻⁴ at 300°C) can cause tapered wires with nonuniform distribution of dopants along their length. The electrical properties of these tapered p-doped GeNW structures would be interesting to examine in order to find out how the dopant incorporation and wire tapering at higher B₂H₆/GeH₄ ratios would affect
the device properties.

A GeNW core can be coated with an n-type shell by choosing the appropriate growth conditions, namely the temperature and the dopant ratio. Deposition of a smooth Ge layer on GeNW sidewalls is possible only when growth temperatures of 500 to 550°C are used. Below or above this range, the surface of coated nanowire becomes rough even in the absence of phosphine and the shell becomes polycrystalline. For the optimum temperature range, the amount of phosphine flown during the growth can also change the morphology. For example, when $\text{PH}_3/\text{GeH}_4$ ratio is set to $5 \times 10^{-2}$ the surface of the coating again becomes rough. Thus, more thorough investigation is required to find the optimum dopant ratio at these temperatures to coat GeNWs with n-type shells that are smooth.

To investigate the effect of structure on the performance of the radial p-n nanowires it would be helpful to measure single nanowires since the contact can be directly made on the n-type shell which could avoid shorting out the device. More radial p-n GeNW array devices should be fabricated and their properties should be studied.

4.6 References

Choi, J. H. Kang, and H. J. Joyce, Nanotechnology 21, 295602.


5.1 Introduction

Besides Si and Ge nanowires discussed so far, yet another interesting material for future group IV semiconductor nanowire electronic and optoelectronic applications is their SiGe alloy. $\text{Si}_{1-x}\text{Ge}_x$ offers a variable system of lattice constants and energy band gaps that can be realized through its adjustable chemical composition. This property has been widely investigated in studies of thin films and has been shown to have a noticeable influence on the electrical and optical characteristics of the alloy.\textsuperscript{1-4} Similar to thin films, the physical properties of $\text{Si}_{1-x}\text{Ge}_x$ alloy nanowires are also expected to depend on their composition. In fact, Yang \textit{et al.} showed that the optical band-edge of $\text{Si}_{1-x}\text{Ge}_x$ NWs could be tuned by varying both the Ge fraction and the nanowire diameter.\textsuperscript{5} Consequently, it is of critical importance to gain control over the chemical composition of $\text{Si}_{1-x}\text{Ge}_x$ nanowires by better understanding the growth mechanism and the effect of growth conditions on the properties of these nanowires.

Previous reports have shown that the Ge fraction of $\text{Si}_{1-x}\text{Ge}_x$ nanowires can be influenced by different growth parameters such as temperature and precursor gases ratio,\textsuperscript{6-8} diameter of the nanowire\textsuperscript{9} and total reactor pressure\textsuperscript{10} as well as dopant gases\textsuperscript{11}. In all these reports, the effect of growth conditions was examined when silane and germane were used as the source gases. Lew \textit{et al.}\textsuperscript{7} found that due to differences in the
thermal stabilities of these two precursors, a narrow range of Ge fraction can be obtained at a constant temperature such that higher temperatures (>400°C) and lower inlet gas ratios favor the growth of Si-rich Si$_{1-x}$Ge$_x$ nanowires (Figure 5-1), whereas lower temperatures (<400°C) and higher gas ratios are required to obtain Ge-rich alloys, otherwise a tapered structure will form due to Ge deposition on the nanowire sidewalls. It was also observed that for both Si-rich and Ge-rich SiGe nanowires, the Ge concentration could strongly depend on the nanowire diameter if wires are thinner than ~50 nm in diameter$^9$ (Figure 5-2).

![Figure 5-1: Effect of growth conditions on the Ge composition in the Si$_{1-x}$Ge$_x$ nanowires grown using SiH$_4$ and GeH$_4$.$^7$](image)

Ideally, it would be technologically attractive to have a growth process that can vary Ge composition in SiGe alloy nanowires from 0 % to 100 % at a constant temperature. Givan et al.$^{10}$ illustrated that this could be achieved if the total reactor
pressure is changed at a constant temperature and precursor gases ratio. However, according to their results, represented in Figure 5-3 (a), lower total pressures yield Si-rich SiGe nanowires and thus, in order to get about 70% germanium fraction at 350°C, pressures as high as 1000 Torr should be used. In addition, the growth of GeNWs is not successful under the conditions used to grow SiGe NWs (Figure 5-3 (b)). Moreover,

![Figure 5-2: Ge concentration as a function of diameter in SiGe nanowires grown using SiH₄ and GeH₄.](Image)
the introduction of dopant gases during the growth increases the Si content, especially in the case of boron doped nanowires which doubles the Si/Ge ratio in comparison to the intrinsic wires (Figure 5-4).

![Graph showing the dependence of Si concentration on growth pressure](image)

Figure 5-3: (a) Dependence of Si concentration of Si$_{1-x}$Ge$_x$ nanowires grown at 350°C using SiH$_4$ and GeH$_4$ on growth pressure. (b) ESEM images of Ge grains obtained under the same conditions of SiGe nanowires at total reactor pressures of 100 (left), 500 (middle) and 1000 (right) Torr.$^{10}$

Taken as a whole, the findings on the growth of SiGe nanowires by using silane and germaine precursors along with the differences in growth conditions of SiNWs and GeNWs from these source gases indicate that the fabrication of certain types of heterostructures may not be readily viable. As shown in chapters 3 and 4, SiNWs are
Figure 5-4: Influence of doping on Si composition of Si$_{1-x}$Ge$_x$ nanowires grown using SiH$_4$ and GeH$_4$ gases under a growth temperature of 350°C and a total reactor pressure of 200 Torr.$^{11}$

normally grown at temperatures above 400°C by using silane, whereas GeNW growth is carried out at lower temperatures (300-400°C). The difference in growth conditions complicates the fabrication of specific types of heterostructures, namely Si/Si$_{1-x}$Ge$_x$ where $x$>0.5 and Ge/Si$_{1-x}$Ge$_x$ with $x$<0.5, both of which are of interest for fundamental studies of nanowire heteroepitaxy as well as device development as it will be discussed in chapter 6.

This limitation shows a need for a different approach to tune the chemical composition of Si$_{1-x}$Ge$_x$ nanowires over a wide range under the growth conditions that additionally yield the fabrication of individual Si and Ge nanowires. Considering the higher reactivity and higher adsorption probability of disilane compared to SiH$_4$
(illustrated in chapter 3), a possible method may be the use of Si$_2$H$_6$ as an alternative Si source gas to grow SiGe nanowires.

The feasibility of Si$_{1-x}$Ge$_x$ NW growth from Si$_2$H$_6$ and GeH$_4$ precursors has previously been reported in low pressure$^{12}$ and ultra high vacuum CVD systems$^{13}$. Both these studies only focused on high growth temperatures above 400°C and examined the influences of growth parameters on Ge fractions less than about 50%. A trend similar to that of SiH$_4$ was observed where increasing total pressure and GeH$_4$/Si$_2$H$_6$ ratio increased Ge concentration. It was also found that the morphology of nanowires can change depending on the Ge concentration.$^{13}$ For x$_{Ge}$ lower than a temperature dependent minimum (for example x$_{Ge}$=0.17 at 400°C), SiGe NWs adopt a Si-like characteristic and grow with Au decorated sidewalls along the $<111>$ direction if lower total pressures are used, while they exhibit Au-free sidewalls grown in $<112>$ direction at higher total pressures. For x$_{Ge}$ greater than the minimum, SiGe nanowires take Ge-like characteristics and follow $<111>$ growth direction with Au-free sidewalls.

Slightly tapered SiGe nanowires that were grown at 450°C by flowing Si$_2$H$_6$ and GeH$_4$ gases have also been used to demonstrate the ability of micro-Raman spectroscopy to determine the distribution of Ge composition in individual nanowires.$^{14,15}$ The analysis confirmed a core-shell structure with a low-Ge composition core and a high Ge composition shell neither of which are uniform, but gradually change along the axis resulting in Ge composition distribution both in the radial and axial directions.$^{14}$

Although disilane has been employed as the Si source to grow SiGe nanowires, its potential has not been fully exploited as of yet to control the chemical composition of these wires over a wide range. In addition, there is still a lack of detailed studies on the
influence of growth parameters on the growth rate of SiGe nanowires when Si$_2$H$_6$ is used. This chapter attempts to fulfill this task by examining the variations in growth rates with growth conditions. Among different growth parameters that were previously shown to impact the process when SiH$_4$ is used, only the effects of temperature and precursor partial pressures are examined here on undoped SiGe nanowire growth. Total growth pressures as well as dopants are also important parameters to be examined in the future.

5.2 Growth conditions

SiGe NWs were grown on oxidized silicon substrates coated with 3 nm Au thin films by flowing Si$_2$H$_6$ and GeH$_4$ gases through the reactor as the sources of Si and Ge, respectively. The influence of the variation in growth parameters on both Ge composition and growth rate of $\text{Si}_{1-x}\text{Ge}_x$ nanowires was investigated by changing the growth temperature and the inlet germane/disilane ratio while the total reactor pressure was kept constant at 13 Torr. Temperatures in the range of 350°C to 425°C were examined. For all these temperatures, the disilane flow rate was fixed at 5 sccm ($P_{\text{Si}_2\text{H}_6} = 0.0065$ Torr), and the flow rate of GeH$_4$ was varied from 5 sccm to 90 sccm (corresponding to $P_{\text{GeH}_4} = 0.013$ - 0.234 Torr) to control the inlet GeH$_4$/Si$_2$H$_6$ ratio over the range of 2 to 36. At 375°C, additional growths were performed by keeping the germane flow rate constant at 60 sccm and changing the disilane flow between 3 and 30 sccm such that similar GeH$_4$/(GeH$_4$+Si$_2$H$_6$) ratios were obtained. During the experiments, the H$_2$ flow rate was adjusted to keep the total flow constant at 100 sccm and the nanowires were grown for 45 min.
5.3 Results

The successful growth of SiGe nanowires over the entire investigated range of temperatures and GeH₄/Si₂H₆ inlet gas ratios enabled studies to explore the consequence of variations in growth parameters on the structure, Ge composition and length of these nanowires as will be discussed in the following sections.

5.3.1 Structural properties of Si₁₋ₓGeₓ nanowires

SiGe NWs with reasonable density and length were obtained for all the growth conditions examined here. As shown in Figure 5-5, at lower temperatures ( ≤ 400°C ), the nanowires are quite uniform in diameter along their length and are not affected by the Ge deposition on their sidewalls even at the highest GeH₄ partial pressure examined. Figure 5-6 demonstrates a TEM micrograph of such nanowires grown at 375°C and GeH₄/Si₂H₆ ratio of 2. The SiGe nanowire grown in the (110) growth direction has smooth surface with a diameter of 41 nm over its entire length, indicating negligible tapering effect. X-ray energy dispersive spectroscopy (XEDS) composition line profiles across the nanowire body (Figure 5-6(g) and (f)) indicate a constant Si to Ge ratio both near the tip and the bottom of the nanowire confirming a homogeneous distribution of Ge in the radial direction. An amorphous region between the tip and the nanowire is evident. XEDS indicates that this amorphous region consists of Au, Si, and Ge, as well as O. From the collected XEDS spectra, the Ge composition is extracted to be (24.4 ± 0.7) at.% near the tip and (25.3 ± 0.6) at.% near the bottom of the nanowire which proves that the chemical composition of the nanowire is homogeneous both radially and axially.
Figure 5-5: Cross-sectional SEM images of SiGe nanowires grown at (a) 350°C (b) 375°C and (c) 400°C with GeH₄/Si₂H₆ = 36.
Figure 5-6: (a) Low-magnification bright-field TEM image of a SiGe nanowire grown at 375°C and GeH₄/Si₂H₆ = 2. (b) and (c) Higher magnification images collected from the bottom (not shown in (a)) and tip regions of the NW, respectively. (d) SAD pattern corresponding to (b). (e) XEDS spectra collected near the bottom of the NW and composition line profiles collected from (f) BB', and (g) CC' indicated in (b) and (c).
The uniformity in nanowire diameter becomes affected as the temperature is increased to 425°C (Figure 5-7). At this temperature, nanowires are uniform in diameter only up to a GeH₄/Si₂H₆ inlet ratio of 14. Once higher germane partial pressures are used to enhance the inlet ratio above 24, the wires become tapered due to Ge deposition on their sidewalls.

Figure 5-7: SEM images of SiGe nanowires synthesized at growth temperature of 425°C and inlet GeH₄/Si₂H₆ ratios of (a) 8, (b) 14, (c) 24, and (d) 36.

In this case, the surface of the nanowire is smooth only near the Au tip and it becomes rough with a high density of defects towards the center and the bottom of the nanowire which is believed to form due to uncatalyzed vapor-solid deposition on the surface. An example of these types of wires is shown in Figure 5-8 for a growth
condition of 425°C and GeH$_4$/Si$_2$H$_6$ = 36. Based on the XEDS composition line profiles, the Ge to Si ratio is constant across the NW body near the tip, except the two points near the NW surface, which is believed to be an artifact. Moving away from the Au tip, the Ge/Si ratio becomes slightly larger near the surface than the center of the NW, suggesting the Ge deposition on the nanowire sidewalls. The composition near the tip and bottom of this SiGe NW is (85.2±0.4) at.% Ge and (88.7±0.3) at.% Ge, respectively.

Figure 5-8: Low-magnification bright-field TEM image of a tapered SiGe nanowire grown at 425°C and GeH$_4$/Si$_2$H$_6$ = 36. (b), (c), and (d) are higher magnification images collected from the bottom, middle, and tip regions of the NW, respectively. (b) and (c) are the XEDS composition line profiles collected from BB’ and DD’, respectively, indicated in (b) and (d).
5.3.2 Composition of Si$_{1-x}$Ge$_x$ nanowires

As described in the previous section, the relative composition of Si and Ge in Si$_{1-x}$Ge$_x$ nanowires of a few samples was determined from the XEDS spectra probed on individual nanowires in the scanning TEM mode. However, the main method used in this study to extract the Ge fraction is grazing incidence x-ray diffraction (GIXRD) on arrays of as-grown nanowires as it is less expensive and less time consuming and it has shown to produce reliable results comparable to that obtained from TEM analysis.\textsuperscript{16} From the resultant GIXRD diffractogram, the two-theta positions of the peaks (111), (220), (400) and (331) corresponding to a diamond structure are used to determine the lattice constant and to eventually obtain the Ge composition based on Vegard’s law (discussed in chapter 2). Figures 5-9(a)-(c) illustrate examples of GIXRD spectra of samples grown at 425°C and different GeH$_4$/Si$_2$H$_6$ inlet gas ratios. Standard peak position of bulk Si and Ge are also included to exhibit the progressive shift in peaks from Ge-rich to Si-rich nanowires. Table 5-1 lists the lattice parameters and chemical compositions of the Si$_{1-x}$Ge$_x$ nanowires related to each inlet gas ratio extracted from Figure 5-9.

Table 5-1: Lattice constant and composition of Si$_{1-x}$Ge$_x$ nanowires grown at 425°C determined from GIXRD analysis in Figure 5-9.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>GeH$_4$/Si$_2$H$_6$</th>
<th>Lattice constant</th>
<th>Ge fraction from XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>5.64613</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>36</td>
<td>5.61215</td>
<td>0.84</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>5.57287</td>
<td>0.66</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>5.53027</td>
<td>0.46</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>5.4899</td>
<td>0.27</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>5.43095</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5-9: GIXRD patterns of as-grown SiGe nanowires grown at 425°C, indicating the two-theta positions of (a) (111), (b) (220), (c) (400) and (331) diffractions for inlet gas ratios listed in Table 5-1.
It should be noted that the Ge fraction at the inlet gas ratio of 36 obtained from XRD analysis compares well to that obtained near the tip of the nanowire using TEM analysis. Table 5-2 lists more comparisons on the Ge compositions at different conditions attained from the two methods and shows a close agreement between the two.

Table 5-2: Comparison of Ge fraction determined from XRD and TEM analysis for SiGe nanowires grown at different conditions.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>GeH₄/Si₂H₆</th>
<th>Ge fraction from XRD</th>
<th>Ge fraction from TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>425°C</td>
<td>36</td>
<td>0.84</td>
<td>0.85 near the tip</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.89 near the bottom</td>
</tr>
<tr>
<td>425°C</td>
<td>4</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>375°C</td>
<td>2</td>
<td>0.23</td>
<td>0.25</td>
</tr>
</tbody>
</table>

At the growth temperature of 425°C and GeH₄/Si₂H₆ ratio of 4, the composition of four nanowires with different diameters were examined by TEM and Ge fractions of 0.38, 0.32, 0.33, and 0.26 were obtained, respectively, for nanowires with diameters of 35, 62, 84, and 106 nm. The average of the four compositions is included in Table 5-2. In diameter range of 35-85 nm where the majority of the nanowires are located, the Ge fraction remains almost the same and is unaffected by the nanowire diameter. A slight drop in Ge content was only observed for larger nanowire which needs further investigation.

Returning to Table 5-1 it can be seen that as expected, the Ge composition increases with increasing GeH₄/Si₂H₆ ratio. The observed dependence suggests a
non-linear behavior where the increase in $x_{Ge}$ occurs more rapidly for GeH$_4$/Si$_2$H$_6$ ratios below 14, while above this point the dependence is reduced. This non-linear behavior is more clearly exhibited in Figure 5-10 which illustrates the effect of inlet gas ratio on the Ge fraction of Si$_{1-x}$Ge$_x$ NWs grown for different growth temperatures. The graph shows that by using Si$_2$H$_6$ and GeH$_4$ sources, Ge compositions ranging from a low of $\sim 20$ atom % to a high of $\sim 80$ atom % can be obtained at each temperature by increasing the GeH$_4$ partial pressure. At a given inlet gas ratio, the Ge fraction is observed to increase slightly with increasing temperature.

Figure 5-10: Ge concentration of Si$_{1-x}$Ge$_x$ nanowires as a function of inlet gas ratio (GeH$_4$/Si$_2$H$_6$) at 13 Torr total reactor pressure and constant Si$_2$H$_6$ flow rate of 5 sccm.
If the Ge composition data (Figure 5-10) are re-plotted to show the change in Ge/Si ratio in Si$_{1-x}$Ge$_x$ nanowire with P$_{\text{GeH}_4}$/P$_{\text{Si}_2\text{H}_6}$ (as in Figure 5-11), a linear relationship becomes apparent:

$$\frac{x_{\text{Ge}}}{1 - x_{\text{Ge}}} = m \frac{P_{\text{GeH}_4}}{P_{\text{Si}_2\text{H}_6}}$$  \hspace{1cm} (5-1)

with the slopes listed in Table 5-3. Interestingly, as it can be seen, the ratio of Ge to Si in the nanowire is only about 1/5 of that in the inlet gas phase. This may be due to the depletion of precursors from the gas phase during their residence time in the reactor, which reduces their partial pressure and thus lowers the effective Ge/Si ratio in the gas phase near the substrate as compared to the inlet partial pressures. Si$_2$H$_6$ has low thermal...
stability and decomposes homogenously at relatively low temperatures (~300ºC) producing SiH₂ species that is highly reactive. The interaction of this species with GeH₄ in the gas phase may change the gas phase composition and thus influence the nanowire growth process. Another explanation could be that the sticking probability of GeH₄ on the liquid Au tip is smaller than that of Si₂H₆. Therefore, even though the amount of Si₂H₆ is lower in the gas phase, it adsorbs more efficiently on the droplet than GeH₄ and thereby reduces the Ge/Si ratio in the Au liquid compared to the gas phase; for example, at the highest GeH₄ partial pressure, 0.05% disilane in the gas phase supplies about 20% of Si in the nanowires. The sticking coefficient of GeH₄ has been reported to be lower than that of Si₂H₆ for the case of Si₁₋ₓGeₓ thin film deposition where the germane to disilane sticking probability was calculated as 0.4 at 430ºC and x ~0.5 (14). This may be the case for nanowires as well, although the sticking coefficients of the molecules on the liquid droplet are expected to be much higher (15). Both these possibilities will be further examined in section 5.4.

Table 5-3: The slope of linear relation between Ge/Si ratio in Si₁₋ₓGeₓ nanowire and P.GeH₄/P.Si₂H₆ shown in Figure 5-11.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>0.091 ± 0.002</td>
</tr>
<tr>
<td>375°C</td>
<td>0.1 ± 0.005</td>
</tr>
<tr>
<td>400°C</td>
<td>0.11 ± 0.006</td>
</tr>
<tr>
<td>425°C</td>
<td>0.14 ± 0.004</td>
</tr>
</tbody>
</table>
5.3.3 Growth rate of Si$_{1-x}$Ge$_x$ nanowires

Variations in growth temperature and GeH$_4$/Si$_2$H$_6$ gas ratios influence not only the Ge composition of SiGe nanowires, but also their growth rate. Figure 5-12 shows the measured dependency of SiGe nanowire growth rate on inlet GeH$_4$/Si$_2$H$_6$ ratio as the germane partial pressure increases at different temperatures while the disilane flow rate is held constant. Similar to Ge composition in Figure 5-10, the growth rate increases nonlinearly with increasing GeH$_4$/Si$_2$H$_6$ ratio and exhibits larger changes for lower germane partial pressures.

Figure 5-12: Variation in the growth rate of SiGe nanowires with the GeH$_4$/Si$_2$H$_6$ gas ratio when Si$_2$H$_6$ flow rate is kept constant at 5 sccm and GeH$_4$ partial pressure changes at $P_t = 13$ Torr.
At each GeH₄/Si₂H₆ ratio, the growth rate increases exponentially with increasing temperature (Figure 5-13). Based on the observed Arrhenius behavior, the apparent activation energies can be calculated from the slope. Table 5-4 lists those values for different inlet gas ratios, along with the activation energies of individual SiNW and GeNW growth under the same total reactor pressure of 13 Torr obtained in chapters 3 and 4. As it can be seen, the presence of Ge lowers the temperature dependency of SiGe nanowire growth compared to SiNW and the activation energy of the process moves away from that of SiNW to that of GeNW as the germanium content of the nanowire increases.

Figure 5-13: Temperature dependence of the growth rate of Si₁₋ₓGeₓ nanowires.
It has been proposed in preceding chapters that the growth of individual Si and Ge nanowires are not controlled by a similar rate-limiting step. Based on the resemblance of activation energies between Si nanowire growth and Si planar film, the adsorption of source gas which is restricted by its low flux is suggested to regulate the SiNW growth process. In case of GeNW, due to the very small apparent activation energy obtained for the process, the growth rate is suggested to be determined by the chemisorption of GeH4, the rate of which is weakly dependent on temperature for GeH4 adsorption on Ge surface. Consequently, the SiGe nanowire growth process can be restricted by either disilane flux or germane chemisorption or a combination of both depending on GeH4/Si2H6 gas ratio which results in transition of $E_a$ from large values close to SiNW growth to small values approaching GeNW growth as the amount of GeH4 is increased in the gas phase.

Table 5-4: The activation energies of Si$_{1-x}$Ge$_x$ nanowire growth calculated for different inlet GeH4/Si2H6 gas ratios.

<table>
<thead>
<tr>
<th>GeH4/Si$_2$H$_6$</th>
<th>P$_{GeH4}$ (Torr)</th>
<th>Ge content (%)</th>
<th>$E_a$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiNW</td>
<td>-</td>
<td>0</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>0.013</td>
<td>23-27</td>
<td>27.2</td>
</tr>
<tr>
<td>8</td>
<td>0.026</td>
<td>27-35</td>
<td>22.6</td>
</tr>
<tr>
<td>14</td>
<td>0.052</td>
<td>39-46</td>
<td>18.9</td>
</tr>
<tr>
<td>24</td>
<td>0.091</td>
<td>54-66</td>
<td>17.1</td>
</tr>
<tr>
<td>36</td>
<td>0.234</td>
<td>77-84</td>
<td>14.6</td>
</tr>
<tr>
<td>GeNW</td>
<td>0.13</td>
<td>100</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The total growth rate can be broken down into the effective growth rates of the Ge and Si components as depicted in Figures 5-14(a) and (b) if it is assumed that the Si and
Figure 5-14: The growth rates of Ge and Si components of Si$_{1-x}$Ge$_x$ nanowire obtained from the experimental data on growth rates and Ge fraction.
Ge incorporation at the growth front (catalyst-wire interface) is proportional to the Si and Ge fraction in the nanowire. It can be seen that the Ge growth rate component increases with increasing germane partial pressure as would be expected. It is interesting to compare these values with the growth rates of GeNW that would be obtained under similar GeH$_4$ partial pressures and temperatures if Si$_2$H$_6$ was eliminated from the process. Figure 5-15 exhibits this comparison and illustrates the changes in the ratio of growth rate of Ge component of SiGe nanowire to that of GeNW as temperature and GeH$_4$ partial pressure vary. The data on growth rate of GeNW as a function of P$_{\text{GeH}_4}$ are extracted from the results already discussed in chapter 4/section 4.4.1.2. Based on Figure 5-15, one can see that both values of the Ge component in the SiGe nanowire and the GeNW agree well at the lowest temperature of 350°C indicating that the presence of Si$_2$H$_6$ does not affect the incorporation of Ge at this temperature. However, as the temperature is raised the ratio deviates from unity and the growth rates of the Ge component in SiGe nanowire become larger than those of GeNW. In addition, the difference is enhanced for smaller GeH$_4$ partial pressures at higher temperatures.

In view of Si incorporation rate in SiGe nanowire in Figure 5-14, it remains almost the same in the range of GeH$_4$ partial pressures examined at T = 350°C. At higher growth temperatures of 375°C and 400°C, the Si growth rate component shows slight increase with P$_{\text{GeH}_4}$ up to 0.052 Torr, followed by a decrease after reaching a peak and at 425°C, it drops with increasing germane partial pressures.

Generally the results show that both the Si and Ge incorporation into the Si$_{1-x}$Ge$_x$ nanowire are affected by the presence of GeH$_4$ during the growth, which in turn influences the total growth rate of the nanowire as the amount of germane is altered.
Figure 5-15: The ratio of growth rate of Ge component of SiGe nanowire to that of GeNW in the absence of Si$_2$H$_6$ as a function of temperature and GeH$_4$ partial pressure.

The variation in growth rate is not limited to GeH$_4$ partial pressure, but it also occurs when the Si$_2$H$_6$ flow rate is changed. This was investigated at the growth temperature of 375°C by keeping the germane flow rate constant at 60 sccm (corresponding to P$_{\text{GeH}_4} = 0.156$ Torr) and changing the disilane flow between 3 and 30 sccm. Disilane flow rates were chosen such that the ratio of GeH$_4$/(GeH$_4$+Si$_2$H$_6$) is similar to the case when the germane partial pressure is changed at constant P$_{\text{Si}_2\text{H}_6} = 0.0065$ Torr. Increasing Si$_2$H$_6$ partial pressure reduces the Ge composition as expected and increases the growth rate nonlinearly similar to what has been observed at constant P$_{\text{Si}_2\text{H}_6} = 0.0065$ Torr. A comparison of the two situations is depicted in Figures 5-16(a) and (b). While similar Ge compositions were obtained in both cases, the growth rates
Figure 5-16: Comparison of the variation in the (a) Ge content and (b) growth rate of Si$_{1-x}$Ge$_x$ nanowires when either germane partial pressure changes at P$_{\text{Si}_2\text{H}_6} = 0.0065$ Torr or disilane flow rate varies at P$_{\text{GeH}_4} = 0.156$ Torr under a growth temperature of 375°C.
differ from each other especially at lower Ge fractions where higher values are measured for \( P_{\text{GeH}_4} = 0.156 \) Torr. In addition, interestingly, the growth rate variation as a function of Ge composition exhibits an opposite behavior in the two cases.

Overall the observed results can be explained by a kinetic model for the reactions of precursors on the Au droplet surface which will be further discussed in section 5.4.

5.4 Discussion

In previous chapters, it has been shown that the net reactions of \( \text{Si}_2\text{H}_6(g) \rightarrow 2\text{Si}(s) + 3\text{H}_2(g) \) and \( \text{GeH}_4 \rightarrow \text{Ge}(s) + 2\text{H}_2(g) \) on the Au droplet surface can be described through adsorption, desorption and decomposition steps leading to nanowire growth which explains the observed dependence of Si and Ge nanowire growth rate on precursor partial pressure. Considering the simultaneous occurrence of these steps in the presence of both \( \text{Si}_2\text{H}_6 \) and \( \text{GeH}_4 \) gases, the \( \text{Si}_{1-x}\text{Ge}_x \) nanowire growth can thus be represented by the following set of equations:

\[
\begin{align*}
\text{Si}_2\text{H}_6(g) & \xrightarrow{k_{a,\text{Si}_2\text{H}_6}} \text{Si}_2\text{H}_6^* \\
\text{Si}_2\text{H}_6^* & \xrightarrow{k_{d,\text{Si}_2\text{H}_6^*}} \text{Si}_2\text{H}_6(g) \\
\text{Si}_2\text{H}_6^* & \xrightarrow{k_{r,\text{Si}_2\text{H}_6^*}} 2\text{Si}(s) + 3\text{H}_2^* \\
\text{GeH}_4(g) & \xrightarrow{k_{a,\text{GeH}_4}} \text{GeH}_4^* \\
\text{GeH}_4^* & \xrightarrow{k_{d,\text{GeH}_4^*}} \text{GeH}_4(g) \\
\text{GeH}_4^* & \xrightarrow{k_{r,\text{GeH}_4^*}} \text{Ge}(s) + 2\text{H}_2^* \\
\text{H}_2^* & \xrightarrow{k_{H_2^*}} \text{H}_2(g)
\end{align*}
\]

In these equations \( k \)'s are the reaction rate constants and asterisked species are surface-adsorbed species. Assuming that the reactions are first order and the
concentration of surface-adsorbed species remains constant under steady state conditions, one would obtain:

\[ \theta_{\text{Si}_2\text{H}_6} = \frac{k_{a,\text{Si}_2\text{H}_6}}{k_{d,\text{Si}_2\text{H}_6} + k_{l,\text{Si}_2\text{H}_6}} \theta_{\text{e}} P_{\text{Si}_2\text{H}_6} \]  

(5-9)

\[ \theta_{\text{GeH}_4} = \frac{k_{a,\text{GeH}_4}}{k_{d,\text{GeH}_4} + k_{l,\text{GeH}_4}} \theta_{\text{e}} P_{\text{GeH}_4} \]  

(5-10)

\[ \theta_{\text{H}_2} = \frac{3k_{l,\text{Si}_2\text{H}_6}}{k_{h_2}} \theta_{\text{Si}_2\text{H}_6} + \frac{2k_{l,\text{GeH}_4}}{k_{h_2}} \theta_{\text{GeH}_4} \]  

(5-11)

where \( \theta \)'s are the fractional surface coverage of adsorbed species. Considering that the overall fraction of empty sites and adsorbed species should equal to one \( (\theta_{\text{e}} + \theta_{\text{Si}_2\text{H}_6} + \theta_{\text{GeH}_4} + \theta_{\text{H}_2} = 1) \), the fraction of empty sites will be:

\[ \theta_{\text{e}} = \frac{1}{1 + \left( 1 + \frac{3k_{l,\text{Si}_2\text{H}_6}}{k_{h_2}} \right) A P_{\text{Si}_2\text{H}_6} + \left( 1 + \frac{2k_{l,\text{GeH}_4}}{k_{h_2}} \right) B P_{\text{GeH}_4}} \]  

(5-12)

with \( A \) and \( B \) being defined as \( A = \frac{k_{a,\text{Si}_2\text{H}_6}}{k_{d,\text{Si}_2\text{H}_6} + k_{l,\text{Si}_2\text{H}_6}} \) and \( B = \frac{k_{a,\text{GeH}_4}}{k_{d,\text{GeH}_4} + k_{l,\text{GeH}_4}} \). Once the concentration of empty sites is known, the deposition rates of Si and Ge constituents of the nanowire according to reactions (5-4) and (5-7) can be given by:

\[ r_{\text{Ge}} = \frac{k_{l,\text{GeH}_4} k_{a,\text{GeH}_4}}{k_{d,\text{GeH}_4} + k_{l,\text{GeH}_4}} \theta_{\text{e}} P_{\text{GeH}_4} \]  

(5-13)

\[ r_{\text{Si}} = \frac{2k_{l,\text{Si}_2\text{H}_6} k_{a,\text{Si}_2\text{H}_6}}{k_{d,\text{Si}_2\text{H}_6} + k_{l,\text{Si}_2\text{H}_6}} \theta_{\text{e}} P_{\text{Si}_2\text{H}_6} \]  

(5-14)

Subsequently, the total growth rate which is assumed to be a linear sum of the individual growth rates for Si and Ge, will be equal to:

\[ r_t = \frac{2k_{l,\text{Si}_2\text{H}_6} A P_{\text{Si}_2\text{H}_6} + k_{l,\text{GeH}_4} B P_{\text{GeH}_4}}{1 + \left( 1 + \frac{3k_{l,\text{Si}_2\text{H}_6}}{k_{h_2}} \right) A P_{\text{Si}_2\text{H}_6} + \left( 1 + \frac{2k_{l,\text{GeH}_4}}{k_{h_2}} \right) B P_{\text{GeH}_4}} \]  

(5-15)

which shows that the SiGe nanowire growth rate can be a non-linear function of both
GeH$_4$ and Si$_2$H$_6$ partial pressures as observed experimentally.

Considering that the ratio of Ge to Si incorporation rate equals the ratio of the Ge to Si in the nanowire, from Equations (5-13) and (5-14) one would obtain:

$$\frac{x_{Ge}}{1-x_{Ge}} = \frac{k_{I,GeH_4}^{*} B P_{GeH_4}}{2k_{I, Si_2H_6}^{*} AP_{Si_2H_6}}$$

Equation (5-16) clearly explains the observed linear relationship in Figure 5-11 for a constant $m = k_{I,GeH_4}^{*} B / 2k_{I, Si_2H_6}^{*} A$ obtained earlier in Table 5-3 as the slope of the graph. By substituting constant $m$ in Eq. (5-15), the growth rate as a function of GeH$_4$/Si$_2$H$_6$ ratio simplifies to

$$r_t = \frac{2 + 2mP_{GeH_4}/P_{Si_2H_6}}{k_{I, Si_2H_6}^{*} AP_{Si_2H_6} + \left( \frac{1}{k_{I, Si_2H_6}^{*} + \frac{3}{k_{H_2}^{*}}} \right) + \left( \frac{1}{k_{I, GeH_4}^{*} + \frac{2}{k_{H_2}^{*}}} \right) 2mP_{GeH_4}/P_{Si_2H_6}}$$

Now if it is assumed that the reaction rate constants are only a function of temperature, then Eq. (5-17) can be fitted to the experimental data for the case of constant $P_{Si_2H_6} = 0.0065$ Torr. This is re-plotted in Figure 5-17 as solid curves with fitting parameters given in Table 5-5. For all temperatures, the corresponding model prediction fits very well with the measured values for the examined germane to disilane ratios between 2 to 36.

If the fits are extrapolated to $P_{GeH_4}/P_{Si_2H_6} = 0$ for the case when Si$_2$H$_6$ with a partial pressure of 0.0065 Torr is flown through the reactor in the absence of GeH$_4$, the model predicts the growth rates of pure SiNW as 0.036, 0.085, 0.15 and 0.34 μm/min, respectively, for growth temperatures of 350, 375, 400, and 425°C.

However, such growth rates for individual SiNWs in the absence of GeH$_4$ are obtained only when much higher disilane partial pressures are used. For example,
Figure 5-17: Theoretical Si$_{1-x}$Ge$_x$ nanowire growth rates (solid lines) fitted to the experimental data (symbols) calculated using Eq. (5-17) with the corresponding fitting parameters given in Table 5-4.

Experimental growths of SiNWs at 350 and 400°C yield growth rates of 0.05 and 0.18 µm/min when a disilane partial pressure of 0.065 Torr is employed. Thus, for a disilane partial pressure ten times lower than this, used during SiGe nanowire fabrication ($P_{Si_2H_6} = 0.0065$ Torr), growth rates of approximately 0.005 and 0.018 µm/min will be expected for pure SiNW at the corresponding temperatures. A better estimate can be obtained for SiNW growth rates from the results presented in chapter 3. It has been shown there that the growth rate of individual SiNWs at $P_{Si_2H_6} = 0.013$ Torr follows an Arrhenius behavior with $r_{SiNW} = 8 \times 10^8 \exp\left(-\frac{31kcal/mol}{RT}\right)$ (Figure 3-12) and is linear
for small partial pressures below 0.013 Torr (Figure 3-8). Extending these results to the growth temperatures of 350, 375, 400 and 425°C estimates the growth rates of individual SiNWs for $P_{Si2H6} = 0.0065$ Torr as 0.005, 0.014, 0.034 and 0.078 µm/min, respectively. These data are also included in Figure 5-17.

Table 5-5: Fitting parameters of Eq. (5-17) to obtain Si$_{1-x}$Ge$_x$ nanowire growth rate as a function of $P_{GeH4}/P_{Si2H6}$ for the case when $P_{Si2H6}$ is kept constant at 0.0065 Torr.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\frac{1}{k_{1,Sl2H6} \cdot AP_{Sl2H6}^* + \left( \frac{1}{k_{1,Sl2H6}^<em>} + \frac{3}{k_{H2}^</em>} \right)}$ (min/µm)</th>
<th>$\frac{1}{k_{1,GeH4}^<em>} + \frac{2}{k_{H2}^</em>}$ (min/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>55.3 ± 7.2</td>
<td>0.054 ± 1.4</td>
</tr>
<tr>
<td>375°C</td>
<td>23.5 ± 1</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>400°C</td>
<td>13.7 ± 0.8</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>425°C</td>
<td>5.8 ± 0.3</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>

Comparison of SiNW growth rates between the values estimated from the experimental results and those predicted by the SiGe model shows that the model calculations are much larger than expected. However, one should keep in mind that the model predictions are based on the assumption that the reaction rate constants are only functions of temperature and remain unaffected by Ge composition. While this assumption seems to be valid for the investigated range of GeH$_4$/Si$_2$H$_6$ gas ratios, it may not be the case for small $x_{Ge}$.

In order to examine this assumption more closely, it is helpful to alternatively investigate the changes in total growth rate with Ge composition of SiGe nanowires. Using Eq. (5-16) to substitute for either $k_{1,GeH4}^*$ or $k_{1,Sl2H6}^* A$ in Eq. (5-15), the total
growth rate as a function of $x_{\text{Ge}}$ can be written as:

$$r(x) = \frac{2}{k_{1,\text{Si}_2\text{H}_6}\cdot A P_{\text{Si}_2\text{H}_6} + \left( \frac{1}{k_{1,\text{Si}_2\text{H}_6}} + \frac{3}{k_{2,h^*}} \right) (1 - x) + \left( \frac{1}{k_{1,\text{GeH}_4}} + \frac{2}{k_{2,h^*}} \right) 2x} \tag{5-18}$$

or alternatively as:

$$r(x) = \frac{1}{k_{1,\text{GeH}_4}\cdot B P_{\text{GeH}_4} + \left( \frac{1}{k_{1,\text{GeH}_4}} + \frac{2}{k_{2,h^*}} \right) (x) + \left( \frac{1}{k_{1,\text{Si}_2\text{H}_6}} + \frac{3}{k_{2,h^*}} \right) \frac{1 - x}{2}} \tag{5-19}$$

When reaction rate parameters are assumed to be independent of $x_{\text{Ge}}$, using Eq. (5-18) along with the fitting parameters listed in Table 5-5 for constant $P_{\text{Si}_2\text{H}_6} = 0.0065$ Torr predicts a non-linear increase in growth rate with Ge composition as it is depicted in Figure 5-18. Based on Eq. (5-19), the model can also be fitted to the experimental data obtained when $P_{\text{GeH}_4}$ is held constant. This is demonstrated in Figure 5-19 for a growth temperature of 375°C. Both increasing and decreasing trends in growth rate observed experimentally can be explained when the fitting parameters are set to

$$k_{1,\text{Si}_2\text{H}_6} A = 7.3 \, \mu\text{m}/(\text{Torr}\times\text{min}), \quad k_{1,\text{GeH}_4} B = 1.46 \, \mu\text{m}/(\text{Torr}\times\text{min}),$$

$$\left( \frac{1}{k_{1,\text{Si}_2\text{H}_6}} + \frac{3}{k_{2,h^*}} \right) = 2.3 \, \text{min}/\mu\text{m}, \quad \left( \frac{1}{k_{1,\text{GeH}_4}} + \frac{2}{k_{2,h^*}} \right) = 2.1 \, \text{min}/\mu\text{m}.$$

If the graph for $P_{\text{GeH}_4} = 0.156$ Torr is extrapolated to $x_{\text{Ge}} = 1$, a growth rate of 0.15 µm/min will be extracted for pure GeNW which interestingly is in close agreement with the experimental value of 0.094 µm/min (Figure 4-15). However, as mentioned earlier, with the assumption that the reaction rate constants are only a function of temperature, the model overestimates the growth rates of pure SiNW even though it reasonably simulates the growth rates of $\text{Si}_{1-x}\text{Ge}_x$ nanowire in the range of $x_{\text{Ge}} = 20$ to 80%.
Figure 5-18: Calculated total growth rates of SiGe nanowire (solid lines) as a function of Ge composition using Eq. (5-18) and fitting parameters in Table 5-5 for the case when $P_{Si_2H_6} = 0.0065$ Torr. The symbols represent raw data.

Interestingly, a closer look on the experimental data at 350, 375 and 400°C shows that the SiGe nanowire growth rate at these temperatures is better presented by a linear relation $r_t(x) = m_1 + m_2x$ which predicts the pure SiNW growth rates more accurately. Furthermore, modifying this relation to

$$r_t(x) = \frac{(m_1 + m_2x)}{1 + m_3(m_1 + m_2x)}$$  \hspace{1cm} (5-20)

best serves as an empirical equation on the correlation between the SiGe nanowire growth rate and the Ge composition when the disilane flow rate is kept constant (Figure 5-20) which explains the observed results at higher temperature of 425°C as well. Table 5-6 gives constants $m_1$, $m_2$, and $m_3$ for each temperature.
Figure 5-19: Calculated total growth rates of SiGe nanowire as a function of Ge composition using Eq. (5-18) and (5-19) when $P_{\text{Si}2\text{H}6}$ and $P_{\text{GeH}4}$ are, respectively, held constant at 0.0065 Torr and 0.156 Torr for a growth temperature of 375°C.

Comparison between the empirical equation of growth rate in Eq. (5-20) and the model in Eq. (5-18) indeed suggests that the reaction rate constants are dependent not only on the temperature but also on the composition of the SiGe nanowire, particularly at lower Ge fractions.

This is further supported if the problem is approached from a different view by comparing the growth rates of Ge constituent of Si$_{1-x}$Ge$_x$ nanowire to that of GeNW in the absence of disilane as depicted earlier in Figure 5-15. Using Eqs. (5-13) and (4-10), the experimental observation translates into a mathematical form of
In chapter 4, it has been discussed that when germane partial pressures in the range of 0.08-0.63 Torr are used at low growth temperatures, the growth is limited by germane decomposition. The hydrogen desorption as well as Ge incorporation into the nanowire occurs fast such that almost all surface sites remain open for adsorption of GeH₄ and thus, the fraction of empty sites equals unity. Therefore, the introduction of Si₂H₆ into the growth process cannot further increase the concentration of empty sites and as a result higher growth rates of Ge component in SiGe nanowire cannot be explained through changes in θₑ.

Table 5-6: constants $m_1$, $m_2$, and $m_3$ obtained from fitting the empirical equation of SiGe nanowire growth rate as a function of $x_{Ge}$ (Eq. (5-19)) to the experimental data

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$m_1$ (µm/min)</th>
<th>$m_2$ (µm/min)</th>
<th>$m_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>0.005</td>
<td>0.16 ± 0.01</td>
<td>0</td>
</tr>
<tr>
<td>375°C</td>
<td>0.012 ± 0.007</td>
<td>0.39 ± 0.05</td>
<td>1.19 ± 0.41</td>
</tr>
<tr>
<td>400°C</td>
<td>0.03 ± 0.02</td>
<td>0.61 ± 0.12</td>
<td>0.84 ± 0.39</td>
</tr>
<tr>
<td>425°C</td>
<td>0.09 ± 0.06</td>
<td>3.63 ± 2.43</td>
<td>1.74 ± 0.3</td>
</tr>
</tbody>
</table>

In view of GeH₄ partial pressure above the substrate, it may be altered by the presence of Si₂H₆ due to homogenous and heterogeneous reactions occurring upstream in the reactor during the residence time of the gas. If homogeneous decomposition of Si₂H₆ and GeH₄ precursors occurs, SiH₂ and GeH₂ species will be produced in the gas
phase. These are highly reactive molecules and their interaction with each other or with other molecules may change the gas phase composition. However, considering Si$_2$H$_6$ and GeH$_4$ gas phase reactions summarized in Tables 3-3 and 4-1, the calculated concentration profiles indicate that GeH$_4$ does not decompose homogeneously over the investigated growth temperatures of 350-425°C and the homogeneous decomposition of disilane is only 1.55% at the highest employed temperature of 425°C. Consequently, germane does not affect the disilane concentration and even if the reaction of SiH$_2$ with GeH$_4$ is taken into account as:

$$\text{SiH}_2 + \text{GeH}_4 \rightarrow H_3\text{SiGeH}_3$$

(5-22)

with $k = 7.93 \times 10^{13} \exp\left(\frac{0.51\text{ kcal/mol}}{RT}\right) \text{cm}^3/(\text{mol.s})$ being the rate constant of the reaction,$^{18}$ despite the increase in germane conversion (for example from 0.00046% to 0.46% at 425°C and $v_{\text{GeH}_4} = 5$ sccm), its homogenous decomposition is still too small to play any role.

As of the heterogeneous reaction of GeH$_4$ on the reactor wall, the model calculations developed in chapter 4/section 4.4.1.2 show that in the absence of Si$_2$H$_6$ the depletion occurs only at higher temperatures and lower germane fluxes as depicted in Figure 5-21. For example when GeH$_4$ with a partial pressure of 0.013 Torr is flown through the reactor at a growth temperature of 425°C, about 60% of the gas deposits on the tube surface reducing the germane flux above the substrate to about 0.4 of that in the reactor inlet. Now even if the germane depletion is totally prohibited in the presence of Si$_2$H$_6$ (due to the formation of SiH$_2$ which has higher reactivity on the surface than GeH$_4$), it will increase the growth rate of Ge component in SiGe nanowire by about 2.5
times compared to that of GeNW. This does not explain the experimentally observed ratio of 18 (Figure 5-15).

![Graph showing total growth rate vs. Ge composition](image)

**Figure 5-20**: Calculated total growth rates of SiGe nanowire as a function of Ge composition using Eq. (5-20) suggested empirically for the case when $P_{Si2H6} = 0.0065$ Torr. The solid lines are the respective model curve fits and the symbols represent raw data.

The foregoing discussion consequently suggests that the term $\frac{k_{t,GeH_4}^*k_{a,GeH_4}}{k_{d,GeH_4}^*+k_{t,GeH_4}^*}$ in Eq. (5-21) increases when disilane also takes part in the growth process and once again this implies that the reaction rate constants may not be only a function of temperature, particularly at lower Ge compositions in a Si-rich SiGe nanowire. Adsorption rate constants of GeH$_4$ and SiH$_4$ on Si$_{1-x}$Ge$_x$ thin films has previously been demonstrated to
depend on Ge composition as well,\textsuperscript{19} which based on the abovementioned discussions may also be the case in Si\textsubscript{1-x}Ge\textsubscript{x} nanowires.

![Graph showing P\textsubscript{GeH\textsubscript{4}} (Torr) at the center of the reactor vs. P\textsubscript{GeH\textsubscript{4}} (Torr) at the reactor inlet for different temperatures.]

Figure 5-21: Simulation of GeH\textsubscript{4} gas in the absence of Si\textsubscript{2}H\textsubscript{6} at the center of the reactor where substrate is located for total pressure and flow rates of 13 Torr and 100 sccm.

5.5 Conclusions

The higher reactivity of disilane compared to silane enables growth of Si\textsubscript{1-x}Ge\textsubscript{x} nanowires with higher Si concentrations at lower temperatures. In general, the composition of the Si\textsubscript{1-x}Ge\textsubscript{x} nanowires are controllable over a wide range from x \textasciitilde 20 – 80 % by varying the inlet GeH\textsubscript{4}/Si\textsubscript{2}H\textsubscript{6} ratio at a constant temperature in the range
of 350-425°C. The Ge/Si ratio in Si$_{1-x}$Ge$_x$ nanowire is a linear function of the GeH$_4$/Si$_2$H$_6$ inlet gas ratio with a slope of about 0.1.

Variations in growth temperature and GeH$_4$/Si$_2$H$_6$ gas ratios influence not only the Ge composition of the SiGe nanowires, but also their growth rate. At a given inlet gas ratio, the growth rate increases exponentially with increasing temperature. The apparent activation energy of the process reduces as the Ge content of the nanowire is enhanced indicating a change in the rate-limiting step of the process. For Si-rich nanowires, the $E_a$ is close to that obtained for SiNW growth which is suggested to be restricted by disilane flux and for Ge-rich nanowires it takes the characteristic of GeNW growth that is suggested to be governed by GeH$_4$ decomposition.

For different growth temperatures, the growth rate of Si$_{1-x}$Ge$_x$ nanowire exhibits a non-linear dependence on variations in either germane or disilane partial pressures and increases with both parameters when the other is fixed. Generally, the incorporation of Ge and Si constituents into the Si$_{1-x}$Ge$_x$ nanowire are larger compared to pure Ge and Si nanowires grown under similar conditions. A kinetic model that describes the reactions of precursors on the Au droplet surface through adsorption, desorption and incorporation steps of precursors explains the observed results. For Ge compositions above 20% investigated in this study if the model assumes that the reaction rate constants are only a function of temperature, then the experimental data on growth rate as a function of Ge composition are satisfactorily reproduced by evaluated model parameters for both cases when either germane or disilane partial pressures vary. This assumption fails for small Ge compositions when the model overestimates the growth rates of pure SiNW. Consequently, it is suggested that the adsorption rate constants are not only a function of
temperature but also Ge fraction, particularly at higher temperatures in the Si-rich regime which needs further investigation.

5.6 References

Chapter 6

Growth Properties of Si$_{1-x}$Ge$_x$/Si and Ge/Si$_{1-x}$Ge$_x$
Axial Heterostructured Nanowires

6.1 Introduction

In addition to compositionally uniform Si, Ge and Si$_{1-x}$Ge$_x$ nanowires, the fabrication of axial heterostructures in which the composition changes along the length of the nanowire is also of particular interest for fundamental studies of carrier confinement as well as nanoscale electronic devices. The importance of axial heterostructure nanowires in the form of Ge/Si and Si/SiGe has been demonstrated for applications such as tunnel field-effect transistors$^1$ and thermoelectric devices$^2$ and thus several attempts have been made to form multicomponent nanowires containing these segments.

Combining pulsed laser ablation and chemical vapor deposition processes, Wu et al.$^3$ succeeded to grow single-crystalline Si/SiGe axial heterostructures via the VLS mechanism. A pure Ge wafer was used to generate Ge vapor and SiCl$_4$ was the gas source of Si species. The periodic modulation of Ge was achieved through the pulsed laser ablation of the Ge target during the growth of Si$_{1-x}$Ge$_x$ segment. Epitaxial growth in the $<111>$ direction was observed on Si(111) substrate covered with 20 nm thick Au film. However, the interfaces of the junctions were non-abrupt with widths on the order of 40 nm for 200 nm diameter nanowires. Similarly, Lew et al.$^4$ observed diffuse interfaces when they grew Si/Ge and Si/SiGe heterostructure nanowires in low-pressure CVD system from SiH$_4$ and GeH$_4$ gas precursors using alumina membranes as the template.
A similar broadening of Si-Ge interfaces has also been seen for nanowires grown using MBE\textsuperscript{5,6} where the same Au starting material is employed but the Si and Ge are supplied by molecular beam epitaxy.

The diffuse interface in the axial heterostructured nanowires has been explained as a reservoir effect happening during the VLS growth due to the fundamental nature of the liquid droplet which contains a high concentration of the growth species\textsuperscript{7,8}. As an example, once Ge source is introduced into the reactor to grow Si/SiGe heterostructure, it takes some time for the liquid to reestablish a stable composition, as the excess Si atoms continue to precipitate out while the number of Ge atoms is increased gradually. Therefore, a non-abrupt interface is formed. The length of the diffuse interface has been theoretically\textsuperscript{7} shown to be equal to the diameter of the nanowire and has been experimentally\textsuperscript{8} verified for Si/SiGe heterostructure nanowires.

Since the formation of compositionally abrupt and structurally perfect interfaces is of critical importance for optimal device performance, particular attention has been given to improve the junction sharpness. Because the interface abruptness is determined by the solubility of the species within the catalyst, lowering the solubility should increase the junction sharpness. So far, two approaches have been followed to reduce the solubility (and as a result the concentration) of Si and Ge atoms in the metal catalyst\textsuperscript{9,10}. One is to pursue the growth via the VSS mechanism by using a solid catalyst. Wen et al.\textsuperscript{9} demonstrated that when Au is alloyed with Al to form AlAu\textsubscript{2}, the eutectic temperature rises from \textasciitilde360°C to 487°C and enables VSS growth of heterostructures at sub-eutectic temperatures that are still high enough to achieve practical growth rates. Using the AlAu\textsubscript{2} solid catalyst, sharp heterojunctions of Si/Ge were formed with transition widths
as narrow as 1.3 nm.

The second method that has been proposed to control the Si and Ge solubility in the catalyst is to similarly use the concept of Au alloying except this time with Ga which allows maintaining the VLS growth mode. Using this method, Perea et al. investigated the formation of Ge/Si heterostructures from Au$_{1-x}$Ga$_x$ metal alloy. The Ge segment was initially grown from Au catalyst. Then Au$_{1-x}$Ga$_x$ metal was formed through in situ alloying by simultaneously flowing vapor phase trimethylgallium (TMGa) with GeH$_4$ precursor from which the Si segment of the heterostructure was eventually grown by removing both TMGa and GeH$_4$ gases and introducing SiH$_4$. The presence of Ga reduced the solubility of Ge such that for ~60 nm diameter nanowires, the transition width decreased from 45 nm for wires grown from pure Au to 11 nm for interfaces grown from a Au$_{0.56}$Ga$_{0.34}$ alloy.

While the growth of axial heterostructured nanowires have been mainly explored for their potential applications in nanoscale devices, another interesting implementation of the heteroepitaxy, which is the aim of this study, is to form selective etch structures for nanowire release. Producing monodisperse silicon nanowires (SiNWs) with uniform length has been a critical difficulty in the bottom-up assembly of nanowire devices. SiNWs grown by the VLS method attach firmly to the growth substrate, making it difficult to remove them for single nanowire device assembly. Ultra-sonic agitation is frequently used to break the wires off of the substrate; however, they break at differing lengths, degrading the yield of successful wire integration and device fabrication. As an example, Figures 6-1(a) and (b) exhibit SEM images of as-grown and ultrasonically released SiNWs that were grown at T = 500°C, P$_t$ = 13 Torr and v$_{Si2H6}$ = 10 sccm. The
corresponding length distributions of each sample are given in Figures 6-1(c) and (d), showing that the distribution in length of nanowires broadens after ultra-sonic agitation.

Figure 6-1: SEM images of (a) as-grown and (b) ultrasonically released SiNWs. A growth temperature of 500°C, total reactor pressure of 13Torr and disilane flow rate of 10 sccm was used to grow these nanowires for 12 min. The histograms in (c) and (d) demonstrate the length distribution of each sample.

In this chapter, the concept of SiGe/Si axial-heterostructure nanowire is used to produce SiNWs with more uniform lengths through selective wet chemical etching process which removes the SiGe segment and releases the SiNW segment. The
procedure is schematically illustrated in Figure 6-2.

Figure 6-2: SiNW release by SiGe selective etching process flow

Preferential etching of Si$_{1-x}$Ge$_x$ alloys over pure Si can be obtained by using hydrogen peroxide (H$_2$O$_2$)$^{11}$ or NH$_4$OH:H$_2$O$_2$:H$_2$O (known as RCA)$^{12}$ solutions. However, for the selective etching process to accomplish successfully, the Ge composition has to be greater than 65% when H$_2$O$_2$ is used$^{11}$ and greater than 30% when RCA is employed.$^{12}$ It has been discussed in chapter 5 that at growth temperatures larger than 400ºC, which is more compatible with SiNW growth conditions, silane results in Si-rich SiGe nanowires but disilane enables the growth of SiGe nanowires with a broader composition range of Ge at higher temperatures. Consequently, to attain Ge-rich SiGe
nanowire segment at temperatures above 400°C, disilane and germane gases are chosen in this study as Si and Ge sources to synthesize SiGe/Si heterostructure nanowires.

In addition, using these two precursors, Ge/Si$_{1-x}$Ge$_x$ heterostructured nanowires with Ge compositions of 92% and 66% in the SiGe segment are also fabricated and the morphology and interfacial compositional profile of the nanowires are examined.

6.2 Growth conditions

The SiGe/Si heterostructured nanowires were grown at a growth temperature of 425°C and a total reactor pressure of 13 Torr. Both oxidized silicon wafers coated with 3 nm Au thin film and silicon substrates coated with 50 nm Au nanoparticles were used as the substrates. To grow the SiGe segment, a disilane flow rate of 5 sccm and a germane flow rate of 90 sccm was chosen to obtain a GeH$_4$/Si$_2$H$_6$ inlet gas ratio of 36 which according to results on SiGe nanowires presented in chapter 5 (Figure 5-10) would result in Ge composition of about 84%. Precursor gases were flown simultaneously for 15 min to get a ~ 4 µm long segment of SiGe. After that GeH$_4$ was terminated from the growth and the flow rate of Si$_2$H$_6$ was increased to 10 sccm and flown over the substrate for 4 min to grow a Si segment of approximately 1 µm in length. For both segments, the flow rate of H$_2$ carrier gas was accordingly adjusted for a total flow of 100 sccm.

To grow Ge/SiGe heterostructure nanowires, a temperature of 375°C and a total reactor pressure of 38 Torr were used. By modulating the gas flow during growth, Ge/SiGe axial heterostructure nanowires with Ge compositions of 92% and 66% in the SiGe segment were fabricated. In both cases, a 5 µm long segment of Ge was initially
grown followed by a Si$_{1-x}$Ge$_x$ segment approximately 1 μm in length. In the first case, after growing the GeNW segment, the GeH$_4$ mixture flow rate was increased abruptly from 50 sccm to 90 sccm and Si$_2$H$_6$ gas mixture with a flow rate of 5 sccm was added to the reactor simultaneously resulting in an inlet GeH$_4$/Si$_2$H$_6$ ratio of 36 to initiate the SiGe segment growth. To obtain a lower Ge concentration in the SiGe segment, the GeH$_4$ mixture flow rate was kept constant at 50 sccm throughout growth of the entire nanowire and 15 sccm of the Si$_2$H$_6$ mixture was added for growth of the SiGe segment at an inlet gas ratio of 6.7.

6.3 Results

6.3.1 SiGe/Si heterostructured nanowires

Upon completion of the growth process and formation of SiGe/Si nanowires, the morphology and structural properties of the heterostructures as well as the Ge composition of SiGe segment were first examined and once the successful synthesis of heterostructures was confirmed, the feasibility of selective etching of SiGe segment over Si segment was then investigated using both H$_2$O$_2$ and RCA solutions.

6.3.1.1 Structural properties of nanowires

Figure 6-3 shows the SEM images of top view and cross-sectional view of the as-grown SiGe/Si heterostructured nanowires fabricated from 50 nm Au nanoparticles. The formation of clustered nanowires is due to the agglomeration of the Au particles
Figure 6-3: SEM images of (a) top and (b,c) cross-sectional view of the as-grown SiGe/Si heterostructures from 50 nm Au nanoparticles indicating straight and kinked nanowires.
during their application process as described in chapter 2, where a colloidal method is used which does not provide precise control over the position of the Au nanoparticles. In the SEM images, the SiGe segment can be distinguished from the Si segment through its tapered structure which is expected to occur under the chosen growth condition based on the results on SiGe nanowires presented in Figure 5-7. The tapering in the SiGe segments is about 40-80 nm/μm (measured for 5 nanowires), but it is negligible for the Si segments with diameters of 51 ± 15 nm. As depicted in Figure 6-3(b), both straight and kinked heterostructure nanowires are observed. TEM analysis shows that in a straight wire both segments are grown along [211] direction (Figure 6-4).

![Figure 6-4](image)

Figure 6-4: (a) Low-magnification bright-field TEM image of a straight nanowire, collected on [\(\overline{1}11\)] zone axis. (b), (c), and (d) are selected area diffraction (SAD) patterns collected from the SiGe segment, the interface region, and the Si segment, respectively.

In a kinked nanowire, the SiGe segment grows in the [111] direction, but the growth direction changes to [110] in the Si segment (Figure 6-5). In some nanowires, the
kinking occurs at many points along the length of the Si segment that causes a curled structure indicated in Figure 6-3(c). Generally, for VLS growth, it is believed that kinking in the nanowire happens because of instabilities in the liquid growth seed induced under the chosen growth conditions which lead to interruption of growth, defect formation, and nanowire kinking.

![Image](image_url)

Figure 6-5: (a) Low-magnification bright-field TEM image of a kinked nanowire, collected on [T10] zone axis. (b), (c), and (d) are SAD patterns collected from the SiGe segment, the kink region, and the Si segment, respectively.

For homogeneous growth of SiNWs from Si$_2$H$_6$ in UHV CVD system, it has been found that low substrate temperatures or high disilane pressures induces instability in the droplet and forms kinked nanowires.$^{13}$ In contrast in an LPCVD system, lower total or disilane partial pressures has been observed to cause kinking in the nanowire due to insufficient supply of Si source to the liquid catalyst as well as diffusion and formation of
Au particles on the nanowire sidewalls.\textsuperscript{14}

In case of Ge/Si heterostructured nanowires, the differences in the growth temperature of Ge (T = 300-400\textdegree{}C) and Si (T > 400\textdegree{}C) segments can result in kinked structure when temperature is increased in vacuum or H\textsubscript{2} ambient (which can destabilize the droplet) to start the growth of Si segment on the previously grown GeNW. It has been shown\textsuperscript{15} that keeping a GeH\textsubscript{4} pressure during the temperature ramp will maintain the epitaxial growth and will reduce the kinking. Furthermore, decreasing the SiH\textsubscript{4} partial pressure and consequently decreasing the growth rate increases the percentage of straight nanowires.

The foregoing discussion opens up the question whether optimizing the growth condition, namely the temperature and/or disilane partial pressure, will prevent kinking and will result in larger number of straight heterostructured nanowires. This is an interesting study from the growth viewpoint that requires further investigation; however, it has not been continued in this chapter. Rather, the focus here has been given to the selective etching method to examine its feasibility for nanowire release with more uniform length.

In addition to the morphology of the SiGe/Si heterostructured nanowires, their compositions and interfacial abruptness have also been examined both for straight and kinked nanowires. As an example, Figure 6-6 demonstrates the results for the straight nanowire shown in Figure 6-4. The composition line profiles from the SiGe/Si interface reveal broad transition regions of about 100 nm (Figure 6-6(c)) and 50 nm (not shown here) for straight and kinked nanowires with respective diameters of \textasciitilde{} 66 and 35 nm in Si segment. The width of transition region is close to the diameter which is typical of VLS
Figure 6-6: HAADF STEM images collected from (a) the interface region and (b) near the Au particle of the straight nanowire shown in Figure 6-3. (c) and (d) are composition line profiles collected along lines AA’ and BB’ shown in (a) and (b), respectively. (e) and (f) are XEDS spectra collected from SiGe and Si segments, respectively.
growth as discussed earlier. The composition of the SiGe segments from XEDS analysis is estimated to be (85.1±0.8) and (90.8±0.9) at% Ge respectively in the straight and kinked nanowire, which are in the range of interest for the selective etching process. This provides samples suitable to explore the influence of H₂O₂ and RCA solutions as SiGe selective etchants which will be discussed in the following section.

6.3.1.2 Selective etching process

6.3.1.2.1 Silicon nanowire release using hydrogen peroxide etchant

Prior to employing the etchants on SiGe/Si heterostructures, the etching effect of H₂O₂ was initially explored on SiGe and Si nanowires grown separately at similar conditions to that of heterostructure nanowires; i.e. T = 425°C, P₁ = 13 Torr, GeH₄/Si₂H₆ = 36 for SiGe nanowires and vSi₂H₆ = 10 sccm for SiNWs. For SiGe nanowires, the growth time was also chosen to be the same (t = 15 min) to get nanowires that are comparable in length with the SiGe segment of the heterostructure.

Samples of the as-grown SiGe and Si nanowires were immersed into the solution of 30% H₂O₂ for 30 minutes. It should be noted that during the period of etching there was no shaking of the samples. Figure 6-7 shows the cross-sectional SEM images of the substrates before and after applying the H₂O₂ solution. It can be seen that the solution rapidly etches the SiGe nanowires but does not affect the SiNWs.

The process was then similarly performed on SiGe-Si heterostructure nanowires. After 30 min time period, the substrate was taken out of the solution and the suspension
was dropped on a bare Si wafer for imaging. Figure 6-8 demonstrates the released SiNWs with uniform diameters along their length which distinguishes them from the tapered SiGe segments. The length of the released nanowires is measured to be 980 ± 178nm, which is in agreement with the expectation from growth duration.

Figure 6-7: Cross-sectional SEM images of (a) SiGe and (b) Si nanowires before applying H$_2$O$_2$ solution. Nanowires were grown on oxidized Si wafers under conditions similar to that of SiGe/Si heterostructures. (c) and (d) SEM images of SiGe and Si nanowire substrates, respectively, after dipping into H$_2$O$_2$ solution. Hydrogen peroxide etches SiGe nanowires but does not affect Si nanowires.

While using H$_2$O$_2$ enabled releasing some SiNWs off of the substrate, the density of the collected wires was too low. Additional increase in the etching duration or replacement of the solution did not make any improvement in the quantity of collected SiNWs.
Figure 6-8: FESEM image of Si nanowires released from SiGe/Si heterostructure by selectively etching the SiGe segment using hydrogen peroxide solution. The wires were released into the solution and the suspension was dropped on a bare Si wafer for imaging.

When the substrate that was left after the etching process was examined, interestingly, it was observed that the SiGe segment was not completely removed. As indicated in Figure 6-9, the clustered nanowires of SiGe segment that were observed prior to growth (Figure 6-3(a)) still exist, even though their surface is more rough suggesting that they have been attacked by H₂O₂ but not completely removed. This is in contradiction to what was expected from the results on single SiGe nanowires (Figure 6-7).

Since H₂O₂ is effective on the latter, it can be suggested that the growth of Si segment may have caused this discrepancy. It is possible that during the growth of Si segment a thin layer of Si is deposited on nanowire sidewalls which interferes the etching process. Based on the results on Si thin film deposition presented in Figure 3-11(b), a growth rate of 0.1 nm/min is probable for radial growth on nanowire sidewalls that will
coat the SiGe segment with 4Å of Si shell. In the presence of the oxidizing agent of H$_2$O$_2$, the Si shell oxidizes and passivates the surface. Since H$_2$O$_2$ is very weak agent for the removal of oxide, the etching process remains incomplete and consequently, reduces the density of released SiNWs. Therefore, the influence of an alternative selective etchant, NH$_4$OH:H$_2$O$_2$:H$_2$O, is investigated next. This solution is widely used for removing several metal contaminants from the surface of silicon wafers and is known under the name RCA standard clean. The RCA solution has been shown to be capable of removing SiO$_2$ as well with an etch rate of approximately 2 Å/min which may improve the selective etching process by removing the thin Si layer from the nanowire sidewalls.

Figure 6-9: FESEM image of the SiGe/Si nanowire substrate after applying the hydrogen peroxide solution indicating that H$_2$O$_2$ is incapable of removing the entire SiGe segment.
6.3.1.2.2 Silicon nanowire release using RCA solution

280 µL of RCA solution was prepared by adding ammonium hydroxide (NH₄OH, 28% solution), H₂O₂ (30% solution) and deionized (DI) water in a ratio of 1:1:5. Similar to hydrogen peroxide, the influence of etchant was first investigated on single SiGe and Si nanowires and it was verified that RCA etches SiGe nanowires but does not affect Si nanowires. Then the process was transferred onto SiGe/Si heterostructure nanowires. The sample was dipped into RCA solution at room temperature for 30 min. Once the etch was completed, the substrate was taken out and the solution was centrifuged at 13000 rpm for 45 min to condense the nanowires at the bottom of the tube. Top portion of the solution (~200 µL) was then removed and replaced with DI water. This process was repeated twice to remove the residues of RCA solution. Finally, the suspension was collected on a bare Si wafer for imaging. Figure 6-10 shows SEM images of the released nanowires as well as the SiGe/Si nanowire substrate after completion of the etching process. It can be seen that in contrast to H₂O₂, RCA completely etches the SiGe segment and therefore, large density of SiNWs are released. It should be noted that not only straight nanowires but also the curled and kinked ones that were produced during the growth (Figure 6-3) have been collected. Measuring the length of the straight nanowires reveals a tight distribution with an average of 772 ± 68 nm (Figure 6-10(c)). The results show that the selective etching process using RCA etchant is a promising method to obtain SiNWs with more uniform length. However, for the process to be completely successful, the unwanted kinked and curled nanowires should be eliminated from the growth as the kinking results in nanowires with non-uniform length, particularly when
Figure 6-10: (a) Cross-sectional SEM image of SiGe/Si nanowire substrate after dipping into RCA solution. The SiGe segments of the nanowires are completely etched away and the Si segment is released into the solution. (b) Top view FESEM image of released nanowires. (c) Length distribution of straight SiNWs.
longer segments of SiNWs are grown. Further investigation should be carried out to optimize the growth condition which will prevent kinking and will result in larger number of straight heterostructured nanowires.

6.3.2 Ge/SiGe heterostructure nanowires

A cross-section SEM image of the Ge/SiGe heterostructure nanowire sample grown using GeH₄/Si₂H₆ = 36 for the SiGe segment is shown in Figure 6-11(a). The nanowires are generally straight although kinking can be observed in some of the wires near the top where the Ge/SiGe interface is expected to occur.

A TEM image of a straight nanowire is shown in Figure 6-11(b). Significant tapering of the nanowire diameter was observed in the Ge segment as a result of simultaneous radial growth due to Ge deposition on the nanowire sidewalls, followed by the growth of SiGe of relatively uniform diameter. In this case, the Ge and SiGe segments grow along the [311] direction as shown in Figures 6-11(c) and (d). High resolution TEM of the Ge segment of the nanowire (Figure 6-11(c)) reveals a thin amorphous layer on the outer surface of the nanowire which is believed to be a native oxide layer. XEDS analysis of the SiGe segment indicates a Ge composition of 92 ± 1 atomic %.

A cross section SEM image of the Ge/SiGe heterostructure nanowire sample grown using GeH₄/Si₂H₆ = 6.7 for the SiGe segment is shown in Figure 6-12(a). In this case, a larger number of kinked nanowires were observed compared to the sample grown with the inlet ratio of 36. A low magnification TEM image of a kinked nanowire is
Figure 6-11: (a) Cross-sectional FESEM image of Ge-SiGe nanowires grown at 375°C and $P_t = 38$ Torr with an inlet GeH$_4$/Si$_2$H$_6$ ratio of 36. (b) Low-magnification bright-field TEM image collected on the [\(\bar{1}12\)] zone axis of the Ge segment. (c) and (d) High-resolution TEM images collected from the Ge segment and near the Au particle, respectively. Insets are the corresponding selected area diffraction (SAD) patterns.

shown in Figure 6-12(b). In this case, the Ge segment grows along the [1\(\bar{1}1\)] direction and the growth direction changes to [110] in the SiGe segment. XEDS analysis of the SiGe segment indicates a Ge composition of 66 ± 1 atomic %. Composition profiles were obtained along the axis of the nanowire near the Ge/SiGe and SiGe/Au interfaces as shown in the dark-field TEM images of Figure 6-12(c) and (d). From the Si profile
Figure 6-12: (a) FESEM image of Ge/SiGe nanowires grown at 375°C, P_t = 38 Torr and an inlet gas ratio of 0.87. (b) Low-magnification bright-field TEM image collected on the [\bar{T}12] zone axis of the Ge segment. (c) and (d) HAADF images collected from the interface region and near the Au particle, respectively. (e) and (f) are composition line profiles collected along lines AA’ and BB’ shown in (c) and (d), respectively.
shown in Figure 6-12(e), the width of the Ge/SiGe interface is on the order of 25 nm, which is similar to the diameter of the nanowire in that region. It has been discussed earlier that the diffuse interface in the axial heterostructured nanowires grown by VLS method occurs due to the reservoir effect of the catalyst and the length of the diffuse interface approximately equals to the diameter of the nanowire,\textsuperscript{7,8} as observed here.

A larger number of kinked nanowires were observed in the Ge/Si\textsubscript{0.34}Ge\textsubscript{0.66} nanowire sample (Figure 6-12(a)) compared to the Ge/Si\textsubscript{0.08}Ge\textsubscript{0.92} nanowire sample (Figure 6-11(a)). This is believed to be due, in part, to the lower lattice mismatch of \textasciitilde 0.3\% for Ge/Si\textsubscript{0.08}Ge\textsubscript{0.92} compared to \textasciitilde 1.3\% for Ge/Si\textsubscript{0.34}Ge\textsubscript{0.66}. Despite the compositionally graded interface, the Ge/Si\textsubscript{0.34}Ge\textsubscript{0.66} nanowire is expected to exhibit greater mismatch strain at the heterointerface compared to the Ge/Si\textsubscript{0.08}Ge\textsubscript{0.92} nanowires which can lead to the formation of misfit dislocations in nanowires of this diameter range\textsuperscript{16} as well as a change in growth direction.

### 6.4 Conclusions

The fabrication of two types of axial heterostructured nanowires are examined using disilane and germane precursors: Si\textsubscript{0.15}Ge\textsubscript{0.85}/Si nanowires and Ge-rich Ge/Si\textsubscript{1-x}Ge\textsubscript{x} heterostructures with two different Ge compositions of 92\% and 66\% in the SiGe segment. In all cases, both straight and kinked nanowires are observed under the growth conditions examined. Moreover, in Ge/ Si\textsubscript{1-x}Ge\textsubscript{x} heterostructures grown with the higher Ge fraction, a larger fraction of straight wires are found due to the lower lattice mismatch; whereas at lower Ge compositions, the nanowires typically exhibit kinking
near the Ge/SiGe interface. All structures have interfacial abruptness comparable to the diameter of wires at the interface as a result of the reservoir effect in the liquid droplet.

Si\textsubscript{0.15}Ge\textsubscript{0.85}/Si axial-heterostructure nanowires are additionally investigated as a possible approach to produce SiNWs with more uniform length by selectively etching the SiGe segment away and releasing the SiNW segment. Between the two selective etchants examined, H\textsubscript{2}O\textsubscript{2} and RCA, the former fails to produce successful results. The deposition of a thin Si film on the SiGe segment during the growth of SiNW segment and the formation of SiO\textsubscript{2} in the presence of H\textsubscript{2}O\textsubscript{2} etchant passivates the surface and prohibits complete removal of SiGe segment. In contrast, the RCA solution which is capable of removing SiO\textsubscript{2}, completely etches the SiGe segment and releases SiNWs with more uniform length. Therefore, the selective etching process is a promising method to obtain SiNWs with more uniform length when RCA is used. However, for the process to be completely successful, the unwanted kinked and curled nanowires should be eliminated from the growth as the kinking results in nanowires with non-uniform length, particularly when longer nanowires are grown.

6.5 References


Chapter 7

Thesis Summary and Future Work

7.1 Summary

Over the past years, semiconducting nanowires (NWs) have received increasing attention as potential building blocks for several applications ranging from nanoscale electronic and photonic devices to chemical and biological sensors. A large number of studies have been carried out on the synthesis of nanowires and their electrical characterization. Group IV single nanowires (Si, Ge, and Si$_{1-x}$Ge$_x$ alloy) and their heterostructures, in particular, have received increasing attention due to their compatibility with current microelectronic industry. Numerous research has been going on (mainly on Si and Ge NWs) to better understand the fundamentals of the growth process and to optimize the growth parameters which will allow controlling different properties of the nanowires such as their diameter, the growth rate, the interfacial abruptness in heterostructures and the composition of alloys.

Different techniques have been employed to synthesize nanowires with chemical vapor deposition (CVD) being one of them. For low temperature low pressure CVD, the majority of reports have primarily used SiH$_4$ and GeH$_4$ as their Si and Ge containing gas sources. However, very little is known about nanowire growth kinetics if Si$_2$H$_6$ is employed as the Si source. Disilane is of interest since it is more reactive than silane and therefore may enable higher growth rates at lower temperature and lower partial
pressures. The lower thermal stability of disilane could also be an advantage to enable the growth of Si$_{1-x}$Ge$_x$ nanowires over the entire composition range at lower temperatures (275°C to 375°C) which are more compatible with the range of conditions typically used for Ge nanowire growth and in turn may enable the fabrication of different types of heterostructures. With this motivation, the goal of this research project was to explore the growth of group IV single and heterostructured nanowires from Si$_2$H$_6$ and GeH$_4$ precursors.

First, the growth kinetics of individual SiNWs from Si$_2$H$_6$ was investigated by examining the effects of growth parameters, namely growth temperature and precursor partial pressure, on the growth rate of SiNWs using disilane. The results were compared to that obtained with silane. In addition, to gain a better insight into the SiNW growth process, the results were also compared with Si films deposited under similar conditions inside the same reactor. Overall compared to SiH$_4$, the use of disilane gas as the Si-containing precursor enabled higher growth rates for both SiNWs and Si films. For both gases, a nonlinearity was observed in the growth rate of nanowire as a function of gas partial pressure which was explained by a simple decomposition mechanism including the adsorption, desorption and incorporation of precursor molecule on the Au droplet surface. The apparent activation energy of the process was found to be identical for both gases under the conditions examined in the present study, suggesting similar rate-determining step in the nanowire growth process from the two precursors. In comparison with the thin film, the Si film deposition from Si$_2$H$_6$ precursor was found to be carried out mainly due to the SiH$_2$ reactive species; whereas, the SiNW growth occurred mainly from Si$_2$H$_6$ molecule directly impinging on the Au droplet surface as the
dominant pathway for the incorporation of Si atoms and the contribution of adatoms diffusing on the nanowire sidewalls as an additional route to the growth velocity was found to be negligible.

Upon completion of studies on SiNW growth, the synthesis parameter space was then determined for undoped GeNWs and the influence of growth conditions on their morphology as well as their growth rate was examined. It was found that the fabrication of GeNWs strongly depends on the growth temperature and is achievable only for very narrow range. To get nanowires with uniform diameter, growth temperature should be kept low otherwise, uncatalyzed radial growth on nanowire sidewalls results in tapered nanowires. The growth rate as a function of temperature revealed an Arrhenius behavior with a small apparent activation energy and was observed to increase linearly with germane partial pressure in the range examined here. Besides the undoped GeNWs, the fabrication of radial p-n junction GeNWs, which are of interest for photovoltaic cells, was also studied and the influence of growth parameters was examined which showed that the morphology of both the p-type core and the n-type shell is influenced by temperature and dopant ratios. p-type GeNWs with uniform diameter can be obtained if the diborane to germane ratio is kept low as the B-enhanced thin film deposition on the nanowire sidewall at higher dopant ratios can cause tapered wires with nonuniform distribution of dopants along their length. Deposition of a smooth n-type Ge layer on GeNW sidewalls is possible only when specific growth temperatures are used. Below or above this range, the surface of coated nanowire becomes rough and the shell becomes polycrystalline.

The outcomes of the studies on undoped GeNWs combined with the results on
SiNWs were next used to explore the growth of Si$_{1-x}$Ge$_x$ nanowires from disilane and germane gases. The variations in Ge fraction as well as growth rate of Si$_{1-x}$Ge$_x$ nanowires with growth parameters such as temperature and precursor partial pressures were studied. In general, the higher reactivity of disilane compared to silane enabled the growth of Si$_{1-x}$Ge$_x$ nanowires with Ge composition over a wide range from $x \sim 20 – 80\%$ which was controllable by varying the inlet GeH$_4$/Si$_2$H$_6$ ratio at a constant temperature. It was observed that at a given inlet gas ratio, the growth rate increases exponentially with increasing temperature and the apparent activation energy of the process reduces as the Ge content of the nanowire is enhanced indicating a change in the rate-limiting step of the process. For different growth temperatures, the growth rate of Si$_{1-x}$Ge$_x$ nanowire was found to have a non-linear dependence on variations in either germane or disilane partial pressures which increases with both parameters when the other is fixed. The observed results were explained through a kinetic model that describes the reactions of precursors on the Au droplet surface through adsorption, desorption and incorporation steps of precursors. For Ge compositions above 20% investigated in this study if the model assumes that the reaction rate constants are only a function of temperature, then the experimental data on growth rate as a function of Ge composition are satisfactorily reproduced by evaluated model parameters for both cases when either germane or disilane partial pressures vary. This assumption fails for small Ge compositions when the model overestimates the growth rates of pure SiNW. Consequently, it is suggested that the adsorption rate constants are not only a function of temperature but also Ge fraction, particularly at higher temperatures in Si-rich regime.

Finally, the information gathered from single nanowire synthesis was used to
fabricate Ge/SiGe and SiGe/Si axial heterostructures, which are of interest for fundamental studies of nanowire heteroepitaxy as well as device development. The SiGe/Si nanowires were further processed as a possible approach to form SiNWs with more uniform length by selectively etching the SiGe segment away and releasing the SiNW segment. Producing monodisperse silicon nanowires (SiNWs) with uniform length has been a critical difficulty in the bottom-up assembly of nanowire devices. SiNWs attach firmly to the growth substrate, making it difficult to remove them for single nanowire device assembly. Currently, ultra-sonic agitation is frequently used to break the wires off of the substrate; however, they break at differing lengths, degrading the yield of successful wire integration and device fabrication. It was shown here that this problem can be mitigated through the use of SiGe/Si axial-heterostructure nanowire. After the fabrication of these structures, the SiGe segment can be selectively removed using NH₄OH:H₂O₂:H₂O solution. The process releases the SiNW segments with narrower length distribution.

7.2 Future work

In this thesis, the studies on SiNW growth from Si₂H₆ precursor have only been focused on undoped nanowires. To create functional devices based on these nanowires, their controlled doping with either phosphorous or boron is required. Therefore, it is of importance to investigate the influence of different dopants on the morphology and growth rate of SiNWs when they are flown through the reactor simultaneously with Si₂H₆ gas. In case of SiH₄, it has been observed that the growth rate of SiNW drops with the
addition of PH$_3$. It is interesting to examine whether replacing silane with disilane could reduce this negative effect or not. Furthermore, it has been found that during the growth of phosphorous doped SiNWs from SiH$_4$, the dopant gets incorporated not only through the Au metal but also the nanowire sidewalls causing axial and radial concentration gradient which results in variation in the resistivity of the nanowire complicating the device fabrication. It has been discussed in chapter 3 that when Si$_2$H$_6$ is employed to grow SiNWs, homogeneous decomposition of the gas phase produces the highly reactive species SiH$_2$, which is the main molecule adsorbing on the nanowire sidewalls. Due to higher reactivity, SiH$_2$ can compete very effectively for surface sites with phosphine and thus, it may block the adsorption of PH$_3$ on nanowire sidewalls improving the homogeneous distribution of the dopant in SiNW.

The impact of dopants on the nanowire growth process is also an interesting study subject for Si$_{1-x}$Ge$_x$ nanowires. As mentioned in chapter 5, this has already been investigated by Givan et al. for the case when SiH$_4$ is used to grow doped SiGe nanowires. It has been found that the introduction of dopant gases during the growth increases the Si content, especially in the case of boron doped nanowires which doubles the Si/Ge ratio in comparison to the intrinsic wires. What influence the addition of dopants will have on the growth process of SiGe nanowire in the presence of Si$_2$H$_6$ precursor is still an open question that needs to be addressed in the future.

An additional parameter of the SiGe nanowire growth that has not been examined in this work is the total reactor pressure, which has shown to effect the Ge composition in case of SiH$_4$, but so far has not been investigated on nanowires grown from Si$_2$H$_6$ and is open area for future research.
Finally, even though the use of Si$_2$H$_6$ enabled the formation of different types of heterstructures, namely SiGe/Si and Ge/SiGe nanowires with different Ge compositions, the specific growth conditions chosen in this study lead to both straight and kinked nanowires. It has been discussed that kinking in the nanowire happens because of instabilities in the liquid growth seed which lead to interruption of growth, defect formation, and nanowire kinking. As mentioned in chapter 6, inappropriate choice of temperature or precursor partial pressure can induce instabilities resulting in kinked nanowires.$^4$-$^6$ Consequently, to increase the percentage of straight heterostructured nanowires, the growth parameters should be further optimized. This specifically becomes important in selective etching process of SiGe/Si nanowires with the aim to release SiNWs with more uniform length. For the process to be completely successful, the unwanted kinked and curled nanowires should be eliminated from the growth as the kinking results in nanowires with non-uniform length, particularly when longer nanowires are grown.

### 7.3 References

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