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I. Accurate 50-200 keV proton stopping cross sections in solids II. Lateral growth of Si wires on Si (100) substrate

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Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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I. Accurate 50-200 keV proton stopping cross sections in solids
II. Lateral growth of Si wires on Si (100) substrate

(Thesis format: Integrated Article)

by

Sergey Dedyulin

Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
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London, Ontario, Canada

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Abstract

Medium energy ion scattering (MEIS) is used to determine the elemental depth profile in the first few hundred angstroms of a sample. The interpretation of MEIS spectra requires an accurate knowledge of the rate at which the ions lose their energy - the stopping cross section, $\varepsilon$. The rate of energy loss has been fairly well investigated, both experimentally and theoretically, in elemental and compound targets at high energies ($E > 400$ keV/amu). However, in the medium ion energy range where stopping cross section typically has a maximum, experimental data are scarce while most of the existing theories fail to give accurate predictions.

In this work, we report accurate measurements of stopping cross sections for $\sim 55-170$ keV protons in thin film of Si, Ti and SrTiO$_3$ using MEIS. We developed a new methodology of calculating stopping cross sections from the MEIS spectra. Measured $\varepsilon_{\text{Si}}$ and $\varepsilon_{\text{Ti}}$ agree with the values reported in the NIST database within experimental uncertainties. On the other hand, $\varepsilon_{\text{SrTiO}_3}$ data are systematically lower over the entire energy range probed. Among several factors that could contribute to the observed discrepancy, the following were eliminated: i) the proposed method for calculating stopping cross sections from MEIS spectra is not accurate ii) $\varepsilon_{\text{Ti}}$ literature values used to calculate $\varepsilon_{\text{SrTiO}_3}$ are underestimated.

In the second part of this thesis, we report an observation of self-assembled lateral Si wires (ridges) grown by a vapour-liquid-solid mechanism in a molecular beam epitaxy system. We show that at a sufficiently low flux of Si atoms and high substrate temperature, gold droplets are propelled forward horizontally along two orthogonal $<011>$ directions by the growing silicon wires. The reticular growth closely resembles a self-avoiding random walk in two dimensions, as we confirmed by using a Monte Carlo simulation. We present the experimental results and thermodynamic arguments showing
the unique role carbon plays in initiating lateral growth of Si wires on a Si (100) substrate and discuss the means of kinetic control of the growth process.

Keywords

Stopping cross section, energy loss, medium energy ion scattering, strontium titanate, Bragg's rule, molecular beam epitaxy, Si wire, lateral growth, vapour-liquid-solid, diffusion.
Co-Authorship Statement

The following thesis contains material from previously published or submitted manuscripts. Dr. Lyudmila Goncharova was co-author on the presented papers and was responsible for the supervision of Sergey Dedyulin over the course of his studies. Dr. Giovanni Fanchini was co-author on the manuscript presented in Chapter 6 and at the time was supervising Sergey Dedyulin while Dr. Goncharova was on maternity leave.

For all manuscripts presented in Chapters 3, 6 and 7, Sergey Dedyulin was the primary author responsible for the majority of experimental work, as well as the writing and revision of all drafts, including final manuscripts. Some statistical analysis of scanning electron microscope images for Chapter 6, Chapter 7 and Appendix C was performed by a summer student Gabe Keenleyside. His contributions are gratefully appreciated.

Dr. Rana Sodhi, of Surface Interface Ontario, University of Toronto, performed the angle-resolved X-ray photoemission experiments and analyzed the results described in Chapter 3 and Appendix B. Dr. Todd Simpson, of the Western Nanofabrication Facility, performed focused ion beam etching of selected Si wires in scanning electron microscope as described in Chapters 6. Dr. M.P. Singh and Dr. F.S. Razavi, of Department of Physics, Brock University, provided amorphous SrTiO₃ samples grown by pulsed laser deposition and were co-authors on the manuscript presented in Chapter 3. Mr. Arash Akbari-Sharbaf, of Physics and Astronomy Department, Western University has performed AFM measurements described in Appendix C. Sergey greatly appreciates their experimental assistance.
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I would like to begin by thanking my supervisor Dr. Lyudmila Goncharova for her patience and continuous support throughout my PhD. She helped me from the first day I arrived to Canada when she kindly offered me to stay in her house until I find a place to stay till last days when she was working hard to return the corrections in a timely manner and, most importantly, to make my thesis read better. Without her help, I'm afraid, I would be the only one who could understand what's written on the next 150 pages.

It was inspiring to work for some time under the supervision of Dr. William Lennard and Dr. Giovanni Fanchini. I will miss their passion for experimental physics, their deep theoretical knowledge and desire to share it with people around them.

I was lucky to work in the Tandetron Accelerator Facility, where literally tonnes of equipment are taken care of by a single man – Jack Hendriks. Without his advice, I wouldn't have been able to measure a single RBS spectrum or grow a single thin film.

During my PhD, I was a frequent visitor to the Physics Machine Shop, where two talented men are working, Frank Van Sas and Brian Dalrymple. In fact, I was there so often during the first year that I got a nickname 'Sergey BrokenOFF'. As one can guess, I would have run out of the necessary working parts at the early stages of my PhD career without their help.

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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>amu</td>
<td>Atomic mass unit</td>
</tr>
<tr>
<td>ARXPS</td>
<td>Angle-resolved X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>BE</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-like carbon (substrate)</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>KKKNS</td>
<td>G. Konac, S. Kalbitzer, C. Klatt, D. Niemann, R. Soll stopping cross sections</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MEIS</td>
<td>Medium energy ion scattering</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>QUARK</td>
<td>QUantitative Analysis of Rutherford Kinematics</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square (vibrational amplitude)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMNRA</td>
<td>SIMulation for Nuclear Reaction Analysis</td>
</tr>
<tr>
<td>SOI</td>
<td>Silicon on insulator</td>
</tr>
<tr>
<td>SRIM</td>
<td>The Stopping and Range of Ions in Matter</td>
</tr>
<tr>
<td>STO</td>
<td>Strontium titanate (SrTiO₃)</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapour-liquid-solid mechanism</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Chapter 1. Introduction

The first experimental observations of the interaction of charged particles with matter were made around 1850s using gas-discharge tubes. The atomistic nature of the processes involved in the discharge was largely unknown at the time. It took several decades of intensive research to understand that inelastic collisions of accelerated electrons with the gas atoms and ions in the tube produced a characteristic light.

The phenomena describing penetration of charged particles (electrons or ions) into matter can be divided into two large categories: scattering (angular deflection) and stopping (loss of kinetic energy). The main focus of this chapter will be on physical concepts involved in the stopping of energetic ions in matter and ways to experimentally measure the main stopping characteristics of the medium.

1.1 Processes involved in the stopping of energetic ions in a medium

An energetic charged particle that impinges on a target will penetrate into it. With a large angle scattering collision being highly unlikely (probability $P < 10^{-2}$%), the particle will push its way straight through the target. It will slow down and its kinetic energy,

$$E = \frac{1}{2} M_l v^2,$$

where $M_l$ is the mass of the particle and $v$ is the particle's speed, will decrease. At moderate velocities ($v \ll c$), several processes may contribute to the slowing down of a projectile [1]: i) excitation or ionization of target particles, ii) transfer of energy to centre-of-mass motion of target atoms and iii) changes in the internal state of the projectile.

The two dominant processes of energy loss for the light projectile atoms and the energy range utilized in our work are excitation or ionization of target particles and transfer of
energy to the centre-of-mass motion of target atoms. The first process may be loosely
described as the “frictional resistance” - a loss of projectile energy into kinetic and
potential energy of target electrons - while the second process characterizes the energy
transfer from the projectile to target nuclei in a multitude of small-angle scattering
collisions. Therefore, the first process is usually called “electronic stopping” and the
second process is usually referred to as “nuclear stopping”. For a 100 keV H or He
projectile, the typical energy loss in individual collisions with target nuclei and electrons
is of the order of 1-10 keV (for scattering events) and 1-10 eV, respectively. However,
due to the much higher probability of the projectile-electron collisions, the electronic
stopping contribution prevails at high ($E > 400 \text{ keV/amu}$) and medium ($40 \text{ keV/amu} < E < 400 \text{ keV/amu}$) ion energies (Figure 1.1). Only in the low energy region ($E < 40 \text{ keV/amu}$) does nuclear stopping start to play a role in the slowing down of the projectile.

![Graph showing stopping cross section of protons in silicon](image)

**Figure 1.1**: Stopping cross section of protons in silicon (values are taken from PSTAR
database). Shaded blue area labelled 'Bethe-Bloch' indicates the energy region where
Bethe-Bloch theory is applicable. Shaded red area labelled 'MEIS' corresponds to the
operating energy region for medium ion energy scattering (MEIS).
The simplest experiment to determine the energy loss is shown schematically in Figure 1.2. A beam of monoenergetic particles of energy \( E_0 \) is directed at the thin foil of a known thickness \( \Delta x \). The energy of transmitted particles, \( E_0 - \Delta E \), is then measured at the back of the foil. Due to the random nature of the energy transfer processes, each particle \( i \) from the beam loses a slightly different amount of energy \( \Delta E_i \) to the target. For a large enough number of collisions, the \( \Delta E_i \) are normally distributed around the average energy loss value, \( \Delta E \), measured in the experiment. It is therefore common to assign the energy loss per unit length, \( \Delta E/\Delta x \), as a result of individual contributions of all the atoms in the target exposed to the beam, and introduce the normalized quantity as a stopping cross section, \( \epsilon \):

\[
\epsilon(E_0) = \frac{1}{N} \lim_{\Delta x \to 0} \frac{\Delta E}{\Delta x} = \frac{1}{N} \frac{dE}{dx}(E_0),
\]

(1.1)

where \( N \) is the target atomic density. Stopping cross section is often somewhat misleadingly \[2\] called the stopping power.

![Figure 1.2: Schematic of a transmission experiment to measure energy loss due to a thin film target.](image)

Generally, stopping cross section for a particular material depends on energy, and has the typical form presented in Figure 1.1. As the energy of a projectile changes during the motion through the thin foil in a transmission experiment, so does a stopping cross section. However, this functional energy dependence is frequently neglected and the stopping cross section is approximated by a constant value taken at the initial energy \( E_0 \) (Equation 1.1). Of course, the error produced by using this approximation increases as the
foil used in the transmission experiment becomes thicker or, in other words, as the energy of the ions varies significantly throughout the foil. In that case, other approximations, such as mean energy approximation or numerical methods must be used to estimate the stopping cross section value [3-5]. The latter one is described in detail in the Appendix A as it is relevant to our work.

In addition to the projectile energy, the stopping cross section also depends on the density and composition of the target. Since the early times when the term “stopping power” was first introduced at the beginning of the 20th century, the stopping cross sections were mostly measured experimentally. However getting precise measurements of stopping cross sections for hydrogen and helium ions in the 0.001 – 10 MeV energy range for numerous targets seems like an enormous task considering a variety of inorganic and organic materials and the existing experimental challenges that are described in the next section. Currently, there are three means to simplify the situation: i) at high ($E > 1$ MeV/amu) projectile energies Bethe-Bloch theory [1] gives a reasonable prediction of stopping cross section for elemental targets; ii) semi-empirical fitting functions for hydrogen and helium ions in all elements exist, see e.g. [6-10]; iii) the principle of additivity of stopping cross sections, called Bragg's rule [11], is used to find the stopping cross section for compound targets.

The original Bethe-Bloch relativistic formula for the stopping cross section due to the electronic energy loss for a projectile of mass $M_i$ and charge $Z_i e$, moving at a velocity $v$, has the following form:

$$
\varepsilon_e(E) = \frac{4 \pi e^4 Z^2}{m_e v^2} Z_i^2 \left[ \ln \frac{2 m_e v^2}{I} - \ln (1 - \beta^2) - \beta^2 \right]
$$  \hspace{1cm} (1.2)

where $m_e$ and $e$ are mass and charge of the electron, $Z_2 e$ is the charge of the target particle, the energy $I$ is an average over the various excitations and ionizations of the electrons in a target atom, and $\beta = \frac{v}{c}$. Equation 1.2 can be rewritten in the general form:
\[ \epsilon_e(E) = (Z_2 e)(Z_1 e)^2 f\left(\frac{E}{M_1}\right) \] (1.3)

where \( f(E/M_i) \) is a function that depends only on the target element not on the type of the projectile.

The agreement between experiment and Bethe-Bloch theory can be improved by considering corrections which correspond to powers of \( Z_i \) and \( Z_j \) [1]. These are called the shell correction (\( \sim C/Z_2 \)), density correction (\( \sim f(E, Z_i, Z_j) \)), Barkas correction (\( \sim Z_i^3 \)) and Bloch correction (\( \sim Z_i^4 \)). Equation 1.3 gives erroneous predictions as the ion energy decreases since: a) the ion can trap an electron and thus the effective charge of the projectile decreases; b) the number of the target atom electrons contributing to the energy loss decreases; c) nuclear energy loss increases. The ability to predict stopping cross section around and below the maximum is not as good as in the high velocity range, as shown for the case of a Cu target by Semrad et al. [12].

In the absence of a reliable theory in the medium and low energy ion range, one has to rely on existing semi-empirical formulas or tabulated data for the stopping cross section. The most frequently used amongst these are the following: Northcliffe and Shilling [6], Andersen and Ziegler [7, 13], Ziegler et al. [8], the program code SRIM – the Stopping and Range of Ions in Matter [10], NIST database “Stopping-Power and Range Tables for Electrons, Protons, and Helium Ions” [14]. For example, proton electronic stopping cross sections \( \epsilon_{H} \) [eV·cm²/10¹⁵ atoms] above 25 keV may be obtained from a simple analytical fitting function:

\[ \epsilon_H = \frac{S_{LOW} S_{HIGH}}{S_{LOW} + S_{HIGH}} \] (1.4)

where

\[ S_{LOW} = A_1 E^{A_2} \] (1.5)
and $A_1 - A_5$ are tabulated in [7]. The precision of the fit around the stopping power maximum is estimated by the authors to be around 10%. For comparison, the accuracy of stopping cross section calculated by the program SRIM, based on the experimental data used in [7, 13] and the semi-empirical Ziegler formalism [8], is reduced to 4.6% around the stopping power maximum [10]. The aims of these formulas are: i) to deduce a best fit value for several projectile-target combinations, where sufficient measurements in a broad energy region exist; ii) to predict stopping cross section for other projectile-target combinations based on interpolation guided by some theoretical assumptions; iii) to deduce a best fit value for predicted stopping cross sections. To illustrate this, the fitting procedure from [7] is outlined below.

First, Andersen and Ziegler chose 27 and 24 elements with sufficient amount of experimental data in the high ($400 \text{ keV/amu} < E < 100 \text{ MeV/amu}$) and low ($10 \text{ keV/amu} < E < 400 \text{ keV/amu}$) energy region, respectively. They calculated the stopping cross section of 27 elements in the high energy region using the Bethe-Bloch theory (Equation 1.2) with an initial set of $<I>$-values taken from the literature. Those theoretical values were subtracted from the trusted experimental data in order to obtain experimental shell-corrections, $C/Z_2$. The emergent basic set of shell-corrections for 27 elements was then fitted by the power series:

$$\frac{C}{Z_2} = a_0 + a_1 \ln E + a_2 (\ln E)^2 + a_3 (\ln E)^3 + a_4 (\ln E)^4$$  \hspace{1cm} (1.7)

Next, the assumption was introduced that $C/Z_2$ varied smoothly with $Z_2$, which made an additional adjustment of some of the $<I>$ and $C/Z_2$ values necessary. Shell corrections for elements with an insufficient amount of experimental data were obtained by linear interpolation in $Z_2$, and a similar series was fitted to these interpolated values. Finally, corrected Bethe-Bloch values (Equations 1.2 with shell corrections combined with Equation 1.7) for all elementary targets were fitted to the function $S_{HIGH}$ (Equation 1.6).
In the low-energy limit, experimental stopping cross sections for 24 elements were fitted to the function $S_{\text{low}}$ (Equation 1.5). It was found that $A_2 = 0.45$ produces the best fit for all fitted elements. This $A_2$ value was further used to deduce the stopping cross section for the rest of the elementary targets. The missing $A_i$ values for unmeasured elements were interpolated from the tabulated He stopping cross sections based only on the judgement of the authors that H and He stopping cross section behave similarly.

It should be emphasized that subjective judgement was used in choosing both relevant experimental data and basic assumptions for interpolation in all semi-empirical formalisms. An improved accuracy of a formalism by Ziegler et al. [15, 16] is achieved by a wider selection of relevant experimental data and additional semi-empirical corrections to the Bethe-Bloch formula (Equation 1.2) used in the high-energy region.

For a compound target material, it is common to use Bragg's rule to calculate stopping cross section. Bragg's rule, first postulated by Bragg and Kleeman for molecules [11], is based on the assumption that a projectile particle interacts with only one target atom at a time. According to that postulate, any modification of an electronic density of an element due to the formation of a chemical bond in the chemical compound or change in the physical state does not affect the resultant stopping cross section. Thus, the energy loss in a material composed of various atomic species, $\epsilon(A_mB_n)$, is the sum of the losses in the constituent elements, weighted proportionally to their stoichiometric coefficients:

$$\epsilon(A_mB_n) = m \epsilon(A) + n \epsilon(B)$$  (1.8)

There are several examples of violations of the Bragg's rule in organic compounds [17-22] in oxides [23-28] or other compounds [24, 29] in which one element is a gas in elemental form. These deviations are presumed to be either due to chemical effects – a modification of the atomic electronic density in the compound - or due to physical effects - an atomic $\epsilon$ is obtained for a different physical state than that of the compound. Generally, the deviations from Equation 1.8 are believed to be less than 10%.
1.2 Experimental methods for measuring stopping cross section

There are two main experimental approaches to measure the stopping cross section of ions. It can be done either in transmission or backscattering geometry, respectively. A thorough evaluation of experimental data reveals methodical deficiencies inherent in both techniques, as becomes evident from the scattering of the data in the Andersen and Ziegler compilation [7, 13]. To illustrate the scattering of the experimental data, in Figure 1.3 we show the stopping cross section of silicon as measured by both transmission and backscattering techniques. The discrepancies can reach up to 20% around the stopping power maximum between the different data sets, despite the reported uncertainties in individual measurements of the order 1-5%. It is clear that none of the methods necessarily guarantees correct results unless a certain set of experimental conditions is fulfilled as described in [45, 46].

The transmission measurements, as described in Section 1.1, are usually understood to be a direct and clear procedure because the stopping cross section for the average energy, \( E = E_0 - \Delta E/2 \), is obtained directly from Equation 1.1. This relation holds quite satisfactory in the limit of the very thin foils (1-100 nm), for which \( \Delta E \ll E_0 \). The problem then becomes to eliminate the uncertainties in the measured mean ion energy loss, \( \Delta E \) [eV], and foil thickness, \( N \Delta x \) [at/cm\(^2\)]. The following issues should be addressed: i) calibration of the initial energy of the beam; ii) calibration of the film thickness by independent technique; iii) surface and bulk contamination; and iv) angular dependence of the energy loss in polycrystalline and single crystalline targets. If the precautions are taken by an experimentalist to eliminate all the uncertainties listed above, then the accuracy of the transmission method can be < 3% [46].
Figure 1.3: Stopping cross section for protons in silicon in the 10-250 keV range. The symbols in the figure correspond to published experimental works: SRIM [10], PSTAR [14], a [30], b [31], c [32], d [33], e [34], f [35], g [36], h [37], i [38], j [39], k [40], l [41], m [42], n [43], o [44].

The energy calibration of an accelerator directly influences experimental energy losses due to the nonlinear dependency of stopping cross section on the energy of the beam (Figure 1.1) with the most dramatic effects observed at and below the stopping power maximum. To reduce the measurement uncertainty, the primary calibration of the energy of the beam is best performed with nuclear reactions. In the case of protons, 991.90±0.04 keV $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$ resonance and 429.57±0.09 keV $^{15}\text{N}(p, \alpha\gamma)^{12}\text{N}$ are generally used [9]. For very accurate energy calibrations, it is usually not enough to calibrate the energy at just one point. In addition, consecutive scans over the energy distribution of transmitted
ions should be subsequently performed to ensure an absence of the possible energy drift due to accelerator voltage drift, sputtering of the target foil or gas desorption. For example, when a foil has been recently introduced into a vacuum chamber from the atmosphere and is analyzed for the first time, it will exhibit an additional energy loss up to 1 keV for 300 keV protons due to surface contamination, as pointed out by Mertens in [46].

From the fact that the typical target thicknesses used in transmission experiments do not exceed several hundred atomic layers, it is clear why areal densities of bulk material and bulk impurities should be known as well as the surface contamination. Quartz crystal microbalance was typically used to calibrate the thickness which leads to uncertainties from 1 to 10% [46]. For example, for a specimen size of 1 cm² a weight uncertainty of 2 µg may lead to an uncertainty in the areal density of the foil of 9% for 100 nm carbon and of 1% for 100 nm gold. The uncertainty due to the thickness measurement can be minimized if a set of target foils of different thickness can be prepared and the stopping cross section is determined by applying linear regression. Contamination of a target foil can be detected by means of a nuclear reaction analysis, Rutherford backscattering spectrometry (RBS), medium energy ion scattering (MEIS) or X-ray photoelectron spectroscopy (XPS).

Finally, energy loss measurements in a single crystalline foil and, partially, in polycrystalline foil can be affected by channeling since the energy loss exhibits an angular dependence with a clear minimum along the specific crystallographic directions in a single crystal [43, 47-51]. To minimize the channeling contribution in the crystalline samples, the measurements should be performed away (> 2°) from the specific crystallographic directions in single crystals or texture axis in polycrystalline samples.

In a typical backscattering experiment, one measures the energy loss of ions which travel through the target film, then scatter back from the top of the low Z₂ substrate or from the buried high Z₂ marker layer and finally travel back through the target film into the detector (Figure 1.4). The measured energy loss consists of three parts: energy loss of the
ion on the way in, energy loss of the ion in the scattering event, and energy loss of the ion on the way out. Energy loss of the ion on the way in and out can be related to the stopping cross section of the target film via Equation 1.1. Energy loss of the ion in the scattering event can be calculated from the conservation of energy and momentum, as described in detail in Section 2.2.1. The methodical difficulty arises from the fact that the stopping cross sections on the way in and out of the film are evaluated at different energies, since additional energy loss in a scattering process happens between the two events:

\[ \Delta E = \Delta E_{in} + \Delta E_{bs} + \Delta E_{out} = \varepsilon(E_0) \frac{N \Delta x}{\cos \theta_1} + \Delta E_{bs} + \varepsilon(K E_0) \frac{N \Delta x}{\cos \theta_2} \]  \hspace{1cm} (1.9)

where \( \Delta E_{bs} \) is the energy lost in the scattering event and \( K \) is the kinematic factor, which depends only on the scattering angle and mass of the projectile and target atoms. Note: we have used the surface energy approximation to write the Equation 1.9. In other words, from one single measurement of energy loss two unknown stopping cross sections, \( \varepsilon(E_0) \) and \( \varepsilon(K E_0) \), have to be determined.

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![Figure 1.4: Schematic of a backscattering experiment to measure energy loss in a thin film target.](image)

One way to circumvent this problem is to assume that the stopping cross section is proportional to energy [6, 52, 53], which gives the following relation:
\[ \varepsilon(E) = A_v E^\nu \]  

(1.10)

where, for protons, \( \nu = \frac{1}{2} \) for \( E \leq 25 \text{ keV} \), \( \nu = 0 \) for \( 80 \text{ keV} \leq E \leq 200 \text{ keV} \) and \( \nu = -1 \) for \( E > 200 \text{ keV} \).

However, the linear relationship clearly breaks down around the stopping power maximum, where the stopping cross section depends on energy non-linearly. Another solution has been proposed by Warters [54] and includes Taylor expansion of the stopping cross section up to the first order around energy \( E_x \) lying somewhere in between \( E_0 \) and \( KE_0 \). The exact value of energy \( E_x \) is then determined by setting the coefficient in front of \( (d\varepsilon/dE)|_{E_x} \) equal to zero and solving Equation 1.9 with respect to \( \varepsilon(E_x) \). However, it was found by Aumayr et al. [55] that the systematic uncertainty of Warter's evaluation increases: i) for thicker targets, reaching 5% for 200 \( \mu \text{g/cm}^2 \) copper film; ii) for low \( Z_2 \) targets, reaching 10% for 100 \( \mu \text{g/cm}^2 \) Al film; iii) in the vicinity of the stopping power maximum. An alternative way to solve Equation 1.9 is to use an iterative procedure, where the target film is divided into thin sublayers, with the stopping cross section changing only slightly within each sublayer. A trial \( \varepsilon \) function, e.g. the Andersen and Ziegler formulation for protons or helium [7, 13], can then be used to evaluate the energy loss in the target film, and, if the \( \Delta E_{\text{calc}} \) and \( \Delta E_{\text{meas}} \) disagree with each other, the correction multiplication coefficient to the trial function, \( \Delta E_{\text{calc}}/\Delta E_{\text{meas}} \), is introduced and the procedure is repeated again (see Appendix A). An analogous iterative procedure can be used to improve the accuracy of Warter's method [36, 56].

It was shown [45], that RBS from thin evaporated targets is a simple and extremely accurate method (total uncertainty < 3%) for obtaining stopping cross section for energies from 30 to 700 keV, provided the following requirements are met in the experiment: i) careful calibration of the accelerator energy and compensation for the energy drift; ii) evaporation in a good vacuum onto a low \( Z_2 \) substrate; iii) careful measurement of the target thickness with an independent check of the result; iv) check for the bulk impurities; v) use of a detector of good energy resolution (<3 keV) and rather thin targets (\( \Delta E_{\text{meas}} \sim 10-25 \text{ keV} \)); vi) measurement of an amorphous target or by rotating the sample during the
experiment in order to avoid channeling; vii) measurement at several energies and application of an iterative data evaluation.

Most of the requirements for a backscattering experiment are similar to the requirements for the transmission experiment discussed earlier. The thickness calibration for deposited thin films is complicated by the fact that the target film is essentially attached to a much heavier substrate, so that direct weighing introduces large errors. One has to use multiple techniques, such as transmission electron microscopy, RBS, MEIS, ellipsometry, X-ray photoelectron spectroscopy, etc., to ensure that the uncertainty in the thickness measurement is within 1-2% limit. The requirement for rather thin targets is dictated by the increased uncertainty of the iterative procedure for thicker films. In an RBS measurement, one may forget many of the points which cause trouble in a transmission experiment [46], such as: i) target texture; ii) surface impurities or iii) target inhomogeneities [45].

If the sources of errors discussed above are eliminated, both backscattering and transmission measurements of stopping cross section should agree with each other. In [57], stopping cross section values for hydrogen isotopes on Cu have been carefully measured in the range from 70 keV/amu to 550 keV/amu using both backscattering and transmission methods. For each method, errors of about 3.0% for the data points are expected. The data agree within this uncertainty and no systematic deviations have been found.

To summarize, a reliable theory to predict stopping cross section is absent in the medium ion energy region and experimental data are scarce and often contradict each other which greatly increases the uncertainty of existing semi-empirical predictions. On the other hand, P. Bauer [45] and P. Mertens [46] meticulously describe all the possible sources of errors for measuring stopping cross section in backscattering and transmission geometry, respectively. Their results suggest that accurate values of stopping cross sections in the medium energy region can, in theory, be obtained if all the sources of errors are eliminated or minimized. Moreover, at the end of the 1980s, a variation of Rutherford
backscattering spectrometry emerged, called medium ion energy scattering. Its high energy resolution of the detector \( \frac{\Delta E}{E} < 10^{-3} \) and operating energy range near the stopping maximum are particularly well suited for accurate stopping cross section measurements.

Accurate knowledge of the ion stopping cross sections is essential for depth-sensitive measurements in a variety of ion beam analysis techniques, such as Rutherford backscattering spectrometry, medium energy ion scattering and etc., as described in detail in Section 2.2.3. With an ever shrinking size of transistors in modern computers, accurate non-destructive measurement techniques that can probe elemental composition with a sub-nanometer depth resolution are highly desirable. Medium energy ion scattering can be one of such techniques, provided that the values of the stopping cross sections for all the elements of interest are known with better precision.

1.3 Scope of Part I of the thesis

The present study was undertaken to accurately measure the stopping cross sections of protons for several high-quality solid targets grown by molecular beam epitaxy (MBE) using MEIS. In Chapter 2, I describe experimental methods including MBE, RBS and MEIS techniques that are used extensively throughout this work, and SEM and XPS methods that were utilized as complimentary analytical tools. The idea is to provide the reader with the necessary background in order to be able to understand Chapters 3 and 4 where I report accurate measurements of stopping cross section for 50 - 200 keV protons in elementary Si and Ti targets and ternary oxide SrTiO\(_3\), respectively. I have developed a new methodology on how to calculate stopping cross section from MEIS spectra, since MEIS has never been used before for measuring stopping cross section. This method is described in detail in Appendix A. Appendix B contains additional information on the structure and composition of SrTiO\(_3\) films that are described in Chapter 3.
1.4 References


[54] W. D. Warters, The elastic scattering of protons by 7Li, California Institute of Technology, Pasadena, California, 1953.


Chapter 2. Experimental methods

Molecular beam epitaxy was used in the present work to obtain both high quality ultra-thin targets for stopping cross section measurements and lateral Si wires. In this chapter, the details of the MBE growth system pertinent to deposition of ultra-thin films and Si wires are discussed.

Ultrathin films were probed by a complementary techniques, specifically by XPS, RBS and MEIS. In Chapter 3, XPS was used to characterize the chemical composition of the SrTiO$_3$ film and to obtain depth-resolved chemical information (angle resolved XPS). The absolute concentrations of Sr, Ti and O were obtained from RBS and MEIS. In Chapter 4, XPS was used to confirm the partial oxidation of Ti film. The thickness of Si, Ti and TiSi$_2$ films was monitored in situ by using a quartz crystal monitor and estimated from combined RBS and MEIS measurements.

Silicon wires described in Chapters 6 and 7 were characterized by scanning electron microscopy (SEM). From these measurements we obtained information about the orientation, length and width of the silicon wires. The distributions of C, O, Si and Au along the individual wire were analyzed by using energy dispersive X-ray analysis (EDX).

2.1 Molecular beam epitaxy

Several evaporation sources from which a thermal beam emanates after evaporation of a high purity solid or liquid are the defining elements of a MBE chamber (Figure 2.1). MBE generally involves the deposition of atoms, though dimers, trimers, etc. can constitute some fraction of the evaporated vapour. Typically, Knudsen cells are used as evaporation sources [1]. A Knudsen cell is composed of a heatable crucible placed behind a small aperture from which a directional but highly divergent beam propagates. In our case, electron beam evaporation sources were used instead, in which high purity Au, Ti
and Si ingots were heated by a focused high energy (E ~ 9-10 keV) electron beam. This source of heat is absolutely clean and, when combined with ultra-high vacuum in the chamber (P < 10^{-9} Torr), allows one to produce the purest materials. The purpose of using ultra-high vacuum in MBE is thus i) to reduce scattering of molecular beam species from the atoms of residual gases present in the chamber, and ii) to prevent substrate surface and growing material from reacting with residual gases.

**Figure 2.1:** A schematic of the MBE chamber used in the present work. The Si substrate was mounted on a molybdenum (Mo) holder using indium (In). K-type thermocouples were used to monitor the temperature of the heated substrate.

A beam of evaporated material was directed by a relatively large aperture (r ~ 1.5 cm) toward both the substrate and the quartz crystal monitor to control the deposition rate. Shutters are placed in front of the apertures so that the flow of gas can be rapidly turned on and off. This allows for precise control of the amount of deposited material at the submonolayer level.

Another defining characteristic of MBE is the use of a piece of polished single crystal, e.g. Si, as a substrate which acts as a seed crystal to achieve epitaxy. The deposited film may lock into one or more crystallographic orientations with respect to the substrate.
crystal and a crystalline oriented (epitaxial) film will be produced. However, amorphous or polycrystalline substrates can also be used to produce amorphous or polycrystalline films.

Surface mobility plays a major role in MBE growth. Thus, deposition is conventionally carried out at high substrate temperatures. Room temperature depositions of Ti and Si carried out in the present work on amorphous carbon and crystalline silicon substrates resulted in amorphous thin films. On the other hand, growth of the silicon wires at elevated temperatures ensured epitaxial wire growth.

### 2.2 Rutherford backscattering spectrometry

In RBS, a beam of monoenergetic and collimated ions impinges on the target. A small fraction of ions (<10^{-2} %) gets scattered back due to close encounters of the incident particles with the nuclei of target atoms (Figure 2.2). Some of the ions scatter in the direction of a detector where they generate an analog signal. Typically, the detector is a silicon barrier detector and the analog signal is linearly proportional to the energy of the scattered particle. Small deviations from the linearity of the detector [2] can be ignored in most of the cases. The signal is processed by a multichannel analyzer which subdivides its magnitude into a series of equal increments. Each increment is numbered and referred to as a channel. An event whose magnitude falls within a particular channel is registered there as a count. The raw RBS spectrum thus represents a series of counts contained in the various channels. The relation between the energy of detected particle and the channel number in which that particle is counted must be determined experimentally by performing an RBS measurement of a standard.

The conversion of individual signals in the RBS spectrum to depth distributions of atomic concentrations in a sample relies on three physical quantities: i) the kinematic factor; ii) the scattering cross section; and iii) ion energy loss or stopping cross section.
2.2.1 Kinematic factor $K$ and elemental sensitivity

When a particle of mass $M_1$ moving with a known energy $E_0$, collides with a stationary particle of mass $M_2$, energy will be transferred in a collision to the stationary particle (Figure 2.2). The interaction between $M_1$ and $M_2$ can be described by a simple elastic collision of two isolated particles if: i) the projectile energy significantly exceeds the binding energy of the atoms in a target, and ii) nuclear reactions and resonances are absent. Both conditions for He$^+$ ions are fulfilled within the $1 \text{ keV} < E_0 < 2 \text{ MeV}$ ion energy range [3]. The simple elastic collision of two masses $M_1$ and $M_2$ can then be fully solved by applying the conservation of energy and momentum laws. The ratio of the scattered projectile energy after the elastic collision, $E_1$, to that before the collision, $E_0$, called kinematic factor $K$, can then be found:

$$K = \frac{E_1}{E_0} = \left( \frac{1 - \left( \frac{M_1}{M_2} \right)^2 \sin^2 \theta + \frac{M_1}{M_2} \cos \theta}{1 + \frac{M_1}{M_2}} \right)^2$$  \tag{2.1}$$

\textbf{Figure 2.2:} Schematics of an ion scattering experiment.
The kinematic factor depends only on the ratio of the projectile to the target masses and on the scattering angle $\theta$.

Equation 2.1 contains the essence of how RBS acquires its ability to sense the mass of an atom. If the initial energy $E_0$ and mass $M_1$ of the projectile are known and if the energy $E_i$ after the elastic scattering event is measured at a known angle $\theta$, then the mass $M_2$ is the only unknown quantity in Equation 2.1. When a target contains two types of atoms that differ in their masses by a small amount, it is important that this difference in mass produces the largest possible change in the measured energy $E_i$ of the ion after the collision in order to ensure large separation between the signals in the RBS spectrum. Figure 2.3 shows the scattering angle dependence of the kinematic factor for protons incident upon strontium, titanium, silicon, oxygen and carbon atoms. For fixed $M_1$, a change of $M_2$ gives the largest change of $K$, and hence $E_i$, when $\theta = 180^\circ$. However, at this angle the detector will obstruct the path of the incident particles, so it is usually positioned at some large backward angle, such as 170°.

Figure 2.3: Plot of the kinematic factor as a function of scattering angle for different elemental targets for an H$^+$ incident beam.
While separation between peaks of different elements is larger at scattering angles of $\theta > 120^\circ$, the scattering cross sections and hence intensities of the peaks are actually lower at those angles, as described in the next section. When there is a need to improve the sensitivity of detection, forward scattering experiments are also possible.

2.2.2 Scattering cross section and RBS spectrum yield

The average differential scattering cross section is used in RBS to answer the question of how often an elastic collision between the projectile and the target atom result in a scattering event at a certain angle $\theta$. If $Q$ is the total number of particles that have hit the target and $dQ$ is the number of particles recorded by a detector with a solid angle $d\Omega$, then the differential cross section $\frac{d\sigma}{d\Omega}$ is defined as:

$$\frac{d\sigma}{d\Omega} = \frac{1}{N \Delta x} \times \frac{1}{Q} \times \frac{dQ}{d\Omega} \tag{2.2}$$

where $N$ is the volume density of atoms in the target and $\Delta x$ is the target thickness. To calculate the differential cross section for an elastic collision, the laws of conservation of energy and momentum must be combined with the specific assumptions about the force acting between the projectile ion and the target atom during the collision. If the distance of the closest approach is large compared with nuclear dimensions, then the interaction between the projectile of energy $E$ and target atom may be described as a Coulomb repulsion between the two nuclei, and differential cross section is given by Rutherford's equation [3]:

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{e}} = \left( \frac{Z_1 Z_2 e^2}{4 E} \right)^2 \frac{4}{\sin^4 \theta} \left( 1 - \left( \frac{M_1}{M_2} \right) \sin \theta \right)^2 + \cos \theta \left( 1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2 \right)^2 \tag{2.3}$$
From Equation 2.3, it follows that the ion scattering cross section or, in other words, sensitivity to detect a particular element, is: (a) proportional to \(Z_1^2\), i.e., the backscattering yield for a given atom with a He beam \((Z_1 = 2)\) is 4 times higher than with a H beam \((Z_1 = 1)\); (b) proportional to \(Z_2^2\), i.e., for a given projectile, heavy atoms have larger cross sections than light atoms; (c) inversely proportional to the square of the projectile energy, so the backscattered ion yield rises rapidly with decreasing ion energy; (d) approximately inversely proportional to the fourth power of \(\sin(\theta/2)\), when \(M_1 \ll M_2\), so the yield rapidly increases as the scattering angle is reduced.

Some deviations from the Rutherford scattering cross section exist at small scattering angles and at the very low and very high projectile energies. Small scattering angles correspond to distances of closest approach between the projectile ion and the target nuclei larger than the radius of the innermost electron shell of the target atom. At these distances, the electrostatic interaction is between screened nuclei instead of bare nuclei, as assumed by the Rutherford formula. A similar situation exists at low projectile energies where one must use scattering cross sections derived from a potential which includes electron screening [3]. For sufficiently high energies \(E_b\), the distances of closest approach between the projectile ion and the target nuclei are reduced to nuclear sizes. At these distances, the short-range nuclear forces might start influencing the scattering process and the scattering process would become inelastic. For example, the deviations from the Rutherford formula for protons become pronounced in most targets at energies \(E < 100\) keV and \(E > 1.5\) MeV, when the screening effects and nuclear reactions, respectively, start playing a role.

The average differential scattering cross section for a small detector angle \(\Omega\) is introduced as:

\[
\sigma = \frac{1}{\Omega} \int_{\Omega} \frac{d\sigma}{d\Omega} d\Omega
\]  

(2.4)
It converges to a differential scattering cross section (Equation 2.3) in the limit of a very small solid angle of the detector. Note: somewhat confusingly, the differential scattering cross section \( \frac{d \sigma}{d \Omega} \) is sometime called \( \sigma(\theta) \) in the literature.

For experimental conditions in which a laterally uniform beam of particles hits a homogeneous target much larger than the beam size, the total number of particles \( A \) registered by a detector can be written as:

\[
A = \sigma \times \Omega \times Q \times N \Delta x
\]  

(2.5)

If \( \sigma \) and \( \Omega \) are known, and the numbers of incident (\( Q \)) and detected (\( A \)) particles are counted, then the number of target atoms per unit area, \( N \Delta x \) [atoms/cm\(^2\)], can be calculated from Equation 2.5.

In practice, Equation 2.5 is not used directly since the effective solid angle of the detector is often not accurately known. Instead, a commonly used procedure for the determination of \( N \Delta x \) is to calibrate the product \( Q \times \Omega \) with respect to a backscattering standard (e.g., Si), in which an accurately known number (\( N \Delta x \)) of heavy atoms (e.g., Bi) is implanted per unit area [3]. Then one obtains:

\[
N \Delta x = \left( \frac{d \sigma}{d \Omega} \right)_s \frac{A}{A_s} (N \Delta x)_s
\]

(2.6)

where \( \left( \frac{d \sigma}{d \Omega} \right)_s \) is the differential scattering cross section (Equation 2.3) from the implanted species in the standard.
2.2.3 Stopping cross section and depth sensitivity

An energetic ion that hits a target will not only scatter from the surface atoms but also will penetrate into the target. As the ion passes through the target, it loses energy. The energy loss process is described by the stopping cross section $\varepsilon$ defined in Equation 1.1. If the stopping cross section for a given target is known, then one can find the energy of an ion at any distance $x$ along the ion path:

$$E(x) = E_0 - N \int_0^x \varepsilon \, dx$$  \hspace{1cm} (2.7)

And vice versa, if the energy $E(x)$ of an ion is known, the depth $x$ can be found:

$$x = \frac{1}{N} \int_{E(x)}^{E_0} \frac{1}{\varepsilon} \, dE$$  \hspace{1cm} (2.8)

As follows from Equation 2.7, the energy of ion in the backscattering experiment depends on the depth, where scattering from the target atom has occurred. By performing a computer simulation, the depth profile of the target atoms can be extracted from the measured scattered ion energy distribution.

The numerical calculation proceeds from Equation 2.7 with tabulated values for $\varepsilon(E)$ for all elements and initial guesses of the target's composition and thickness. The stopping cross section of the target, which contains more than one element, is calculated using Bragg's rule. A common numerical approach, as realized for example in the program code QUARK [4], is to divide the depth into many slabs of equal width $\Delta x$, which must be small enough so that $\varepsilon$ can be taken to be constant for the given slab. The calculation starts from the surface layer. The energy of an ion at the surface of the 2nd slab $E^{in}(1)$ is equal to the energy at the surface $E_0$ minus the product of stopping cross section evaluated at the surface energy and the effective path length $\Delta x / \cos \theta_i$ (Figure 2.4):

$$E^{in}(1) = E_0 - \varepsilon(E_0) \left( \frac{N \Delta x}{\cos \theta_i} \right)$$  \hspace{1cm} (2.9)
The energies at the two boundaries of the \((n+1)^{th}\) slab can be related by the recursion relation:

\[
E^{\text{in}}(n+1) = E^{\text{in}}(n) - \varepsilon \left( E^{\text{in}}(n) \right) \left( \frac{N \Delta x}{\cos \theta_1} \right)
\]  

(2.10)

In this way, one obtains the energy of the incident particles before scattering at each slab boundary. If the number of incident particles \(Q\) and solid angle \(\Omega\) of the detector are known a priori from RBS measurements of the standard as described in Section 2.2.2, the number of backscattered ions in \((n+1)^{th}\) slab can be calculated from Equation 2.5, where the scattering cross section is evaluated at the local energy \(E^{\text{in}}(n)\). Upon scattering, the energy of the ions in each slab is reduced by the kinematic factor \(K\). Along the outgoing path, the energy lost in each slab is equal to the product of stopping cross section evaluated at the local energy and the effective path length \(\Delta x / \cos \theta_2\). The emerging particles will have energies \(E^{\text{out}}(1), E^{\text{out}}(2), ..., E^{\text{out}}(n)\), etc., where \(E^{\text{out}}(n)\) is the energy of an ion emerging after a collision in the \(n\)-th slab. Therefore:

\[
E^{\text{out}}(1) = K E^{\text{in}}(1) - \varepsilon (K E^{\text{in}}(1)) \left( \frac{N \Delta x}{\cos \theta_2} \right)
\]  

(2.11)

The energy \(E^{\text{out}}(2)\) of an emerging particle scattered after traversing inward and outward through two slabs is:

\[
E^{\text{out}}(2) = K E^{\text{in}}(2) - \varepsilon (K E^{\text{in}}(2)) \left( \frac{N \Delta x}{\cos \theta_2} \right) - \varepsilon (E_{12}) \left( \frac{N \Delta x}{\cos \theta_2} \right)
\]  

(2.12)

The energy at the 1, 2 interface \(E_{12}\) at which the last term must be evaluated is identical to that given in the parentheses preceding that last term. Iterating the procedure, one can find energies \(E^{\text{out}}(i)\) from all the slabs and reconstruct the RBS spectra corresponding to the initial guess of the composition and thickness of the target. One can then make the necessary adjustments to the initial guess in order to match the experimental spectrum. The procedure is repeated until the simulated and experimental spectra match each other.
2.2.4 Sample RBS spectrum

In Figure 2.5, a schematic RBS spectrum is shown for a homogeneous thin film of a heavy element A on the top of a lighter substrate B. In this example, we assume that the elements A and B are known and below we show how this information is transformed into a backscattering spectrum. In practical cases, the problem is reversed.
When an ion beam of energy $E_0$ collides with the sample surface, some of the ions get scattered into a detector with an energy $K_A E_0$, where $K_A$ is the kinematic factor for ions scattered from an element A. In the absence of the thin film A, the ions scattered from the surface atoms B would have energy $K_B E_0 < K_A E_0$ as follows from Equation 2.1 and Figure 2.3. *Atoms with heavy masses are detected at high energies and atoms with light masses are detected at lower energies in the RBS spectrum.*

All the ions that didn't get scattered from the surface continue to travel through the film A, losing kinetic energy on the way (Section 1.1). Occasionally, they collide with an atom below the surface and some of the ions scatter back in the direction of the detector. These ions will have energy lower than $K_A E_0$ due to energy loss and they contribute to the 'trapezoidal' peak from film A. The signal has a trapezoidal shape due to the $E^{-2}$ dependency of scattering cross section on the projectile energy $E$, as described in Section 2.2.2. As the ion goes deeper into the substrate and its energy decreases, the scattering cross section increases, and so does the yield. The energy width of the trapezoidal peak is proportional to the thickness (Equation 2.7) – a thicker film A produces a wider peak. The ions that scatter from the substrate B after traversing film A will contribute to the trapezoidal signal from B of lower height as follows from Equations 2.3 and 2.5. *Elements with high atomic numbers give high yields in RBS spectrum and elements with low atomic numbers give low yields.*

The final backscattering spectrum is a linear superposition of two signals from A and B. We assumed a sufficiently thick substrate so that the signal from B goes all the way to zero energy, corresponding to ions stopped in the substrate. If a concentration profile of element A varies with depth, the height of a signal will vary accordingly (see Equation 2.5). *An RBS spectrum is thus an image of elemental depth distributions.*

### 2.3 Medium energy ion scattering

Medium energy ion scattering uses the same physics as Rutherford backscattering spectrometry: ions impinge on the target, travel through it until eventually they get
scattered in a close collision with a target nucleus, and some of them scatter in the
direction of the detector that determines their energy. Two main differences from RBS
that allow MEIS to analyze surface layers with sub-nanometer depth resolution are: i)
using medium energy ions \(40 \text{ keV/amu} < E_0 < 150 \text{ keV/amu}\) instead of high energy ions
\(E_0 > 150 \text{ keV/amu}\) and ii) using a movable toroidal electrostatic energy analyzer with a
channel plate detector instead of a fixed silicon barrier detector. First, lower energy ions
do not penetrate as deep into the substrate, hence the increased surface sensitivity of
MEIS. The surface sensitivity is further increased since stopping cross sections for
protons and helium in most of the target elements have maxima near the medium ion
energy region (Figure 1.1). This implies that the same measured energy losses for
medium and high energy protons \(\Delta E\) correspond to to smaller probed depth \(\Delta x\) for
medium energy protons according to the Equation 1.1. Second, the electrostatic analyzer
simultaneously detects ions of a fixed energy \(E\) for a range of scattering angles \(\theta\) with
high energy resolution \((\frac{\Delta E}{E} < 10^{-3})\). Finally, the movable detector allows one to align it
with specific crystallographic directions in the substrate (blocking direction). Combined
with channeling conditions for the incident beam, this so-called double channeling
geometry minimizes the substrate's yield and ensures great surface sensitivity (e.g.,
relaxation of the surface layers in thin epitaxial films on single crystalline substrates can
be detected with an accuracy \(\pm 0.01 \text{ Å}\) in favourable cases [5]).

2.3.1 Scattering cross section

Due to the lower ion energy used in MEIS compared to RBS, charged particles cannot
penetrate through all the electron shells in a close collision. As a result of screening by
target atom's innermost electrons, interaction between the projectile and the target atom
in the collision event cannot be described by the Coulomb potential. Therefore, the
Rutherford scattering cross section formula (Equation 2.3) needs to be modified.
To account for screening effects, a screened Coulomb potential is used to derive the scattering cross section at medium ion energies. For a positively charged projectile with atomic number $Z_1$ and target nuclei with atomic number $Z_2$, the screened Coulomb potential will have a general form

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \phi \left( \frac{r}{a} \right)$$

(2.13)

where $\phi(r/a)$ is the screening function and $a$ is the screening length. Screening effects become unimportant at distances larger than the screening length. Typically, a Molière potential [5] is adopted for MEIS using light projectile ions ($H^+$ and He$^+$), for which the screening function has the form

$$\phi(x) = 0.35 e^{-0.3x} + 0.55 e^{-1.2x} + 0.10 e^{-6.0x}$$

(2.14)

and the Thomas-Fermi screening length for a partially ionized projectile is defined as:

$$a = \frac{0.885 a_0}{\sqrt{Z_1 + Z_2}^{2/3}}$$

(2.15)

where $a_0 = 0.529$ Å is the Bohr radius.

In the Molière approximation, the differential scattering cross section is given by a Rutherford expression (Equation 2.3) corrected by the screening correction factor $F$:

$$F = 1 - \frac{0.042 Z_1 Z_2^{2/3}}{E \text{[keV]}}$$

(2.16)

Depending on the ion-target combination and ion energy, the screening term lies typically in the range $0.85 \leq F \leq 1$ [5].
2.3.2 Shadowing and blocking

When a beam of energetic light ions (H\(^+\) or He\(^+\)) hits an atom, a shadow is cast as shown in Figure 2.6. The shadow cone arises from small-angle deflections of the ions in the screened Coulomb potential of the atom's nuclear charge. For an unscreened Coulomb potential, the corresponding shadow cone radius at a distance \(r\) from an atom producing a shadow is:

\[
R_C = 2\sqrt{\frac{Z_1 Z_2 e^2 r}{E}}
\]

It follows from the dependence of the shadow cone radius on energy that it is increased if lower energy light ions are used in MEIS experiments. An increased shadowing of the atoms lying deep into the target means that it is mostly surface atoms that contribute to the MEIS spectrum.

\[\text{Figure 2.6: Scattering from an ideal periodic and static lattice for an ion beam incident on a crystal along a low index direction. See ref. [5].}\]

If one uses the Molière potential (Equation 2.14), then no analytical expression exists for the shadow cone radius and it can only be found numerically in the form

\[
R_M = \xi(R_C) \times R_C
\]

where the parameter \(\xi(R_C)\) is called the screening parameter and plots of the screening parameter as a function of unscreened Coulomb radius \(R_C\) are available in the literature, see e.g. [5]. The conclusion regarding the increased surface sensitivity for low-Z medium
energy ions still remains valid due to the functional dependence of screened cone radius $R_M$ on its unscreened Coulomb counterpart $R_C$.

The surface sensitivity on single crystals using MEIS is obtained by aligning the ion beam with a major crystal direction (channeling direction). For Si, which crystallizes in a diamond cubic crystal structure (Figure 2.7), a major crystal direction with the largest channel area is $<110>$ (Figure 2.7) and most MEIS experiments are done by aligning incoming and outgoing beams with it. For an ideal periodic and static lattice, as in the example given in Figure 2.6, only the top layer of atoms is fully exposed to the beam, since the atoms in the following layers are located in the shadow and, hence, cannot scatter. In a practical case, the number of visible atoms per row would be larger due to lattice imperfections and thermal motion of the atoms, which would make lower layers visible to incoming ion beam.

![Figure 2.7: Model of the Si crystal along the <100> and <111> crystallographic directions.](image)

If the scattering atom is located beneath the surface layer, the backscattered projectile may be blocked on its way out by another atom in the upper layer. It can be shown that
the opening angle, $\beta$, of the blocking cone is given by $\beta = \frac{R_M}{r}$, where $R_M$ is given by Equation 2.18 and $r$ is the distance between the emitting and blocking atom.

A theoretical calculation of the backscattering yield in MEIS is cumbersome and a Monte Carlo simulation of the scattering process is often done instead. In the following example, we describe the computational scheme known as the 'nuclear encounter probability method' pioneered by Barrett [6].

Consider the situation when the scattering occurs from a single atomic row ('single row approximation'). This condition is fulfilled if the shadow cone radius remains much smaller than the distance between adjacent rows within the depth of interest. The scattering process can be treated as a sequence of discrete small-angle deflections by the screened Coulomb potentials of the atoms along the row as shown in Figure 2.8 for one specific track. It is further assumed that the atoms are vibrating independently. The ion enters parallel to the $z$-axis at a distance $x_0$ from the origin, deflected from thermally displaced atoms 1 to $n-1$ at positions $(x_1', x_2', \ldots, x_{n-1}')$, and finally collides with the atom in plane $n$ located exactly at $x_0 + \Delta_n$. The probability density $p_n(x_0)$ for such a track to occur is given by

$$p_n(x_0) = G_i(x_0 + \Delta_n) \prod_{j=1}^{n-1} G_j(x_j')$$

(2.19)

where $G_j(x_j')$ designates the Gaussian probability density for the thermal displacement of atom $j$:

$$G_j(x_j') = \frac{1}{2\pi \langle u^2_j \rangle} \exp \left( -\frac{|x_j' - x^0_j|^2}{2\langle u^2_j \rangle} \right)$$

(2.20)

Here, $x^0_j$ is the equilibrium position of atom $j$ projected on plane $j$ and $\langle u^2_j \rangle$ is its one-dimensional RMS vibrational amplitude. To obtain the hitting probability of atom $n$, one
should integrate Equation 2.19 over all possible positions \( \{ x'_j \} \) and track starting positions \( x_0 \).

![Figure 2.8: Ion trajectory along a row containing \( n \) atoms. The ion undergoes discrete small-angle deflections from the thermally displaced atoms in the row. Symbols are defined in the text. See ref. [5].](image)

In the Monte Carlo method, first a random point \( x_0 \) is chosen uniformly from a sufficiently broad impact area surrounding the atomic row. Then points \( x'_j \) are chosen quasi-randomly in accordance with the Gaussian probability densities (Equation 2.20) of atoms 1, 2, ..., \( n-1 \). After calculation of the track, the probability density for a nuclear encounter \( G_n(x_0 + \Delta x_n) \) is evaluated. The procedure is repeated for many tracks, while accumulating the sum over \( p_n(x_0) \) (Equation 2.19). After appropriate normalization this sum gives \( p_n \) [5], which is the hitting probability of atom \( n \).
2.3.3 Instrumentation: RBS and MEIS

The 50 - 170 keV H$^+$ ions and the 500 keV He$^+$ ions in our MEIS and RBS experiments, respectively, are produced in the 1.7 MeV Tandem accelerator (Figure 2.9) located in the Tandetron Lab, Western University. The positive He$^+$ ion beam is generated in the duoplasmatron source, and passes through a sodium vapour to produce negative He$^-$ ions. The negative ions are accelerated toward the high-voltage terminal, where electrons are stripped from each ion in the nitrogen stripper canal producing positively charged He$^+$ ions. Positive ions are now repelled by the high-voltage terminal and return to ground potential, again gaining kinetic energy. The final energy of the He$^+$ ion beam is $E = 500$ keV. The negative H$^-$ ion beam is generated in a cesium (Cs) sputter source with a titanium hydride target (TiH$_2$) (High Voltage Engineering Europa), which can be preaccelerated to a maximum kinetic energy of 158 keV. The ion beam then goes through the same acceleration scheme as outlined for He ions. The only difference is that for energies lower than ~160 keV, H$^-$ ions are used without converting them to the H$^+$ ions. In other words, the Tandetron low energy accelerating column accelerates the ions and the Tandetron high energy accelerating column decelerates the ions by exactly the same amount to the energy they had prior to entering the columns.

The ion beam is focused by three quadrupole electromagnets and directed into the RBS or MEIS beamline by a high-energy switching magnet. The He beam is then collimated by two beam defining slits which are typically 0.4 - 0.5 mm in size and are separated by a distance of 2 m. The size of the beam spot on the sample is less than 0.5×0.5 mm. The H beam is collimated by a beam defining slit of less than 0.5×1.5 mm size before entering the analysis chamber. The ion dose is measured by intercepting the beam with a Faraday cup, which blocks and measures ion beam current typically for 1 s in every 4 s time interval.

A high precision 4-axis manipulator in the RBS chamber allows targeting of the sample within ±0.5 mm and allows orientation of the sample with respect to the ion beam.
direction within ±0.1°. A high-precision 3-axis goniometer in the MEIS chamber allows the orientation of the sample with respect to the ion beam direction to within 0.1°.

![Diagram of Tandem Accelerator Layout](image)

**Figure 2.9:** 1.7 MeV Tandem accelerator layout (Tandetron Lab, Western University).

The analysis of the energy distribution of backscattered He⁺ ions is realized by using a surface barrier silicon detector (Ortec) located at a 170° scattering angle above the sample in the so-called 'Cornell' geometry [7]. The energy resolution of the detector is 12 keV, and typically it has solid-angle-defining aperture (slit) of 2.0 mm × 6.1 mm with the longer dimension oriented horizontally.

An Sb implanted Si standard with a known total content of Sb $4.93 \times 10^{15}$ at/cm² and a maximum of Sb distribution lying at ~20 nm depth was used to determine the detector solid angle (see Sec. 2.1.2 for the details of the procedure). Backscattered ion energy distributions were simulated using SIMNRA v. 6.05 [8].

The analysis of the energy distribution of backscattered H⁺ ions is realized by using a toroidal electrostatic analyzer (High Voltage Engineering Europe) [9], shown schematically in Figure 2.10. The analyzer can rotate around the sample and permits simultaneous detection of ions in a ±10° range of scattering angles around its bisector.
The trajectories of the scattered ions entering into the analyzer via an entrance slit, which is much larger than the beam spot, are bent by an electric field between two deflecting plates. An applied voltage \( V \), producing an electric field between the plates, determines the central pass energy \( E_c \) of the analyzer according to \( E_c \ [\text{keV}] = V \ [\text{kV}] / 0.06 \). Only ions having a kinetic energy within \( \sim 2\% \) of the \( E_c \) value will reach the exit slit and hence will be detected. It is worth mentioning that the maximum possible voltage \( V = 10 \text{ kV} \) and the small pass energy window of \( \pm 0.02E_c \) limit the use of electrostatic detectors to scattering of medium energy ions and analysis of relatively small energy ranges. After passing through the exit slit of the analyzer, the ions impinge on a channel electron multiplier in a form of two microchannel plates with a gain of \( 10^6 - 10^7 \). The resulting electron cloud is collected by a position sensitive charge-dividing collector [10], where its energy and angle position are analyzed.

Figure 2.10: Schematic of a toroidal electrostatic analyzer.

Since an electrostatic analyzer measures ions only, Equation 2.5 for measured backscattering yield should be modified by introducing the measured ion fraction \( \eta^+ \) (or \( \eta^- \) if the negative ions are detected):

\[
A = \eta^+ \times \sigma \times \Omega \times Q \times N \Delta x
\]

(2.21)
In the medium energy range, $\eta^+$ is found to be independent of the backscattering depth and of the azimuthal and polar angle at which the ion leaves the surface. However, its value depends on the ion energy, the type of ion (H$^+$ or He$^+$) and the surface composition [5]. Quantitative analysis of MEIS spectra according to the procedure outlined in Section 2.2.2 requires accurate knowledge of the ion fraction for both sample and standard.

The ion fraction can be determined directly by means of a silicon barrier detector located alongside the electrostatic analyzer, as described in [11]. The silicon barrier detector detects both ions and neutrals, while an electrostatic analyzer detects ions only. Comparison of the two signals should give $\eta^+$ after correction for differing solid angles and angular positions. Typically, the charge fraction of positive ions is in the 0.6 - 0.75 range. An alternative method to do a quantitative analysis of MEIS spectra has been used in this work. After MEIS measurements, the samples of interest were consecutively analyzed by RBS with an Sb implanted Si standard. The content of the heaviest element determined by RBS was then used as a secondary standard in MEIS.

The sample rotation and spectrum acquisition are simultaneously controlled by software developed in LabView. The software does automatic corrections for image distortions and proton charge distribution as described in detail elsewhere [11, 12]. The total system energy resolution is defined by the energy spread and divergence of the original ion beam, the beam defining apertures and the resolution of the toroidal electrostatic analyzer. It is found to be 215 eV for an 95 keV H$^-$ ion beam [11].

2.3.4 Sample MEIS spectrum

A toroidal electrostatic analyzer allows us to measure both the scattering angle and energy at the same time. As a result, MEIS spectra end up looking somewhat different from conventional RBS spectra. In Figure 2.11, we show an MEIS spectrum of ~4 nm SrTiO$_3$ film on a Si (100) substrate. The scattering angle is shown on the $x$-axis and the energy of backscattered ions is shown on $y$-axis. The colour shows the intensity of the signal (number of counts) at a given scattering angle and energy. The bright bands
correspond to ions scattered from Sr, Ti, Si, O and C. Sr and Ti peaks are overlapping due to similar kinematic factors $K$. The backscattering yield from the Si substrate was minimized by aligning the incident proton beam with the Si <110> direction, so that only the bright 'Si, surf' band is clearly visible due to scattering from several surface layers of Si atoms. The substrate's yield is further reduced at a scattering angle of 90° (darker vertical band), which corresponds to the Si <110> blocking minimum.

![Figure 2.11: MEIS spectrum of protons scattered from a SrTiO$_3$ film on Si (100) substrate. The incident beam is aligned with the Si <110> direction. Incident energy is 95 keV. The blocking minimum at 90° is visible in Si yield.](image)

It is easier to look at the energy distribution by taking a cut through the 2D data parallel to the $\gamma$-axis at a scattering angle of 90° (Figure 2.12). In the energy distribution, we can see peaks corresponding to each of the bright bands and containing information about the depth distribution of the different species in the sample. This spectrum tells us that the sample consists of a 3.5 nm SrTiO$_3$ film on the top of Si substrate. The model curve does not coincide very well with experimental one for the Si peak due to an overestimated
stopping cross section for SrTiO$_3$ as described in detail in Chapter 3. The small carbon peak corresponds to carbon contamination on the surface of the film.

![Graph showing energy spectrum](image)

**Figure 2.12:** 2D energy spectrum cut at the 90° scattering angle from the MEIS spectrum shown in Figure 2.11, which corresponds to [110] direction for the Si (100) substrate. Positions of surface peaks for Sr, Si, O and C are indicated by arrows.

### 2.4 X-ray photoelectron spectroscopy

In X-ray photoelectron spectroscopy, the surface of a sample is irradiated with a beam of monoenergetic photons, and the kinetic energies of ejected inner shell electrons are analyzed. Because the energy of the X-ray photon is known, the binding energy of each of the emitted electrons can be calculated from conservation of energy [13]:

\[
h \nu = E_B^k(k) + E + \phi_{\text{spec}} \tag{2.22}
\]
where \( h \nu \) is the energy of the incident X-rays, \( E_{\text{BF}}(k) \) is the binding energy with respect to the Fermi level of the sample, \( E \) is the kinetic energy of electrons measured inside the spectrometer analyzer, and \( \phi_{\text{spec}} \) is the spectrometer work function.

The binding energy of inner shell electrons depends on the chemical and electronic state of an element. For example, Figure 2.13 shows the Sr 3d XPS peaks for a 3.5 nm SrTiO\(_3\) film on a Si (100) substrate after Shirley background [14] subtraction. The angle between the surface and outgoing electron (take-off angle) is 22°. Photoemission from p, d and f electronic states, with nonzero angular momentum, produces a spin-orbit doublet due to the spin-orbit interaction between unpaired electrons in the atom [13, 15] such as the 3d\(_{3/2}\) – 3d\(_{5/2}\) states in Figure 2.13. The binding energies of Sr 3d\(_{5/2}\) state in strontium titanate and strontium silicate, formed on the interface, are 132.4 and 133.0 eV, respectively, and the spin-orbit splitting is 1.79 eV for both doublets. The two doublet peaks are clearly visible in the spectrum. The sensitivity of XPS to the chemical state of an element was the reason why we used this method as complementary to MEIS, because MEIS can provide elemental depth distribution, but no information about chemical phases.

The photoelectron signal intensity is attenuated exponentially with depth. 95% of the total intensity comes from a sampling depth of \( 3\lambda \), where \( \lambda \) is the mean free path of the photoelectron. The sampling depth can be varied by changing the detection (incidence) angle of the photoelectrons, as realized in angle-resolved XPS (ARXPS). As shown schematically in Figure 2.14, ARXPS can be used to detect compositional changes within the thin film. In the example above, an XPS spectrum of a SrTiO\(_3\) film at a 22° take-off angle would correspond to the angle \( \theta_1 \) in Figure 2.14. Thus, most of the photoelectrons come from the SrTiO\(_3\) film and not the underlying Si substrate. Increasing the take-off angle to \( \theta_2 = 90° \) would decrease the signal intensity from the SrTiO\(_3\) film and increase the intensity from the underlying Si substrate, since more electrons would now come from a larger depth.
Figure 2.13: Sr 3d XPS peaks for a 3.5 nm SrTiO$_3$ film on a Si (100) substrate.

The area under the photoelectron peaks can be used for quantitative analysis. The area under the peak or intensity, $A$, for an element in a homogeneous thin target can be expressed as [15]

$$A_x = n_x S_x,$$

(2.23)

where $n_x$ is the atomic concentration of the element in the sample and $S_x$ is called the sensitivity factor. The sensitivity factor is determined experimentally for each spectrometer-element combination by using calibrated standards. It includes experimental parameters such as the incoming flux of photons, photoelectric cross section for the atomic orbital of interest, detection efficiency, etc. A generalized expression for the determination of the atom fraction of any constituent in a sample, $C_x$, can be written as an extension of Equation 2.23:

$$C_x = \frac{n_x}{\sum n_i} = \frac{A_x}{\sum A_i S_i},$$

(2.24)
2.5 Scanning electron microscopy

Scanning electron microscopy uses a focused beam of high-energy (typically 1 keV– 30 keV) electrons for imaging the sample. The wavelength of the electron beam depends upon its acceleration voltage, with the wavelength being given by de Broglie equation. For a non-relativistic electron of charge $e$, accelerated by a potential difference of $V$, $\lambda$ is given by formula

$$\lambda = \frac{h}{\sqrt{2m_e e V}}.$$  \hspace{1cm} (2.25)

For an electron microscope with 20 kV accelerating voltage, the wavelength of an electron would be 0.009 nm, which is much smaller than a distance between atoms in a solid. The small wavelength of imaging electrons in SEM gives great lateral resolution ($\geq 10^{-10}$ m) at a very high magnification ($> 100000X$). In addition, inelastic scattering of imaging electrons from the surface of a sample allows one to obtain qualitative and quantitative chemical analysis information.

The schematic of a scanning electron microscope is shown in Figure 2.15. The electrons are produced by an electron gun located at the very top of the SEM column. Electron guns are typically either thermionic guns or field emission guns. The former applies
current to a tungsten filament to extract electrons by thermal emission, while the latter uses a strong electrical field to pull electrons away from the atoms of the cathode. The emitted electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Magnetic scanning coils at the end of the column scan the focused beam along the sample surface. Once the incident beam of electrons hits the sample, it produces elastically scattered primary electrons, secondary electrons from the sample due to inelastic scattering, X-rays and visible light, which are collected by detectors and converted into a signal which is sent to the computer and contains information about the sample topology and composition. Scanning over the area of the sample produces a gray-scale image of sample surface.

Figure 2.15: The schematic of scanning electron microscope

Measuring the yield of secondary electrons emitted by excited atoms of the sample is the most common method of detection. The yield of secondary electrons is a function of the angle between the surface and the beam. Scanning the sample and detecting the variation of electron yield allows one to obtain information about the surface topology of the sample. Scintillator type detectors (Everhart-Thornley) are used for secondary electron imaging.

The second most common imaging method is backscattering mode. The yield of backscattered electrons is strongly related to the atomic number \(Z\) of the element, with a
brighter image produced by high-Z elements. Thus the images in backscattering mode can provide qualitative information about the distribution of different elements in the sample. Detectors for backscattered electrons can be scintillator types or a solid-state detector.

In addition to secondary electrons, excited atoms of the target produce characteristic X-rays. If calibrated against a reference standards, these can be used to obtain quantitative chemical analysis information about the sample surface composition. The technique is usually complementary to standard SEM and is known as energy dispersive X-ray analysis.

2.6 References


Chapter 3. Energy loss of protons in SrTiO$_3$ studied by medium energy ion scattering*

3.1 Introduction

The energy loss concept plays a central role in the interaction of an ion beam with solid matter. Relevant to energy loss are the derived quantities stopping power (or stopping force) $S$ and the stopping cross section $\varepsilon$. For thin film targets, these entities are defined as $\Delta E/\Delta x$ and $\Delta E/N\Delta x$ respectively, where $\Delta E$ is the ion energy loss along the path $\Delta x$, and $N$ is the number of atoms (or molecules) per unit volume of the stopping medium. If the target represents a chemical compound, Bragg's rule [1] is usually assumed to be valid. The rule states that $\varepsilon$ for the compound is simply the sum of the atomic $\varepsilon$-values for the constituent elements taken with stoichiometric coefficients; thus for a two-element compound $A_nB_m$:

$$\varepsilon(A_nB_m) = n\varepsilon(A) + m\varepsilon(B)$$

(3.1)

where $\varepsilon(A, B)$ are atomic $\varepsilon$-values.

Energy loss can be divided into an energy transfer to target nuclei (nuclear energy loss) and a loss of projectile energy into kinetic and potential energy of target electrons (electronic energy loss) [2]. The first process prevails when the energy of an ion is low ($E<10$ keV/amu), while the second is dominant at higher energies. Substantial deviations of measured $\varepsilon$-values for compounds from those calculated using Equation 3.1 have been observed near the stopping power maximum, i.e., near 100 keV for protons. These deviations are presumed to be either due to chemical effects (modification of the atomic electronic density in the compound) or due to physical effects (if atomic $\varepsilon$ is obtained for

a different physical state than that of the compound). For a list of past investigations of Bragg's rule as applied to organic and inorganic compounds, the reader is referred to the thorough reviews by Powers [3], Thwaites [4, 5], Ziegler [6] and references therein.

Stopping powers can be measured in several different ways: from the energy loss of projectiles transmitted through a thin foil [7], from the energy distribution of backscattered ions [8, 9], by calorimetric methods [10], etc. Analysis of published works reveals a wide spread of data and comparatively large uncertainties in the results for many pure elements and chemical compounds, which may be an indication of inherent methodical deficiencies. Some of the common problems relate to the thickness determination of the thin films or foils, the mechanical stability of thin foils, surface contamination, presence of interfacial layers, limited applicability of RBS to energies above the stopping maximum \( E > 200 \text{ keV/amu} \), etc [11]. Possible systematic errors can be eliminated if one uses complementary techniques both for characterizing the target material and for measuring stopping powers [12].

In the past decade, the energy loss of projectiles at medium energies has been studied extensively by MEIS [13]. The high energy resolution of the detector \( \frac{\Delta E}{E} < 10^{-3} \) and energy range near the stopping maximum make the MEIS technique particularly well suited for energy loss studies. For example, in [14] the authors were able to measure an increase in the stopping of \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ionic clusters in SiO\(_2\) in the energy region between 70 and 100 keV/amu. According to the authors, the observed 50-75\% increase may be due to the plasmon excitation contribution to the stopping power of ionic clusters. The impact-parameter dependence of \( \text{H}^+ \) electronic energy loss at medium energies was shown both experimentally and by theoretical simulations based on \textit{ab initio} coupled-channel calculations [15-17].

This work focuses on the energy losses and derived stopping cross sections for \(~55-170\) keV protons in the ternary oxide SrTiO\(_3\) (STO) measured by MEIS. It is shown that, if the thickness and structure of the interfacial layer may be deduced, the validity of Bragg's
rule for strontium titanate can be tested. The methodology established herein can be extended to many other thin film systems.

### 3.2 Experimental details

Measurements of energy loss and stopping cross sections with high precision require high quality targets. Ideally, the thin film target should have an atomically sharp interface, atomically flat surface and a uniform thickness and composition over a suitably large surface area. Molecular beam epitaxy is a technique that can produce such an ideal thin film target.

An epitaxial SrTiO$_3$ film on Si(001) was grown by MBE. A SiO$_2$-free 2×1 Si(001) surface was obtained by heating in UHV to ~980 °C. Upon it ~1/2 ML of strontium was deposited at a substrate temperature of 700 °C. This formed an interfacial strontium silicide layer, that functions to protect the underlying silicon from oxidation. The wafer was then cooled to near room temperature (<200 °C as measured by an infrared pyrometer), where in UHV an additional 1/2 ML of strontium was deposited. This strontium remains metallic and serves as an additional buffer layer to prevent Si substrate oxidation. With the substrate still at the room temperature, oxygen was then introduced to a background pressure of 4×10$^{-8}$ Torr and additional strontium was deposited in the presence of the oxygen to form a total of 3 ML of epitaxial SrO. Metallic strontium is also oxidized during this step. On top of the 3 ML of crystalline SrO, 2 ML of amorphous TiO$_2$ was deposited in a oxygen background pressure of 3×10$^{-7}$ Torr. The heterostructure was then annealed in UHV at ~550 °C for ~30 min with the oxygen source turned off to recrystallize a SrTiO$_3$ layer through a topotactic reaction between TiO$_2$ and SrO. The extent of TiO$_2$ diffusion was monitored by reflection high-energy electron diffraction. Further growth of the epitaxial SrTiO$_3$ layer was done on this 2.5 unit-cell-thick SrTiO$_3$ template layer through the repeated codeposition (Sr + Ti + O$_2$ molecular beams) of an amorphous SrTiO$_3$ layer near room temperature followed by recrystallization at 550 °C.
The resultant thickness of the strontium titanate film was 9 unit cells (i.e., 3.51 nm). Details of the experimental procedure are described elsewhere [18].

Rutherford backscattering spectrometry using 0.5 MeV $^4$He$^+$ ions was performed for several spots on the sample to check the uniformity, stoichiometry and crystallinity of the STO layer. Both rotating random and channeling incidence along the Si [001] crystallographic direction were used with a silicon barrier detector mounted at 170° at the Western University Tandetron Accelerator Facility. Simulated backscattered spectra were calculated using SIMNRA software, v. 6.05 [19]. MEIS measurements were performed using incident 55-170 keV H$^+$ ions in both double aligned and random geometries. The details of the experimental setup and MEIS image corrections may be found in Kim et al. [20]. QUARK software [21] was used for MEIS data analysis.

The chemical composition of the interface was analyzed by angle-resolved X-ray photoelectron spectroscopy using a Thermo Scientific Theta Probe Spectrometer (ThermoFisher, E. Grinstead, UK) located at the University of Toronto. The sample was analyzed both in a standard mode, i.e., all angles collected (60° angular acceptance) for the survey spectra, and in the ARXPS mode (16 different angles) for the elemental spectra. A monochromatic Al K$_\alpha$ X-ray source was used. Where necessary, charge compensation was provided utilizing a flood gun. The energy calibration was adjusted to place the main C 1s feature (C-C bond) at 284.6 eV. The data were collected in both low resolution (pass energy = 150 eV) and in high resolution (pass energy = 30 eV). All data were processed using software (Avantage) provided with the instrument.

Since one is interested in the stopping powers in a random (i.e. non-channeling) direction, the crystallographic channeling directions of SrTiO$_3$ and/or Si should be avoided: first, the beam was aligned with the Si substrate $<101>$ channeling direction, then all 3 rotation angles were changed by $\sim$0.5-1° in order to maximize the Si, Sr, and Ti yields, and MEIS spectra were recorded. Backscattered energy spectra for several scattering angles were extracted from the MEIS energy-angle scans. These energy spectra were typically integrated over a $\sim$0.5-1° angular window to improve statistics. Although the energy...
resolution as evidenced by the steepness of the silicon edge might deteriorate due to the
kinematic factor dependence on the scattering angle, the position of the inflection point
remains unchanged after integration since symmetric angular intervals relative to the
central scattering angle position were used. The exact position of the inflection point of
the Si or Sr edge could then be found by differentiating the backscattered spectral yield
with respect to energy. In order to obtain smooth functions for differentiation, the spectra
were first fitted manually using the QUARK program. Since one is interested in the best
fit of the edge, the sample's detailed interface structure was ignored at this step. Finally,
the energy difference for protons scattered from thin SrTiO$_3$ film-covered and clean Si
surface was calculated as following:

$$\Delta E_{STO} = E_{Si}^{STO/Si} - E_{Si}^{surf} = K_{Si} E_{Si}^{surf} - K_{Sr} E_{Sr}^{surf}$$

(3.2)

where the $K$-values are kinematic factors for Si and Sr. Note that a direct estimate of the
proton energy loss from the width of Ti and Sr scattering components is not possible due
to overlapping of the peaks at the scattering angle range used in this work.

For selected proton energies, an alternative procedure was used to calculate $E_{Si}^{surf}$. MEIS
spectra for a thick (280 nm) SiO$_2$/Si(001) sample were measured immediately after the
STO sample using the same beam parameters and manipulator angle settings. The Si
surface energy position was then found following the same procedure as for the STO/Si
sample. The incident beam energies obtained from these two measurements were
consistent within $\pm 20$ eV ($\frac{\delta (\Delta E)}{\Delta E} < 0.5 \%$).

Backscattering yield measurements give information on the stopping cross section factor,
$\epsilon$, which in our case may be written in the surface energy approximation [22] as

$$[\epsilon_o] = \frac{\Delta E}{N \Delta x} = \frac{K_{Si}}{\cos \theta_1} \epsilon (E_o) + \frac{1}{\cos \theta_2} \epsilon (K_{Sr} E_o)$$

(3.3)
where $\Delta E$ is the ion energy loss in a thin film, $N\Delta x$ is the thickness of the film in atoms(or molecules)/cm$^2$, $\Delta x \sec \theta_{1,2}$ account for the ingoing and outgoing projectile pathlength enlargement for the tilted target, and $E_0$ is the incident energy. Since Equation 3.3 contains two unknowns, $\varepsilon(E_0)$ and $\varepsilon(K_{Si}E_0)$, a value of $\varepsilon(E_0)$ was found by an iterative procedure as described in Appendix A, which produces a constant multiplier to the Andersen and Ziegler stopping power values [23]. The calculations were performed for different scattering angles, $\theta$ (where $\theta = 180^\circ - \theta_1 - \theta_2$), and incident energies, $E_0$.

In Equation 3.3, the major sources of uncertainty are the energy loss in the STO thin film, $\Delta E_{STO}$, and the thin film thickness value, $N\Delta x$. The uncertainty in $\Delta E_{STO}$ is determined by the quality of the fits of the backscattered spectra. It was found that different fits within the scattering of the data points at the Si edge produce a typical uncertainty of $\delta(\Delta E) < 0.05$ keV. Thus, for an energy loss of 2 keV, a relative uncertainty of $\sim 3\%$ is introduced. The $N\Delta x$ value was obtained from RBS measurements using an Sb-implanted standard as described in Section 3.3 below. The uncertainty in $N\Delta x$ is estimated to be $\sim 2\%$ and is limited by the accuracy of the standard. Using these estimates, the total uncertainty is expected to be $< 4\%$.

### 3.3 Results and discussion

A typical MEIS spectrum for 95 keV protons scattered from the 3.5 nm strontium titanate film is shown in Figure 3.1. Even for an assumed random incident direction, several blocking minima are still evident. For example, there are pronounced minima at 99.6°, 104.1° and 107.6° in Figure 3.1 Panel a, which should be avoided. The backscattered energy spectrum was created by a slice at $98.0^\circ \pm 0.2^\circ$ (as indicated by the yellow line in Figure 3.1, Panel a), see Figure 3.1, Panel b. This spectrum was fitted using pure Si and the simulated spectrum after differentiation is shown in the bottom of Panel b together with a quadratic polynomial fit. This procedure was repeated for several different scattering angles and beam energies. The energy loss was then calculated using Equation 3.2.
To calculate the stopping cross section factor for $\text{SrTiO}_3$ (Equation 3.3), the thickness of the strontium titanate thin film, $N\Delta\chi_{\text{SrTiO}_3}$, must be known with high precision. In addition, the energy loss in any interfacial layers must be subtracted from the total energy loss measured from the shift in the Si edge position. It is well known that the $\text{SrTiO}_3/\text{Si}$ interface is thermodynamically unstable [24]. One possible reaction with standard Gibbs free energy of reaction at 1000 K, $\Delta G^0_{1000} < 0$ (spontaneous reaction) results in the formation of $\text{SrSiO}_3$ and $\text{TiSi}_2$ products. Therefore, to stabilize the interface and ensure epitaxial growth, strontium silicide is formed at the silicon surface prior to strontium titanate deposition (see Section 3.2). Recent studies of thin MBE-grown strontium titanate films on silicon by XPS indicate the formation of a $\text{SrSiO}_x$ layer at the interface due to oxygen diffusion through the film [25].

Figure 3.1: a) 95 keV $\text{H}^+$ MEIS spectrum for 4 nm strontium titanate film recorded at random incidence direction in the Si region. b) Top: Backscattered energy spectrum at 97.97° (vertical yellow line in Panel a) summed over 0.5° interval and fitted using pure Si as a model; Bottom: derivative of the simulated spectra with respect to energy fitted with the quadratic polynomial, where $a_0 = 7.8 \times 10^6 \text{ counts/keV}$, $a_1 = -1.8 \times 10^5 \text{ counts/(keV)}^2$ and $a_2 = 1100 \text{ counts/(keV)}^3$.

In order to obtain the chemical composition and relative order of interfacial layer(s) we have analyzed the $\text{SrTiO}_3/\text{Si}$ sample by ARXPS. The analysis is described in detail in Appendix B. It was found that the Ti 2p peak shows only one component which is identified as originating from $\text{SrTiO}_3$ using literature data. On the contrary, the Sr 3d
peak has an additional component that can be assigned to the non-stoichiometric strontium silicate interfacial layer. Thus within the sensitivity limits of XPS, no Ti-containing species was observed at the interface. Analysis of photoelectron spectra at the fixed detector angle combined with the results of maximum entropy calculations for ARXPS (Appendix B) suggest the following sequence of layers from the surface down: C | SrTiO$_3$ | SrSiO$_x$ | Si (substrate). This model was further refined in RBS and MEIS spectra simulations.

For quantitative RBS analysis, an Sb-implanted sample with a known Sb content of (4.93±0.10)×10$^{15}$ at./cm$^2$ located 23 nm below the surface (primary standard) was measured using incident 0.5 MeV $^4$He$^+$ ions in order to calibrate the product of total charge collected, $Q$, and the solid angle of the silicon detector, $\Delta\Omega$. $\Delta\Omega$ was determined by fitting the spectrum of this standard using SIMNRA. Assuming that all the Ti signal in the RBS spectrum of SrTiO$_3$ arises from the STO film, according to XPS results, the value $N \Delta x_{STO} = 31.5 \times 10^{15}$ molecules/cm$^2$ is found from SIMNRA simulations. (The choice of stopping powers used in SIMNRA simulations is irrelevant when one is only concerned with peak areas.) Note that the Ti and Sr peaks are totally resolved in the $^4$He$^+$ RBS spectrum, and the Sr:Ti atom ratio is 1.07±0.02.

This procedure then provides for the Ti signal from the STO film to serve as a secondary standard in MEIS measurements at scattering angles where the Ti and Sr peaks do not overlap, and for random proton trajectories. Thus $Q\Delta\Omega$ can be determined for the MEIS experimental configuration with the additional reasonable assumption that the detector solid angle is independent of scattering angle.

The MEIS spectrum of SrTiO$_3$/Si was then collected in a double aligned geometry with both the incident beam and detector aligned along the Si <011> channeling direction (90° scattering angle). In this way, the C and O signals (from adventitious amorphous C at the surface, and O from the STO film and amorphous silicate interface) were pronounced. SIMNRA simulations yielded values for $N \Delta x_C = 3.5 \times 10^{15}$ at./cm$^2$ and $N \Delta x_{Sr_{0.06}Si_{0.30}O_{0.64}} = 5 \times 10^{15}$ mols./cm$^2$ for the interfacial layer. The latter value can be
converted to ~0.63 nm using $7.83 \times 10^{22}$ mols./cm$^3$ as the SiO$_2$ density, which agrees reasonably well with a reported value of ~1.3 nm as measured by high-resolution transmission electron microscopy for a thicker STO sample prepared by the same group [26].

Finally, these refined thickness values for the strontium titanate film with a strontium silicate interface were used in the calculations via the iterative procedure described in Appendix A. The energy loss in the interfacial strontium silicate layer was calculated using Andersen and Ziegler stopping powers for Si and corrected Andersen and Ziegler stopping powers for strontium and oxygen with the correction coefficient set equal to that of SrTiO$_3$. The possible uncertainty introduced due to chemical effects for the interfacial layer is estimated to be $\leq 1\%$. The energy loss in the adventitious C layer was not considered in the calculations, since its presence leads to an equivalent shift of the Sr surface energy, $E_{\text{Sr surf}}$, which was used to find the incident proton energy.

The pairs of $\varepsilon_{\text{STO}}$ at (i) the incident energy and (ii) energy after a backscattering event are shown in Figure 3.2 for different scattering angles and incident energies. The data points are grouped according to the $\theta_2$ values in order to show that there is no systematic trend in the behavior of $\varepsilon_{\text{STO}}$ as a function of scattering angle. The absolute uncertainty is indicated for one of the data points at 160 keV. It is evident that the variation of $\varepsilon_{\text{STO}}$ with scattering angle, as represented by different symbols on Figure 3.2, is larger than the uncertainty. One possible explanation for the observed behaviour would be an underestimation of the uncertainty in $\Delta E_{\text{STO}}$. Small variations in determining the Si edge position, and hence $\Delta E_{\text{STO}}$, would introduce a large relative uncertainty for the small energy losses observed in the thin STO film. Note: for the thicker (13nm) polycrystalline STO sample grown by pulsed laser deposition (not shown) the stopping cross section does not vary with the scattering angle. This might be expected, since the relative uncertainty in the energy loss for the thicker sample will be largely reduced. The presence of a residual channeling effect is also not excluded. Note: the impact parameter-dependence for electronic energy loss at the medium H$^+$ energies reported in [17] will be insignificant due to the large number of atomic layers involved in stopping.
Comparison of experimental data with the prediction of Bragg's rule in Figure 3.2 may indicate that there is a chemical effect present in the stopping of SrTiO$_3$, i.e., a strong modification of the valence electron density in STO. All experimental data lie systematically lower than the Bragg's rule curve and the maximum of the stopping curve appears to be shifted to higher projectile energies. This finding disputes the idea...
expressed by Ziegler et al. [6] that, except for hydrocarbons, measurable deviations from Bragg's rule for compounds with heavier atoms disappears. This last conclusion is supported by recent studies of the stopping of He$^+$ ions in TiO$_2$ [27], where no deviations from Bragg's rule were found. In addition, studies of the chemical bonding in SrTiO$_3$ with X-ray diffraction analysis suggest a pure ionic or mixed ionic and covalent character of the bonding with dominant ionic contribution [28,29]; hence, no measurable modifications of valence electron density should be expected.

On the other hand, the observed discrepancy between the experimental data and the Bragg's rule prediction may be explained by incorrect stopping powers for constituent elements: Sr, Ti and/or O. It is noted that the stopping powers of Sr obtained from SRIM2003 [30] give unreasonably high values, as compared to widely used 5 or 8 coefficient fits to stopping power data [23, 31]. This will shift the resultant stopping curve for strontium titanate upwards and the stopping maximum towards lower energies. An additional argument for the incorrect stopping power data is the different behavior for the three different Bragg-rule predictions, even though the two of them were obtained by fitting to essentially the same experimental data.

3.4 Conclusions

The stopping cross section of strontium titanate, $\varepsilon_{\text{STO}}$, for protons in the energy range 55 - 170 keV has been determined by an iterative procedure from MEIS spectra. To reduce the uncertainties involved in determining the SrTiO$_3$ film thickness and structural parameters of the interfacial layer, we rely on complimentary results from XPS, RBS, MEIS and film growth. Comparison of calculated $\varepsilon_{\text{STO}}$ values with the predictions of Bragg's rule may indicate that there is a chemical effect present in the stopping of SrTiO$_3$. This finding contradicts recent discussions in the literature stating that chemical effects are negligible in high-Z compounds and suggests an alternative explanation: Andersen and Ziegler stopping powers [23] overestimate the actual values by ~10%. The multiple-technique approach proposed herein is also applicable to cases where interface layer
thickness is significant (> 20% of the film thickness). Nevertheless, further investigation is needed to confirm the accuracy of stopping cross sections as determined by an iterative procedure from MEIS spectra.

3.5 References


[26] Private communication with Prof. D. G. Schlom.


Chapter 4. Energy loss by keV protons in Si and Ti

In Chapter 3, we found that the stopping cross section of strontium titanate $\varepsilon_{\text{STO}}$ measured by medium energy ion scattering (MEIS) is systematically lower than the Bragg's rule prediction obtained by using atomic $\varepsilon$-values from the program SRIM [1]. Several explanations of the observed discrepancy were proposed: i) the method for calculating stopping cross section from MEIS spectra is not accurate; ii) SRIM atomic $\varepsilon$-values are overestimated for one of the elements and iii) Bragg's rule is invalid.

In order to test the validity of the proposed method for stopping cross section calculations, we prepared a series of mono-elemental ultra-thin films of Si and Ti, and measured $\varepsilon_{\text{Si}}$ and $\varepsilon_{\text{Ti}}$ for protons in the 50-170 keV energy range, as described below. This allowed us to eliminate the first and, partially, the second of the listed above hypotheses. The verification of Bragg's rule with titanium silicide ultra-thin films turned out to be challenging. We will comment on this at the end of this chapter.

4.1 Sample preparation and characterization

The growth experiments were carried out in an ultra-high vacuum (UHV) molecular beam epitaxy (MBE) chamber (Kurt Lesker), containing two sources with Si (Alfa Aesar, 99.9999% purity) and Ti (Alfa Aesar, 99.999% purity), that are evaporated from water-cooled graphite crucibles using electron beam heating. The deposition rate was controlled using quartz crystal monitors that were calibrated by means of independent Rutherford backscattering measurements. 10×10 mm pieces of double-side-polished diamond-like carbon (DLC) or 8×10 mm pieces of single-side-polished n-Si(100) wafers (Silicon Valley Microelectronics) were used as the substrates for our depositions. In the latter case, after removing the native silicon oxide layer by etching for 60 sec in an HF buffer solution, a 1 nm marker layer of osmium was deposited in the Nanofabrication Facility (Western University) prior to loading the sample into the UHV MBE chamber. Any
adsorbate had been removed by outgassing DLC substrates at 500 °C for 1 h at a 4×10^{-9} Torr base pressure prior to the deposition process. Amorphous Si and Ti targets were deposited at room temperature at 1×10^{-8} Torr base pressure. All samples were transferred into the MEIS chamber in an Ar-purged glove bag to prevent oxidation and MEIS spectra were recorded using incident 55-170 keV H^+ ions.

After the energy loss measurements, Rutherford backscattering spectrometry was performed for several spots on the sample to check the purity, uniformity and stoichiometry of the deposited thin films using 0.5 MeV 4He^+ ions. Rotating random incidence was used with a sample tilted 5° off the channeling axis and then rotated azimuthally during the measurements. Simulated MEIS and RBS spectra were calculated using SIMNRA software, v. 6.05 [2]. Chemical composition of the surface oxide layer for Ti films was analyzed by angle resolved X-ray photoelectron spectroscopy (Surface Science Western) with a monochromatic Al Kα X-ray source. The energy calibration was adjusted to place the main C 1s feature (C-C bond) at 284.6 eV. Simulated photoelectron spectra were calculated using CasaXPS software [3].

MBE-grown samples that have been used for evaluating the stopping cross section of Si and Ti are listed in Table 4.1. Any oxide layer present at the surface (interface) is formed by diffusion of oxygen species at T << 1000 °C [4-7]; therefore, oxide layer composition close to its boundaries is not strictly stoichiometric. However, in our assignment of the oxide layer stoichiometry, we ignored such a small compositional variation and deduced the oxide layer thickness from the total oxygen content as measured by MEIS and RBS and the step width corresponding to the oxide layer at the leading Si(Ti) edge (see below). Any uncertainty thus introduced is negligible due to a small relative contribution of a transitional oxide layer to the total energy loss. For Ti films, the presence of Ti_2O_3 was additionally confirmed by ex situ XPS.

As an example, our treatment of data is shown in Figure 4.1 for a Ti/DLC target. In a two-dimensional MEIS spectrum (Figure 4.1a), there are signals which correspond to oxygen at the surface (O, surf) due to a surface titanium oxide layer and oxygen at the
Ti/C interface (O, int) beside the lines corresponding to the scattering from the Ti film and carbon substrate (C sub). The O, int peak overlaps with an adventitious carbon signal (C, surf) due to contamination from oil pumps. The backscattered energy spectrum was created by slicing the MEIS energy-angle 3D spectrum at 124°±0.25° scattering angle (as indicated by the yellow line in Figure 4.1a) and is shown in Figure 4.1b. The energy spectrum at an angle of 124° is relatively smooth and has higher yield compared to spectra at higher scattering angles. This spectrum was fitted using $20.5 \times 10^{15}$ at/cm$^2$ Ti$_2$O$_3$/55.2$ \times 10^{15}$ at/cm$^2$ Ti (solid blue line, model 1 in Figure 4.1c).

**Figure 4.1:** a) 95 keV H$^+$ MEIS spectrum for Ti film on the top of DLC substrate. b) Backscattered energy spectrum at 124° (vertical yellow line in (a)) fitted using model 1 (solid blue line); 2 (dashed red line) or 3 (dash-dotted orange line) shown in c). All thicknesses are listed in units of $10^{15}$ at/cm$^2$. 
**Table 4.1:** A summary of elementary targets grown by MBE. Composition in nm is calculated using bulk density values \( \rho_{\text{Si}} = 2.322 \text{ g/cm}^3 \), \( \rho_{\text{Ti}} = 4.520 \text{ g/cm}^3 \), \( \rho_{\text{SiO}_2} = 2.648 \text{ g/cm}^3 \), and \( \rho_{\text{Ti}_2\text{O}_3} = 4.49 \text{ g/cm}^3 \).

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (in ( 10^{15} ) at/cm(^2))</th>
<th>Composition (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/DLC</td>
<td>( \text{SiO}_2 (2.8)</td>
<td>\text{Si (55.5)}</td>
</tr>
<tr>
<td>Si/DLC, h×2</td>
<td>( \text{SiO}_2 (2.8)</td>
<td>\text{Si (128)}</td>
</tr>
<tr>
<td>Si/Os/Si</td>
<td>( \text{SiO}_2 (6)</td>
<td>\text{Si (43)}</td>
</tr>
<tr>
<td>Ti/DLC</td>
<td>( \text{Ti}_2\text{O}_3 (20.5)</td>
<td>\text{Ti (55.2)}</td>
</tr>
<tr>
<td>Ti/DLC, h×2</td>
<td>( \text{Ti}_2\text{O}_3 (18.0)</td>
<td>\text{Ti (125.5)}</td>
</tr>
</tbody>
</table>

For comparison, in Figure 4.1b we show two alternative fits for the Ti/DLC spectra. One with an oxide layer at the Ti/C interface instead of at the surface (dashed red line, model 2 in Figure 4.1c) - fits the Ti front edge very poorly, and another - with a slightly thicker oxide layer (dash-dotted orange line, model 3 in Figure 4.1c) - shows a systematic shift from experimental data at the Ti front edge (inset in Figure 4.1b). For the thicker oxide layer, the total Ti content was kept constant. Despite a 14% increase in the oxide thickness and a visible difference between the solid and dash-dotted line, the Ti stopping cross section was decreased by only ~3%, which is less than the claimed 4% experimental uncertainty (Section 3.2).

### 4.2 Stopping cross section calculations

Simulated energy spectra for targets from Table 4.1 for incident energy \( E_0 \) in the 55-170 keV range were differentiated to find the exact positions of the Ti(Si) and C(Os) edges. The energy loss was then calculated using an equation similar to Equation 3.2; e.g., for the Ti/DLC sample discussed above, one obtains the expression

\[
\Delta E_{\text{Ti/DLC}}^{\text{surf}} = E_{\text{C}}^{\text{Ti/DLC}} - E_{\text{C}}^{\text{surf}} = E_{\text{Ti/DLC}}^{\text{surf}} - \frac{K_{\text{C}}}{K_{\text{Ti}}} E_{\text{Ti}}^{\text{surf}},
\]  

(4.1)
where the first term is the position of the C edge in the spectrum of the Ti/DLC film and the second term is the position of the C edge for the uncovered DLC substrate at the same energy and the $K$-values are kinematic factors for C and Ti. We have ignored any adventitious carbon layer in our simulations since it will introduce an equal energy shift for all the elements in a MEIS spectrum, and will therefore not affect the result of Equation 4.1.

The Si and Ti stopping cross sections are calculated from the measured energy loss by an iterative procedure (Section 3.2 and Appendix A). The results are shown in Figure 4.2. For comparison, the most commonly used semi-empirical Si and Ti stopping cross sections from the program SRIM [1] and the database PSTAR [8] are also plotted. For a given incident energy $E_0$ of protons, two values of the stopping cross section are reported: $\varepsilon(E_0)$ and $\varepsilon(KE_0)$, where $K$ is the kinematic factor of the substrate. In the case of Ti, we have not attempted to measure the stopping cross section at 170 keV because of the low signal-to-noise ratio and, consequently, the largely increased experimental uncertainty. Multiple symbols for each energy correspond to the different scattering angles in a MEIS spectrum. In our previous work (Chapter 3), we have shown that there is no systematic trend in the behaviour of $\varepsilon$ as a function of scattering angle. It was suggested that the observed scattering of $\varepsilon$-values can be due to experimental uncertainty.

As one can see, our experimental data are in excellent agreement with each other and with the literature values from the NIST database PSTAR, whereas SRIM underestimates the stopping cross section around the peak position for both Si and Ti. An agreement between the measured Si and Ti stopping cross sections and PSTAR literature values thus confirms the validity of the iterative procedure for calculating stopping cross section from the energy loss measured by MEIS.

However, our findings still cannot explain why $\varepsilon_{STO}$ is overestimated since SRIM underestimates $\varepsilon_{Ti}$. The remaining possibilities are: i) Bragg’s rule is invalid (see the discussion of chemical effects in Chapter 1), ii) $\varepsilon_{Sr}$ is overestimated and iii) one cannot
use in solid SrTiO$_3$ the $\varepsilon_O$ values obtained for the gaseous target (see the discussion of physical effects in Chapter 1).

**Figure 4.2:** Si and Ti stopping cross section. Different symbols correspond to different scattering angles. Error bars for one single measurement are also indicated.

Next, we intended to verify Bragg's rule by measuring stopping cross sections for medium energy protons in TiSi$_2$ ultra-thin films. Measured $\varepsilon_{\text{TiSi}_2}$ can be directly compared with the sum of confirmed $\varepsilon_{\text{Ti}}$ and $\varepsilon_{\text{Si}}$ PSTAR values. However, all our attempts to grow smooth homogeneous 10 nm films of titanium silicide have been unsuccessful so far. We tried to grow TiSi$_2$ by depositing Ti films on DLC, Si (001) or Si (111) substrates at room temperature and annealing them at different temperatures. At low temperatures ($T < 650 \,^\circ\text{C}$), titanium oxide is formed. At high temperatures ($T > 850 \,^\circ\text{C}$), titanium silicide forms islands. In the intermediate temperature region ($650 \,^\circ\text{C} < T < 850 \,^\circ\text{C}$), titanium silicide
films have very rough surfaces with multiple cracks due to the lattice parameter mismatch between the film and Si substrate.

### 4.3 References


Chapter 5. Si wires: introduction

The first publication on the growth of silicon filamentary crystals dates back to the late 1950s [1]. Depending on the diameter $d$, filamentary crystals are commonly referred to as silicon whiskers ($d \gg 1 \mu m$), silicon wires ($d \sim 1 \mu m$) or, more recently, silicon nanowires ($d \leq 100 \text{ nm}$), however this distinction is often omitted and term 'silicon wire' is used generically. In the last decade, silicon-wire research experienced a remarkable increase when its potential in the areas of photonics and electronics was fully recognized (see Figure 5.1).

![Figure 5.1](image_url)

Figure 5.1: Plot of the number of Si "whisker", "wire" and "nanowire" publications as function of publication date. Source: ISI Web of Knowledge. Search date: August 7, 2013. Note the logarithmic scale.

Surprisingly, little has been added to the vapour-liquid-solid (VLS) growth model first proposed by Wagner and Ellis in 1964 [2] regarding the mechanism of silicon wire growth. Until today, the VLS growth model has been the central paradigm of semiconductor wire research. It has been applied in order to explain peculiarities of
growth, not only for silicon but also for a much broader range of wire materials, including Ge, III-V semiconductors (GaAs, GaP, InP, InAs), II-IV semiconductors (ZnO), etc. [3].

In this chapter, the VLS growth model and its alternatives will be briefly discussed in Sections 5.1 and 5.2. We will compare the theoretical predictions with key experimental observations and touch on the deficiencies of the VLS model. The chapter will conclude with a discussion of the published research on the lateral growth of Si wires in Section 5.3. For additional information on the different aspects of silicon wire growth and means to control it, the reader is referred to the classic text by Givargizov [3] and thorough reviews by Schmidt et al. [4, 5], Barth et al. [6] and Fan et al. [7].

5.1 Vapour-liquid-solid growth model

The VLS growth model was put forward by Wagner and Ellis [2] for silicon whiskers grown by disproportionation reaction of SiI$_2$ or by the hydrogen reduction of SiCl$_4$. The observation of a hemispherical globule at the tip of the whisker and a microprobe analysis of its composition, which showed a significant amount of the metals that had been added to the silicon source (gold, copper, silver, etc.) were the key facts which led to the concept. Analyzing phase diagrams of the metals and silicon, Wagner and Ellis concluded that the globule was a solution of silicon in the metal and that the globule was liquid at the typical crystallization temperature (850 - 1050 °C).

The process of Si growth with gold as a catalyst is illustrated in Figure 5.2. If a small particle of Au is placed on the Si (111) substrate and the substrate is heated to a temperature above the eutectic for a Si-Au mixture, T = 363 °C (point 1 in Figure 5.2a), then over time a gold-silicon alloy is formed corresponding to the gold-rich (point 2 in Figure 5.2a) or silicon-rich branch of the phase diagram (point 3 in Figure 5.2a). If a mixture of SiCl$_4$ and H$_2$, or any other Si precursor, is then introduced, almost no deposition proceeds on solid surfaces in the absence of gold up to 950 - 1000 °C [3]. However, the reduction reaction easily occurs at the surface of Si-Au droplet, owing to
the relatively high sticking coefficient of the vapour-phase species on liquid surfaces. The droplet becomes supersaturated with Si to a value critical for the growth of a whisker to start at the liquid-solid interface (point 3 in Figure 5.2a). The excess Si is deposited on the {111} planes and the liquid droplet rises from the substrate on the tip of the growing faceted crystal (Figure 5.2b). If thermodynamic equilibrium conditions are maintained, the liquid droplet and Si wire compositions correspond to points 3 and 4 in Figure 5.2a., respectively.

Thus, the main feature of the vapour-liquid-solid model is that a layer of liquid (in which the crystal material is soluble) is situated between the vapour and the growing crystal. The two introduced interfaces, namely vapour-liquid and liquid-solid, play an important role in the growth process.

The surface of the liquid has a large sticking coefficient and is therefore a preferred site for deposition. The seeded growth of silicon whiskers has been demonstrated experimentally in the early work by Wagner and Ellis [8]. These authors also determined the growth rates of Si on Pt-Si and Au-Si liquid alloys in comparison with those on crystalline Si substrates alone. They found the growth rate for Pt-Si and Au-Si alloy to be
about 60 and 20 times higher, respectively, than the growth rate of silicon film directly on the Si substrate at 900 °C. Bootsma and Gassen [9] compared the axial and radial rates for Si and Ge whisker growth with the growth rate of Si and Ge thin film over a range of temperatures. As Figure 5.3 shows, the radial and the substrate rates (both related to the vapour-solid interface) are essentially the same, whereas the axial rates by the VLS process (vapour-liquid and liquid-solid interfaces) are higher by several orders of magnitude for both Si and Ge.

![Arrhenius plots of the growth rate, \( g \), of Si and Ge as a function of substrate temperature \( T_s \) with Au as a catalyst.](image)

**Figure 5.3:** Arrhenius plots of the growth rate, \( g \), of Si and Ge as a function of substrate temperature \( T_s \) with Au as a catalyst. \( \dot{l}_w \) - average whiskers' length (axial) growth rate, \( \dot{d}_w \) whiskers – average whisker's diameter (radial) growth rate, \( \dot{w} \) substrate – average substrate's thickness growth rate. See ref. [9].

One of the underlying assumptions of the VLS model is that the growth takes place under local thermodynamic equilibrium conditions close to the liquid-solid interface. An existence of local thermodynamic equilibrium implies that the growth of a silicon wire is determined by minimization of the total Gibbs free energy. Under fixed total pressure and temperature, the change in Gibbs free energy, \( \delta G \), is given as:
\[
\delta G = \delta N (\Delta \mu_\infty) + \sum_i \delta A_i \gamma_i
\]

(5.1)

where the first term is the variation of the free energy of the system due to the transfer of \(\delta N\) atoms from the vapour phase to the crystal, \(\Delta \mu_\infty\) denotes the supersaturation over a catalyst surface with infinite radius of curvature, and the second term is the increment of the crystal's free energy due to its increasing surface area \(\delta A_i\), and \(\gamma_i\) denotes the specific free energy of the surface \(i\) [3].

In Table 5.1, the low-index surface energy order for silicon is listed. Surface energy relationships combined with the minimization of surface-to-volume ratio can alone predict Si wire shapes and orientations. Minimization of the gold droplet/silicon interface energy dictates that sufficiently large silicon wires preferentially grow along the \(<111>\) silicon crystallographic direction with a hexagonal cross section formed by \{110\} and \{112\} facets [2, 8, 14]. Conversely, a different trend is observed for smaller wires. The lateral surface energy contribution dominates over the gold droplet/silicon interface energy for silicon nanowires and wires of a relatively small diameter. As a result, silicon (nano)wires are oriented along the \(<110>\) crystallographic direction [15-18], with a hexagonal cross section formed by four \{111\} and two \{100\} facets [17, 19]. Interestingly, there is experimental evidence [17] that the liquid-solid interface remains \(<111>\) oriented and is V-shaped to accommodate for the Si nanowire \(<110>\) growth direction.

While growth rates, shapes and orientations of Si wires are consistent with predictions of the VLS growth model, the typical range of temperatures in which Si wires grow is not. Silicon wires usually grow only at temperatures that are significantly higher than the Si-Au eutectic temperature [5], in spite of the fact that the eutectic can be lower for gold droplets with nanometre sizes [20]. Moreover, the necessity of the liquid droplet to ensure (nano)wire growth has been widely debated recently [21-25].
Table 5.1: Ordering of low-index surface energies for silicon.

<table>
<thead>
<tr>
<th>Relative order</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ(111)&lt;γ(100)&lt;γ(311)&lt;γ(110)</td>
<td>Equilibrium shape of Si voids; clean Si surface</td>
<td>[10]</td>
</tr>
<tr>
<td>γ(111)&lt;γ(110)&lt;γ(100)</td>
<td>Faceted cavities in He-implanted Si</td>
<td>[11]</td>
</tr>
<tr>
<td>γ(111)&lt;γ(110)&lt;γ(100)</td>
<td>Density-functional tight-binding simulations; H-terminated Si nanowires</td>
<td>[12]</td>
</tr>
<tr>
<td>γ(111)&lt;γ(110)&lt;γ(100)</td>
<td>Plane wave pseudopotential calculations; unrelaxed clean Si surface; relaxed/reconstructed clean Si surface; H-covered Si surface;</td>
<td>[13]</td>
</tr>
</tbody>
</table>

5.2 Dislocation-diffusion and diffusion-droplet models

Wagner and Ellis [2, 8] regarded the VLS growth model as an alternative to the dislocation-diffusion model first proposed by Sears [26]. The dislocation-diffusion model postulated that each whisker contained an axial screw dislocation which created a permanent growth step on the tip, in accordance with the well known suggestion of Frank of the importance of screw dislocations for crystal growth [27]. The axial growth proceeded mainly due to atoms which were adsorbed by the side faces of the whisker and/or by substrate, and then diffused to the tip of a whisker containing a screw dislocation.

Even though no experimental evidence was found of the screw dislocation necessarily present at the tip of the growing wire [3, 8], the diffusion part of the Sears' model is still valid. For example, if a Si substrate covered with Au droplets is exposed to a uniform flux of Si atoms in a MBE UHV chamber [28-31] and the atoms are allowed to freely diffuse on the surface, the preferential incorporation of the silicon atoms into the droplets causes Si wires to form. Thus, a 'diffusion-droplet' model instead of 'dislocation-diffusion' model should be considered, where the liquid droplet instead of a screw dislocation serves as an active sink on the wire tip [3].
The diffusion assisted growth of whiskers was investigated theoretically in the 1960s by Dittmar and Neumann, Blakely and Jackson, Ruth and Hirth, and others [32-35]. Following Dittmar and Neumann [32], similar equations were written and solved for different approximations and different boundary conditions, as summarized below.

The fundamental differential equation describing the areal density of adatoms on the substrate surface, \( n_s \) [at/cm\(^2\)], in the 'diffusion-droplet' model can be written in the general form [36]

\[
\frac{\partial n_s}{\partial t} = D_s \nabla^2 n_s - \frac{n_s}{\tau_s} + R_s. \tag{5.2}
\]

Here \( R_s \) [cm\(^2\)s\(^{-1}\)] is the impingement flux from the vapour phase; \( \tau_s = \frac{1}{\omega} \) is the mean time of stay of an adsorbed atom before re-evaporation, where the desorption frequency is \( \omega = \nu \exp(-\frac{\Delta H_{des}}{kT}) \), where \( \nu \) is the surface vibrational frequency and \( \Delta H_{des} \) is the free energy of desorption of an adatom. In other words, Equation 5.2 is a diffusion equation complemented by terms that take into account adatom desorption and the atom deposition from the vapour.

A coupled equation, similar to Equation 5.2, can be written for the areal density of adatoms on the sides of the wire, \( n_w \). The length growth rate of the wire, \( \frac{dL}{dt} \), can be expressed as the adatom flux from the wire sides into the metal particle at the tip multiplied by the circumference, divided by the cross-sectional area of the wire plus the contribution from direct impingement on the metal particle:

\[
\frac{dL}{dt} = -D_w \frac{d}{dz} n_w(L) \times \frac{2}{r_w} \frac{\Omega}{r_w} + 2 \Omega R_{top}, \tag{5.3}
\]
where \( D_w \) is the diffusivity of adatoms on the side of the wire, \( \Omega \) is the atomic (or molecular) volume of the growth species, \( r_w \) is the radius of the wire, \( z \) is the vertical coordinate along the wire growth axis and \( R_{\text{top}} \) is the deposition rate on the wire top.

The 'diffusion-droplet' formalism [36] predicts that at the later stages of growth, i.e., when \( L \gg \lambda_w \), where \( \lambda_w \) is the surface diffusion length, the length growth rate is inversely proportional to wire radius, \( \frac{dL}{dt} \propto r_w^{-1} \), in excellent agreement with experimental observations [28, 36].

Note that the VLS model predicts that wires with a larger radius should grow faster than those with a smaller radius due to the increase of supersaturation as a function of wire radius, the so called Gibbs-Thompson effect [3]:

\[
\frac{\Delta \mu}{kT} = \frac{\Delta \mu_0}{kT} - \frac{2\Omega \gamma_{ss}}{kT} \frac{1}{r_w} \tag{5.4}
\]

where \( \Delta \mu \) is the effective difference between the chemical potentials of Si in the nutrient (vapour or liquid) phase and in the wire, \( \Delta \mu_0 \) is the same difference at a plane interface (\( r_w \rightarrow \infty \)) and \( \gamma_{ss} \) is the specific free energy of the wire surface. However, Schubert et al. [28] have demonstrated that Si wires grown by molecular beam epitaxy at 525 °C exhibit an opposite trend (Figure 5.4). It has been shown later [36], that the Gibbs-Thompson effect can be neglected in this case, since it operates at much lower supersaturation, and a diffusion model should be used instead. When the substrate temperature is increased to 700 °C and accordingly Si wire growth is not diffusion limited anymore, the \( \frac{dL}{dt} \propto r_w \) dependence is restored [30].
Figure 5.4: Correlation between the length, $l$, and diameter, $d$, of Si whiskers. The growth was performed in MBE UHV chamber at a uniform Si flux 0.5 Å/s at 525 °C for 240 min. See ref. [28].

5.3 Horizontal growth of Si wires (ridges)

As was discussed in Section 5.1, the solid-liquid interface for a silicon wire is the close-packed plane (111). So for the commercially available Si (100), Si (110) and Si (111) substrates, silicon wires will generally grow in a direction that is either vertical or angled from the substrate (see Figure 5.5). The vertical-type geometry is not ideal for practical applications. It complicates device fabrication and requires advanced processing techniques [16, 37]. There are generally two approaches to in-plane silicon wire growth: a) grow wires from etched facets (such as sidewalls and V-grooves) on the substrate surface and b) grow wires in the plane of the substrate surface under unconventional growth conditions.

The first approach, growth from side walls and V-grooves, was initially demonstrated for GaAs [38] wires and has been widely used for Si later [39-42]. On the Si (110) substrate, deep trenches with (111)-oriented sidewalls can be easily formed with an anisotropic chemical etch. Au (nano)particles can then be deposited and (111)-oriented Si (nano)wires can nucleate on one (111) sidewall and bridge over to the adjacent sidewall
This method was successfully used to grow silicon photovoltaic elements with tunable power output and nanowire-based AND and OR diode logic gates [39]. However, a conventional Au-deposition step with subsequent annealing to form gold droplets allows little control over the positioning of Si wires on the (111) sidewall. Thus, an additional improvement to the method will inevitably involve an extensive use of expensive lithography techniques.

Similarly, Quitoriano et al. [43, 44] etched commercial silicon-on-insulator Si (001) substrates in order to partially expose an underlying buried oxide layer with the top Si ledges forming an overhanging trench. Si nanowires growing toward the buried oxide layer were forced to grow in a &lt;110&gt; crystallographic direction when they came in contact with the oxide. The liquid-solid interface remained &lt;111&gt; -oriented for the whole time until the adjacent ledge was reached and an isolated FET was formed. Quitoriano et al. further extended this guiding technique by patterning small oxide windows on a Si

**Figure 5.5:** Schematic illustration of &lt;111&gt;-oriented Si wires grown epitaxially on different Si substrates. See ref. [51].
(001) substrate with Au and forcing Si nanowires to grow vertically on the substrate in an energetically unfavourable <100> direction [44].

Figure 5.6: a) Schematics illustrating the direct growth of a p-type Si nanowire resistor (top) and a p-i-n Si nanowire diode (bottom). (b) SEM images of Si nanowires bridging two electrodes of different gaps. See ref. [39].

An example of using the second approach is an in-plane solid-liquid-solid growth of Si nanowires demonstrated by Yu et al. [45, 46]. They formed liquid indium nanoparticles embedded into an amorphous silicon layer and annealed the sample in a gas-free environment, which caused Si wires to grow. In a solid-liquid-solid growth mechanism, amorphous Si on one side of the liquid In droplet is dissolved. It is diffused through the liquid and is transformed into the crystalline Si nanowire on the other side of the liquid droplet. The In droplet is propelled forward by the growing wire. Unlike VLS growth, solid-liquid-solid growth usually results in irregularly shaped nanowires, which limits possible practical applications of the method.

Recently, Rathi et al. [47] have demonstrated epitaxial single-crystal Si nanowires grown laterally along <110> crystallographic directions on Si (111) substrates that have been miscut toward [112]. Au droplets were formed by a conventional annealing procedure and disilane (Si₂H₆) was used as a precursor for nanowire growth. The horizontal nanowires grow together with the conventional vertical ones (Figure 5.7). The ratio of lateral-to-vertical nanowires increases as the miscut angle increases and as disilane pressure and substrate temperature decrease. The authors admit that experimental
observations cannot conclusively identify the mechanism leading to lateral nanowire growth but suggest that it should involve pinning of the gold droplets at the hillocks on the miscut substrate surface.

Spontaneous lateral (nano)wire growth similar to that described in [48] which follows the VLS mechanism has been also reported for III-V [48-51] and II-VI [51-53] semiconductor materials. Theoretical explanations usually attribute the observed behaviour to the stability of the vapour-liquid-solid trijunction [54-57]. When the stability criteria are not met, as discussed in the following, there are two possible outcomes: either the wire radius vanishes after a finite period of growth or the droplet becomes unpinned during growth. Due to the existence of alternative equilibrium droplet configurations, the latter outcome can result in growth of 'crawling' (nano)wires observed experimentally.

Figure 5.7: SEM image acquired 70° away from Si [111] toward the Si [112] direction showing both lateral and vertical nanowires. See ref. [47].

A liquid droplet stays in contact with the substrate at the initial stage of growth for vertical wires and during the entire growth for lateral wires. If one assumes that any compositional and structural changes in the droplet are rapid on the time scale of wire growth (quasistatic approximation), then a droplet maintains mechanical equilibrium with a rigid solid substrate and both tangential and normal components of the net force with respect to the solid-liquid interface are equal to zero. The situation of a droplet resting on a flat solid substrate (Figure 5.8a) is then characterized by the Young contact angle $\theta_Y$ – the angle subtended by the liquid at the line where it meets the solid [54]:
\[
\cos \theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}.
\]  

Equation 5.5

In Equation 5.5, the Young angle \( \theta_Y \) is given in terms of three surface energies: \( \gamma_{sv} \) (solid-vapour), \( \gamma_{sl} \) (solid-liquid) and \( \gamma_{lv} \) (liquid-vapour). Note that surface tension (force/unit length) and surface energy (free energy/unit area) are interchangeable definitions with the same units \([\text{J/m}^2 = \text{N/m}]\) and even though they are both scalars they are often represented by their respective forces as in Figure 5.8a.

**Figure 5.8:** Balance of forces corresponding to solid-vapour, solid-liquid and liquid-vapour surface energies for a) a droplet on the flat surface and b) a droplet on the top of a Si wire.

In a more general case, e.g. development of a droplet-wire system (Figure 5.8b), an additional inclination angle \( \phi \) of the wire flank is introduced. At thermodynamic equilibrium, when the wire growth velocity is small compared to the velocity with which the droplet reacts to the changes of the boundary conditions, an equation similar to Equation 5.5 can be derived. For a contact line pinned at a location where the solid subtends an angle of \( \phi \), the range of contact angles which liquid may subtend is [54]:

\[
\theta_Y \leq \phi \leq (\pi - \phi) + \theta_Y
\]  

Equation 5.6

Equation 5.6 is derived from the requirement that a virtual displacement \( \delta x \geq 0 \) along either part of the solid surfaces meeting at the corner should do positive work. If \( \phi = \pi \),
the solid is continuous at the point of contact (there is no corner) and the inequalities (5.6) yield \( \theta = \theta_Y \). With constraint (5.6), a range of droplet and (nano)wire geometries exist, consistent with mechanical equilibrium in the sense that virtual displacements of the contact lines in these geometries increase the energy of the system.

Roper et al. [54] explored the consequences of near-equilibrium steady wire growth. This occurs through the pathway which minimizes the Gibbs free energy. Maximum decrease in Gibbs free energy occurs when the work due to the surface energy is minimized and the steady growth corresponds to the condition \( \frac{d r_w}{d z} \to 0 \), where \( r_w \) and \( z \) are the radius and the height of the growing wire, respectively. This occurs when

\[
-\cos \theta_f = \frac{Y_{sl}}{Y_{lv}} \leq 1 ,
\]  

where \( \theta_f \) is the limiting value of \( \theta \) obtained during steady growth. For cases where \( \frac{Y_{sv}}{Y_{lv}} > 1 \), steady growth is not established: the radius of the wire vanishes after a finite period of growth. Combined with Equation 5.6, only angles in the range

\[
\theta_Y \leq \theta_f \leq \theta_Y + \frac{\pi}{2}
\]  

are allowable if the droplet is to remain pinned atop the wire. Note: Equation 5.7 will be modified in the presence of line tension at the trijunction [58], which applies to very small catalyst droplets (\( r < 20 \) nm).

Inequalities in Equations 5.7 and 5.8 predict multiple outcomes during VLS growth which depend on the ratios of surface energies \( \frac{Y_{sl}}{Y_{lv}} \) and \( \frac{Y_{sv}}{Y_{lv}} \), as shown in Figure 5.9. In the shaded triangular regions, the liquid will leave the solid substrate either completely wet (upper-left) or completely dry (lower-right). VLS growth is only feasible in the unshaded regions: a) red – straight growth, pinned trijunction, b) blue – steady growth not
possible, unpinned trijunction and c) white – radius vanishes, pinned trijunction. The blue region is the one that can possibly lead to the growth of lateral (nano)wires. It should be noted that Roper et al. have assumed isotropic surface energies in their derivations. In general, faceted (nano)wires are observed in the experiment (see Section 5.1), with the solid-vapour and liquid-solid interfaces forming different crystallographic planes, which leads to richer variety of configuration of liquid droplet and solid wire, as shown by Schwarz and Tersoff [56, 57]. Nevertheless, the main conclusion remains valid for the faceted wires: namely an existence of a range of parameters $\frac{\gamma_{sl}}{\gamma_{lv}}$ and $\frac{\gamma_{sv}}{\gamma_{lv}}$, which lead to unpinning of the trijunction and resultant lateral growth.

![Figure 5.9](image)

**Figure 5.9:** Multiple outcomes that can be realized during VLS growth, depending on the location in the surface-energy space. See ref. [54].

We would like to emphasize that the theoretical approaches described above, while illustrating real effects, e.g., kinking of a wire or growth of 'crawling' wires, do not represent a unique determination of the detailed mechanism in specific experiments. The main reason is that little is known about the structure and energetics of semiconductor facet edges, or the microscopic processes by which new facets are introduced during wire
growth. Rather, they demonstrate how the observed complex behaviour can grow naturally out of the interplay of a few simple elements, such as solid-liquid, liquid-vapour and solid-vapour surface energies and the energy required to introduce a new facet.

5.4 Scope of Part II of the thesis

In contrast to the well-studied growth of vertical Si wires by VLS (Section 5.1) or diffusion-droplet mechanism (Section 5.2), the spontaneous growth of lateral Si wires described in Section 5.3 is poorly understood. In the following chapters, I will present experimental evidence of the importance of surface diffusion for lateral wire growth in MBE (Chapter 6) and apply the diffusion-droplet model to explain some aspects of lateral growth of Si wires in MBE (Chapter 7).

Controlled lateral wire growth has a lot of potential applications in electronics and photonics. In electronics, guided linear growth of lateral Si wires from placed gold seeds can be used to produce interconnections between the two metal electrodes deposited on the surface similar to growth of silicon logic gates reported by Kim et al [39]. In photonics, Si wire networks can be used for improving efficiency in solar cells since they lead to broadband antireflection as well as enhanced light trapping efficiency [59].

5.5 References


Chapter 6. Horizontal reticular growth of silicon wires: random walk in two dimensions*

In this chapter, we report an observation of arrays of self-assembled Si ridges grown by the vapour-liquid-solid mechanism in a molecular beam epitaxy chamber. The growth experiments are conducted on Si (100) substrates using Au droplets as seeds for growth of Si ridges. We show that at a sufficiently low flux of Si atoms, gold droplets are propelled forward along two orthogonal <011> directions by the growing silicon ridges. The reticular growth closely resembles a self-avoiding random walk in two dimensions, as we confirmed by Monte Carlo simulation. The result is the formation of a network of Si ridges with a topological complexity and connectivity that depends on the growth time as well as the starting diameter of the Au droplets. Based on our experimental results, we elaborate on the role of diffusion in the MBE growth of Si ridges.

6.1 Experimental methods

Si ridge growth experiments were carried out in an ultrahigh vacuum (UHV) MBE chamber (Kurt Lesker) containing two sources with Si (Alfa Aesar, 99.9999% purity) and Au (Canadian Mint, 99.999% purity), that are evaporated from water-cooled graphite crucibles using electron beam heating. The deposition rate was controlled using quartz crystal monitors that were calibrated by means of independent Rutherford backscattering measurements. The substrates were heated by an electron beam heater (VG Ltd., Hastings) and their temperature was controlled by K-type thermocouples (OMEGA). Pieces of single-side-polished n-Si(100) wafers (Silicon Valley Microelectronics) of 8×10 mm size were used as substrates for our depositions.

Prior to loading the samples in the UHV MBE chamber, the native silicon oxide layer on the substrate was removed by etching for 60 s in an HF buffer solution (Transene Company Inc.). The substrate was subsequently mounted on a Mo sample holder using indium (Sigma Aldrich, 99.99% purity) as an adhesive and was transferred to the UHV MBE chamber via a load-locking chamber. Any silicon oxide layer that may have been formed on the substrates during the transfer is then removed by outgassing them at 600 °C for 15 min and subsequently heating the substrate at 850 °C for 10 min at 4×10⁻⁹ Torr base pressure prior to the deposition process. After the substrate had cooled to room temperature, thin gold films of 1 or 2 nm thickness were deposited at 4×10¹⁵ atoms×cm⁻²×min⁻¹ growth rate on the Si (100) wafers. Substrates covered with 1 or 2 nm Au film were annealed at 650 °C for 30 min in order to form gold droplets of 90 or 60 nm diameter, respectively. These droplets served as a catalyst for the growth of the ridges. The reported values correspond to the maximum of gold droplet size distribution. Si was deposited at a rate of 5×10¹⁴ atoms×cm⁻²×min⁻¹ 30 to 360 min at 650 °C and 1−2×10⁻⁸ Torr pressure.

The Si ridges were analyzed by using different scanning electron microscopes: a LEO (Zeiss) 1530 SEM and a LEO (Zeiss) 1540 XB FIB/SEM. The Monte Carlo simulation program for modelling the growth of Si ridges was written in Python (version 2.6.5) and is described in detail in Supplementary Information (Appendix D).

6.2 Results and discussion

In our MBE system, we carried out a set of growth experiments by changing two relevant parameters: the time of growth (30 to 360 min) and the average thickness of Au thin film (1 and 2 nm). Upon anneal, 1 nm Au films formed droplets of 90 nm diameter with an average separation Δr_avg = 409±96 nm and areal density 2.336×10⁶ nm⁻². In comparison, 2 nm Au films formed droplets of 60 nm diameter with an average separation Δr_avg = 262±86 nm and areal density 7.190×10⁶ nm⁻². These droplet-covered substrates were exposed to a uniform flux of silicon atoms for various length of time.
If the system is limited by transport phenomena, then adsorption of a silicon atom from the vapour phase onto a Si (100) wafer may result in two competing outcomes. The first possibility is the epitaxial silicon layers grow by island coalescence [1] which takes place if the surface diffusion length of silicon atoms, $L_D$, is much smaller than the average distance between the gold droplets, $L_D < \Delta r_{avg}$. The second outcome is the dissolution of the silicon adatoms into a gold droplet which takes place if $L_D \sim \Delta r_{avg}$. At the specific temperature of 650 °C and a low Si flux of $5 \times 10^{14}$ atoms×cm$^{-2}$ min$^{-1}$ optimized in the present work, the diffusion length of the adatoms exceeds $L_D = 200 \text{ nm}$ [2,3]. Under these conditions, the growth proceeds by preferential incorporation of silicon into gold droplets for both 1 and 2 nm Au films because $L_D$ and $\Delta r_{avg}$ have the same order of magnitude. In accordance with the VLS growth model, liquid droplets then capture material from the vapour and deposit it onto the solid in the form of ridges (Figure 6.1), with longer silicon deposition time resulting in longer ridges.
Figure 6.1: SEM planar views of Si ridges obtained on Si (100) substrates at $T = 650 \, ^\circ\text{C}$ using 90 nm Au droplets (a-c) and 60 nm Au droplets (d). The Si deposition times are as indicated on the figures.

The ridges have a width that is determined by the diameter of the Au droplets. If the size and shape of the droplets do not change during the growth process, one would expect that the final distribution of the width of the silicon ridges to reflect the initial distribution of the gold particle diameters. In addition, the final areal density of the gold droplets should be equal to the initial areal density of the gold droplets. Figure 6.2a and 6.2b show that this is not the case. These figures report the ridge width distribution after 30 min of Si deposition and average gold droplet areal density as a function of time, respectively. Even after 30 min of growth, when the ridges are less than 1 μm long and not colliding with each other, the diameters of silicon ridges are much larger than the initial Au droplet diameters. This suggests that significant Ostwald ripening [4] of the droplets - a process in which larger gold droplets ripen at the expense of the smaller ones - has taken place.
This conclusion is further supported by observing that the gold areal density is inversely proportional to the growth time (Figure 6.2b).

Figure 6.2: Ostwald ripening of 90 nm Au droplets. a) Changes in the gold droplet diameter after 30 min of silicon deposition. The initial single-peak size distribution of the gold droplets (maximum at 90 nm) becomes distinctly bimodal. b) Decrease in the areal density of gold droplets as a function of growth time.

We argue that Ostwald ripening is responsible for roughening of the Si film between the Si ridges in the case of 60 nm Au droplets (Figure 6.1d). Smaller relative size and the higher areal density of the droplets formed upon anneal of 2 nm Au film lead to the formation of multiple small silicon ridges in between the larger ones. During the growth, small gold droplets at the tip of those small ridges evaporate as a result of Ostwald ripening, leaving behind small silicon islands. Growth and coarsening of these islands causes a rough Si film to grow on the substrate surface.

For the CVD growth by the VLS mechanism, it is well known that wires with larger diameter Au droplet at the tip should grow faster than those with smaller diameter droplet due to a Gibbs-Thompson effect [5]. In contrast, we observe in our MBE experiments the opposite trend: thinner ridges grow faster than thicker ones as shown in Figure 6.3. Similar results were obtained for the MBE growth of vertical Si wires on Si (111) substrates [6] and explained theoretically by incorporating surface diffusion of silicon into VLS growth model [7]. Additional experimental evidence of the role of diffusion in
the MBE growth of Si ridges is discussed further below. Note: broad length distribution of silicon ridges might be caused by complex growth dynamics. Multiple turns and collisions between the ridges can result in redistribution of Au at the tip of the growing ridge which in turn will cause changes in its growth rate.

Our observations indicate that low silicon flux rate and Si (100) substrate morphology are crucial factors in the growth of silicon ridges. First, increasing the silicon flux to $1.3 \times 10^{16}$ atoms$\times$cm$^{-2}$ min$^{-1}$ leads to Si layer growth by island coalescence as shown in Figure 6.4. Under these conditions, the areal density of silicon adatoms on the surface is high enough to allow nucleation of multiple stable silicon islands in between the Au droplets. Growth and coarsening of these islands causes rough Si film to grow. Second, using Si (111) substrates in a similar MBE deposition system [6,8,9] resulted in the growth of vertically aligned silicon wires.

We attribute this behaviour to the impact of surface energy of the ridge's facets and their growth rate on the stability of vapour-liquid-solid trijunction of the growing wire, as it has been previously considered in 2D continuum model [10,11]. The model captures many experimentally observed (nano)wire morphologies, including kinking from one direction to another for the vertical wires or crawling along the surface.
Figure 6.3: Correlation between the length $L$ and width $d$ of Si ridges. In this specific case, the growth experiment was performed at temperature $T = 650 \, ^\circ\text{C}$ and flux $F = 5 \times 10^{14} \, \text{atoms}\times\text{cm}^{-2}\times\text{min}^{-1}$ for 1 h using 90 nm Au droplets. The solid line is the least square fit to the function $Cd^{-1}$, where $C$ is a constant, predicted by 'diffusion-droplet' model [7].

Figure 6.4: SEM micrograph of a diffusion limited growth of Si ridges using 60 nm Au droplets. The growth temperature $T = 650 \, ^\circ\text{C}$ and flux $F = 1.3 \times 10^{16} \, \text{atoms}\times\text{cm}^{-2}\times\text{min}^{-1}$. 
In this 2D continuum model, lateral growth is initiated when the liquid droplet rolls off the tapered (nano)wire base due to failed edge formation at the transition from the tapering pedestal to a uniform wire [11]. Difficulty in introducing new facets can be affected by absorbed gases, growth temperature, impurities, and so forth. We speculate that this failure of edge formation may be related to the observed faceting of ridges sidewalls (see Supplementary Information for details). In addition, simulations in 2D continuum model suggest that the growth rate can strongly affect the occurrence of kinking and crawling [11].

As it was mentioned before, the ridge growth rate is very slow, about 900 nm/h for the longest ridges at silicon atom flux $F = 5 \times 10^{14}$ atoms cm$^{-2}$ min$^{-1}$. We argue that this slow growth rate ensures epitaxial growth of Si ridges on Si (100) substrate. The ridges are aligned with the Si $<011>$ crystallographic direction with occasional turns at 90° primarily caused by a collision with another ridge at the later stages of growth. In Figure 6.5a, we show a single Si ridge with a schematically drawn orientation for ridge surfaces. The $<011>$ axes have been assigned based on the known crystallographic orientation of the original Si substrate with respect to the ridge growth directions (see Supplementary Information). The Au liquid-solid interface is $<111>$-oriented as follows from the analysis of a cross-sectional SEM image of an individual silicon ridge along the direction of growth (Figure 6.5b). This observation agrees with the predictions of the VLS model for large diameter silicon ridges. On the other hand, the silicon ridges maintain a semicircular cross section for the first 0.5-1 μm from the gold droplets (Figure 6.5c and 6.5d). This disagrees with the VLS model that predicts a faceted shape of the wire cross section dominated by $\{110\}$ or $\{112\}$ facets. In our case, ridges assume faceted cross sections only at relatively large distances, $r$, from the droplets, $r > L_D$. This behaviour underlines the critical role of surface diffusion in our growth process. If the length of the ridge is smaller than the surface diffusion length of Si adatoms on the Si (100) surface, the ridge maintains a semicircular cross section through its entire length (Figure 6.5d).
Figure 6.5: Individual silicon ridge shape and orientation. a) SEM micrograph of Si ridge facets. b) High resolution SEM image of the Si ridge cross-section along the growth direction. c) SEM image of the Si ridge after 4 h silicon deposition. Arrows indicate the following: 1 – surface diffusion of Si adatoms on the Si (100) substrate, 2 – the region of the silicon ridge where Si surface diffusion dominates, 3 – the region of the silicon ridge where the bulk diffusion dominates. d) SEM planar view of a Si ridge after 30 min silicon deposition.

In order to further elucidate the mechanism responsible for reticular growth of silicon ridges, we performed Monte Carlo simulations of ridge length evolution as a function of silicon deposition time (see Supporting Information for the details of the code). We have modelled the behaviour of individual ridges according to the rules of a self-avoiding random walk in two dimensions [12]. The individual walker is randomly placed on a 2D square lattice and allowed to go in one of the two orthogonal directions. Once chosen, the direction of the walk and step size are kept fixed until the walker intercepts another walk path. In that case, there is a chance for the walker to turn left or right from the direction it
was following or to stop. The probabilities for each particular outcome of the collision are determined from counting statistics after 4 h of silicon deposition. The individual steps in the simulation correspond to 10 min of silicon deposition. The important parameters, such as areal density of the walkers and average distance between the walkers or average step size, were taken from the experiment after 0 min or 30 min of silicon deposition, respectively. We have also introduced a decaying termination rate in order to simulate the effects of Ostwald ripening: at each step the random walker has a chance to stop, which is inversely proportional to the total walk length.

Figure 6.6 shows schematically four walkers following the rules of a self-avoiding random walk in two dimensions after the first (Figure 6.6a) and the second step (Figure 6.6b). The random walk step length in this example is 2 squares per step for walker A, 2 squares for walker B, 1 square for walker C and 4 squares for walker D, which corresponds to an average value of 2 squares per step. The randomly chosen initial directions of the walk are as follows: walker A – to the right, walker B – to the left, walker C, D – up. Since at the second step, the paths of walkers A and D would intercept the paths of walkers D and B, respectively, the following outcomes of the collision are randomly chosen: walker A – termination, walker D – turn right in order to avoid the collision. Figure 6.6c compares experimental and Monte Carlo simulation results for Si ridge length distribution after 4 h of Si deposition. The self-avoiding random walk combined with termination of the ridges due to Ostwald ripening describes well the experimental distribution of silicon ridge lengths. Collisions between the ridges with termination as a result of the collision cannot alone contribute to the peak at small ridge lengths. Thus gold loss plays an important role in the ridge growth mechanism. This issue should be addressed as a means to support the growth of longer ridges. Note: frequent drops in simulated probability values for longer ridges are due to fixed discrete size of random walk steps. Decreasing the size of the step, which is equivalent to increasing the time resolution, will make the simulated results smoother, but at the same time will increase the computational cost.

In summary, the epitaxial growth of silicon ridges by MBE was observed on Si (100) substrates. It is shown that for sufficiently long silicon deposition times, the ridges form a
two-dimensional network on the substrate surface that can be successfully simulated by a self-avoiding random walk in two dimensions if the effects of Ostwald ripening are taken into account. Due to peculiarity of MBE growth, our silicon ridges maintain semi-spherical cross-section in the vicinity of the gold droplets – a manifestation of the surface diffusion of silicon atoms.

**Figure 6.6:** A Monte Carlo simulation of Si ridge growth. Schematics illustrating the rules for Monte Carlo simulations: a) after the first step and b) after the second step. c) The Si ridge length distribution after 4 h of silicon growth (90 nm Au droplets): experimental and Monte Carlo simulation results. For the simulation, the result without a rule that postulates a decay in walkers’ areal density, inversely proportional to the walk length, is shown for comparison.
6.3 References


Chapter 7.  Thermodynamic vs. kinetic control of the lateral Si wire growth*

Reproducible lateral Si wire growth can be realized on the Si (100) surface, as was shown in Chapter 6. In this chapter, we present experimental evidence showing the unique role that carbon plays in initiating lateral growth of Si wires on a Si (100) substrate. Once initiated in the presence of ~5 ML of C, lateral growth can be achieved in the range of temperatures, \( T = 450 \div 650 \, ^\circ\text{C} \), and further controlled by the interplay of the flux of incoming Si atoms with the size and areal density of Au droplets.

7.1 Experimental methods

Si wire growth was carried out in an ultrahigh vacuum MBE chamber described in detail in Section 6.1. A n-Si(100) wafer was covered with photoresist (Shipley 1827) to prevent small debris from spreading in the clean room environment and cut into 8×10 mm pieces. After removing the photoresist with acetone and isopropanol, these pieces were used as substrates for MBE depositions. Si substrates cut without using photoresist were also prepared as control samples.

Any SiO\(_2\) layer on Si substrates was removed by etching in HF buffer solution prior to loading into the UHV MBE chamber and by subsequent heating of the substrates in UHV to 850 °C for 10 min as described in detail in Section 6.1. Next, a 1 nm thick gold film was deposited at room temperature at a growth rate of \( 4 \times 10^{13} \, \text{atoms} \times \text{cm}^{-2} \times \text{min}^{-1} \) followed by annealing at 600 °C for 30 min in order to form catalytic gold droplets of 90 nm diameter. The reported size of gold droplets correspond to the maximum of the Weibull distribution. In the next step, Si was deposited at a rate of \( 2.3 \times 10^{14} \) or \( 5 \times 10^{14} \, \text{atoms} \times \text{cm}^{-2} \times \text{min}^{-1} \) for 15 to 360 min at 450, 550 and 650 °C and \( \sim 1 \times 10^{-8} \, \text{Torr} \) pressure.

* The content of this chapter has been submitted to *Applied Physics Letters*
The samples were analyzed by scanning electron microscopy (LEO (Zeiss) 1530 SEM and LEO (Zeiss) 1540 XB FIB/SEM, NanoFab UWO) and medium energy ion scattering (95 keV $H^+$ beam, Tandetron Lab, UWO). The length of the wires were measured manually in ImageJ software [1].

### 7.2 Results and discussion

Typical SEM images of Si wires after 30 min and 240 min Si deposition are presented in Figure 7.1. Here, the growth temperature was 650 °C and silicon deposition rate was $5 \times 10^{14}$ atoms cm$^{-2}$ min$^{-1}$. The lateral wire growth is only observed for silicon substrates previously covered with photoresist. On the control Si substrate (without photoresist), Si wires grow only around carbon-based contamination particles (Figure 7.2a). After the removal of photoresist and subsequent thermal treatment, the Si (100) surface remains covered with carbon, as confirmed by ex-situ medium energy ion scattering and energy dispersive X-ray analysis carried with the SEM microscope. MEIS shows that ~ 5 ML of C (1 ML $\approx 6.8 \times 10^{14}$ at/cm$^2$ for Si (100)) need to be present on the surface to initiate Si wire growth. After Au deposition, carbon has a tendency to agglomerate in gold droplets as illustrated in EDX images in Figure 7.2b, showing superposition of Au and C signals. This is not surprising if one takes into account the relatively high (up to 4.7 at.% [2]) solubility of carbon in liquid gold and extremely low (up to $9 \times 10^{-4}$ at.% [3]) solubility of carbon in solid silicon. It should be noted that oxygen and carbon have long been recognized as the two major contaminants on wet etched Si surfaces [4,5], and carbon is the most difficult to remove by heating Si in ultrahigh vacuum [5,6].

In order to explain lateral wire growth, we start with one of the underlying assumptions in the VLS model, namely that growth takes place under local thermodynamic equilibrium conditions close to the liquid-solid interface. The existence of local thermodynamic equilibrium implies that the growth of a silicon wire is determined by the minimization of the total Gibbs free energy; i.e., it is thermodynamically controlled. Next, we compare the
main thermodynamic parameters controlling Si wire growth in the vertical and horizontal growth regimes.

**Figure 7.1:** SEM planar views of Si wires on Si (100) substrate after a) 30 min and b) 4 h of Si deposition.

Under fixed total pressure and temperature, the change in Gibbs free energy, $\delta G^{Si}$, for a vertical wire can be written as [7]

$$\delta G^{Si} = \delta N^{Si} (-\Delta \mu^{Si}_{\infty}) + \sum_{i} \delta A^{Si}_{i} \gamma^{Si}_{i},$$

(7.1)

where the first term is the variation of the free energy of the system due to the transfer of $\delta N^{Si}$ silicon atoms from the gas phase to the crystal, $\Delta \mu^{Si}_{\infty}$ denotes the supersaturation over a gold surface with infinite radius of curvature and the second term is the increase of the free energy of the wire due to its increasing surface $\delta A^{Si}_{i}$ and $\gamma^{Si}_{i}$ denotes the specific free energy of the surface $i$. $\Delta \mu^{Si}_{\infty}$ can be estimated as

$$\Delta \mu^{Si}_{\infty} = k_B T \ln \frac{P^{Si}}{P_{\infty}},$$

(7.2)

where $P^{Si}$ and $P_{\infty}$ are the silicon vapour pressure over the gold droplet and bulk gold with infinite radius of curvature, respectively. For vertical wires, it was shown [8] that Si
surface energy relationships combined with the minimization of surface-to-volume ratio can alone successfully predict Si wire shapes and orientations.

![SEM planar view of the Si wire growth initiated around C-containing contamination (black arrow) present on the control Si substrate.](image)

**Figure 7.2:** a) SEM planar view of the Si wire growth initiated around C-containing contamination (black arrow) present on the control Si substrate. b) EDX analysis of Au and C distribution in the highlighted area of Electron Image.

For lateral silicon wires, the substrate surface diminishes with growth. Therefore, one has to consider the system including both the lateral wire and the underlying substrate when calculating the surface energy change during growth. As a result, the second term in Equation 7.1 should be modified by including in the sum the corresponding surface energy of the substrate with a negative sign, $-\delta A_s^{\text{Si}} y_s^\text{Si}$.

In addition, we argue that the change in Gibbs free energy, $\delta G^{Au}$, for a gold droplet should also be taken into account for lateral growth:

$$\delta G^{Au} = \delta N^C (-\Delta \mu_{Au}^{Au}) + \sum_i \delta A_i^{Au} y_i^{Au},$$

(7.3)

where the first term is the variation of the free energy of the system due to dissolving of $\delta N^C$ carbon atoms from the Si substrate into gold droplet, $\Delta \mu_{s}^{Au}$ represents the change in the chemical potential of the Au due to formation of Au (C) liquid solution, and the second term is the decrease of the free energy of the gold droplet due to dissolution of C. Overall, minimization of $\delta G^{Au}$ is responsible for initiating the lateral growth.
It is thermodynamically more favourable for a gold droplet to stay in contact with a carbon covered Si substrate (Figure 7.3a). This way, the Au droplet lowers its chemical potential $\Delta \mu_{\text{Au}}^{\text{Si}}$ and, possibly, the surface tension $\gamma_{\text{Si}}^{\text{Au}}$ by dissolving more carbon; in other words, minimizes $\delta G^{\text{Au}}$. Additionally, lateral growth minimizes the fraction of exposed Si (100) plane, which is known to have larger surface energy density $\gamma_{\text{Si}}^{\text{Si}}$ than the Si (111) plane [9-11]. The observed preferential incorporation of C into Au droplets (Figure 7.2b) and its high solubility in liquid gold [2] both suggest that the chemical potential of a gold droplet is indeed reduced upon dissolving carbon impurities. We were not able to find any published data on the influence of carbon impurities on the surface tension of liquid gold. However, introducing surfactants, e.g. As and Sb, during thin film growth has been known to change the growth mode from island formation to layer-by-layer growth by lowering surface tensions of the growing materials [12,13].

![Figure 7.3: a) Schematic of nucleation of a lateral Si wire: an Au droplet lowers its Gibbs free energy by consuming C impurities on the surface. b) The stages of Si wire growth in MBE: 1 - mass-transport in the gas phase; 2 - surface diffusion; 3 - incorporation into liquid droplet; 4 - diffusion in the liquid phase; and 5 - incorporation in the crystal lattice.](image)

While we showed the evidence that nucleation of lateral Si wires is thermodynamically controlled, their subsequent growth is controlled kinetically as discussed further below. By analogy to the growth of thin films, the process that is thermodynamically controlled at the nucleation stage may be driven from equilibrium into a regime where kinetic parameters determine the film morphology. Temperature and pressure (flux) are typically used for that purpose [14]. The temperature of the substrate controls the diffusion and desorption rates of adatoms, sticking coefficients and surface energies. The pressure in
the gas phase controls the impingement rate of adsorbing atoms. In our MBE system, the
temperature of the substrate and deposition (impingement) rate of silicon atoms can be
controlled independently, which offers a unique playground for testing various
hypotheses regarding the wire growth mechanism and thereof developing growth recipes
for possible applications.

A schematic of lateral wire growth process is shown in Figure 7.3b. Five principal steps
can be distinguished: (1) mass-transport in the gas phase; (2) surface diffusion; (3)
preferential incorporation of atoms into liquid droplets; (4) diffusion in the liquid phase;
and (5) precipitation of Si into a growing wire. Here we have adopted four growth steps
(1, 3, 4 and 5) characteristic to vertical wire growth by CVD [7] and added a surface
diffusion step (2) specific to MBE wire growth [15]. Several of these stages (1, 2, 3) can
be a rate-determining step for the formation of the silicon wire network. For example, we
have shown previously (Chapter 6) that increasing the gold coverage will make step 3 a
rate-determining one. In that case, higher areal density and smaller relative size of gold
droplets lead to the formation of the multiple small silicon islands. Growth and
coarsening of those islands caused rough multilayer Si film to grow.

The mass-transport regime (step 1) will be a rate limiting step at relatively high growth
temperatures $T$ and low fluxes of silicon atoms $F$. In this regime, all silicon atoms landing
on the substrate will have enough time to reach a Au droplet by surface diffusion and
precipitate into a growing Si wire. Under these conditions, the steady state solution to the
diffusion equation for Si adatoms on Si (100) surface (see Supplementary Information in
Appendix E) predicts that the length of a lateral Si wire will be directly proportional to
the Si deposition time, $t$, and incoming Si flux, $F$:

$$L = c(r_{Au}, \lambda_s) F t,$$

(7.4)

where $c(r_{Au}, \lambda_s)$ is a constant factor that depends on the radius of the gold droplet $r_{Au}$
and diffusion length $\lambda_s$ of Si adatoms. To confirm this, we measured the average length of
Si wires at $T = 650 \, ^\circ C$ and $F = 5 \times 10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$ for different Si deposition times
(Figure 7.4). In agreement with theoretical predictions, we found linear growth for short
Si deposition times ($t < 3$ h). Deviation from linear growth at longer Si deposition times are caused by a decrease in the Si flux $F$ over time as revealed by in situ measurements with crystal quartz monitor [16].

In MBE, the silicon atoms are thermally evaporated and typically have low kinetic energies ($k_B T \sim 0.1$ eV) when they arrive at the surface [17]. Low energy deposition conditions imply that atoms attach at the sites very near to the impingement point of the atom with the surface, unless they are thermally activated on the surface. If the deposition rate $F$ is high, or the substrate's temperature $T$ is low, the atoms are unable to diffuse to gold droplets nearby and they nucleate a new island instead. The growth of individual Si islands is thus competing with incorporation of Si atoms into Au droplets, and as a result a rough Si film develops.

![Image of a graph showing wire length as a function of time.](image)

**Figure 7.4:** The length of lateral Si wires as a function of Si deposition time. Constant growth rate, $L=vt$, is also shown for comparison.

In Figure 7.5, we show how the diffusion regime (step 2) can be activated by lowering the growth temperature to 450 °C and keeping the flux the same, $F = 5 \times 10^{14}$ atoms×cm$^{-2}$×min$^{-1}$. In this case, the surface diffusion coefficient, $D = D_0 \exp(-E_a/k_BT)$, where $E_a$ is the diffusion barrier, is lower by a factor of 2 [18], so that adatoms tend to stay where they have landed, nucleating multiple silicon islands. When a slow-moving gold droplet encounters one of these islands, the island blocks its path. The silicon wire
can then either turn or cease growing. Minimizing the island density will thus decrease the number of turned or terminated wires.

The island density $N$ should decrease with a decrease of flux $F$ and/or increase of diffusion coefficient $D$ (or temperature $T$) and has the qualitative form $N \sim F^p/D^q$ [19]. The values of $p$ and $q$ are positive and are dependent on the nucleation and growth mechanisms. It is then possible to compensate the low temperature effects by decreasing the flux of Si atoms. Indeed, we were able to grow Si wires at 450 °C by lowering the Si flux, $F = 2.3 \times 10^{14} \text{ atoms} \times \text{cm}^{-2} \times \text{min}^{-1}$ (see Supplementary Information in Appendix E). However, lower growth rate and incomplete suppression of island formation render such growth conditions impractical.

![SEM micrograph of a diffusion limited growth of Si wires. The growth temperature was $T = 450$ °C and flux $F = 5 \times 10^{14} \text{ atoms} \times \text{cm}^{-2} \times \text{min}^{-1}$.](image)

**Figure 7.5:** SEM micrograph of a diffusion limited growth of Si wires. The growth temperature was $T = 450$ °C and flux $F = 5 \times 10^{14} \text{ atoms} \times \text{cm}^{-2} \times \text{min}^{-1}$.

In summary, we have presented thermodynamic arguments proving that carbon deposits on the level of ~ 5 ML initiate the lateral growth of silicon wires on the Si (100) substrate. Controlled deposition of a carbon layer after the substrate's cleaning stage can thus be used to initiate the lateral growth of semiconductor wires which otherwise grow vertically.

Upon nucleation, Si wire growth is controlled kinetically by the following three parameters: the flux of incoming silicon atoms (mass-transport regime), the surface diffusion of Si adatoms (the diffusion regime) or the areal density of Au droplets (the Au-incorporation-limited regime). Among these three regimes, the mass-transport regime,
realized at high deposition temperatures \((T \geq 650 \, ^\circ C)\), low Si fluxes \((F \leq 5 \times 10^{14} \, \text{atoms} \times \text{cm}^{-2} \times \text{min}^{-1})\) and large interwire separation \((\Delta r_{\text{avg}} > \lambda_s)\), is beneficial for future applications. In this regime, the wires grow linearly with time, provided the temperature and flux are kept constant. This fact can be used to produce interconnections between two metal electrodes deposited on the surface similar to growth of silicon logic gates reported by Kim et al. [20]. Adding precise positioning of catalyst droplets and using miscut substrates with atomic steps to guide the wire growth can further result in self-assembled wire arrays of desired complexity.

### 7.3 References


[16] Decreasing of the Si flux over time may be caused by geometric shadowing from the edges of the hole formed on the surface of silicon source due to evaporation.


[18] We have used a lowest reported value for $E_a = 0.6$ eV calculated by G. Brocks et al., Phys. Rev. Lett. 66 (1991), 1998 for diffusion of Si adatoms along the dimer rows on Si (100) surface.


Chapter 8. Conclusions and future work

In the first part of this thesis, a new methodology was developed for calculating proton stopping cross sections $\varepsilon$ from MEIS spectra in both crystalline and amorphous thin film targets. The details of the procedure on how to extract accurate energy loss values from recorded MEIS energy-angle scans are described in Section 3.2. An iterative method that calculates a set of $\varepsilon$-values from the measured energy loss values is presented in Appendix A along with the computer code implementation.

We first applied this method to measuring the stopping cross section $\varepsilon_{STO}$ for protons of ~55 - 170 keV energy in a crystalline 3.5 nm strontium titanate film (Chapter 3). To reduce the uncertainties, we thoroughly characterized the structural parameters of the film by a combination of surface- and bulk-sensitive techniques: ARXPS, RBS and MEIS. We found that calculated $\varepsilon_{STO}$ values are systematically lower than the Bragg's rule prediction, $\varepsilon_{Sr} + \varepsilon_{Ti} + 3\varepsilon_{O}$, over the probed energy range. Atomic $\varepsilon$-values were obtained from the widely used program SRIM. Several explanations of observed discrepancy were proposed: i) the method for calculating stopping cross section from MEIS spectra is incorrect; ii) SRIM atomic $\varepsilon$-values are overestimated for one of the elements and iii) Bragg's rule is invalid.

In order to eliminate the first explanation and part of the second, we measured $\varepsilon_{Si}$ and $\varepsilon_{Ti}$ for protons of 50-170 keV energy in a set of thin films of different thicknesses prepared in a MBE chamber (Chapter 4). Our experimental data for both silicon and titanium are in excellent agreement with each other and with the literature values from the NIST database PSTAR, whereas SRIM underestimates the stopping cross section around the peak position for both Si and Ti. An agreement between measured Si and Ti stopping cross sections and PSTAR literature values thus confirms the validity of the iterative procedure for calculating stopping cross sections from the energy loss measured by MEIS. However, our findings still cannot explain why $\varepsilon_{STO}$ is overestimated since SRIM underestimates $\varepsilon_{Ti}$. The remaining possibilities are: i) Bragg's rule is inaccurate (see the
discussion of chemical effects in Chapter 1) ii) $\varepsilon_{Sr}$ is overestimated and iii) one cannot use in solid SrTiO$_3$ the $\varepsilon_O$ values obtained for the gaseous target (see the discussion of physical effects in Chapter 1). Unfortunately, one cannot confirm SRIM values for both $\varepsilon_{Sr}$ and $\varepsilon_O$ directly. Sr thin films are highly reactive and form strontium carbonate, SrCO$_3$, strontium oxide or hydroxide upon exposure to the traces of CO$_2$, O$_2$ and(or) H$_2$O. The stopping cross section of oxygen gas is usually measured in transmission geometry in a well defined differentially pumped volume filled with a gas. Such measurements are not possible in the current design of the MEIS chamber.

We propose the following future experiments to eliminate possibilities i) and iii). First, Bragg's rule can be tested separately by measuring $\varepsilon$ for TiSi or TiSi$_2$ thin film targets and by comparing the values with Bragg’s rule predictions. PSTAR literature values for $\varepsilon_{Ti}$ and $\varepsilon_{Si}$ can be used for the latter.

If the validity of Bragg's rule is confirmed, the presence of the physical effect in $\varepsilon_O$ can be tested by measuring $\varepsilon$ for TiO$_2$ thin film targets. Experimental $\varepsilon_O$ values can then be found by inverting Bragg's rule:

$$\varepsilon_O = \frac{1}{2}(\varepsilon_{TiO_2} - \varepsilon_{Ti})$$  \hspace{1cm} (8.1)

If the values obtained from Equation 8.1 and PSTAR literature values for $\varepsilon_O$ agree with each other, one can conclude that $\varepsilon_{Sr}$ is overestimated in the program SRIM. The latter fact might not be surprising, since the current Sr stopping cross section values are based on a single measurement by Ch. Epaher et al. [1].

In the second part, we presented experimental evidence that lateral Si wires (ridges) can grow epitaxially on Si (100) substrates in MBE. A three-step growing process involves depositing a uniform Au film of 1 or 2 nm thickness, annealing of a Au film to form an array of Au droplets of 90 or 60 nm diameter, respectively, and evaporating Si at rates of $2.3\times10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$ or $5\times10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$ for 30 to 360 min at 450 - 650 °C.
The growth process can be described by the VLS growth model (Chapter 6). According to this model, silicon in the vapour phase impinges on a substrate covered with liquid gold (nano)particles. At sufficiently high substrate temperatures and low flux of incoming Si atoms, silicon atoms landing on Si substrate can diffuse to the nearest gold droplet and dissolve into it. When Si concentration in the droplet exceeds the saturation point, excess silicon crystallizes as a solid wire at the droplet/substrate interface. Gold droplets are propelled forward along two orthogonal <011> directions by the growing silicon wires forming an orthogonal network of Si wires.

As discussed in Chapter 7, the nucleation of the wires is controlled thermodynamically. The Gibbs free energy of the lateral wires is lower compared to their vertical counterparts for several reasons. First, the chemical potential of gold droplets in contact with the substrate is decreased by dissolving C present on the surface. We showed that C on the level of ~ 5 ML are essential for initiating the lateral growth. Second, lateral growth minimizes the fraction of exposed Si (100) plane, which is known to have a larger surface energy density $\gamma_{(100)}^{\text{Si}}$ than does the Si (111) plane.

Upon nucleation, Si wire growth is controlled kinetically by one of the following three parameters: the flux of incoming silicon atoms (mass-transport regime), the surface diffusion of Si adatoms (the diffusion regime) or the areal density of Au droplets (the Au-incorporation-limited regime) (Chapter 7). Among these three regimes, the mass-transport regime, realized at high deposition temperatures ($T \geq 650$ °C), low Si fluxes ($F \leq 5\times10^{14}$ atoms×cm$^{-2}$min$^{-1}$) and large interwire separation ($\Delta r_{\text{avg}} > \lambda_s$), is the most attractive for practical applications. In this regime, Si wire length is directly proportional to time and flux of incoming silicon atoms, as we showed both experimentally (Chapter 7) and theoretically (Appendix E). For sufficiently long silicon deposition times, the wires form a two-dimensional network on the substrate surface (Chapter 6) that can be successfully simulated by a self-avoiding random walk in two dimensions (Appendix C and Appendix D).
For future work, it will be interesting to test the means of controlling the lateral wire growth proposed in Chapter 7. For example, carbon deposit can i) have no effect on the growth at very low coverage; ii) initiate the growth at intermediate coverage or iii) terminate epitaxial growth at higher coverage. Controlled deposition of a carbon layer after the substrate's cleaning stage can thus be used to identify the range of C coverages beneficial for lateral growth of silicon wires. The next step is to test if controllable C deposition can switch on the lateral wire growth in other semiconductor systems, such as Ge and GaAs.

As suggested in Chapter 7, Si wire turns might be completely eliminated by utilizing guided wire growth along the atomic steps on miscut Si (100) wafers. Combining guided growth with precise positioning and size control of gold droplets might be seen as the ultimate goal of the crystal growth part of the project. If diameter of Au droplets is reduced, or Au clusters of controlled diameter are utilized to initiate Si wire growth, additional applications can be envisioned. Linear growth of lateral Si wires from placed gold seeds can be used to produce interconnections between the two metal electrodes deposited on the surface similar to growth of silicon logic gates reported by Kim et al [2]. Alternatively, Si wire networks can be used for improving efficiency in solar cells since they lead to broadband antireflection as well as enhanced light trapping efficiency [3].

8.1 References


Appendices

Appendix A  Computer simulation for calculating stopping cross section

When the energy loss of protons in a target of known composition and thickness is measured, it is possible to calculate the correct stopping cross sections by using an iterative procedure. A Python code has been used to calculate the energy loss in an ideal laminar target with constant composition for a given incident energy, $E$, incident angle, $\theta_1$, and detector position angle $\theta_2$.

The program slices a film of interest into $N$ sublayers of equal thickness $\Delta z$ and the energy loss of an incoming ion in each sublayer is first estimated using Andersen and Ziegler stopping power values \[A1\] according to the equation

$$
\frac{\Delta z}{\cos \theta_1} \int_0^{\Delta z} \varepsilon(E(x)) \, dx = N \frac{\Delta z}{\cos \theta_1} \varepsilon^{(1)}(E_{\text{in}}(i)) 
$$

(A.1)

In Equation A.1 the stopping cross section is assumed constant throughout sublayer $i$ and evaluated at the ion energy $E_{\text{in}}(i)$ at the front surface of the sublayer (surface energy approximation). The energy at the front surface of sublayer $i+1$ is therefore given by

$$
E_{\text{in}}(i+1) = E_{\text{in}}(i) - \Delta E_{\text{in}}(i) 
$$

(A.2)

The energy loss along the outgoing path is calculated in the same way as for the incoming path. In the special case of a thin film on the top of a substrate, the calculated energy loss is

$$
\Delta E_{\text{calc}}(E) = KE_{\text{in}}(N+1) - \sum_i \Delta E_{\text{out}}(i) - KE 
$$

(A.3)
where $K$ is the kinematic factor for the substrate, $E_{\text{in}}(N+1)$ is the energy of the beam before the scattering event, and $E$ is the incident beam energy. The corrected stopping cross sections are then calculated according to

$$
\epsilon_{\text{new}}(E_{\text{in}}(i)) = \epsilon_{\text{old}}(E_{\text{in}}(i)) \frac{\Delta E_{\text{meas}}(E)}{\Delta E_{\text{calc}}(E)}
$$

(A.4)

where $\Delta E_{\text{calc}}(E)$ and $\Delta E_{\text{meas}}(E)$ are the calculated and measured energy losses at energy $E$. The iterative procedure is then repeated again until the measured and calculated energy losses at energy $E$ are the same within the experimental uncertainty.

#program allows you to calculate stopping powers if the files with target compositions and the energy losses are provided

1 import numpy as np
2 import os
3
4 def Kfactor(M1, M2, angle):
5     "function calculates kinematic factor"
6     return np.power((M1/(M1 + M2)), 2)*np.power((np.cos(np.radians(angle))
7         + np.sqrt(np.power((M2/M1), 2) - np.power(np.sin(np.radians(angle)), 2))), 2)
8
9 def Stopping_Power_kkk(x, s, a0, a1, a2, a3, b):
10    "functional form for KKKNS stopping powers"
11    slow = np.power(0.001*x, s)*np.log(np.exp(1) + b*0.001*x)#energy is in the units MeV/amu
12    shigh = a0 + a1*np.power(0.001*x, 0.25) + a2*np.power(0.001*x, 0.5) +
13        a3*np.power(0.001*x, (1+s))
14    return slow/shigh
15
16 def Stopping_Power_az(x, a1, a2, a3, a4, a5):
17    "functional form for Andersen and Ziegler stopping powers"
18    slow = a1*np.power(x, a2)
19    shigh = (a3/x)*np.log(1+a4/x+a5*x)
20    return slow*shigh/(slow + shigh)
21
22 def StoppingLayer5(Energy, Correction, Layer):
23    "function calculates the stopping power at given Energy for the Layer using
24 Corrected Andersen and Ziegler values (REFERENCE) or KKKNS stopping powers
26    Sum = 0
27    for index in range(int(Layer[3])):
Element = int(Layer[2*index+4] - 1) #to skip fitting option, thickness and
number of layers/elements
if Element == 13:#if Si, then use KKKNS stopping powers
    Sum += Correction[Element]*Concentration*Stopping_Power_kkk(Energy,
0.37, 4.16e-002, -1.47e-001, 1.80e-001, 2.79e-001, 15.7)
else:#for other elements use Andersen and Ziegler
    Sum += Correction[Element]*Concentration*Stopping_Power_az(Energy,
Stop5Coeff[Element][0],Stop5Coeff[Element][1], Stop5Coeff[Element][2],
Stop5Coeff[Element][3],Stop5Coeff[Element][4])
return Sum

Stop5Coeff_str = [line.strip().split() for line in open("Andersen_Ziegler_5_H.dat")]
AZ coefficients a1-a5 from the file
Stop5Coeff = np.array([[float(another) for another in item] for item in
Stop5Coeff_str])
PeriodicTable_str = [line.strip().split() for line in open("PeriodicTable.dat")]
# atomic weights of elements
PeriodicTable = np.array([float(item[2]) for item in PeriodicTable_str])

TargetFile = open(raw_input("Please, enter the name of the target file: "))
Target = []#to store target layers
ToFit = []#to store elements for which one fits the stopping powers
for line in TargetFile:
    item = line.strip().split()
    if item[0] == '0':#layer's stopping power is fixed
        Target.append([float(another) for another in item])
    elif item[0] == '1':#layer's stopping power needs to be fitted
        LayerOfInterest = Target[-1]# to store the layer for which one fits the stopping
        powers
        ToFit = [int(item[2*i + 4]) for i in range(int(item[3]))]
    elif item[0] == '-1':#substrate layer
        Substrate = int(item[4]) - 1
EnergyLoss_str = [line.strip().split() for line in open(raw_input("Please, enter the
name of energy loss file: "))]
EnergyLoss_exp = np.array([[float(another) for another in item] for item in
EnergyLoss_str])#Experimental energy loss
CorrectionCoeff = np.ones((len(EnergyLoss_exp), len(Stop5Coeff)))#all the
correction coefficients are initially set to 1
OutputFile = open(raw_input("Please, enter the name of the output file: "), 'w')
Energy_calc = []
for i in range(len(EnergyLoss_exp)):
    Energy_calc.append([])
EnergyLoss_calc = 0
flag = 0
K = Kfactor(PeriodicTable[0], PeriodicTable[Substrate], EnergyLoss_exp[i][3])
while np.abs(EnergyLoss_calc - (K*EnergyLoss_exp[i][0] - EnergyLoss_exp[i][4])) > 0.03:
    if flag == 1:
        Energy_calc.pop()
        Energy_calc.append([])
    Energy_calc[i].append(EnergyLoss_exp[i][0])
    for j in range(len(Target)):
        SublayerThicknessIn = (Target[j][1]/Target[j][2])/(np.cos(np.radians(EnergyLoss_exp[i][1]])*np.cos(np.radians(EnergyLoss_exp[i][2])))
        for k in range(1, int(Target[j][2]+1)):
            Energy_calc[i].append(Energy_calc[i][-1] - 0.001*StoppingLayer5(Energy_calc[i][-1], CorrectionCoeff[i], Target[j])*SublayerThicknessIn)
        Energy_calc[i].append(K*Energy_calc[i][-1])
    EnergyLoss_calc = K*Energy_calc[i][0] - Energy_calc[i][-1]
    for item in ToFit:
        CorrectionCoeff[i][item-1] = CorrectionCoeff[i][item-1]*(K*EnergyLoss_exp[i][0] - EnergyLoss_exp[i][4])/EnergyLoss_calc
    flag = 1
else:
    OutputFile.write("%0.2f %0.2f\n" % (EnergyLoss_exp[i, 0], StoppingLayer5(EnergyLoss_exp[i, 0], CorrectionCoeff[i], LayerOfInterest)))
OutputFile.close()
References:

Appendix B  The results of XPS analysis of SrTiO$_3$/Si sample

The core level binding energies (BE) extracted from C 1s, Sr 3d, Ti 2p, O 1s and Si 2p XPS spectra obtained in the standard mode are listed in Table B.1 along with the published data. The results can be summarized as follows:

• An adventitious C layer is present at the surface of the sample as indicated by the pronounced C 1s peak A at 284.6 eV.

• A single Ti 2p$_{3/2}$ peak D at 458.0 eV is attributed to a STO layer as follows from a comparison with literature data for a STO single crystal. TiSi$_x$ species are then absent at the interface, which contradicts previously published results for MEIS analysis of MBE-grown SrTiO$_3$ on Si(001) [B4].

• Sr 3d$_{5/2}$ and O 1s components, B and E respectively, can be assigned to the SrTiO$_3$ film if compared to SrTiO$_3$ single crystal XPS data.

• The Sr 3d$_{5/2}$ and Si 2p$_{3/2}$ peaks, K and I respectively, originate from the non-stoichiometric strontium silicate interface. Thus, the latter Si 2p$_{3/2}$ peak may be directly compared with the 102.4 eV peak in [B1]. The difference in the Si 2p3/2 binding energy found here arises from the different choice of reference peaks: i.e. C 1s (C-C bond) here, Si 2p$_{3/2}$ from the substrate in [B1].

• Two additional broad peaks at higher BE (F and G) can originate from the interfacial layer as well as from residual hydrocarbons at the sample surface. Due to the low photoelectron cross section for O 1s, the assignment of components to the separate layers based on the angular dependence of the XPS signal is somewhat ambiguous.
From the fitted ARXPS spectra at 16 different angles, the relative depth distribution of chemical species was obtained using Maximum Entropy calculations [B5] (Figure B.1) with Avantage software. The most probable profile is shown in Figure B.1a.

**Table B.1:** Summary of the measured core level binding energies in eV for a 4 nm SrTiO$_3$/Si(001) sample compared to the literature data. Letters in front of the binding energy values were used in the discussion. Numbers in parentheses are the full width at the half maximum.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C 1s</th>
<th>Sr 3d$_{5/2}$</th>
<th>Ti 2p$_{3/2}$</th>
<th>O 1s</th>
<th>Si 2p3/2</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$/Si(001)</td>
<td>A: 284.6(1.3)</td>
<td>B: 132.4(0.9)</td>
<td>D: 458.0(1.1)</td>
<td>E: 529.4(1.2)</td>
<td>F: 530.9(1.3)</td>
<td>G: 531.9(1.7)</td>
</tr>
<tr>
<td>SiO$_2$/Si(001)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.3(-)</td>
<td>101.3(-)</td>
</tr>
<tr>
<td>SrTiO$_3$/Si(001)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.3(-)</td>
<td>101.2(-)</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>284.6(-)</td>
<td>132.5(0.95)</td>
<td>457.9(1.0)</td>
<td>529.0(1.1)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>284.6(-)</td>
<td>132.6(1.5)</td>
<td>-</td>
<td>530.0(1.5)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SrCO$_3$</td>
<td>284.6(-)</td>
<td>132.7(1.6)</td>
<td>-</td>
<td>530.9(1.9)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TiSi</td>
<td>-</td>
<td>-</td>
<td>452.8(-)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The totality of the XPS data suggests the following sequence of layers: C| SrTiO$_3$| SrSiO$_x$| Si (substrate) (Figure B.1b). The peaks in Figure B.1 are broadened by detector resolution and low photoelectron yields, so that the exact thickness of layers cannot be deduced. The presence of strontium oxide at the surface supports the finding of Goncharova et al. [B4], that these SrTiO$_3$ films are SrO-terminated. Overlapping layers of SrO and SiO$_2$ at the interface are represented as SrSi$_x$O$_y$ in Figure B.1b.
Figure B.1: a) Reconstruction of ARXPS profiles for SrTiO$_3$/Si(001) by using maximum entropy calculations (Avantage software). The corresponding binding energies used for the fitting are indicated in the brackets, the notation is adapted from Table B.1. The ratios of elemental signals coming from the same chemical species were fixed to stoichiometric ratios. b) The schematic representation of SrTiO$_3$/Si(001) structure from ARXPS data.

References:


Appendix C  Supplementary information for Chapter 6

This appendix contains the Supplementary Information which was published together with the material presented in Chapter 6.

Silicon wire growth direction

The original n-Si (100) wafers (Silicon Valley Microelectronics) polished on a single side were cut in 8×10 mm rectangular pieces using K&S 780 Dicing Saw (Nanofab, Western University) as shown in Figure C.1a (inset). The orientation of the wires with respect to the substrate edges is shown in Figure C.11a (low magnification) and Figure C.1b (high magnification). When comparing them with Figure s1a (inset), it is clear that the wires grow parallel to Si <110> crystallographic direction.

![Figure C.1: Direction of silicon wire growth. a) SEM micrograph of the Si(100) rectangular substrate with Si wires after a 2 h Si deposition (90 nm Au droplets) at low magnification (×100). b) The same wires at higher magnification (×3770).](image)

Orientation of side facets of a silicon wire

We measured an incline angle between the wire side facet and substrate surface by using two different techniques: analyzing a cross section image obtained by a focused ion beam (FIB) etching of a selected Si wire in a scanning electron microscope (LEO (Zeiss) 1540...
XB FIB/SEM, Nanofab, Western University) and analyzing line profiles extracted from topography scans obtained in an atomic force microscope (Witec AlphaSNOM 300, Prof. Giovanni Fanchini group, Western University).

**Figure C.2:** Individual silicon wire cross section. a) SEM micrograph of the two wires on a Si (100) substrate obtained after a 2 h Si deposition (90 nm Au droplets) prior to a FIB etching. b) The cross section of silicon wire on the right obtained using a FIB etching. The schematic shows measured angles for the facets with respect to a (100) normal direction.

Figure C.2 shows an SEM image of silicon wires obtained after a 2 h Si deposition (90-nm Au droplets) prior to a FIB etching (Panel a) and after etching part of the wire perpendicular to the growth direction (Panel b). In Panel b, the white dashed line is a 4 nm osmium coating used to remove possible charging effects, and the thick amorphous layer on the top of the wire is a platinum coating used to prevent possible rounding of wire edges by an ion beam. The angles were determined using an image processing software ImageJ [C1] and are indicated schematically in Panel b. The observed angles of 27±5° and 22±5° match the theoretical value of 25.2° for the Si (311) plane within experimental uncertainty. Si (311) facets have been previously observed for Si nanowires grown in situ in transmission microscope [C2]. There is experimental evidence that the Si (311) facet is stabilized on a Si (100) surface by carbon impurity [C3]. The experimentally observed values of 44±2° and 43±2° cannot belong to (110) direction since the facet's normal should lie in the plane perpendicular to the direction of growth.
We speculate that the measured value of 45° corresponds to an average angle measured for a vicinal facet with a staircase of atomic steps. Ross et al. in [C4] have suggested that kinetic factors could in principle allow growth of such a sidewall with 'forbidden' orientation.

**Figure C.3:** AFM image of individual silicon wires. a) AFM amplitude image (forward scan) for silicon wires on a Si (100) substrate after 6 h Si deposition (60 nm Au droplets). b) A, B and C line profiles extracted from the AFM topography scan. The lines A, B and C are shown schematically in Panel a. All axes are labelled in nm.

Figure C.3 shows the AFM amplitude image for silicon wires obtained after a 6 h Si deposition (60-nm Au droplets) (Panel a) and the extracted line profiles A, B, C (Panel b). The linear background subtraction and angle measurements were done using software for data processing and nonlinear curve fitting Fityk [C5]. The three angles observed in the topography profiles in Panel b are: 18°±5°, 25°±5° and 45±5°. We speculate that the 18° angle belongs to the Si (411) plane which has a theoretical value of 19.4°. The presence of high index (411) planes may be due to the change of wire surface curvature from a positive angle to a negative one at the top of the silicon wire.

It is worth mentioning that essentially different samples and wires were analyzed in an atomic force microscope and a scanning electron microscope which might contribute to
the difference between the observed values. In addition, presence of systematic uncertainties due to electron beam aberration in SEM and a finite tip size effects in AFM cannot be excluded.

Ostwald ripening of gold droplets

**Figure C.4:** Au droplet areal density as a function of Si deposition time. Indicated time values include the initial annealing of a Au film for 30 min at 600 °C and a Si deposition time at 650 °C.

Figure C.4 and Table C.1 highlight the change in gold droplet areal density as a function of silicon deposition time. The data indicate that the gold droplet areal density decreases by more than a factor of 10 in the first 30 minutes of Si deposition compared to the areal density right after the annealing of the initial gold film. The same phenomenon is present for both 60-nm and 90-nm Au droplets. Similar behaviour of gold droplet areal density has been observed by P. Werner et al. for vertical Si wire growth in a MBE chamber at 525 and 545 °C [C6]. The authors attribute the observed phenomena to the effect of Ostwald ripening.

According to the mathematical investigation of Ostwald ripening by Lifshitz and Slyozov [C7], the average volume of all particles grows proportionally to time in a diffusion limited process. In a closed system, the average density of all the particles should then decrease, which agrees with our observations.
Table C.1: Areal density of gold droplets as a function of time. Indicated time values include the initial annealing of the Au film for 30 min at 600 °C and a Si deposition time at 650 °C. Superscript 'a' corresponds to 90-nm droplets, superscript 'b' – to 60-nm droplets.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Au areal density, $10^9$ nm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30$^a$</td>
<td>2424</td>
</tr>
<tr>
<td>45$^a$</td>
<td>206</td>
</tr>
<tr>
<td>60$^a$</td>
<td>146</td>
</tr>
<tr>
<td>150$^a$</td>
<td>67</td>
</tr>
<tr>
<td>270$^a$</td>
<td>65</td>
</tr>
<tr>
<td>390$^a$</td>
<td>58</td>
</tr>
<tr>
<td>30$^b$</td>
<td>7190</td>
</tr>
<tr>
<td>60$^b$</td>
<td>218</td>
</tr>
<tr>
<td>270$^b$</td>
<td>153</td>
</tr>
<tr>
<td>390$^b$</td>
<td>88</td>
</tr>
<tr>
<td>500$^b$</td>
<td>103</td>
</tr>
</tbody>
</table>

Silicon wire collisions

Table C.2 reports the statistical analysis of silicon wire collisions in terms of what fraction of the collisions results in the wires turning right, left or stopping. If collided, silicon wire has a higher chance of turning than stopping completely: 80% and 20% respectively. As expected, the probability of the wire turning left or right are equal to each other. The higher probability of the colliding wire to turn can be explained if one takes into account the non-ideal semicircular shape of the gold droplet at the tip of the wire. The slightest shift of the gold droplet's centre of mass away from the Si wire <110> growth direction will result in the shear force present at the gold-silicon interface in the collision. This shear force can “squeeze” gold droplet to the side of the colliding wire so that the growth may continue in a direction perpendicular to the original one.
Table C.2: The results of silicon wire collisions as a function of silicon deposition time.

Superscript 'a' corresponds to 90-nm droplets, superscript 'b' – to 60-nm droplets.

<table>
<thead>
<tr>
<th>Si deposition time, min</th>
<th>Total # of collisions</th>
<th>Wires turned left</th>
<th>Wires turned right</th>
<th>Wires stopped</th>
</tr>
</thead>
<tbody>
<tr>
<td>240&lt;sup&gt;a&lt;/sup&gt;</td>
<td>49</td>
<td>23</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>360&lt;sup&gt;a&lt;/sup&gt;</td>
<td>22</td>
<td>10</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>240&lt;sup&gt;b&lt;/sup&gt;</td>
<td>26</td>
<td>17</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>360&lt;sup&gt;b&lt;/sup&gt;</td>
<td>74</td>
<td>29</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>470&lt;sup&gt;b&lt;/sup&gt;</td>
<td>262</td>
<td>94</td>
<td>114</td>
<td>54</td>
</tr>
<tr>
<td>Total fraction</td>
<td>0.4</td>
<td>0.41</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

Monte Carlo simulation code details.

The Monte Carlo simulation code was written in Python (v. 2.6.5). In order to generate random numbers, we used a Python Random module. The flow-chart diagram for the code is shown in Figure C.5.

The code starts with randomly positioning $n_{Au}$ walkers in the nodes of the two-dimensional square grid, which is the equivalent of $n_{Au}$ gold droplets formed on a Si (100) surface after the annealing of a gold film. As a first step, $n_{Au}$ pairs of pseudo random integer numbers $0 \leq x, y < 2000$ are generated, which represent walker coordinates on the square grid of $2000 \times 2000$ squares. The size of one grid square used in the simulation is $15 \times 15$ nm$^2$. For each generated pair, it is then tested if there is already another walker in the 409 nm radius area. If the answer is positive, a new pair of random numbers $x, y$ is generated. The procedure is repeated until the number of walkers on the Si surface is equal to the $d_{Au} \times (15 \times 15$ nm$^2 \times 2000 \times 2000$), where $d_{Au}$ is the experimentally measured areal density of gold droplets before the Si deposition ($2424 \times 10^{-9}$ droplets/nm$^2$).

In order to determine the step length of each walker, the average silicon wire length after a 10 min Si deposition was first estimated from the wire length distribution after a 30 min Si deposition (90 nm Au droplets). The corresponding values were $489 \pm 89$ nm and $160 \pm 30$ nm after a 30 and 10 min silicon deposition, respectively. $n_{Au}$ normally
distributed pseudo random numbers are then generated representing a fixed step length $s_i$ for each walker $i$. The mean of the Gaussian distribution is equal to $160/15 = 11$ squares and the standard deviation is equal to $30/15 = 2$ squares. Defined in this way, each step in the simulation corresponds to a 10 min silicon deposition in the experiment. For example, to simulate a 240 min deposition, each of the walkers is required to make $N_{\text{tot}} = 24$ steps of fixed length $s_i$, unless it was terminated prematurely as explained in the following.

**Figure C.5:** A Monte Carlo simulation of Si wire growth on a Si (100) surface. The flow chart is shown for an individual walker $i$.

For each walker $i$, a walking direction $d_i$ is randomly chosen. The integer pseudo random numbers ranged from 1 to 4, where 1 is walking North, 2, 3 and 4 are walking East, South and West respectively. The numbers are uniformly distributed, which corresponds to
equal probabilities of growing in any of the Si $<011>$ directions for silicon wires observed in the experiment. Once chosen, the direction of the walk for any given walker $i$ is fixed unless the paths for any two walkers $i$ and $j$ intercept at the next step. In that case, instead of continuing along the same path, which would lead to a collision, the walker $i$ has a 40% chance of turning left, a 40% chance of turning right and a 20% chance of stopping. These percentages are taken from the experimental observations, as explained in the previous section. If the walker $i$ “decides” to turn, the new direction of motion is chosen and the walk continues until the final number of steps, $N_{\text{tot}}$, is reached or another collision happens.

We have also introduced the probability of the walk terminating prematurely in order to explain why the wire length distribution peaks at small lengths. At each step for each walker $i$, a uniformly distributed random number between 0 and 1 is generated and compared with $A/L_i$, where $L_i$ is the walk length. If the random number is less than $A/L_i$, the walk is terminated. The constant $A$ is chosen to fit the experimental length distribution ($A = 3$ for a 240 min Si deposition experiment).

After the total number of steps, $N_{\text{tot}}$, is reached, the histogram of simulated silicon wire lengths is plotted and compared to the experimental distribution.

References:

Appendix D  Computer simulation of Si wire growth (Au thickness = 1 nm, deposition time = 240 min)

1 import matplotlib.pyplot as plt
2 import numpy as np
3 import random as rnd
4
5 #the square screen is defined in terms of growth velocity: for 1nm Au is estimated to be ~490 nm/0.5 hr,
6 #if 1 grid segment = 15 nm, then average speed of a nw = 11 segments per time step that corresponds to 10 min
7 screen_size = 2000
8 gold_density = 0.000002424#density of gold seeds per nm^2, taken from the experiment at 0 min Si deposition
9 time_steps = 24#total number of time steps, each time step is equal to 10 min
10 gold_seeds = int(gold_density*screen_size*screen_size*15*15)#number of gold seeds per screen area
11 grid = np.zeros((screen_size,screen_size))#creating empty grid for nw to grow
12 nw = np.zeros((gold_seeds+1, 6))#nw([0,0,0,0,0,0],[nw1 head x, nw head y, nw1 diameter, if nw1 is terminated/not, nw1 length, nw1 direction of growth], ...)
13
14 def closer(center_x, center_y, proximity_radius):
15     "checks if there is a gold droplet in the circle of PROXIMITY_RADIUS around CENTER_X, CENTER_Y"
16     for k in range (0, 5):
17         for l in range (0, 5):
18             if (((k - center_x)**2 + (l - center_y)**2) <= proximity_radius**2) and (grid[(k % screen_size), (l % screen_size)] > 0):
19                 return 1
20
21 def vacant(x, y, direction, step_value):
22     "checks if the next STEP_VALUE nodes along DIRECTION from X, Y are vacant"
23     for w in xrange(1, int(step_value+1)):
24         if direction == 0 and grid[((x-w) % screen_size)][y] != 0:
25             return 0
26         elif direction == 1 and grid[x][((y+w) % screen_size)] != 0:
27             return 0
28         elif direction == 2 and grid[((x+w) % screen_size)][y] != 0:
29             return 0
30         elif direction == 3 and grid[x][((y-w) % screen_size)] != 0:
31             return 0
32     return 1
def step(x, y, direction, value, step_value):
    "changes the value of the node next to X, Y in the given DIRECTION to the same VALUE as node at X, Y"
    if vacant(x, y, direction, step_value):
        if direction == 0:
            for u in range(1, int(step_value+1)):
                grid[((x-u) % screen_size)][y] = value
                nw[value][0] = ((x-step_value) % screen_size)
                nw[value][4] += step_value
                nw[value][5] = 0
        elif direction == 1:
            for u in range(1, int(step_value+1)):
                grid[x][((y+u) % screen_size)] = value
                nw[value][1] = ((y+step_value) % screen_size)
                nw[value][4] += step_value
                nw[value][5] = 1
        elif direction == 2:
            for u in range(1, int(step_value+1)):
                grid[=((x+u) % screen_size)][y] = value
                nw[value][0] = ((x+step_value) % screen_size)
                nw[value][4] += step_value
                nw[value][5] = 2
        else:
            for u in range(1, int(step_value+1)):
                grid[x][((y-u) % screen_size)] = value
                nw[value][1] = ((y-step_value) % screen_size)
                nw[value][4] += step_value
                nw[value][5] = 3
    else:  # the nw has 2:2:1 chances to turn left: turn right: terminate if collided with another nw
        k = rnd.randint(1, 5)
        if k == 1:
            nw[value][3] = 1  # terminate
        elif k == 2 or k == 3:
            step(x, y, ((direction-1) % 4), value, step_value)  # turn left
        else:
            step(x, y, ((direction+1) % 4), value, step_value)  # turn right

# creating gold seeds at random sites of (screen_size x screen_size) grids, not repeating position
i=1
while i<=gold_seeds:
    x_coordinate = rnd.randint(0, screen_size - 1)
    y_coordinate = rnd.randint(0, screen_size - 1)
#only if the node has no gold seed:
if not closer(x_coordinate, y_coordinate, 27):# should be 27 = no seeds in ~410 nm distance around
    grid[x_coordinate][y_coordinate] = i
#memorizing the position of nw head
nw[i][0] = x_coordinate
nw[i][1] = y_coordinate
v = rnd.gauss(11, 2)#speed of the growing wire is normally distributed - exp. data are taken from 30 min sample
nw[i][2] = int(round(v))
nw[i][5] = rnd.randint(0, 3)
i += 1

for t in range(1, time_steps+1):#growth
    for i in range(1, gold_seeds+1):
        if not nw[i][3]:
            step(nw[i][0], nw[i][1], nw[i][5], i, nw[i][2])
l = rnd.random()#generates random float number in [0;1]
if l < 3/nw[i][4]:#an MC simulation of Ostwald ripening, 3/nw length is found manually to fit the experiment
    nw[i][3] = 1#terminate
print "...", t, "..."

#plotting the resultant nw network
#plotting experimental distribution of nw lengths
experiment_x = []
experiment_y = []
data2plot_string = [line.strip().split() for line in open('SNW11_length_150nmbin.dat')]
for item in data2plot_string:
    experiment_x.append(float(item[1]))
    experiment_y.append(float(item[0]))
experiment_np_x = np.array(experiment_x)
experiment_np_y = np.array(experiment_y)
p1, = plt.plot(experiment_np_x, experiment_np_y/float(np.sum(experiment_np_y)), marker = 'o', label = 'experiment')

#plotting simulated distribution of nw lengths
length_array = np.zeros(gold_seeds)
for i in range(1, gold_seeds+1):
    length_array[i-1] = nw[i][4]*15#1 segment is equal to 15 nm
answer = 'n'
#finding the satisfactory size of the bins in the histogram
while answer == 'n':
    l_bin_size = int(raw_input("Input the bin size:"))
    l_bin_number = int((max(length_array)-min(length_array))/l_bin_size)
    hist, bin_edges = np.histogram(length_array, bins = l_bin_number)
    mc_simulation_x = np.delete(bin_edges+l_bin_size/2, l_bin_number)
    mc_simulation_y = hist/float(np.sum(hist))
    plt.xlabel("Length, nm")
    plt.ylabel("Frequency")
    p2, = plt.plot(mc_simulation_x, mc_simulation_y, linestyle = 'None', marker = '*',
    label = 'simulation')
    plt.legend( loc='upper right', numpoints = 1 )
    plt.show()
    answer = raw_input("Are you satisfied with the bin size (y, n)?")
if answer != 'n' and answer != 'y':
    print "wrong input!"
    raise SystemExit
filename = raw_input("Enter the name of the output file:")
if not filename:
    print "You haven't entered the name!"
    raise SystemExit
f = open(filename, 'w')
for i in range(0, l_bin_number):
    f.write ("%0.0f %0.5f
    % (mc_simulation_x[i], mc_simulation_y[i]))
Appendix E  Supplementary information for Chapter 7

'Diffusion-droplet' model

In this section, we describe the mass-transport-limited model for lateral growth of Si wires. A generalized version of this theory is explained in Section 5.2. The general assumptions of the model are that 1) the growth occurs only at the site occupied by a liquid gold droplet which is treated as a sink absorbing all the Si atoms arriving at its surface; 2) the droplet is a quarter of a sphere with a growing wire attached to one of its flat sides (Figure E.1); 3) there is a steady state diffusion of silicon adatoms on the substrate; 4) the diffusion of silicon within the metal particle and the nucleation of the silicon wire at the wire/droplet interface are fast compared to the surface diffusion of silicon adatoms and can be disregarded; and 5) the separation between the wires is relatively large.

![Figure E.1: SEM planar view of Si wire after 30 min silicon deposition. 1 nm Au layer was used to form Au droplets, Si flux $F = 5 \times 10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$, substrate temperature $T = 650$ °C. The projection of the Si wire on Si (100) plane used in the 'diffusion-droplet' model is shown schematically. It is assumed that the Au droplet absorbs Si atoms only along the area which is not in contact with the growing wire.](image-url)
As was shown in our previous work [E1], if silicon deposition takes place at a relatively high temperature ($T \geq 650$ °C) and low silicon flux ($F \leq 5 \times 10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$), then assumption (1) is valid. A high deposition temperature and low flux of incoming silicon atoms ensure high diffusivity and long diffusion time of silicon adatoms respectively, so that they preferentially incorporate into gold droplets. The fundamental differential equation describing the areal density of adatoms on the substrate surface, $n_s$, in the 'diffusion-droplet' model can be written in the general form [E2]:

$$\frac{\partial n_s}{\partial t} = D_s \nabla^2 n_s - \frac{n_s}{\tau_s} + F$$  \hspace{1cm} (E.1)

Here $D_s$ is the surface diffusivity of adatoms on the substrate; $\tau_s$ is the mean time an atom stays adsorbed before re-evaporation and $F$ [atoms$\times$cm$^{-2}$s$^{-1}$] is the impingement flux from the vapour phase. In other words, the Equation E.1 is a diffusion equation complimented by the terms that take into account adatom desorption and deposition from the vapour phase. For typical growth situations, incorporation dominates over desorption. Therefore, we interpret $\tau_s$ as the average time an adatom diffuses before being incorporated into the wire. For this quantity, it is only possible to estimate an upper limit, which is the average time required to replace an adatom by an atom from the vapour, $\tau_s = N_s/F$, where $N_s$ is the density of surface sites [E2].

In order to retain a rotational symmetry in the diffusion equation (Equation E.1), we first assume that the gold droplet is hemispherical in order to calculate the flux of silicon adatoms absorbed into the gold droplet. Later on, we divide that flux by two in order to get back to the assumption 2 and calculate the growth rate of lateral Si wire from a quarter-of-a-sphere droplet. Note: if one takes into account the realistic geometry of the Au droplet and Au-Si interface, this will simply result in a constant multiplication factor in the final equation for wire length as a function of time. For a hemispherical gold droplet, the Laplacian in Equation E.1 is given by $\nabla^2 = \partial^2/\partial r^2 + r^{-1} \partial/\partial r$, i.e., polar coordinates with no angular dependence. The steady-state solution to Equation E.1,
obeying boundary condition \( n_s(r_{Au}) = 0 \), where \( r_{Au} \) is the radius of the gold droplet, can then be expressed in terms of the modified Bessel function of the second kind [E3], \( K_0(x) \)

\[
n_s(r) = F \tau_s \left[ 1 - \frac{K_0(r/\lambda_s)}{K_0(r_{Au}/\lambda_s)} \right]
\]

(E.2)

where \( \lambda_s = \sqrt{D_s \tau_s} \) is the surface diffusion length.

If assumption (5) is not valid, i.e., if the separation between the gold droplets is less than \( \lambda_s \), then individual wires compete for the available material and each wire cannot be treated independently. In that case, adatom density \( F \tau_s \) is not reached between the wires in Equation E.2. However, this is not the case for 1 nm gold film, which upon annealing forms droplets separated on average by \( \Delta r_{avg} = 409 \pm 96 \) nm [E1], which is larger than the silicon adatom diffusion length at \( T = 650 \) °C, \( \lambda_s = 200 \) nm [E4,E5].

The adatom flux into the gold droplet, \( J \), which is equal to the flux of silicon atoms incorporated into the wire, is given by

\[
J = -\frac{1}{2} D_s \nabla n_s = -\frac{1}{2} D_s \left( \frac{\partial n_s(r)}{\partial r} \right)_{r_{Au}} = \frac{1}{2} F \lambda_s \frac{K_1(r_{Au}/\lambda_s)}{K_0(r_{Au}/\lambda_s)},
\]

(E.3)

where the factor of \( \frac{1}{2} \) appears due to the assumption 2 about the droplet shape as it was discussed earlier.

The length growth rate \( dL/dt \) of the wire can be expressed as the adatom flux from the substrate into the metal particle multiplied by the droplet circumference, \( \pi r \), divided by the cross-sectional area for growing wire, \( \pi r^2/2 \), plus the contribution from direct impingement on the metal particle,

\[
\frac{dL}{dt} = J \frac{\Omega}{r^2} + 2 \Omega F = 2 F \Omega \left[ 1 + \frac{\lambda_s}{r_{Au}(t)} \frac{K_1(r_{Au}(t)/\lambda_s)}{K_0(r_{Au}(t)/\lambda_s)} \right]
\]

(E.4)
where $\Omega$ is the atomic volume of the growing species. The factor of two appears in the second term due to the fact that the surface area of the quarter-of-a-sphere droplet, $\pi r^2$, divided by the cross-sectional area of the wire, $\pi r^2/2$, is equal to 2.

In order to find the silicon wire length as a function of time from Equation E.4 and compare it to the experiment, one needs to know the radius of a gold droplet as a function of time, $r_{Au}(t)$, which changes during the growth process as a result of both Ostwald ripening of gold droplets and collisions between the wires [E1]. However, as shown in Figure E.2, the average radius of gold droplets reaches its maximum value already after the first 30 min of silicon deposition, so for the purpose of the current discussion, we treat the gold droplet radius as a constant in Equation E.4. We then find that wire length $L$ changes linearly with time,

$$L(t) = C t$$

with the constant of proportionality $C$ equal to

$$C = 2 F \Omega \left[ 1 + \frac{\lambda_s}{r_{Au}^a} \frac{K_1(r_{Au}^a/\lambda_s)}{K_0(r_{Au}^a/\lambda_s)} \right]$$

(E.6)

where $r_{Au}^a$ is the asymptotic value for the average droplet radius (see Figure E.2).

From Equations E.5 and E.6 it follows that any changes in the flux of incoming Si atoms $F$ will affect the wire length as discussed in more detail in the main text of the manuscript.
Figure E.2: Au droplet areal density and radius as a function of Si deposition time. Indicated time values include the initial annealing of a 1 nm Au film for 30 min at 600 ºC and a Si deposition time at 650 ºC. The dashed line shows the asymptotic value of 260 nm for the average droplet radius $r_{\text{Au}}^\circ$.

Low temperature, low flux growth

As was mentioned in the main text of the manuscript, we were able to grow lateral Si wires at 450 ºC by lowering the Si flux, $F = 2.3 \times 10^{14}$ atoms$\times$cm$^{-2}$min$^{-1}$. Figure E.3 shows a representative electron microscopy image for this growth regime.
Figure E.3: Lateral growth of Si wires (circled) on Si (100) substrate at $T = 450$ °C after 2 h.

References:


# Curriculum Vitae

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<table>
<thead>
<tr>
<th>Institution</th>
<th>Location</th>
<th>Degree</th>
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<tbody>
<tr>
<td>Moscow State University</td>
<td>Moscow, Russia</td>
<td>B. Sc. (Materials Science)</td>
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PbS(001) surface with O₂ and air studied with photoelectron spectroscopy and ab initio modeling, Surf. Sci. 605 (2011) 473-482.

