X-ray Absorption Spectroscopy of Ultrathin Nickel Silicide Films: A Theoretical and Experimental Investigation

by

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ABSTRACT

X-RAY ABSORPTION SPECTROSCOPY OF ULTRATHIN NICKEL SILICIDE FILMS: A THEORETICAL AND EXPERIMENTAL INVESTIGATION

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Previous studies have attempted to probe the structure of ultra-thin Nickel silicide films as they evolve in the manufacturing process with limited success. These studies have used ultra-thin Nickel silicide films that were quenched during the manufacturer’s annealing process at select temperatures. This study aims to determine the structure of quenched ultra-thin Ni-Si films using Grazing Incidence X-Ray Absorption Near Edge Spectroscopy (GI-XANES) and ab-initio calculations (FDMNES). Successful calculations were prepared for the $\delta$ and $\theta-Ni_2Si$ phases, as well as the $Ni_3Si_2$, $NiSi$ and $NiSi_2$ phases. The GI-XANES experimental data was taken at the Canadian Light Source, at the Hard X-Ray Microanalysis Beamline (HXMA). XANES and FDMNES are used to identify two phases of the ultra-thin films: the as – deposited phase as a low-ordered $Ni_3Si_2$ phase, and the epitaxial $NiSi_2$ phase was found in samples annealed past 400°C.
Dedication

"There’s a puzzle I work on endlessly, and I’ve got the sides and all the corners, but there’s a space; lost some pieces I can’t replace" - Dan Mangan

For Alicia...
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# Contents

Dedication ................................................................. iii

Acknowledgements ......................................................... iv

1 Introduction ............................................................. 1

1.1 Motivation and History ............................................. 1

1.2 Brief Overview of Project ........................................... 4

2 Theory and Background ................................................. 5

2.1 Introduction to X-ray Absorption Spectroscopy ................. 5

2.2 Finite Difference Method Near Edge Spectroscopy ............ 9

   2.2.1 Interaction of Light with Matter ......................... 10

   2.2.2 Calculation Schematic: Finite Difference Method ....... 13

   2.2.3 Density Functional Theory: The Potential ............... 16

   2.2.4 Multiple Scattering Theory vs. FDM .................... 19

3 Experimental Data and Analysis .................................... 22

3.1 Bulk Standards: The H-Series .................................... 23

   3.1.1 Bulk Standard Methodology .............................. 24

3.2 Ultra-thin Temperature Series ................................... 25
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1 Bragg Peak Elimination</td>
<td>77</td>
</tr>
<tr>
<td>5.2.2 Core Hole</td>
<td>78</td>
</tr>
<tr>
<td>5.2.3 Temperature Resolution</td>
<td>78</td>
</tr>
<tr>
<td>Appendix A</td>
<td>79</td>
</tr>
<tr>
<td>Appendix B</td>
<td>82</td>
</tr>
<tr>
<td>Appendix C</td>
<td>85</td>
</tr>
<tr>
<td>Bibliography</td>
<td>86</td>
</tr>
</tbody>
</table>
List of Tables

3.1 The seven standard H-series samples used in this study . . . . . . . . . 23
3.2 Edge Shifts of the ultra-thin film temperature series . . . . . . . . . . 32
4.1 Internal basis of FDMNES. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 53
# List of Figures

2.1 X-ray Absorption Spectroscopy experimental schematic for transmission mode. .................................................. 6

2.2 Schematic of spectra from an isolated atom and cluster of atoms. ................................................................. 7

2.3 Discrete line of points at $r + h^+$ and $r - h^-$ .............................................................. 14

2.4 FDMNES calculation schematic [13] .......................................................... 17

2.5 The muffin-tin, approximation and full periodic potential schematics [13] 20

3.1 Bulk Nickel silicide phase diagram [5]: Showing a wide selection of Nickel phases dependent upon % silicon, and temperature. ........................................... 24

3.2 Bulk standard sample spectra [18], and their derivatives, both to be used as reference for theoretical modelling with FDMNES. ........................................ 25

3.3 Experimental set-up for XANES measurements of the temperature series samples. .......................................................... 27

3.4 Temperature series spectra for $E_\parallel$ and $E_\perp$ are virtually indistinguishable. 28

3.5 Temperature series spectra for 200°C, 300°C, 400°C, 500°C and 700°C 29
3.6 Top: Temperature series spectra, overlaid to make apparent the variation between spectra. Below left: the Nickel rich bulk phases: $H4-H6$, $\theta-Ni_2Si$, and their derivatives that are comparable to as–deposited $200^\circ C, 300^\circ C$. Below right: $NiSi$ and $NiSi_2$ and their derivatives, comparable to $400^\circ C, 500^\circ C$ respectively.

3.7 Edge shifts of the ultra-thin film temperature series.

3.8 Experimental set-up for XANES measurements of the control $\theta-Ni_2Si$ samples.

3.9 Comparison of the IBM Watson center $\theta-Ni_2Si$ samples, and two control samples: 10nm and 50nm thick.

4.1 Structure of $\delta-Ni_2Si$, Ni in green (site 1) and yellow (site 2), and Si in grey.

4.2 Best fit model of $\delta-Ni_2Si$.

4.3 Site specific spectral calculations for $\delta-Ni_2Si$ overlaid with bulk standard spectra.

4.4 Structure of $\theta-Ni_2Si$, Ni in green (site 1) and yellow (site 2), and Si in grey.

4.5 Best fit model of $\theta-Ni_2Si$.

4.6 Site specific spectral calculations for $\theta-Ni_2Si$.

4.7 Structure of $Ni_3Si_2$, Ni in blue, and Si in grey.

4.8 Best fit model of $Ni_3Si_2$.

4.9 Site specific spectral calculations for $Ni_3Si_2$.

4.10 Structure of $NiSi$, Ni in blue, and Si in grey.

4.11 Best fit model of $NiSi$.

4.12 Structure of $NiSi_2$, Ni in blue, and Si in grey.
4.13 Best fit model of NiSi$_2$. ................................. 47
4.14 Polarization Dependence Modelling of $\delta - Ni_2Si$ and NiSi$_2$. ............................... 51
4.15 Polarization plane generated for a rotation about axis (1,0,0), with rotation point at (0.5,1,0). ........................................ 55
4.16 Modelled effect of sample rotation during spectral measurements for select surface orientations of $\delta$ and $\theta - Ni_2Si$. ............................. 56
4.17 Individual spectral calculations for $\theta - Ni_2Si$ rotated about perpendicular axes. ......................... 57
4.18 Cluster size dependence of NiSi, taken at Ni shell +0.1Å, for approximately 1Å intervals, from 2Å- 8.05Å. ............................. 60
4.19 The bulk as – deposited spectral comparison with Nickel foil. ........................................... 62
4.20 2nm as – deposited spectral comparison with Nickel rich phases. ........................................... 63
4.21 2nm as – deposited spectral comparison with FDMNES model of $\delta$ and $\theta$ for long range order, and short range (inclusion of the first Ni shell information only). ................................. 67
4.22 2nm as – deposited spectral comparison with FDMNES small grain model of $\delta$. ........................................... 68
4.23 2nm as – deposited spectral comparison with FDMNES small grain model of Ni$_3$Si$_2$. ......................... 71

1 The 4 node computer cluster, for FDMNES calculations. ................................. 80
Chapter 1

Introduction

1.1 Motivation and History

The interest in Nickel silicides’ application in electronics began in the mid-1970’s. It started predominantly as an interest in the chemical phase of silicide $NiSi_2$. The particular interest lay primarily with the sharp atomic transition between $NiSi_2$ and $Si$ as an ideal system for modelling Shottky barrier height that occurs when preparing conductive contact materials in microelectronics.

The Shottky barrier is a potential that is created between conductive materials and semiconductors – $\sim 0.7eV$ for $NiSi_2$ when they are attached to one another; whereby a depletion or accretion region of electrons forms at the interstitial boundary between materials. The result being that the contact point of a metallic material with a semiconductor can be used to create n-type or p-type diodes. This formation is undesirable in the fabrication of conductive contact materials, for obvious reasons. It is thought that the Shottky barrier height is determined by the interface between substrates and the metallic material.

In the case of $NiSi_2$ the lattice constant mismatched with $Si(001)$ by only 0.4%
The result is a relatively low barrier height, when compared to other transition metals, attributed to the almost matching interfaces of Si and NiSi₂, meant that the use of this phase as a conductive material would ensure a more ohmic contact at the terminals of transistors.

There were however a litany of drawbacks to using NiSi₂ as a conductive contact material. First of all, NiSi₂ is not a very good conductor. Another drawback to NiSi₂ is that the very thing that lead to the interest in the material in the first place: the matching lattice constants, also leads to epitaxial growth on silicon substrates. This creates inherent complications with the manufacturing of these films: since the material favours growth directions along the crystalline substrate, it would often form outside of the intended contact areas.

Further complicating things, the phase diagram of nickel silicides includes 6 phases that are stable at room temperature. It proved difficult to create a fool-proof manufacturing process for consistently producing any one phase of nickel silicide. With this, despite there being interest in the study of nickel silicides for microelectronics since the seventies, it took a back seat in the nineties to other silicides with less complicated bulk phase diagrams, like Ti − Si and Co − Si. Nearing the end of the nineties however, there was a rebirth of interest in these materials by manufacturers.

The renewed interest in nickel silicide films began, in particular, after the failures of Ti − Si and Co − Si as conductive materials for use below 0.2μm. The breakdown in the operation of the Ti and Co based films came from discontinuity between the known bulk material properties and those of their nanoscale films. These Ti and Co nanoscale materials would enter new phases, previously not known (or available to them) in the energies used in the standard manufacturing process. Sometimes this would result in phases of high resistivity or worse, agglomeration in the films which
would create a physical break in the circuit. [30] [17]

It turns out that the whole nickel silicide series phase diagram is well behaved with film thickness down to 45nm—the standard in use today. So, the search began for a suitable bulk phase of nickel silicide for use as a contact material. As mentioned, the presence of high resistivity phases within integrated circuits is undesirable. These are the silicon rich phases, such as $NiSi_2$. Nickel rich phases, however, diffuse rapidly into silicon leading to unexpected and varying resistances. The phase of choice for manufacturers was then $NiSi$ which offers a trade-off between resistivity and diffusivity.

As with $Ti-Si$ and $Co-Si$, however, nickel silicides will cease to abide by the current bulk phase diagram as the films are pushed to even smaller thicknesses. So, as electronic devices move below the 45nm form factor it is crucial to understand the formation and structure of these nickel contact materials in order to avoid forming the highly resistive or diffusive phases. [17] [3] [8]

The current understanding of nickel silicide films’ phase sequence fails as film thicknesses drop below 10nm. If one can characterize the phases present in these so-called ultra-thin nickel silicide films, it will aid in the future application of these silicides for uses below 10nm. Here, then is the crux and motivation for this project: To identify any phases of ultra-thin nickel silicide films in samples that have been annealed to different temperatures. This will be accomplished through a combination of x-ray Absorption spectroscopy and ab-initio calculations using density functional theory.
1.2 Brief Overview of Project

With motivation in hand, it is worth momentary pause to discuss the format of this thesis project. Offered below is a brief synopsis of the upcoming chapters, summaries that serve to map the execution of this theoretical and experimental investigation.

The hardest feat to tackle with this project turned out to be the use of ab-initio calculations. The theoretical modelling software that was used is expansive (to say the least) and so, much of the discussion in Chapter 2 will be a background on the modelling and its relation to x-ray absorption spectroscopy.

Chapter 3 will present an overview of the experimental results. These consist of known Ni-Si bulk samples recaptured from previous work by Kevin Miller [18], these will be used as standards, as well as a series of ultra-thin (2nm) Ni-Si films for which the phases are unknown. A comparison between bulk standards and the unknown samples is talked about in this chapter as well, and some ultra-thin films are identified.

In Chapter 4, the uses of the theoretical model are established by first fitting the bulk standard spectra, and preforming analysis. A novel use of the theoretical model that was used to detect a systematic problem within the x-ray Absorption experiments will be presented. Finally, the pièce de résistance, comes at the end of Chapter 4 where the theoretical model is used to identify the parent phase of the ultra-thin film series.

The Conclusion, Chapter 5, will then wrap up the project, summarizing and discussing the results of this work. At the end of Chapter 5 there will be some discussion on the future outlook for this project, what should be looked at in future, and how the experimental technique can be tweaked for improvement.
Chapter 2

Theory and Background

2.1 Introduction to X-ray Absorption Spectroscopy

The experimental side of this project was solely based on a technique referred to as X-ray Absorption Spectroscopy, or XAS. There are multiple derivatives of XAS, the technique applied in this study being: X-ray Absorption Near Edge Spectroscopy, or XANES, which is not much unlike Extended X-ray Absorption Fine Structure, or EXAFS. These two techniques being the most common experimental derivatives of XAS.

As the name suggests, the XAS technique refers to the process of measuring the absorption of x-ray light through a sample. Of course, there is a broad spectrum of x-rays that could be used for XAS, in particular, the focus of this discussion will be on using hard x-rays. The basic setup for any XAS experiment requires four components. The first component required is a monochromatic x-ray source, often this source is a synchrotron beam-line equipped with an insertion device (undulator or wiggler). The second component is a detector to measure the incoming photon flux, or intensity ($I_0$) of the source while being practically transparent to the source itself. Often this
is accomplished using an ion chamber. The third, and the most crucial part of any experiment is the sample, here it is placed downstream from the first detector. The final component required is a second detector, depending on the experiment (sample concentrations, geometrical considerations), there are two configurations: either an ion chamber downstream from the sample is used to measure transmitted intensity ($I_1$), or an area detector (e.g. a solid state detector), perpendicular to the beam is used to measure the light fluoresced by the sample (the area detector must be perpendicular to the sample in order to avoid measuring scattered light resulting from excited electron dipoles within the material). The first configuration is referred to as transmission mode, and is the simplest to consider for the purposes of this introduction; a schematic of the setup can be seen in Figure 2.1. Both configurations, however can be used to measure the x-ray absorption. Though it should be noted that transmission is particularly adept at measuring samples with large concentrations, and fluorescence necessitates low concentrations to avoid the effects of self absorption.

Figure 2.1: X-ray Absorption Spectroscopy experimental schematic for transmission mode.

When an x-ray enters a material, there are different ways that its intensity is attenuated or absorbed. As the X-ray penetrates deeper into a material, its intensity
is attenuated in an exponential fashion:

\[ I_1 = I_0 e^{\mu \cdot x} \]  \hspace{1cm} (2.1.1)

where, \( \mu \) is the x-ray absorption, and \( x \) is the sample thickness, for which it is standard practise to prepare the sample such that \( x \approx \frac{1}{\mu_0} \). Here \( \mu_0 \) is the resonant absorption amplitude. The natural log of equation (2.1.1) then becomes:

\[ \mu = \ln \left( \frac{I_0}{I_1} \right). \]  \hspace{1cm} (2.1.2)

where \( \mu_0 \) has been normalized. An absorption spectrum can be obtained by measuring incoming and transmitted beam intensities for a range of incoming x-ray energies.

An x-ray absorption curve is in general monotonically decreasing, but at certain x-ray energies, which coincide with the energy of a particular bonding orbital, will result in a resonant absorption. Figure 2.3(a) shows schematically the K-edge absorption
spectrum for an isolated atom, which occurs when the energy of the incoming photon is tuned to the binding energy of the 1s electron.

Once the K-shell electron has absorbed a photon, it is ejected from its atomic potential well. With multiple atoms present within the vicinity of the absorption centre, the ejected photoelectrons scatter off of neighbouring atoms introducing an intensity modulation to the single atomic spectrum. This means that the oscillation seen in Figure - 2.3(b) contains information about the scattering path of the ejected photoelectrons, that is, the atomic structural information.

When focused on the energies immediately following the K-edge jump, XAS is referred to as K-edge XANES. XANES is defined in this thesis as the spectral region up to $\sim 50\text{eV}$ after the edge jump. Here, the ejected photo-electron wave has just barely enough energy to escape the atomic potential well, and so it is sensitive to the inter-atomic, or molecular potential dictated by the configuration of the neighbouring atoms.

These spectra serve as unique chemical fingerprints which can then be used to identify materials through the known spectra taken from relevant reference materials. This methodology requires a large catalogue of fingerprint spectra to compare against, and so without access to large database of spectra, can be difficult to enact and is sometimes impossible.

Most of this summary section was sourced from Introduction to XAFS, by G. Bunker [1], which is a good knowledge-base for all things X-ray Absorption. This section should have provided a thorough enough understanding of how one can obtain absorption spectra, however, and any further inquiries can be directed to the text just noted.

The following section offers a look at a different methodology from that previously
mentioned for identifying materials and shows how one can use a computational model to produce absorption spectra.

2.2 Finite Difference Method Near Edge Spectroscopy

Coupled with the experimental XANES, this thesis incorporates a theoretical tool for modelling XANES spectra computationally. The tool that is used is a software package, entitled Finite Difference Method Near Edge Spectroscopy, or FDMNES \[13\]. In order to have any reliance upon any theoretical model it is paramount that the physics behind the calculation is understood. As well, it is important to have a working knowledge of the limitations inherent with the specific physical model, or computational schematic. It is the intent that in the following section the full-potential theoretical model calculation performed by the program FDMNES will be explained with enough rigour so as to instil faith in its output. As well, it is the aim to emphasize the strengths and the limitations of the FDMNES method so as to develop a sense of what experimental systems this tool is expected to be in agreement with, and ultimately to establish an intuitive sense as to the degree to which it can be relied on.

The first step in understanding FDMNES is in taking a more in depth look at the x-ray absorption process. Specifically, the interaction of light with matter. Following this, it will be necessary, albeit not intuitive, to describe the numerical finite difference method; with a thorough understanding of the FDM in hand the usage and connection to our discussion of light’s interaction with matter will become apparent. The next step is to solidify the preceding steps by describing a rough schematic of how to use the finite difference method in the atomic cluster framework prescribed by Joly.
Lastly, once convinced of the usefulness of this computational method, the gaps remaining in the schematic will be filled by a discussion about the calculation of the inter-atomic potential in the cluster.

2.2.1 Interaction of Light with Matter

As is the case with the majority of interactions, it is useful to start by looking at the general Hamiltonian,

\[ H = H_{\text{matter}} + H_{\text{light}} + H_{\text{int}} \]  \hspace{1cm} (2.2.1)

where \( H_{\text{matter}} \) and \( H_{\text{light}} \) are the Hamiltonians of the material and the electromagnetic field respectively. \( H_{\text{int}} \) is the time-dependent interaction between light and matter. There is little to be gained through the quantum mechanical treatment of light, and so the classical description of light is adopted; as well, for the remainder of this discussion the dipole approximation will be used. Since the matter Hamiltonian can be thought of as time independent, the full Hamiltonian can be expressed in terms of the interaction picture as:

\[ H \approx H_{\text{matter}} + H_{\text{int}}(t) = H_0 + V(t), \]  \hspace{1cm} (2.2.2)

where,

\[ H_0 = \frac{\hat{p}^2}{2m} + qV, \]  \hspace{1cm} (2.2.3)

\( V \) is the potential within the material, and \( V(t) \) is a small, radiative field induced, perturbation to the otherwise neutral atomic cluster (matter) Hamiltonian, caused by the presence of light,

\[ V(t) \approx \frac{e}{m} \hat{p} \cdot \vec{A}. \]  \hspace{1cm} (2.2.4)
where \( e, m, \) and \( \vec{A} \) are the electron charge, electron mass, and the E & M vector potential, respectively. Using the fundamental result of time-dependent perturbation theory, \( V(t) \) can be used to calculate the probability of transition from one state to another:

\[
W_{fi} = \frac{2\pi}{\hbar} \cdot |\langle f | V(t) | i \rangle|^2 \cdot \rho_f, \tag{2.2.5}
\]

where, \( \rho_f \) is the density of states at \( E_f \), and \( \langle f \rangle \) and \( |i\rangle \) are final and initial electron states, respectively. Equation \( 2.2.5 \) is known as Fermi’s Golden Rule, it gives the transition probability, per unit time. Specific to this case, it gives the probability that a photon of specific energy \( \hbar \omega \) will induce a transition of an electron at a given point in k-space all dependent upon the electromagnetic perturbation, \( V(t) \). \( W_{fi} \) can be expressed less formally as:

\[
W_{fi} = \text{transition probability/} \text{unit time}. \tag{2.2.6}
\]

In the case of x-ray absorption spectroscopy, the probability of an atomic state transition occurring is contingent upon an absorption event occurring for a given frequency of light, and hence \( W_{fi} \) is linearly related to the linear absorption coefficient \( \mu_{abs} \), which is defined as:

\[
\mu_{abs}(\omega) = \frac{\text{number of transitions/unit volume/unit time}}{\text{incident photon flux}}. \tag{2.2.7}
\]

The number of transitions per unit volume per unit time is simply the multiplication of the \( W_{fi} \) by the number of absorbing atoms per unit volume, that is \( \rho_a \), the atomic density. The incident photon flux is nothing more than the time averaged magnitude of the Poynting vector, \( \langle S \rangle \), divided by energy \( \hbar \omega \). Now, putting this all together with Equation \( 2.2.5 \), one obtains a more workable definition of absorption:

\[
\mu_{abs}(\omega) = \frac{\rho_a \cdot \frac{2\pi}{\hbar} \cdot |\langle f | V(t) | i \rangle|^2 \cdot \rho_f}{\langle S \rangle / \hbar \omega}. \tag{2.2.8}
\]
For monochromatic plane wave light, working in the coulomb gauge and concerning ourselves with only the real component:

\[
\vec{A} = \vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)
\]

\[
\vec{E} = -\frac{d\vec{A}}{dt} = \vec{E}_0 \sin(\vec{k} \cdot \vec{r} - \omega t)
\]

\[
\vec{B} = \vec{\nabla} \times \vec{A} = \vec{B}_0 \sin(\vec{k} \cdot \vec{r} - \omega t)
\]

where, \(\vec{B}_0 = \frac{\hbar}{c} \vec{E}_0\), \(\vec{E}_0 = \omega \vec{A}_0\) and,

\[
\vec{A}_0 = \vec{\varepsilon} \cdot \sqrt{\frac{\hbar}{2 \varepsilon_0 V \omega_k}}.
\]

One can then calculate the time averaged Poynting vector to be:

\[
\langle S \rangle = \frac{1}{\mu_0} \langle \vec{E}_0 \times \vec{B}_0 \sin^2(\vec{k} \cdot \vec{r} - \omega t) \rangle
\]

\[
= \frac{1}{2 \mu_0} (\vec{E}_0 \times \vec{B}_0) = \frac{1}{2 \mu_0 c} E_0^2
\]

\[
= \frac{1}{2} \sqrt{\frac{\varepsilon_0}{\mu_0}} E_0^2 = \frac{\varepsilon_0 c}{2} E_0^2.
\]

The absorption coefficient is quantum mechanical in nature Equation - \(2.2.8\). It is still helpful to think of the absorption process in a classical analogue, in terms of the directly related cross-section, which is: \(\sigma = \frac{\hbar \omega}{\mu_0}\); this relation with the linear absorption coefficient can be used in conjunction with Equations - \(2.2.8\) and \(2.2.11\) to give an expression for the cross-section:

\[
\sigma = \sum_f \frac{\hbar \omega \cdot \frac{2\pi}{\hbar} \cdot |\langle f| \frac{e}{m} \vec{p} \cdot \vec{A} |i \rangle|^2 \cdot \rho_f \cdot \varepsilon_0 c}{\frac{\varepsilon_0}{2} E_0^2}.
\]

Here, \(\vec{A}\) in Equation - \(2.2.9\) can be rewritten as:

\[
\vec{A} = \frac{\vec{A}_0}{2} (e^{i(k \cdot \vec{r} - \omega t)} - e^{-i(k \cdot \vec{r} - \omega t)}).
\]

Now, the only component of \(\vec{A}\) that will invoke a transition that absorbs energy has the time dependency of \(e^{-i\omega t}\), and so the \(e^{i\omega t}\) (emission transition) term can be
dropped [21]. Using this, Equation - 2.2.12 becomes,

\[
\sigma = \frac{4\pi \omega}{\varepsilon_0 c} \cdot \frac{e^2}{m^2} \cdot \frac{A_0^2}{4E_0^2} \sum_f |\langle f | \hat{\epsilon} \cdot \hat{p} e^{i\hat{k} \cdot \hat{r}} | i \rangle|^2 \cdot \rho_f
\]

\[
= \frac{\pi \omega}{\varepsilon_0 c} \cdot \frac{e^2}{m^2} \cdot \frac{E_0^2}{E_0^2} \sum_f |\langle f | \hat{\epsilon} \cdot \hat{p} e^{i\hat{k} \cdot \hat{r}} | i \rangle|^2 \cdot \rho_f
\]

\[
= 4\pi^2 \frac{\hbar}{m^2 \omega} \cdot \frac{e^2}{4\pi \varepsilon_0 \hbar c} \cdot \sum_f |\langle f | \hat{\epsilon} \cdot \hat{p} e^{i\hat{k} \cdot \hat{r}} | i \rangle|^2 \cdot \rho_f
\]

\[
= 4\pi^2 \frac{\hbar}{m^2 \omega} \cdot \alpha \cdot \sum_f |\langle f | \hat{\epsilon} \cdot \hat{p} e^{i\hat{k} \cdot \hat{r}} | i \rangle|^2 \cdot \rho_f
\]  

(2.2.14)

where, \( \alpha \) and \( \hat{\epsilon} \) are the fine structure constant and light polarization vector, respectively. It can be helpful to visualize the electrons in the sample material as a collection of moving targets that change their cross-section depending upon which final states are available, the energy of the incoming x-rays, and the density.

The end game of the theoretical model will be to complete the integral in (Equation - 2.2.14) computationally. This will be done by either calculating values for the available final states, and then solving for \( \sigma \) directly, or alternatively, using a self consistent multiple scattering theory calculation using Green’s functions. Once a value for the cross sectional area is calculated for all energies to be in the calculated spectrum, a theoretical absorption spectra can be produced.

### 2.2.2 Calculation Schematic: Finite Difference Method

The numerical method used in FDMNES to solve the Schrödinger equation, is called the finite difference method, which allows for the use of exact potentials. The finite difference method is a generalized way to solve differential equations, it works by discretizing second order derivatives [13].

It is a worthwhile endeavour to look at how one can discretize the Laplacian found in the Schrödinger Equation. This can be done by first looking at the Laplacian in one
The figure illustrates a discrete line of points at \( r + h^+ \) and \( r - h^- \). The second step is to express the electron wavefunctions at \( r + h^+ \) and \( r - h^- \) in terms of a Taylor expansion up to third order, that is,

\[
\psi(r \pm h^\pm) = \psi(r) \pm h^\pm \psi'(r) + \frac{h^\pm 2}{2} \psi''(r) \pm O(h^\pm 3). \tag{2.2.15}
\]

Defining \( \psi(r + h^+) \equiv \psi^+ \) and \( \psi(r - h^-) \equiv \psi^- \), then the two expressions in Equation 2.2.15 can be summed as:

\[
\psi^+ + \psi^- = h^+ \psi'(r) - h^- \psi'(r) + 2\psi(r) + \frac{h^+ 2}{2} \psi''(r) + \frac{h^- 2}{2} \psi''(r) + O(h^\pm 3). \tag{2.2.16}
\]

If the inter-space lengths are equivalent, then this sum simplifies,

\[
\psi^+ + \psi^- = 2\psi(r) + h^2 \psi''(r) + O(h^3). \tag{2.2.17}
\]

With some further rearranging of Equation 2.2.17 and expressing \( \psi''(r) \) as \( \frac{d^2 \psi(r)}{dr^2} \), the following expression for the Laplacian in one dimension is obtained:

\[
\frac{d^2 \psi(r)}{dr^2} = \frac{1}{\hbar^2} [\psi^+ + \psi^- - 2\psi(r)]. \tag{2.2.18}
\]

The form of Equation 2.2.18 indicates that second order derivatives of \( \psi(r) \) can be represented in terms of the wavefunctions of nearest neighbours at \( r + h \) and \( r - h \), and \( r \). This is the discretized Laplacian in 1-D.

By substituting our recently derived discretized Laplacian into the Schrödinger equation, one obtains a one dimensional, linear, equation, in which each wavefunction...
solution is interdependent with the wavefunction solution at the nearest neighbouring points. That is the Schrödinger equation,

\[ [-\nabla_i^2 + V(r_i)]\psi(r_i) = E(r_i)\psi(r_i), \]

becomes,

\[-\frac{1}{\hbar^2} \left( \psi^+ + \psi^- - 2\psi(r_i) \right) + V(r_i)\psi(r_i) = E(r_i)\psi(r_i). \]

If the boundary conditions for the line are known, in principle, the linear equations can be iteratively solved for the wavefunction’s value at each point on the line. This expression can be generalized to 3 dimensions in a natural way (see Equation - (2.2.19)) to obtain one large system of linear equations connecting the values of wave functions at every point on the grid to the wave functions of its nearest neighbours. In a three-dimensional (3-D) net of points, naming \( \psi_j \) the values of the wave function on the neighbouring points of central point \( i \), one gets for the Schrödinger equation on point "i" [13]:

\[ -\sum_{j=x,y,z} \left( \frac{\psi_j^+ + \psi_j^-}{\hbar_j^2} \right) + 2\psi_i \left( \frac{1}{\hbar_x^2} + \frac{1}{\hbar_y^2} + \frac{1}{\hbar_z^2} \right) + V_i \psi_i = E_i \psi_i. \quad (2.2.19) \]

This 3-D linear system would be difficult to solve by hand, fortunately it can be solved computationally through the Gauss-Seidel method [2], so long as there are valid boundary conditions on the calculation.

The boundaries, which allow for the iteratively produced solution, in the case of our calculation the atomic cores distributed in the crystalline structure, and the edge of our spherical calculation space decided upon at run time. This completely determines the calculation schematic seen in Figure - [2.4] [13]. The entire calculation is divided into three zones:
• The first zone contains the atomic cores, here the wavefunctions are approximated by the standard radial atomic wavefunctions. The potential is the spherical coulombic potential.

• In the third zone the wavefunctions are assumed to be free, a complete set of wavefunctions is expressed in terms of an expansion of spherical harmonics. Here the potential is assumed constant, akin to a muffin-tin potential approximation (more on this in Section 2.2.4), but for all points exterior to the calculation range.

• In the second zone the Finite Difference Method is used to solve the Schrödinger Equation for the inter-atomic wavefunctions, this region shares two boundaries of continuity, one between the atomic core region, Zone 1, and the other being the outer sphere region determined by calculation cluster size, Zone 3. The molecular orbital potential that comprises this region is determined via a density functional theory calculation.

2.2.3 Density Functional Theory: The Potential

Density Functional Theory is increasingly popular tool being used across a broad spectrum of scientific disciplines (See for example [23]). The intent of this section is to outline in brevity the core components of density functional theory (DFT), and to describe the particulars of its use in calculating a full potential for our cluster model.

First off, a little bit of background, DFT had its first real introduction to the world in 1965, the mathematical preliminaries being developed by Kohn and Sham together in their paper entitled "Self-Consistent Equations Including Exchange and Correlation Effects" [16]. In which they describe a method, similar to that of Hartree
Fock, that allows for a self consistent calculation of potentials of inhomogeneous electron gases, one that includes exchange and correlation effects similar in spirit to "the well known methods of Thomas-Fermi and the Slater exchange hole" [16]. They start first by expressing the ground state energy of inhomogeneous system as follows:

$$E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + G[n(\mathbf{r})],$$

where the first term is the Coulomb interactions between the electrons and the nuclei, the second term is the Coulomb interactions between pairs of electrons and the third term $G[n(\mathbf{r})]$ is a function of the function of electron density, $n(\mathbf{r})$, read: a functional of electron density. That is $G$ is a mapping of electron density to energy, and can be expressed as the sum of two components, the kinetic energy of non-interacting electrons, $T[n(\mathbf{r})]$, and the exchange and correlation energy of an interacting system, $E_{xc}[n(\mathbf{r})]$ [16].

The most important thing to grasp from the above is that the ground state energy
of the system is being expressed entirely in terms of density. Furthermore, even though the explicit form of the functional $E_{xc}[n(r)]$ is unknown, what is known is that, whatever the form, the correct electron density must minimize the ground state energy. The distillation of the work of Kohn and Sham is that one can use the one-electron Schrödinger equation,

$$\left\{ \frac{\nabla^2}{2} + \left[ \phi(r) + \mu_{xc} \right] \right\} \psi_i(r) = \epsilon_i \psi_i(r),$$  \hspace{1cm} (2.2.21)

and $\phi(\vec{r})$ is the Hartree potential:

$$\phi(\vec{r}) = v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r'},$$  \hspace{1cm} (2.2.23)

and $\mu_{xc}[n(\vec{r})]$ is the chemical potential coming from the exchange and correlation potential, $\epsilon_{xc}$ (which is defined phenomenologically and differently across individual DFT algorithms),

$$\mu_{xc}[n(\vec{r})] = \frac{dn \epsilon_{xc}(n)}{dn}.$$  \hspace{1cm} (2.2.24)

Equations 2.2.20-2.2.24 can be used to calculate the electron density self-consistently. The process is straightforward, one starts by guessing a form for $n(\vec{r})$, this is used to calculate the Hartree potential 2.2.23 and the chemical potential 2.2.24. Once the potentials are calculated, they can be used to solve for the one-electron wavefunctions in the one-electron Schrödinger Equation 2.2.21. Then finally, with the one-electron wavefunctions in hand, the density function can be updated using 2.2.22. If the density function obtained from solving 2.2.21 is the same as the density function used to calculate the potentials initially (within some tolerance value), then this is a good
representation ground state density function. If the two functions are not within some threshold, then one updates \[2.2.23\] - \[2.2.24\] by checking which values of \( n(r) \) minimize \[2.2.20\] and repeats the process again until the density functions are the same.

Now, so far an integral part to the calculation has been glossed over—the exchange and correlation functional. The form of which has yet to be disclosed. The exchange and correlation functional is the piece of the puzzle that separates out different Density Functional Theory based solutions. In the case of Finite Difference Method, the exchange correlation functional is of the Hedin-Lundqvist type \[13\].

**Hedin-Lundqvist** One of the difficulties in applying the Kohn-Sham theory to aid in the calculation of a XANES spectra, is that our potential is no longer in the ground state. In fact, any material under investigation with x-ray absorption would find the ground state potential altered by the existence of quasi-holes due to a missing core-level electron. What Hedin-Lundqvist \[7\] offered in their paper in 1971 is an interpolation scheme to construct an excitation energy independent exchange and correlation potential that attempts to model the excited state effects. The method is more of phenomenologically based model, but the end result is a more realistic calculation of the potential using DFT. \[6\]

### 2.2.4 Multiple Scattering Theory vs. FDM

Multiple Scattering Theory, or MST is an alternative method for calculating the x-ray absorption probability. This model of solution is tried and tested in software such as FEFF \[22\], so an in depth review of the calculation method is not necessary.

The most important defining difference between MST and FDM is in the potential used for calculations. Figure - \[2.6(a)\] shows the 2-D potential for FDM method, while
Figure 2.5: The muffin-tin, approximation and full periodic potential schematics

(a) Full molecular orbital modeling

(b) Muffin-tin potential

Figure - 2.6(b) shows the potential for MST. The finite difference method allows for the use of a full potential for the atomic cluster; whereas, the MST method relies upon the so-called muffin-tin potential. The muffin-tin potential carries a fairly crude approximation in the inter-atomic region. The problem with this approximation is that XANES is primarily dealing with ejected photoelectron excitation energies that are just barely able to escape the atomic potential well. In this sense, XANES is particularly sensitive to the shape of the inter-atomic potential. This means that FDM is expected to produce a more accurate calculation of XANES when compared to MST [13].
The question then becomes: why use MST calculations at all? The answer is one of a practical nature, MST calculations are much less computationally expensive than their FDM counterparts. Analogously, this means that a calculation that could take hours with the MST method, may take days using FDM. Secondly, the less physically relevant potential used in MST is not that inaccurate an approximation when dealing with higher photoelectron energies.

The decision of when to use MST or FDM can often be a difficult one. There is no set rule in weighing the trade-off between computational speed and physical accuracy. In some cases, one is forced to use MST on account of the FDM calculation requiring more computational resources than those available. In others the FDM calculation must be used in order to obtain satisfactory results. The calculations performed for this study aimed to use FDM whenever computationally possible, reserving MST only for the cases in which FDM could not feasibly be used.
Chapter 3

Experimental Data and Analysis

For the purposes of this study, all but two samples were prepared at IBM Watson Research Centre, in processes mimicking the industrial processes used by IBM. The samples can be subdivided into three sets: the bulk IBM H-Series, the IBM ultra-thin film temperature series, and two other samples provided by IBM that were produced elsewhere as controls on the reproducibility of the sample preparation process.

This chapter will focus on the introduction of these three sample types, giving a schematic as to their preparatory processes, an overview of the experiments performed, and the data obtained will be provided here. Following the reported spectral data for each series a methodology will be charted out for their inclusion into this project. A brief preliminary discussion and analysis is performed here as well to lay the groundwork for the case studies which will be discussed in Chapter 4, with special focus taken on the ultra-thin film materials.
3.1 Bulk Standards: The H-Series

The first preparatory process results in the development of bulk material standards. These are referred to by IBM as the H-Series, and were used in a previous study done by Kevin Miller [18]. Of the ten standard samples used in his study, only seven are used here, as seen in Table - 3.1. Also included in Table - 3.1 are the lattice constants extracted from the diffraction data previously obtained by M. Tremblay [26].

Table 3.1: The seven standard H-series samples used in this study

<table>
<thead>
<tr>
<th>Phase:</th>
<th>Bulk Structure:</th>
<th>Sample Code</th>
<th>Lattice Constants</th>
<th>w.t.% Silicon</th>
<th>Stratum Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>$Fm - 3m$</td>
<td>H2</td>
<td>$a, b, c = 3.524$</td>
<td>0</td>
<td>200nm</td>
</tr>
<tr>
<td>Ni$<em>{31}$Si$</em>{12}$</td>
<td>$P3_21$</td>
<td>H4</td>
<td>$a, b = 6.671$ ; $c = 12.288$</td>
<td>$\sim 14$</td>
<td>200nm</td>
</tr>
<tr>
<td>$\delta - Ni_2Si$</td>
<td>$Pcmn$</td>
<td>H5</td>
<td>$a = 7.39$ ; $b = 9.90$ ; $c = 7.03$</td>
<td>19.3</td>
<td>200nm</td>
</tr>
<tr>
<td>$\theta - Ni_2Si$</td>
<td>$P63mmc$</td>
<td>Theta</td>
<td>-</td>
<td>26.5</td>
<td>110nm</td>
</tr>
<tr>
<td>Ni$_3$Si$_2$</td>
<td>$Cmc2_1$</td>
<td>H6</td>
<td>$a = 12.29$ ; $b = 10.8050$ ; $c = 6.924$</td>
<td>$\sim 24$</td>
<td>200nm</td>
</tr>
<tr>
<td>NiSi</td>
<td>$Pnma$</td>
<td>H7</td>
<td>$a = 5.233$ ; $b = 3.258$ ; $c = 5.659$</td>
<td>32.4</td>
<td>200nm</td>
</tr>
<tr>
<td>Ni$_3$Si$_2$</td>
<td>$Fm - 3m$</td>
<td>H8</td>
<td>$a, b, c = 5.416$</td>
<td>48.9</td>
<td>200nm</td>
</tr>
</tbody>
</table>

The standards are created by first vapour depositing silicon onto a silicon (001) substrate, and then allowing exposure to oxygen to form a $SiO_2$ cap. Following this, nickel is vapour deposited atop the $SiO_2$ layer, and the sample is annealed up to the appropriate temperature, using the standard ramping process at IBM, and the known phase diagram in Figure - 3.1 at which point it is quenched. Further information about the samples is available from previous work done by K. Miller [18].
3.1.1 Bulk Standard Methodology

X-ray Absorption spectra of these standard samples were taken in previous studies done at the HXMA-CLS beam-line, by K. Miller. These spectra can be seen in Figure 3.2 and are used in the study as benchmark points for the theoretical modelling of spectra, and for further understanding of these phases. Using the crystallography data, obtained from XRD, and XANES spectra an adequate modelling of these bulk samples is possible, opening the door for the modelling of Ultra-thin Nickel silicide samples.
Figure 3.2: Bulk standard sample spectra [18], and their derivatives, both to be used as reference for theoretical modelling with FDMNES.

3.2 Ultra-thin Temperature Series

There is a second process for the creation of ultra-thin nickel silicide films. These materials are formed with a nickel deposition thickness of 2nm - 10nm, as verified by STEM. Each of these samples are prepared by IBM using a vapour deposition process of Nickel onto a silicon (001) substrate at room temperature. The thin film sample is then chemically etched to remove any unbound nickel from the surface. After the etching, the samples are then annealed with a standardized ramping temperature under vacuum; baking the individual samples until the temperature reaches pre-determined values. After reaching the pre-determined temperature the samples are then quenched in vacuum, (heat is turned off), through radiative cooling. After annealing, the film thickness increases to $\sim 5 - 7\text{nm}$, due to the variance between annealed sample thickness, for simplicity the films will be referred to by their deposition
thickness only. The sample set provided from IBM for this investigation consisted of 2nm of deposited nickel annealed on silicon, individually quenched at temperatures of 200, 300, 400, 500 and 700°C. IBM also supplied a sample taken at room temperature, prior to the annealing process, but after the chemical etching has occurred; this sample is referred to as the as-deposited sample.

3.2.1 Temperature Series Measurements

Grazing Incidence - XANES data were taken at HXMA-CLS beam-line [11]. The beam-line wiggler was at 2.1T, providing a flux of \( \sim 2 \times 10^{12} \text{photons/s/0.1\%BW} \) at about 10keV. The Si(111) crystal was selected in the double bounce monochromator, and the Rh stripe was used for the collimating and toroidal mirrors. The mirrors were adjusted by use of a YAG Crystal image to produce a beam profile suitable for grazing incidence experiments. The first ion chamber detector was filled with \( N_2 \), with a flow rate of \( \sim 1 \text{bubble/sec} \) in 5mm of water: This flow rate has been chosen quasi-empirically to ensure that the ion chamber remains in the linear region [19]. The second crystal of the monochromator was detuned at 500eV + 8333eV so that only 50% of light intensity is allowed to pass: this significantly limits the higher harmonics contents of light reaching our sample.

The data for the temperature series samples was collected in fluorescence mode, using a 32-element germanium detector, and the grazing incidence set-up as in previous work was adopted [18]; including the Bragg Peak solution and methodology whereby the samples are mounted atop a rotor which is spinning at 500Hz. A diagram of the experimental setup can be seen in Figure - 3.3. The spectra were taken in both \( E_\parallel \) and \( E_\perp \) modes for each sample in Figure - 3.4.
$E_\parallel$ and $E_\perp$: Synchrotron light is highly elliptically polarized. So much so, that it can be thought of as being entirely linearly polarized tangent to the electron storage ring (horizontal). This means that the two configurations mentioned above – that is $E_\parallel$ and $E_\perp$ – refer to the samples orientation with respect to this linearly polarized light. When the sample surface is parallel to the polarized light (i.e. lying horizontal), then the setup is called $E_\parallel$. Alternatively, when the sample surface runs perpendicular to the polarized light (i.e. mounted vertically), then the setup is referred to as $E_\perp$.

Figure 3.3: Experimental set-up for XANES measurements of the temperature series samples.

3.2.2 Temperature Series Data Processing

For the temperature series repeated scans were taken for each sample, for both the $E_\parallel$ and $E_\perp$ modes. The reported results are the average of these scans. The 32-element detector provides 32 channels in total for each measurement. Using the standard X-ray Absorption Analysis software package Athena [21], these spectra were loaded in individually and analyzed and contrasted with other channels from the
Figure 3.4: Temperature series spectra for $E_{\parallel}$ and $E_{\perp}$ are virtually indistinguishable.

(a) Temperature series spectra, taken in $E_{\parallel}$ mode.  
(b) Temperature series spectra, taken in $E_{\perp}$ mode.

same measurement. Any outlier channels, that is, those that appeared to have been saturated or offline, were then removed. Following this an average spectra is calculated using Athena’s merge normalized function.

Subsequently, upon viewing the averaged spectral results, there appears to be no difference between the $E_{\parallel}$ and $E_{\perp}$ modes for any of the temperature series samples. The comparison of the parallel and perpendicular data can be seen in Figure - 3.4. This came as a surprise, normally one expects thin film samples to exhibit some properties reflecting their single crystalline structure (in this case many of the sample’s structures are not cubic). This result is investigated in further detail as a case study in Section - 4.2. The temperature series data that is used for the bulk of this project in Figure - 3.5 is consequently the average of all data sets, both $E_{\parallel}$ and $E_{\perp}$. This, in effect, allows for higher quality "powder like" spectral data.
3.2.3 Temperature Series: Phase Formation

One of the more interesting things that becomes readily apparent through just glancing at the temperature series samples, is that the ultra-thin nickel silicide films have a notably different phase formation sequence compared to the H-Series [3.1]. In Figure - 3.7(a) where the spectra are overlaid. It is of note that the epitaxial phase, which resembles $NiSi_2$, begins to form at a temperature of 400$^\circ$C, and that it appears to become more crystalline with an increase in temperature: 500$^\circ$C and 700$^\circ$C; by contrast, the bulk $NiSi_2$ formation occurs at 800$^\circ$C. It appears that the formation of $NiSi$, was skipped altogether, though it is possible with higher annealing temperature resolutions, that $NiSi$ is formed briefly somewhere in-between 300$^\circ$C and 400$^\circ$C.

Looking at the lower temperature region it looks as though the temperature series samples: as – deposited, 200$^\circ$C & 300$^\circ$C, are almost indistinguishable from one
another, and at first glance have some similarity to the Nickel rich phases: $H4$ to $H6$, as well as the $\theta - Ni_2Si$ phase. This observation will be investigated further in more detail, with the aid of our theoretical model, in Section - 4.3. For now however, upon reviewing the bulk standard phase formation and contrasting each temperature series sample to known bulk phases: one can establish an overarching trend that the ultra-thin nickel silicide films tend to follow a similar phase formation sequence that operates over a smaller temperature range. However, the differences between these two phase formation sequences are non-trivial. The fact that there are significant differences in the phase formation sequence makes some intuitive sense, in that the energies required for each phase to exist is much more dependent upon the surface/interface effects of the material, than with bulk materials. One can no longer think of these phases as ad infinitum crystallizations, the domain boundaries now play a significant role in determining the phase formation.

### 3.2.4 X-ray Absorption Edge Shifts

Further insight to the temperature series can be gained through looking at the edge shifts $E_0$, that is the shifts of the first inflection point away from the known $E_0$ of nickel metal of $8333eV$. These edge shifts reflect changes in the electronic structure, and are dictated by the local inter-atomic potentials, and as such are a useful fingerprint in determining chemical composition using XANES. Figure - 3.7 shows the results of edge shifts and their errors for each sample in the temperature series. The working value of edge shift was calculated as the average across all scans taken both in $E_\perp$ and $E_\parallel$, since there was no detectable difference between these spectra. The error in the edge shift was determined conservatively for each sample to be half the range of the edge shifts coming from individual scans.
Figure 3.6: Top: Temperature series spectra, overlaid to make apparent the variation between spectra. Below left: the Nickel rich bulk phases: $H_4 - H_6$, $\theta - Ni_2Si$, and their derivatives that are comparable to as – deposited 200°C, 300°C. Below right: NiSi and NiSi$_2$ and their derivatives, comparable to 400°C, 500°C respectively.
The table provided below lists the edge shifts for different samples at various temperatures:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>0.2008 ± 0.206</td>
</tr>
<tr>
<td>200°C</td>
<td>0.4413 ± 0.303</td>
</tr>
<tr>
<td>300°C</td>
<td>0.5000 ± 0.126</td>
</tr>
<tr>
<td>400°C</td>
<td>0.7687 ± 0.236</td>
</tr>
<tr>
<td>500°C</td>
<td>1.1000 ± 0.473</td>
</tr>
<tr>
<td>700°C</td>
<td>1.1980 ± 0.306</td>
</tr>
</tbody>
</table>

Looking at Figure 3.6, the earlier speculation on the structure of the 700°C sample can be affirmed further by comparing the edge shifts. Previous work measured the edge shift of NiSi₂ to be 1.29 – 1.60 eV [18]. This is consistent, within error, with the edge shifts determined for the 500°C and 700°C phases, adding to the affirmation that these annealed phases are in fact NiSi₂. The edge shift of 0.7687 for the 400°C phase edge shift seems to be slightly lower than what is expected from the bulk phase of NiSi₂, and is quite close to the edge shift of 0.78 – 0.99 eV of NiSi [18]. This could imply some imperfections within the lattice structure, also consistent with the previous conjecture that this phase is the beginning of the formation of NiSi₂.

Therefore residual components of other phases may still be detectable. It is possible given this edge shift, that the ultra-thin temperature series does pass through NiSi during the annealing process, but that the temperature resolution was too coarse.

Focusing on the lower temperature ranges (20°C - 300°C) in Figure 3.6, one can obtain the edge shifts of the proposed Nickel rich portion of the series. The edge shift of δ-Ni₂Si was determined previously to be 0.16 – 0.17 [18]. This is slightly lower.
than the nominal edge shift of the as–deposited phase. The edge shifts of 0.4413 and
0.5000 from the 200°C and 300°C phases are close in magnitude to the edge shifts of
the \( \theta - Ni_2Si \) and \( Ni_3Si_2 \) bulk standard phases alike. This suggest that all four of
these phases carry a similar chemical environment.

3.3 Other \( \theta - Ni_2Si \) Samples

Two control samples of the \( \theta - Ni_2Si \) phase were measured at HXMA-CLS us-
ing the experimental set-up seen in Figure - 3.8. The XANES spectra were taken
with almost identical conditions to those of the temperature series, and IBM bulk
standards, however the detectors used where different. HXMA had purchased new
ion chambers prior to the run, and at the time the 32-element germanium detector
was being repaired. The 4-element germanium detector from Vortex was used for
fluence mode instead.

Figure 3.8: Experimental set-up for XANES measurements of the control \( \theta - Ni_2Si \)
samples.

The results from these experiments are in Figure - 3.9 The purple curve is for a
sample prepared as for the bulk series, with a deposition thickness of 10\textit{nm} heated to 420 \textdegree C, with 46% silicon. The green curve is for similar sample prepared with a deposition thickness of 50\textit{nm}. The black curve is the bulk $\theta - Ni_2Si$ phase to be used as a standard. There is no discernible difference between any of these three spectra. In the XANES region these three spectra are identical, forgiving the noise inherent in using a 4-element detector in lieu of a 32-element. It is therefore safe to conclude that these control samples posses an identical phase to that produced at the Watson centre.

Figure 3.9: Comparison of the IBM Watson center $\theta - Ni_2Si$ samples, and two control samples: 10\textit{nm} and 50\textit{nm} thick.

(a) XANES Spectra of theta phase samples taken at HXMA-CLS

(b) Derivative of theta phase samples.
Chapter 4

FDMNES and the Calculation of XANES

The following chapter is comprised of three sections, the collective purpose of which are to report and analyse the findings determined through use of the theoretical calculations using FDMNES. The first section will present the calculated spectra modelling the bulk standard H-Series samples covered in Chapter - 3. Discussion about the individual phases, information extracted from the theoretical model, and the corresponding quality of the fits will be reported here. The following two sections concern themselves with two case studies using FDMNES which are of particular note: Section - 4.2 will show how the FDMNES package was used to unearth the reason for some subjectively mysterious experimental results; and in Section - 4.3 the method through which FDMNES helped identify the projected composition of one of the ultra-thin film phases will be discussed.

In general, these calculated spectra were produced using the May 2012 FDMNES version, using self consistency. Cluster size for the calculations was dependent upon
symmetry, and in some cases MST calculations were required due to a lack of computational power. Most calculations were attempted on SHARCNET (Shared Hierarchical Academic Research Computing Network), but due to the shared nature of the resources and seven day runtime restriction, it was difficult to complete some calculations. In lieu of this, a 4-node computer cluster was assembled and configured. The particulars of this cluster are discussed in Appendix A.

4.1 Bulk Sample Theoretical Fits

The first step in using any theoretical model is to start by modelling known systems. After which one can begin to grow and expand the model to include conjectures on unknown systems. For the purposes of this project, it was paramount that adequate simulated spectra be calculated for the H-Series samples. The point to which this task was completed for each of the bulk IBM samples (less \( H2 \) and \( H4 \)) is presented and discussed in this section.

4.1.1 \( \delta - Ni_2Si \)

This phase is orthorhombic, with space group \( Pbmn \), (a variant notation for \( Pcmn \) due to different origin choice) also referred to as "pseudo-hexagonal". The structure of this phase can be seen in Figure - 4.1, the two graphics show the structure looking along the [001] and [010] axes. From these structure diagrams, one can see that there are two distinct absorption sites for Nickel and in the [010] perspective the layered structure containing the pseudo-hexagonal sheets can be seen. This can complicate the modelling slightly, in that the relative \( E_0 \) (as discussed in Section - 3.2.4) of the separate absorption sites can change the linearly combined spectral form quite
Figure 4.1: Structure of $\delta - Ni_2Si$, Ni in green (site 1) and yellow (site 2), and Si in grey.

(a) View of structure along [001].  
(b) View of structure along [010].

drastically.

Figure 4.2 shows the best fit calculated for $\delta - Ni_2Si$. It was obtained using the multiple scattering method, with the Muffin-tin potential. The calculation was performed with a cluster size of 7Å, but exhibited no discernible differences between DFT and MST at smaller cluster sizes of approximately 4Å. The lattice constants were contracted by 3% in order to achieve this best fit. This contraction value was determined through the use of parameter optimization, resulting in a reliability factor of 0.0018 (determined as in Appendix C). The reason for the discrepancy between lattice constants require for this optimized fit is unknown, but the results offer a significantly better agreement with experiment.

**Site Sensitivity** One of the most difficult tasks in modeling XANES spectra can be in systems with more than one absorption site. These models are particularly
sensitive to the $E_0$ calculation of each site, a slight shift between individual K-edge absorption values can change the whole resultant spectrum. In the case of $\delta - Ni_2Si$ it turns out that FDMNES calculates the relative K-edges absorption values with good accuracy. A good fit for materials with multiple absorption sites allows for the decomposition of the spectra into its linear contributions from each site. Figure 4.3 shows just that: the separate absorption spectra overlaid with the bulk standard spectra for $\delta - Ni_2Si$. Here, it is easy to see that the peak splitting in the white line region is the result of the unique white lines from the two separate absorption sites. It is also evident that the two shoulders on the rising edge are both an average contribution from the two absorption sites.

The power that comes with this kind of understanding is immense. One can envision future experiments made easy, where the monitoring of site occupancy, perhaps changed by oxidation or some other controllable mechanism, can be accomplished
by first performing a calculation for a bulk crystalline material, decomposing absorption sites, and picking features specific to the absorption site of concern. One could track this feature over multiple samples and determine site occupancy with relative ease. This combination of theory with experiment provides a number of previously untapped opportunities to expose the information rich content of XANES measurements.

Figure 4.3: Site specific spectral calculations for $\delta-Ni_2Si$ overlaid with bulk standard spectra.

![Graphs showing absorption and first derivative of Ni2Si.]

4.1.2 $\theta-Ni_2Si$

This phase is hexagonal, with space group $P6_322$, with lattice constants $a, b = 3.805\text{Å}$ and $c = 4.890\text{Å}$. The structure of this phase can be seen in Figure - 4.4, the two graphics show the structure looking along the $[001]$ and $[110]$ axes. From these structure diagrams, one can see that there are two distinct absorption sites for Nickel.
Figure 4.4: Structure of $\theta - Ni_2Si$, Ni in green (site 1) and yellow (site 2), and Si in grey.

(a) View of structure along [001].
(b) View of structure along [110].

in this phase as well (not surprisingly).

Figure - 4.5 shows the best fit calculated for $\theta - Ni_2Si$. It was obtained using the density functional theory method, with full inter-atomic potentials. The calculation was performed with a cluster size of 6Å. A metric of best fit was determined through the parameter optimization function in FDMNES, giving a reliability factor of 0.0036. The absorption sites were adjusted to promote one half electron charge from the 4s orbital to the 3d, to obtain this best fit. This is a lower quality fit than that obtained for the $\delta - Ni_2Si$. The main difficulty in modelling this material is peak intensity. All attempts to improve the intensity through parameter optimization resulted in larger disagreements between spectra.

**Site Sensitivity**  As previously discussed with the $\delta$ phase, a good fit in the case of multiple absorption sites allows for the decomposition of the spectra into its linear
contributions from each site. The quality of the best fit acquired for the $\theta$ phase limits the reliability of the decomposition, however, there is still information to be gathered in doing so. Figure 4.6 shows the separate absorption spectra for $\theta - Ni_2Si$ overlaid with calculated best fit. One can still use this method to determine that the peak splitting of the white line is the result of the two underlying white lines of the absorption sites. This decomposition also exposes that the peak intensity calculated for absorption site 2 is the main source of discrepancy between the best fit and the experimental data. The ability to decompose the spectra allows also for further insight as to how to improve the model. To date, most attempts to improve upon the fit have been directed towards the properties of the second absorption site. It should be also be noted that, similar to the $\delta - Ni_2Si$ case, the two shoulders on the rising edge in the experimental data (Figure 4.5) in this case also come from an average contribution from the two absorption sites.
Figure 4.6: Site specific spectral calculations for $\theta - Ni_2Si$.

(a) Site specific spectra for $\theta - Ni_2Si$. (b) Site specific spectral derivatives.

4.1.3 $Ni_3Si_2$

This phase is hexagonal, with space group $Cmc_1$, lattice constants $a = 12.23\text{Å}$, $b = 10.80\text{Å}$ and $c = 6.92\text{Å}$. The structure of this phase can be seen in Figure - 4.7, the two graphics show the structure looking along the [001] and [100] axes. Though it is difficult to determine visually, there are eight unique absorption sites within the unit cell.

Figure - 4.8 shows the best fit calculated for $Ni_3Si_2$. It was obtained using the density functional theory method and calculation was preformed with a cluster size of 4.5Å. A metric of best fit was determined giving a reliability factor of 0.0043. The absorption sites were assumed neutral. This is a lower quality fit than for either of the $Ni_2Si$ phases. The main difficulty in modelling this material is computational time. Larger cluster size may be possible to calculate, which would ultimately lead to a better fit, but would require weeks for computation.
Figure 4.7: Structure of $Ni_3Si_2$, Ni in blue, and Si in grey.

(a) View of structure along [001].

(b) View of structure along [100].

Figure 4.8: Best fit model of $Ni_3Si_2$.

(a) Bulk data comparison with best fit of $Ni_3Si_2$.

(b) Derivative comparison of best fit and XANES data.
Site Sensitivity As stated previously, there are eight absorption sites within the unit cell for $Ni_3Si_2$. This largely chaotic distribution of overlapping spectra produces the almost "feature-less" quality of the $Ni_3Si_2$ spectrum. An interesting thing to note about these spectra is that they are segregated into two groups for relative intensity. The absorption sites along the flat layers at $0a$ and $\frac{1}{2}a$ of the unit cell contribute half as much to the calculated spectrum, due to the site occupancy ratio difference. Whereas, the spectra from absorption sites within the puckered layers at $\frac{1}{6}a$ and $\frac{1}{3}a$ are the main contributors to the spectral form.

4.1.4 $NiSi$

This phase is orthorhombic, with space group $Pbnm$ (a variant notation for $Pnma$, due to different origin choice), with lattice constants $a = 5.233\,\text{Å}$, $b = 3.258$ and $c = 5.659\,\text{Å}$. The structure of this phase can be seen in Figure - 4.10, the two graphics
show the structure looking along the [001] and [010] axes. There is only one absorption site in this nickel silicide phase. To produce this structure, using $Pbnm$ (origin choice 4 of Spacegroup No. 62), an offset by 0.25 of the lattice constant $c$ to the layers prescribed along the $c$–axis in Toman’s paper [25] was required.

Figure 4.10: Structure of $NiSi$, Ni in blue, and Si in grey.

![Figure 4.10: Structure of $NiSi$, Ni in blue, and Si in grey.](image)

(a) View of structure along [001].

(b) View of structure along [010].

Figure - 4.11 shows the best fit calculated for $NiSi$. It was obtained using the density functional theory method, with full inter-atomic potentials; the potential calculated used neutral atoms. The calculation was preformed with a cluster size of 8.05Å. Due to the large computational requirements, no parameter optimization was calculated, and hence there is no reliability factor to report. However, qualitatively speaking, this is a high quality fit. Every feature is accounted for, with minimal energy offsets, with relatively good agreement on feature intensity. The derivative also shows agreement with the theoretical model, and the feature rich $NiSi$ spectra, again with only slight disagreement in the relative intensities.
Figure 4.11: Best fit model of NiSi.

4.1.5 NiSi$_2$

This phase is cubic, with space group $Fm - 3m$, with lattice constants $a, b, c = 5.395$ Å taken from ASM Specialty Handbook [5]. This lattice constant is 0.7% smaller than the one determined through diffraction measurements at École Polytechnique de Montréal [26], but provides a more suitable fit. The structure of this phase can be seen in Figure - 4.12, the two graphics show the structure looking along the [001] and [010] axes. As can be seen from the structure diagram, there is no directional dependence in this phase as it is a simple cubic (CaF$_2$) structure.

Figure - 4.13 shows the best fit calculated for NiSi$_2$. It was calculated with the full atomic potential, using DFT. The calculation was preformed with a cluster size of 8.0Å with quadrupolar terms included. Qualitatively speaking, the calculated fit is quite good: all major features are accounted for, however some minor inflection
Figure 4.12: Structure of \(NiSi_2\), Ni in blue, and Si in grey.

(a) View of structure along [001].  
(b) View of structure along [010].

Figure 4.13: Best fit model of \(NiSi_2\).

(a) Bulk data comparison with best fit of \(NiSi_2\).  
(b) Derivative comparison of best fit and XANES data.
4.2 Consequences of the Bragg Peak Averaging

In the thin film absorption experiments performed by K. Miller, there were problems with the initial grazing incidence setup, in that the penetration depth of the incoming x-ray's was large enough to extend past the film itself and reach the crystalline silicon substrate. The problem with the x-ray’s reaching the substrate was that occasionally the Bragg condition would be satisfied resulting in the formation of bright spots called Bragg peaks somewhere in the $2\pi$ steradians above the sample.

The experimental geometry, and the somewhat lower concentrations of Nickel called for the indirect measurement of absorption using a solid state germanium detector to measure fluorescence. Germanium solid state detector electronics can be easily saturated by these Bragg peaks, which can have adverse effects when measuring an XAS signal by introducing artefacts and spoiling otherwise usable data.

The solution described by K. Miller [18] to reduce the effect of these Bragg peaks by averaging the Bragg peak intensity over $2\pi$ radians. This was accomplished by physically spinning the sample during the experiment, reducing the total counting rate in the solid state detector. This allowed for the energy discrimination function of the detector to be used to isolate the fluorescent signal, and eliminate artefacts. The unintended consequences of that decision will be covered later in Subsection - [4.2.2] Before this, however, in the following subsection: a discussion about some polarization modelling with FDMNES that aided in the understanding of the effect of rotation.
4.2.1 Polarization Dependence

Thin and ultra-thin nickel silicide films alike exhibit epitaxial growth upon their respective silicon substrates. These silicide films are crystalline, and are very sensitive to the polarization of light with which our absorption experiments are conducted. This can be verified by revisiting Equation 2.2.14. Synchrotron radiation sources emit highly elliptical light; this light can be approximately treated as linearly polarized in the tangential direction with respect to the electron storage ring [9].

Recall, from the explanation of FDMNES in Chapter 2, that the software model is designed to calculate spectra with polarization dependence. In order to verify its output, a test was devised to compare the calculations for two samples, and their respective polarized spectra.

The two samples that were decided upon for this case study were the bulk H5, or δ – Ni$_2$Si phase, which has an orthorhombic structure (Pbnm) [25] and the bulk H8, or NiSi$_2$ phase, which has a cubic structure (Fm – 3m) [4]. The aim in choosing these two samples was to determine whether the FDMNES package predicts the polarization independent nature that is inherent in a cubic structure. That is: FDMNES should produce no difference in spectra for different polarizations for Fm – 3m. Conversely, FDMNES should predict some polarization dependence for the orthorhombic Ni$_2$Si structure.

Figure 4.14 (a) shows the spectra for H5, overlaid with the calculated spectrum with no polarization dependence and two spectra with polarization along the [100] and [010] directions, (b) shows the derivatives of the same. For each case, FDMNES models the polarization dependent spectra to be starkly different from one another. The non-polarized light calculation is the best fit for the bulk standard spectra previously reported in Section 4.1.
Interestingly, the spectrum calculated for light polarized along [110] is quite similar to the spectrum calculated for Absorber 1 in Figure - 4.3, though the second shoulder before the white-line still appears in this calculated spectrum. This may indicate that light polarized along this axis sees a larger cross sectional area from Absorber 1, than Absorber 2. This insight, though perhaps not critical for the scope of this project, does give some weight to the power FDMNES offers when trying to dissect all of the subtleties at the atomic level that ultimately are expressed in every XANES spectra. The polarization along [010] shows little site specific information.

The driving point of this case study though, rears its head in Figure - 4.14 (c) and (d). Here, in fact, there are four spectra: the spectrum of H8, the non-polarized spectral calculation, a calculated spectra for light polarized along [110] and [010]. The cubic structure spectral calculations show no discernible difference between polarized and non-polarized light calculations. This is what was expected, and so, FDMNES indeed is self consistent for polarization calculations, it correctly predicts changes (or in this case, the absence of them) in spectra based on the polarization of light.

It was the intention that after the calculated spectra had been verified in this manner, that a pursuit to understand the polarization dependence in the ultra-thin film temperature series could be embarked upon. To this end, for a long time these efforts remained fruitless, as there were no subtle spectral features with which one could attempt to drive the model towards. For each sample the spectral measurements of the temperature series remained insensitive to polarization changes. In the proceeding section, however, there will be discussion over how FDMNES helped uncover a possible reason for this mysterious insensitivity.
Figure 4.14: Polarization Dependence Modelling of $\delta - Ni_2Si$ and $NiSi_2$.

(a) Polarization dependent calculations for [110], [010], and [000] of $\delta - Ni_2Si$.

(b) Derivative of polarization comparison for $\delta - Ni_2Si$.

(c) Polarization dependent comparison for [110], [010] and [000] of $NiSi_2$.

(d) Derivative of polarization comparison for $NiSi_2$. 

51
4.2.2 Modelling the Effects of Rotation

The polarized nature of a synchrotron light source can be both a blessing and a curse when dealing with epitaxially grown thin films such as the ultra-thin nickel silicide temperature series. On one hand it can be exceedingly useful: for instance, when one is interested in extracting the film growth direction through absorption spectroscopy; it can also be a slight nuisance: when one is attempting to cross-identify bulk (read: polycrystalline) phases within highly ordered (read: quasi-crystalline) thin or ultra-thin epitaxial films.

In order to be able to then preserve the ability to compare the polycrystalline bulk spectra with the ultra-thin films, it was necessary to be able to identify any polarization dependence in the thin films experimentally. This was accomplished through measuring the absorption spectrum of the sample in two geometric configurations, one with it parallel (horizontal) and one with it perpendicular (vertical) to the polarization of the incoming beam.

An entirely unexpected result occurred, however; neither parallel nor perpendicular configurations offered any differing features between the spectral measurement and their identified bulk counterparts (when identified). This was perplexing, to say the least. There were only two conclusions that could be drawn from this, neither of which seemed very plausible, initially. Either the ultra-thin films were in fact polycrystalline, an outlier to most everything thought to be known about these supposedly epitaxial films, or second, perhaps by spinning our samples planarly the subspace of final states available with the polarizations explored was sufficiently large enough to sequester any directional dependent data.

The latter notion was initially thought to be equally as absurd as the former, in that this technique of spinning to eliminate Bragg peaks is a standard way of
measuring X-ray absorption of thin films to avoid the Bragg peaks from the crystalline substrate [10] [12]. However, a scheme was devised using FDMNES to test the seemingly improbable validity of this notion.

The first challenge in building an appropriate model with FDMNES was the fact that the Polarization vectors, when entered into the program have to be defined within the internal coordinates of the program. Much effort was taken in determining, via the verbose output files, exactly how FDMNES calculates its standard basis. The projection is broken down in Table 4.1 for the specific case where $c \perp a \& b$, which covers all samples of interest for this project.

Once this challenge had been met, a small program was written that would take in crystal lattice vectors $(a, b, c, \alpha, \beta, \gamma)$ a spin rotation axis $(u, v, w)$, a point $(x, y, z)$ through which the polarization vector would pass onto/through the rotation axis, and a rotational resolution $\theta$. The source code for this application was written in C++ and is available in Appendix B. It was decided to concentrate upon the effect of rotation upon polarization dependence for the worst case scenario. That is, the rotation would be modelled in $E \parallel$ mode, where the polarization vector is perpendicular to the rotation axis. Then comparisons would be made for orthogonal sample orientations within this configuration to test for polarization sensitivity. In the idealized $E \perp$ setup, it should be noted that, rotation should not have any effect, but the grazing incidence angle in the experimental setup used would result in some component of polarization remaining perpendicular to the axis of rotation.
The program works by first doing a change of basis upon the crystal lattice vectors to the internal basis of FDMNES, likewise for the rotation axis and point. It then projects the polarization point on to the transformed rotation axis \((j, k, l)\), the difference between these points gives the polarization vector. The point is then rotated about the rotation axis by applying to following matrix:

\[
A(\theta) = \frac{1}{L} \times \\
\begin{bmatrix}
  u^2 + (v^2 + w^2) \cos \theta & uv(1 - \cos \theta) - w\sqrt{L}\sin\theta & uw(1 - \cos \theta) + v\sqrt{L}\sin\theta \\
  uv(1 - \cos \theta) + w\sqrt{L}\sin\theta & v^2 + (u^2 + w^2) \cos \theta & vw(1 - \cos \theta) - u\sqrt{L}\sin\theta \\
  uw(1 - \cos \theta) - v\sqrt{L}\sin\theta & vw(1 - \cos \theta) + u\sqrt{L}\sin\theta & w^2 + (u^2 + v^2) \cos \theta
\end{bmatrix}
\]

where \(L\) is the length of the rotation axis vector. If the point \((x, y, z)\) from above is acted upon by \(A(\theta)\), it will result in a rotation of \(\theta\) degrees about the rotation axis \((u, v, w)\). This process is repeated \(N\) times until \(N \times \theta = 360^\circ\), that is until a discretely outlined rotation has been completed. The rotation points \((x_i, y_i, z_i)\) are then used in conjunction with the initial projection \((j, k, l)\) to determine a plane of discretely rotated polarization vectors. The typical results for one of these calculations can be seen in Figure - [4.15](#).

As can be seen in Figure - [4.15](#), the program properly outputs a plane of polarization vectors, with which one can now convincingly model the rotation of material with a static polarization vector. Once the planar polarization vectors had been calculated they were transferred to an FDMNES input file. The calculation was then performed. Upon completion of the calculation, there were multiple spectra, corresponding to each polarization vector in the input. A linear combination of these spectra was constructed, all with equal weighting, and then normalized. This normalized linear combination of polarization spectra represents the time averaged effect of rotating the sample while taking measurements in \(E_\parallel\) mode.
Figure 4.15: Polarization plane generated for a rotation about axis \((1,0,0)\), with rotation point at \((0.5,1,0)\).

In looking at Figures - 4.16 (a) and (b) one can see the polarized spectra along \([010]\) and \([100]\) are observably different from the combined polycrystalline calculation, and the bulk IBM standard spectra. The choice of polarization planes, when modelling rotation, was chosen to include these two polarization directions within the \(\delta\) - phase (\([100]\) and \([010]\)). Two additional calculations were also performed where the rotation planes were perpendicular to one another. Three calculations were performed all together: one with the plane in the \(span([100],[010])\) rotating about \([001]\), one with the plane in the \(span([010],[001])\) rotating about \([100]\), and one with the plane in the \(span([100],[001])\) rotating about \([010]\). In all three of these calculated cases, the deviation away from the polycrystalline calculation was less than either of the static cases. The rotated samples do maintain some features of the static polarized samples, in that the three rotation calculation derivatives are unique. However, the overarching observation from the effect of rotating a sample is that one can expect the effect of polarization dependence will be sequestered, or smoothed out.
Figure 4.16: Modelled effect of sample rotation during spectral measurements for select surface orientations of $\delta$ and $\theta - Ni_2Si$.

(a) Comparison of $\delta - Ni_2Si$ calculations between static spectral polarizations and their rotated counterparts, non-polarized calculations, and bulk IBM standard.

(b) Derivative of comparison for $\delta - Ni_2Si$.

(c) Comparison for $\theta - Ni_2Si$ between randomly selected rotational polarizations, non-polarized calculations and bulk IBM standard.

(d) Derivative of comparison for $\theta - Ni_2Si$. 
The question that was then asked after seeing the trend form in the $\delta$ phase was:

What would the effect be of an arbitrarily chosen rotation axis, through an arbitrarily chosen lattice point? Figures - 4.16 (c) and (d) show calculations modelling the $\theta$ phase rotating about an arbitrary axis [111] and an orthogonal axis [−101]; the answer to the question posed in this case is: A sample rotated about an arbitrary axis, when compared to its perpendicular counterpart offers little to no detectable polarization dependence. For reference Figure - 4.17 shows the individual spectral calculations along the two perpendicular rotation axes. It is clear from these graphs that there would be a polarization dependence detected between these perpendicular polarization pairs. The features of spectra rotated about [111] are more pronounced than those rotated about [−101]. However, the averaged contribution for each of these directions turns out to be indistinguishable, as in Figure - 4.16 (c).
From the results of these two models it can be concluded, at least for the $E_\parallel$ mode, that the unintended consequence of rotating the sample while measuring absorption spectra is the sequestering of polarization dependent information. For the purposes of some thin film spectral measurements, this result should be considered in future experiments. There are situations where this new result could work in the favour of, or against the experimentalist. Often times it is desirable to use bulk standards for comparison, as in was done in this project. In this case, it proved beneficial that the polarization dependence was all but removed from our measurements, as it allows for direct identification of phases. In other experimental designs, where one is interested in determining the lattice orientation of a single crystalline thin film, it would be necessary to find a different method for eliminating Bragg peak contamination from a crystalline substrate. In either case, this result has implications for the way in which XANES spectral measurements should be taken, and illustrates the use of ab-initio modelling (in this case FDMNES) for the improvement of structural studies using XANES.

4.3 As – deposited: Composition Characterization

In this section, the similarities between the spectra of the Nickel rich phases with the ultra-thin as – deposited phase is explored with the aid of FDMNES. Presented first, in the following subsection, is a case study with $NiSi$ determining the effect of cluster size upon the the spectra, and the physical implications of this parameter when modelling spectra. Lastly, the discussion will be pointed towards how cluster size modelling can be used to aid in the determination of XRD amorphous phases, specifically in the case of the ultra-thin as – deposited sample.
4.3.1 Cluster Size Dependence

One of the key advantages to XANES is the breadth of information that each spectrum contains. Since the local atomic potential is sensitive to long range order, and the absorption spectra are sensitive to changes in the local atomic potential, the spectra also contain long range order information. These fact adds a new facet of complication to appropriately modelling XANES spectra using FDMNES. The amount of long range order, that each simulated spectra is sensitive to is determined by parameter optimization, specifically, the cluster size of the calculation.

The cluster size of the calculation certainly has a dictatorial role in including long range order information, but there is a limit to which one can impose this order. In the photo-electron scattering picture of XAS, the outgoing photo-electron wave must interfere with the scattered photo-electron waves in order for there to be any modulations generated in the absorption spectra. This implies that the spectral features can only be measured for the lifetime of the core-hole generated by the absorption of the incoming x-ray’s, which puts a limit on the physical distance a photo-electron wave can probe. One of the drawbacks to the DFT calculation that is used in our modelling is that the potential it calculates, is not time-dependent. The upshot of not using a time-dependent DFT model, is that the core-hole remains ad infinitum, artificially, possibly leading to a calculated spectrum with physically irrelevant features. The advantage to the time independent model, however, is that it takes less time computationally to generate these theoretical spectra, and as long as one is conscientious of the potential drawbacks, it poses little risk.

To get a feeling for this cluster size/long range order dependence of XANES, and FDMNES modelling multiple calculations where performed for NiSi, as can be seen in Figure - 4.18. The calculations were done for varying cluster sizes, approximately
Figure 4.18: Cluster size dependence of NiSi, taken at Ni shell +0.1Å, for approximately 1Å intervals, from 2Å- 8.05Å.

(a) Theoretical and experimental NiSi XANES spectra.

(b) Derivative of Theoretical and experimental NiSi XANES spectra.

every 1Å, chosen at 0.1Å outside of any Ni shell (to include the whole atomic structure within the boundary), for spherical cluster sizes of 2Å up to 8.05Å. This range was determined somewhat empirically, the minimum cluster size is below any nearest neighbour distances in NiSi, and the maximum cluster size is that of the best fit to date.

These varied cluster sizes show the trend that: as one increases the cluster size, the theoretical spectrum contains more structural information. Starting at R = 2Å, the spectrum is reduced to a spectrum similar to that of a one-atom absorption curve, as the calculations moves to a cluster size of R = 3.4Å, just after the first Nickel shell, the spectra begin to take the approximate form of a regular NiSi spectra. Looking at the derivative, one can see the features that have been denoted b, and d, begin to form somewhere between the shell at 4.35 Å, and 5.68 Å. Feature a, begins to form between
5.68 Å, and 6.51 Å. Further, it is apparent that feature \( c \) does not make it into our theoretical models. It is possible that with a larger cluster size, feature \( c \) may begin to form. This presumption is based on the fact that NiSi is orthorhombic, and has low symmetry. Low symmetry, in general and intuitively, requires larger cluster sizes in order to calculate a complete set of final states. It is also possible, however, that feature \( c \) is the result of multi-electron interactions, or a so-called shake-up peaks [24], in which case the single-electron FDMNES model wouldn’t be expected to reproduce this feature.

4.3.2 \( \text{As} - \text{deposited} \) and the Nickel rich phases

As hinted at earlier when first presenting the temperature series data in Section - 3.2.3, the nickel rich phases uniformly have similar spectra to the "colder" phases in the temperature series. This was further supported by the edge shifts of these phases which was discussed in Section - 3.2.4. These observations are unique to the ultra-thin films. The bulk \( \text{as} - \text{deposited} \) spectrum as in Figure - 4.19 shows that for the bulk case one obtains a pure nickel phase[18], and that no phase transformation has occurred after the initial deposition. By contrast, the ultra-thin \( \text{as} - \text{deposited} \) from the temperature series, looks nothing like the bulk \( \text{as} - \text{deposited} \) or the Nickel foil, indicating that inter-facial nature of the system under consideration.

This all leads to an interesting question: What is the composition of the ultra-thin film \( \text{as} - \text{deposited} \) phase? The answer, as it turns out is not that simple, but it starts in part with the previous observations that the nickel rich phases have similarities to the ultra-thin \( \text{as} - \text{deposited} \) phase. Figure - 4.20 shows the Nickel rich phases stacked and overlaid with the ultra-thin \( \text{as} - \text{deposited} \) spectra. The edges have been aligned to 8333eV for ease of comparison. Additionally, the residual (difference) plot
Figure 4.19: The bulk as - deposited spectral comparison with Nickel foil.

(a) XANES spectra of Nickel and bulk as - deposited (H2).

(b) Derivative of Nickel foil and bulk As Deposited.

(c) XANES spectra of bulk and temperature series as - deposited.

(d) Derivative of bulk and temperature series as - deposited.
Figure 4.20: 2nm as – deposited spectral comparison with Nickel rich phases.

(a) XANES spectra of 2nm as – deposited, δ and θ - Ni$_2$Si, Ni$_3$Si$_2$ and Ni$_{31}$Si$_{12}$.

(b) Spectral derivatives of 2nm as – deposited, δ and θ - Ni$_2$Si, Ni$_3$Si$_2$ and Ni$_{31}$Si$_{12}$.

has been provided for each of these phases with respect to the as – deposited phase.

The four bulk spectra in Figure 4.20 can be subdivided into two classifications: δ - like and θ - like. The δ - like subgroup consists of Ni$_{31}$Si$_{12}$ and δ – Ni$_2$Si, which have very similar spectral features, and as such must have similar chemical environments. The θ-like subgroup consists of Ni$_3$Si$_2$ and θ – Ni$_2$Si based on their chemical similarities, as well.

Comparing θ - like spectra with the 2nm as – deposited spectrum there are some distinct differences: the second shoulder, corresponding to the trough between $b$ and $c$ is broadened slightly when compared with as – deposited data. Specific only to the θ – Ni$_2$Si phase are: the double peak about feature $c$, and after the main peak, the oscillations between 8360 – 8380 eV that can both be seen in the derivative, are not present in the as – deposited spectra. Discrepancies aside though, there are some
matching characteristics: the first shoulder at 8335eV, corresponding the trough between points \( a \) and \( b \) in the derivative, is common to \( \theta \)-like and \( as – deposited \) phases, this implies the potential close to the Fermi level is approximately the same in all cases. The second commonality of note is the shape of the resonant peak (white-line): all spectra show a very broad, but mostly singular peak defining this region.

From the previous section on site specific absorption (4.1.1), it is known that the broad white-line actually comes from the superposition of absorption signals from unique absorption sites. There is some trace of this peak splitting that can be seen in the derivative at around 8360eV, but the magnitude is on the same order of the \( as – deposited \) noise level.

In comparing the \( \delta \)-like spectra with the ultra-thin \( as – deposited \) spectrum, there are also some differences: as with the \( \theta \)-phase, there are common shoulders between \( a \) and \( b \), but for the \( \delta \)-like phases this is slightly sharper than the shoulder in the \( as – deposited \) spectrum. As well the white line for the \( \delta \)-like phases have the characteristic splitting from the two absorption sites which is not present in the \( as – deposited \) spectra. At around 8380eV there is a peak possessed only by the \( \delta \)-like phases, deviating from the \( as – deposited \) phase.

Apart from the qualitative analysis of the similarities/dissimilarities between these two groups of phases, and the ultra-thin \( as – deposited \) spectrum, Figure - 4.20 also includes a quantitative report of the reliability factor measured between each spectra and the \( as – deposited \) spectrum. Using this, one can confirm that indeed the \( Ni_3Si_2 \) phase offers the best overall fit for the \( as – deposited \) phase with a reliability factor of 0.00038, with the \( Ni_{31}Si_{12} \) and \( \delta – Ni_2Si \) phases lagging not too far behind with reliability factors of \( \sim 0.0005 \). The aim at this point was to turn to using FDMNES to model variations of these phases in order to achieve a plausible solution fit to the
as – deposited phase. This poses a slight problem, in that of the Nickel rich phases there have not been satisfactory theoretical spectra produced for either \(Ni_3Si_2\) or \(Ni_{31}Si_{12}\). It is possible however, to divert our attention in the interim to the more successful calculations of \(\theta\) and \(\delta – Ni_2Si\). Keeping in mind that each of these four phases must share very similar chemistry about the Nickel absorption, it is possible to use the \(Ni_2Si\) calculations in the following manner:

- The \(\theta\) - phase material shares several spectral features in common with the \(Ni_3Si_2\) phase. It is assumed then that the \(\theta\) phase calculations can be used a representative of both spectra as \(\theta\) - like materials.

- Similarly, as the \(\delta\) and \(Ni_{31}Si_{12}\) phases share many spectral features, it is assumed that the \(\delta\) phase will stand as an adequate representation of the \(\delta\) - like materials.

- The poor reliability factor reported earlier for \(\theta – Ni_2Si\) spectrum is of some concern. The assumption used in this investigation is that one should expect self consistency within the theoretical results. That is, the reliability factors remain directly comparable among the same material despite deviations from experimental results.

In the previous section, [4.3.1], there was much discussion over the dependence of FDMNES models on the selection of an appropriate cluster size. The fits for \(NiSi\) ranged from one-atom absorption spectra, all the way up to including information from 8.05Å away. With this tool at our disposal, and the known XRD amorphous nature of the ultra-thin as – deposited material, it seems reasonable to ask, "What if the long range order, prevalent in the bulk standards has yet to form in the as – deposited material". On a simply qualitative level, the smaller the grain/texture
size within the material, the fewer and less exaggerated the spectral features become (Figure - 4.18). And so, it is worth while to model both $\delta$ and $\theta$ phases as they might exist if they had yet to form their full single crystal structure.

Using FDMNES to produce small grain models is straightforward and is accomplished as follows: by adjusting the calculations cluster radius one can impose upon the produced spectrum an inclusion of nearest-neighbour information only. The cluster radius is selected in this case to be just beyond the first Nickel shell from an absorption site. For Nickel silicides, this often results in selection of a radius of $\sim 3\text{Å}$. Figures - 4.21 and 4.22 show the results of the small grain modelling for both the $\theta$ and $\delta - Ni_2Si$ phases respectively, overlaid with the spectrum for the ultra-thin $as - deposited$ phase. As well, for comparison, the long range order calculation for the two bulk phases done in the previous section has been provided.

Looking at Figure - 4.21 (a) and (c), not surprisingly the $\theta$ phase model attempt doesn’t agree that well. The small grain model is quantitatively, no better than the bulk model, both achieving a reliability factor of $\sim 0.01$. Leaving that aside one can still see that the expected trend exists: there is an overall smoothing effect synonymous with a small grain model. Focusing on the derivatives now in Figure - 4.21 it can be seen that the small grain model offers an improvement in relative peak intensity between $b$ and $c$, but loses some agreement between $a$ and $b$. The inflection point about $8380eV$ appears in both the bulk and small grain models, and nothing equivalent to this exists in the $as - deposited$ spectra. From an uncertain starting point, this model maintains its poor reliability factor. This measure in conjunction with the disagreement between the experimental $\theta$ spectrum and the ultra-thin $as - deposited$ phase serves as an indication that the $\theta$ phase, specifically, is not a good match for the $as - deposited$ phase.

66
Figure 4.21: 2nm as-deposited spectral comparison with FDMNES model of δ and θ for long range order, and short range (inclusion of the first Ni shell information only).

(a) XANES spectra of 2nm as-deposited, and FDMNES model of θ - Ni$_2$Si at R = 3Å.

(b) Spectral derivatives of 2nm as-deposited, and FDMNES model of θ - Ni$_2$Si at R = 3Å.

(c) XANES spectra of 2nm as-deposited, and FDMNES model of θ - Ni$_2$Si at R = 6Å.

(d) Spectral derivatives of 2nm as-deposited, and FDMNES model of θ - Ni$_2$Si at R = 6Å.
Figure 4.22: 2nm *as – deposited* spectral comparison with FDMNES small grain model of δ.

(a) XANES spectra of 2nm *as – deposited*, and FDMNES model of δ - Ni<sub>2</sub>Si at R = 3Å.

(b) Spectral derivatives of 2nm *as – deposited*, and FDMNES model of δ - Ni<sub>2</sub>Si at R = 3Å.

(c) XANES spectra of 2nm *as – deposited*, and FDMNES model of δ - Ni<sub>2</sub>Si at R = 8Å.

(d) Spectral derivatives of 2nm *as – deposited*, and FDMNES model of δ - Ni<sub>2</sub>Si at R = 8Å.
The small grain and bulk models for the $\delta$-phase can be seen in Figure - 4.22. The small grain model offers a calculated spectra that is closer to the $as-deposited$, approximately quartering the reliability factor to 0.00131. The smaller cluster size predicts smoother spectral features associated with the second absorption site, and so the peak splitting that was seen in the bulk spectra white line has almost vanished. Looking at the derivative however, corresponding to the range $8352 - 8363 eV$, one can see that the the peak splitting has been reduced but not removed. The relative intensities between $a$ and $b$ are improved by the small grain model, however the intensity of the peak between $b$ and $c$ has been reduced. In the small grain model for the $\delta$ phase, it was thought prudent to expand the calculation energy range. In Figure - 4.20 (d), one can see that the plateau beginning around $8380 eV$ in the experimental (as in Figure - 4.19) is reproduced in the FDMNES model with lower intensity than in the experimental. In the small grain model, this plateau remains but is well below the noise level in the $as-deposited$ spectra. It is true that the small grain model of $\delta-Ni_2Si$ creates a close fit for the $as-deposited$ phase, but the derivative reveals a slightly different story. Here the features deriving from long range order have been stripped away, leaving information purely local to the absorption site, and still the near edge spectrum retains features specific to the $\delta$-phase, disparate with the ultra-thin $as-deposited$.

Neither of the above small grain models provide a direct answer to the question posed, however these models for $\delta-Ni_2Si$ and $\theta-Ni_2Si$ do provide some insights. The $as-deposited$ phase appears to be a system with limited long range order, in that it only contains smooth spectral features. Secondly, small grain models of a material allow one to adjust relative intensities to drive the model result towards the expected experimental spectrum. However, as was seen in the small grain model of

69
both the $\theta$ and $\delta$ phase calculations, one can't "smooth out" features originating from areas local to the absorption site; that is, $\delta$-like phases will always retain $\delta$-like features. This is important, as it means that a working small grain model for the ultra-thin $as-deposited$ phase should be unique.

It is likely that the true parent phase is structurally related to $Ni_3Si_2$ given the better initial agreement between the experimental $Ni_3Si_2$ spectrum the $as-deposited$ spectrum. It is also now known from the $\theta$-phase modelling, that one should expect to see an improved agreement between the shoulder edge (defined by inflection points $b$ and $c$) of $\theta$-like materials and the ultra-thin $as-deposited$ phase. To this end, a small grain model of this phase was calculated, the results of which are presented in Figure - 4.23. The results show an agreement with the $as-deposited$ spectrum, with derivative features $a$, $b$, and $c$ all accounted for, and their relative intensities and locations within an acceptable range. The reliability factor for the small grain is also reported in Figure - 4.23 as 0.00232, increasing the agreement between the model and $as-deposited$ phase by a factor of three. This agreement on order with the $\delta$-phase small cluster modelling; however, the results preclude any spectral features not consistent with the $as-deposited$ spectrum. This implies that indeed the $Ni_3Si_2$ small grain model is qualitatively the best calculated result for the $as-deposited$ phase. This observation, in conjunction with the initial agreement between the experimental $Ni_3Si_2$ spectrum and the ultra-thin $as-deposited$ phase, suggests that previously unknown composition of the ultra-thin $as-deposited$ material is in fact a lower-ordered $Ni_3Si_2$ phase.

This is not surprising, given the fact that the $as-deposited$ phase, intuitively, must be Nickel rich: it hasn’t had time/energy to deeply diffuse into the silicon substrate, but it also must be bound to silicon or it would have been removed in the
Figure 4.23: 2nm \textit{as – deposited} spectral comparison with FDMNES small grain model of \textit{Ni}_3\textit{Si}_2.

(a) XANES spectra of 2nm \textit{as – deposited}, and FDMNES model of \textit{Ni}_3\textit{Si}_2 at \textit{R} = 3Å.

(b) Spectral derivatives of 2nm \textit{as – deposited}, and FDMNES model of \textit{Ni}_3\textit{Si}_2 at \textit{R} = 3Å.

(c) XANES spectra of 2nm \textit{as – deposited}, and FDMNES model of \textit{Ni}_3\textit{Si}_2 at \textit{R} = 4.5Å.

(d) Spectral derivatives of 2nm \textit{as – deposited}, and FDMNES model of \textit{Ni}_3\textit{Si}_2 at \textit{R} = 4.5Å.
selective acid etching process. Further adding to the plausibility that the parent phase is $Ni_3Si_2$ is the low formation energy of this phase when contrasted with other Nickel silicide phases at low temperature [4]. Lastly, on a qualitative note, the structure of $Ni_3Si_2$ is of low symmetry and is qualitatively chaotic [20]. It is a natural conclusion that this more chaotic structural configuration describes the as – deposited phase material.
Chapter 5

Conclusions

5.1 Wrap Up: XANES and FDMNES

As was reviewed in Chapter 1 the quest to understand and use nickel silicide films as conductive contact materials in CMOS devices, is one that developed out of the failures of similar materials’ bulk phase models degrading in applicability as manufacturers began developing transistors into the sub $90\,nm$ regime. As the drive for continued computational power pushes manufacturers to keep designing circuitry further down into the nano-scale, it is self evident that surface effects will have a continued role in complicating the understanding of phase formations no matter what the material is, in question. As devices get smaller, it behaves material scientists to understand the phase formations of these ultra-thin films, and to re-characterize their phase diagrams. There will not always be another "nickel" –another material– that will be serendipitously more cooperative at smaller scales than the current production standard.

This project has humbly sought to embark upon this pursuit of ultra-thin film phase formation comprehension. By using experimental tools such as XANES, and
theoretical models such as FDMNES, it has been shown that it is possible to identify the phases of these ultra-thin nickel silicide films. Moreover, it has been shown that these tools can also be combined to give insight into the experimental design and execution.

5.1.1 Temperature Series Phase Identifications

In Chapter 3 the simplest methodology of using XANES, that is the fingerprinting methodology mentioned in Chapter 2, was used to identify the ultra-thin nickel silicide phase that forms at temperatures above 400°C. It was concluded that starting at 400°C the silicon rich phase of NiSi₂ is forming. Further annealing increases the longer range order, resulting in more defined features. This result was unexpected, in that this silicon rich phase forms at much higher temperatures in the regular bulk phase diagram, up past 900°C for the normal 43% silicon concentration.

In the temperature series, no NiSi phase could be identified. This points to the temperature resolution of the samples as being too large to detect the existence of the NiSi phase. Though it is possible that the phase formation sequence skips this phase all together. The samples appear to make drastic changes, going from the typical muted features of nickel rich spectra to the silicon rich spectra between 300°C and 400°C, it is possible that the NiSi phase could be identified within this temperature region, given higher temperature resolved samples.

In Chapter 4, the combination of the information rich technique of XANES with the modelling power of FDMNES saw the identification yet one other ultra-thin nickel silicide phase. The as–deposited phase, the parent phase to all of the ultra-thin temperature series samples, was concluded to be the infancy of a Ni₃Si₂ phase. Through
the fingerprinting methodology, it was noticed that there were many similarities between the \textit{as-deposited} phase and the $Ni_3Si_2$ phase from the beginning. By first ensuring an adequate model of the bulk $Ni_3Si_2$ phase spectra was completed, and then proceeding to model a crystalline phase with decreasing long range order, FDMNES was able to produce a working model for the \textit{as-deposited} phase.

5.1.2 Experimental Design

Phase identification of the ultra-thin nickel silicide films ended up not being the only results of this project. With a stroke of happenstance, the experimental data posed a question of its own: Why is there no polarization dependence for the spectra of these ultra-thin films? The answer came through some creative use of the FDMNES program. A model was created to simulate the effect of the Bragg peak elimination method whereby the sample is rotated while obtaining data. The model emulates the rotation of a sample to determine the impact on the resultant spectra. The results showed that the rotation of a sample made available a larger span of states, resulting in a smearing effect of any polarization dependent information within the spectra. This answered the question posed: Their is likely polarization dependence in the ultra thin films, but that by rotating the sample, this information is suppressed.

This result will have an impact on future experimental designs. It is important to know that in situations where polarization information is desired, it is probably better to not rotate the samples; but conversely, where polarization dependence in not desired, in can be minimized through the rotation of the sample.
5.1.3 FDMNES Modelling Successes and Limitations

In the start of Chapter 4, there were five models of bulk nickel silicide phases presented: $\delta - Ni_2Si$, $\theta - Ni_2Si$, $Ni_3Si_2$, $NiSi$ and $NiSi_2$. Each one of these models resulted in a fit with a reliability factor $< 0.005$, which considered to be a good fit. These models were calculated to be jumping off points in the modelling of unknown phases, and proved their usefulness in the understanding of the as-deposited phase identification, as well as proponents in the understanding of the polarization dependence results. It was also shown that one can successfully decompose XANES spectra with multiple absorption sites, as was the case with $\delta - Ni_2Si$, $\theta - Ni_2Si$, and $Ni_3Si_2$.

There are some limitations to the modelling method, however. The discrepancies in the $\theta$-phase calculation are still cause for some concern. The reliability factor was minimized through the use of non-neutral absorption sites, but there is still room for improvement. The spectral calculation can be improved upon with the adaptation of more complete potentials. This suggests that perhaps the current shielding scheme may not be the most appropriate model for the $\theta$-phase, and perhaps there is some prominent core hole effect that can be accounted for in future.

In the modelling of $\delta - Ni_2Si$, despite calculating a fit with a reliability factor of 0.001, it was only achieved through parameter optimization of the lattice constants. Specifically the scaling of the unit cell by 3%. This amount of contraction upon the unit cell is suspicious, and warrants some consideration. The $H5$ model was developed using the MST method, after lower cluster sizes of $H5$ showed agreement between DFT and MST. Since, the MST calculations are less computationally intensive, and since the $H5$ space group has very low symmetry, it was decided to use MST for the refinement of the best fit. It is assumed then that since the MST method is not as robust in its calculations of the potential, that the non-physical contraction can be
thought of as a correction factor, rather than a true representation of the system. The effect of contracting the lattice in real space is the expansion of points in energy space which are directly interdependent with the muffin-tin constant potential. The correction factor of scaling lattice constants can be thought of as an adjustment of the muffin-tin potential height rather than a geometrical adjustment.

The limitations above point to the fact that although DFT is a robust model, that it does have some drawbacks. The one obvious drawback is that calculation time can be onerous if one is not equipped with the proper facilities. The second limitation is within the model itself, the DFT model is assumed static at some \( t = 0 \), which neglects any contributions from the core hole effect, instead electron cloud shielding is then assumed and parametrized.

5.2 Future Outlook

There is still plenty of work left to be done, and the many facets of this project leads to no shortage of options as to what should be looked at next. There are however three broader areas of interest which can be looked at in future research.

5.2.1 Bragg Peak Elimination

The impact of rotation, it seems is either a cause for concern or aid depending on the system of interest. In the case of the ultra-thin nickel silicide films it was convenient to have polarization independent spectra that could be compared directly with the bulk samples. Before any future data is collected with the intent of looking at polarization dependence, it is imperative that one remediates the Bragg Peak problem in another fashion.
5.2.2 Core Hole

The problem of modelling the core hole, as mentioned in the limitations of FDMNES modelling, is one of concern for anyone doing X-ray Absorption modelling. Future investigations using XANES and FDMNES, should make use of an alternate models: the amount of shielding can be parametrized and chosen optimally within the FDMNES program. Alternatively, the use of different programs for calculating cluster potentials, such as the FLAPW method [28], can be incorporated into the FDMNES calculation of XANES. In using a more robust potential it is expected that there will be an improvement in the determination of final states, and that from this the model of the absorption spectrum will improve in kind.

5.2.3 Temperature Resolution

Further work with the nickel silicide films needs to be completed to identify the unknown phases. However, since the phase of interest, $NiSi$ did not appear within the unknown phases in the ultra-thin nickel silicide films that were measured here, it is worthwhile to measure a new set of samples. If one could obtain a series of samples between the temperatures of $300^\circ C$ and $400^\circ C$, one should be able to identify the $NiSi$ phase if it is formed along the phase formation sequence specific to these ultra-thin Nickel silicide films.
Appendix A

Assembly of a four node cluster for FDMNES Calculations:

Calculations with FDMNES can take weeks to complete on a conventional desktop computer. What’s worse is that in cases where a large cluster size is desirable, most desktop computers lack the required amount of memory to perform the calculation. This is the major downfall of FDM, and DFT, numerically and physically they are precise and elegant, computationally, however, they are a bit like a bull in a china shop. All this to say, if you are planning on doing any serious calculations with FDMNES, you’ll require some serious calculation power.

Fortunately, FDMNES has been coded with MPI (message passing interface), which allows for multiple components of the calculation to be calculated simultaneously. That is so long as you have multiple processors, which can handle these parallel tasks.

Universities in Ontario have the privilege of being able to use SHARCNET, (Shared Hierarchical Academic Research Computing Network) a high performance computing facility that is more than capable of managing any FDMNES calculation one could throw at it. However, there is one problem with using FDMNES for these calculations. The theoretical calculations have many parameters, and in order to
achieve an appropriate model there is a lot of trial and error involved. Since SHARCNET is a shared facility, the more calculations one completes, the lower one’s priority in the queuing system. This has the direct impact that as the calculated model you are working on improves, you are forced to wait longer for the results. This can be infuriating, to say the least.

The best case scenario is to be equipped with the power of SHARNCET, but to not have to share with anyone else. To this end our group embarked upon building a small computational cluster for our FDMNES calculations. The end result can be seen in Figure 1.

The hardware used consists of 4 identical nodes, each with: an 8 core processor, 32Gb of RAM, a 500Gb hard drive, and 1000Mb/s ethernet connection. The four computers were named: Doris, Boris, Delores, and Morris. Boris, Morris and Delores, were all loaded with the same modified version of the Ubuntu operating system, sharing a user account with a home folder loaded from an NFS (network file system) folder. Doris, was loaded with a similar operating system, but was set-up as the
NFS file server for the other three. Doris was also equipped with an extra 1000 Mb/s ethernet adapter for external access.

Once booted up, Doris can be used from any external computer as a login node using SSH (secure shell). From here calculations can be submitted and monitored. The combined machinery results in a 32 core MPI cluster with 128 Gb of RAM, which more or less devours FDMNES calculations.
Appendix B

Polarization Generator Source Code:

```c
#include <stdio.h>
#include <string.h>
#include <stdlib.h>
#include <iostream>
#include <fstream>
#include <math.h>

#define PI 3.14159265

int main(int argc, char *argv[]) {
    double hkl[3], crysa, crysb, crysc, angA, angB, angC, pttx, pnty, pntz, angle_cone=0;
    int select, resolution, i;
    std::ofstream polarize;

    /*Begin list of cases for command line input, load into corresponding variable*/
    for (i=1; i<argc; i++) {
        if (strcmp(argv[i], "-M") == 0) select = 1;
        if (strcmp(argv[i], "-R") == 0) select = 2;
        if (strcmp(argv[i], "-abc") == 0) select = 3;
        if (strcmp(argv[i], "-ARR") == 0) select = 4;
        if (strcmp(argv[i], "-pnt") == 0) select = 5;
        if (strcmp(argv[i], "-angle") == 0) select = 6;
    switch(select) {
    case 1:
        if(argc >= 16) {
            sscanf(argv[i+1], "%lf", &hkl[0]);
            sscanf(argv[i+2], "%lf", &hkl[1]);
            sscanf(argv[i+3], "%lf", &hkl[2]);
        } else {
            printf("Usage: ./polgen -M 0 1 0 -R 9 -pnt 1 2 3 -abc 1 2 1 -ABG 90 90 120 \n*\n");
            return(1);
        }
    select = 10;
    break;

    ...
    Cases removed for brevity...
```
case 10:
    break;
default:
    if(argc <= 10) {
        break;
    } else {
        printf("Usage: ./polgen -W 0 1 0 -R 9 -pnt 1 2 3 -a 1 2 1 -a6G 90 90 90 120 \n\n");
        return(1);
    }
    break;
}

/* Convert hkl to integral R2 basis*/
//
// k = a
// y = c

double x1[]={1,0,0}, y1[]={0,1,0}, z1[]={0,0,1}, crysa_p1[]={1,0,0}, crysb_p1[]={0,1,0};
double crysc_p1[]={0,0,1};
if ((angA == 90) & (angB == 90)) {
    crysa_p[0] = crysa;
    crysc_p[3] = crysc;
    crysb_p[0] = crysb*cos(angCPI/180);
    crysb_p[1] = crysb*sin(angCPI/180);
    polarize.open("output.txt");
} else {
    std::cout<<"Case not accounted for"<<std::endl;
    return 0;
}

/*Convert HKL to the R2 basis*/
double hkl_p[3][3], mno[3][3];
    hkl_p[0] = hkl[0];
    hkl_p[1] = hkl[1]*sin(angCPI/180);
    hkl_p[2] = hkl[2];
    mno[0] = -1*hkl_p[2];
    mno[1] = 1*hkl_p[0] - 1*hkl_p[2];
    mno[2] = 1*hkl_p[1];
/*Create point to rotate around hkl*/
    double proj_m, hkl_m, proj[3][3], rotptn[3];
    double pol_m, proj_shift, pol_p[3][3];
    rotptn[0] = pntx;
    rotptn[1] = pnty;
    rotptn[2] = pntz;
    proj_m = rotptn[0]*hkl_p[0] + rotptn[1]*hkl_p[1] + rotptn[2]*hkl_p[2];
    hkl_m = sqrt((hkl_p[0])*(hkl_p[0]) + (hkl_p[1])*(hkl_p[1]) + (hkl_p[2])*(hkl_p[2]));
if(angle_cone != 0){
    pol_m[0] = rotptn[0] - proj[0];
    pol_m[1] = rotptn[1] - proj[1];
    pol_m = sqrt((pol_m[0])*(pol_m[0]) + (pol_m[1])*(pol_m[1]) + (pol_m[2])*(pol_m[2]));
    proj_shift = pol_m*tan(angle_cone*PI/180);
proj_n = fabs(proj_n - proj_shift);
std::cout << "Opposite length is: " << proj_shift << std::endl;
}
proj[0] = proj_n * (hkl_p[0]/hkl_m);
proj[1] = proj_n * (hkl_p[1]/hkl_m);
proj[2] = proj_n * (hkl_p[2]/hkl_m);
std::cout << "Projection is: " << proj[0] << " t" << proj[1] << " t" << proj[2] << std::endl;
polarize << "0.0" << " t" << "0.0" << " t" << "0.0" << " t" << proj[0] << " t" << proj[1] << " t" << proj[2] << std::endl;
polarize << "0.0" << " t" << "0.0" << " t" << "0.0" << " t" << hkl_p[0] << " t" << hkl_p[1] << " t" << hkl_p[2] << std::endl;
polarize << "0.0" << " t" << "0.0" << " t" << "0.0" << " t" << rotpt[0] << " t" << rotpt[1] << " t" << rotpt[2] << std::endl;
/* Create rotated point*/
double rotmat[3], l, cos_t, lsin, plan_vec[3];
l = sqrt(pow(hkl_p[0],2) + pow(hkl_p[1],2) + pow(hkl_p[2],2));
for(i=0; i<360; i=resolution) {
    cos_t = cos(i*pi/180);
    lsin = sqrt(l)*sin(i*pi/180);
    rotmat[0] = (1/l)*rotpt[0]*(pow(hkl_p[0],2) + pow(hkl_p[1],2) + pow(hkl_p[2],2))*cos_t
    rotmat[1] = (1/l)*rotpt[0]*(pow(hkl_p[1],2) + pow(hkl_p[2],2))*cos_t
    rotmat[2] = (1/l)*rotpt[0]*(pow(hkl_p[2],2) + pow(hkl_p[0],2) + pow(hkl_p[1],2))*cos_t
    plan_vec[0] = rotmat[0] - proj[0];
polarize << "0.0" << " t" << "0.0" << " t" << "0.0" << " t" << plan_vec[0] << " t" << plan_vec[1] << " t" << plan_vec[2] << std::endl;
}
polarize.close();
return 0;
}
Appendix C

**Reliability Factor:** The parameter optimization feature in FDMNES can be incredibly useful in trying to determine a best fit for experimental data. It works by minimizing the reliability factor for a range of energies on experimental data, given a range of parameter values over which to interpolate, or extrapolate from.

In this study, it was found that the conventional R factor \[29\] which is calculated by FDMNES was sufficient enough to determine the best fit. Determined by calculating:

\[
R_x^i = \frac{13}{6} \frac{\sum_e |c_i f_{th}^i(e) - f_{exp}^i(e)|^2}{\sum_e |f_{exp}^i(e)|^2}
\]

where, \( c_i \) is a normalization factor, for each theoretical fit \( i \).

FDMNES then calculates several spectra comparing the reliability factor’s associated with each parameter. For more than one parameter, a multidimensional grid of calculations is performed. This can be rather time consuming. Thus, not all spectra were calculated with optimized parameters, and so not all spectral calculations in this project can be provided with a Reliability factor.
Bibliography


