$^{11}\text{B}_4\text{C}$ containing Ni/Ti neutron multilayer mirrors

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$^{11}\text{B}_4\text{C}$ containing Ni/Ti neutron multilayer mirrors

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In such ugly times, the only true
protest is beauty.

Phil Ochs

About the cover

The cover shows the result of a neutron reflectometry measurement performed as part of this thesis. The measurement was done on a Ni/Ti multilayer that was co-deposited by $^{11}\text{B}_4\text{C}$. This particular measurement is shown in $\omega - 2\theta$ formalism, where the 2θ angle is described by the y-axis and the ω rocking angle is described by the x-axis. For aesthetic reasons, the measurement has been mirrored over the x-axis, meaning the ω direction increases from right to left. Around the middle on the front page, a diffraction spot can be seen at the first Bragg peak, as well as a so-called Bragg sheet. This Bragg sheet indicates that some form of roughness correlation is present between the layers. This is the first full neutron reflectometry measurement done during the course of my PhD thesis, marking an important personal milestone. This particular measurement is also essential to the analysis described in this thesis.

Abstract

The work in this thesis covers the design, growth and characterisation of neutron multilayers. The performance of these multilayers is highly dependent on the obtained interface width between the layers, even a modest improvement can offer a substantial increase in reflectivity performance. As multilayers are such an integral component of many neutron optical instruments, any improvement in terms of reflectivity performance has broad implications for all neutron scattering experiments. This project has been carried out with the construction of the European Spallation Source (ESS) in mind, but the principles extend to all neutron scattering sources.

Ni/Ti is the conventional material system of choice for neutron optical components due to the high contrast in scattering length density (SLD). The reflected intensity of such components is largely dependent on the interface width, caused by the formation of nanocrystallites, interdiffusion, and/or intermixing. Apart from hampering the reflectivity performance, the finite interface width between the layers also limits the minimum usable layer thickness in the mirror stack. The formation of nanocrystallites has been eliminated by co-depositing of B_4C . This has been combined with a modulated ion assistance scheme to smoothen the interfaces. X-ray reflectivity (XRR) measurements show significant improvements compared to pure Ni/Ti multilayers. This has further been investigated using low neutron-absorbing $^{11}B_4C$ instead. After deposition, the $^{11}B_4C$ containing films have been characterized using neutron reflectometry, X-ray reflectivity, transmission electron microscopy, elastic recoil detection analysis, X-ray photoelectron spectroscopy. A large part of his work has focused on fitting X-ray and neutron reflectivity measurements in order to obtain structural parameters.

The fits to the experimental data suggest a significant improvement in interface width for the samples that have been co-deposited with $^{11}B_4C$ using a modulated ion assistance scheme during deposition. Any accumulation of roughness has been eliminated, and the average initial interface width at the first bilayer has been reduced from 6.3 Å to 4.5 Å per bilayer. The respective reflectivity performance for these structural parameters have been simulated for a neutron supermirror ($N = 5000$) for both materials at a neutron wavelength at $\lambda = 3$ Å using the IMD software. The predicted reflectivity performance for the $^{11}B_4C$ containing samples amounts to about 71%, which is a significant increase compared to the pure Ni/Ti samples which have a predicted reflectivity of 62%. This results in a reflectivity increase from 0.84% to 3.3% after a total of 10 reflections, resulting in more than 400% higher neutron flux at experiment.

Populärvetenskaplig sammanfattning

Neutronspridning är en populär teknik som kan användas för att studera olika materialegenskaper. Tekniken är på många sätt jämförbar med röntgenspridning, men det finns några viktiga skillnader mellan de två teknikerna. Röntgenstrålning interagerar med elektronmolnen runt en atom medan neutroner interagerar med själva atomkärnan. Den här skillnaden ger neutronspridning flera fördelar jämfört med röntgenspridning. Atomkärnan utgör bara en väldigt liten del av atomen som till största del består av tomrum. Det gör det möjligt för neutroner, som enbart interagerar med atomkärnan, att tränga långt in i material de flesta material. Detta möjliggör undersökning av tjockare bulk-lager. En annan fördel med att använda neutroner är att de växelverkar med magnetiska material och därför kan mäta magnetiska egenskaper, något som inte är möjligt med röntgenstrålning. Spridningsegenskaperna, som beskriver hur en neutron interagerar med ett material, är tillsynes helt slumpmässiga. Till exempel så kan två olika isotoper av samma grundämne till och med ha helt olika egenskaper. Eftersom röntgen- och neutronspridning ger helt oberoende mätvärden som beskriver samma egenskaper har en kombination av teknikerna använts för att analysera material i det här arbetet.

Eftersom neutroner har en begränsad livslängd på 15 minuter behöver experimenten utföras vid en neutronkälla där neutronerna utvinns. Redan under 90-talet bestämdes det att en ny neutronkälla skulle byggas i Europa. År 2014 började konstruktionen av European Spallation Source (ESS) i Lund, och de första experimenten förväntas ske 2023. Byggandet av ESS medför ett större behov av ny kunskap kring neutronspridning i Sverige. Det är därför forskarskolan SwedNess grundades, som det här projektet är en del av.

Det här projektet är inriktat på så kallade multilager, som används i många används i många optiska komponenter vid neutronkällor. Multilager består av väldigt tunna lager av olika material. Ett sådant multilager är neutronspegel som behövs för att transportera neutronerna från källan till platsen där experimentet utförs. Hur många neutroner som reflekteras av en neutronspegel beror på multilagrets kvalitet. En viktig faktor är hur jämnt och slätt gränssnittet mellan de olika lagren är. Även en väldigt liten förbättring i jämnheten har en stor påverkan på den totala reflektansen. Eftersom multilager är så pass viktiga i så många olika komponenter har en liten förbättring därmed en stor betydelse för alla neutronmätningar som utförs. Det här arbetet försöker att förbättra reflektiviteten genom att belägga så jämna lager som möjligt. De olika strukturella parametrarna som beskriver multilager undersöktes genom

en kombination av neutronspridning och röntgenspridning. En teoretisk modell anpassades till de experimentella mätvärdena för att ta fram de strukturella parametrarna av materialet. Resultatet visar en betydlig förbättring jämfört med de neutronspeglar som finns på marknaden idag, och är därmed mycket lovande för framtiden.

Preface

Most of this work has been written during the midst of the global COVID-19 pandemic. While these times are a challenge for all of us, our slow approach out of the situation with the largest vaccination program in history does make me proud to call myself a member of the scientific community. As we will hopefully approach some form of normality after the summer of 2021, I am more eager than ever to start working on site again. While writing on my licentiate thesis is a perfect fit for a work-from-home environment, the situation does not come without its own set of challenges. From a limited access to direct communication or social contacts to a simple lack of physical office space with air-conditioning and ergonomic equipment. There are therefore a number of people that I am extremely thankful for during the first half of my PhD, and particularly during this period as well.

In no particular order, I would want to name **Kenneth Järrendahl** who responded to my request to do a small project in the European Erasmus program in the first place back in 2016. I can not understate the influence that this particular project had on my future trajectory. This was during a period when I was less sure where I was heading with regard to my future studies, and this project turned out to be a major catalyst that led me to where I am today. In the same sense, I owe a lot to **Jens Birch** who acted as my secondary supervisor for this project and is the one who granted me this project in the first place. I am extremely thankful for the trust that has been put into me by giving me this opportunity. It is a great advantage to be able to work so close to someone that has that much feeling for the field, all meetings with Jens have truly been extremely insightful one way or another. I'd also like to thank **Fredrik Eriksson** who acted as my main supervisor for most of this project. I have been impressed with the extensive help from day one. Both his patience and pedagogical skills have been a huge help for me in this project. While I still have much to learn, without Fredrik's expertise with X-ray scattering in particular I would not become close to the level that I am now and subsequently in the field of neutron scattering. I should also mention **Naureen Ghafoor** for her involvement in this project. Naureen has been a very positive contributor during project meetings and has been vital to the foundation that of this project. I would in particular like to thank Naureen for the help with TEM images. Another person outside of LiU that I should mention is **Alexei Vorobiev**, who has been our contact person at ILL. In particular I would want to thank Alexei, and all folks at SuperAdam for the warm welcome during my extended stay in 2019. It's been a very informative period. I would also like to mention SwedNess and all people involved for setting up these projects and opening up a plethora of

opportunities. Finally I would like to say a word about the people that supported outside of the university environment. First my family at home back in the Netherlands. I know it's not easy that we couldn't meet for this long, and a trip to Dronten is definitely the first thing up on my agenda when international travel is in the cards again. Finally I should mention **Karin Stendahl**, the working from home situation would have been infinitely more difficult without you on my side forcing me to follow my much-needed routines. I can not express how much your love and companionship means to me. It still remains a mystery to me how I haven't completely bored you to death with my eternal chatter about whatever pops up in my mind.

It would be nearly impossible to mention every single person, but I am very thankful for everybody at the department. Both for the meaningful discussions, but for the meaningless ones as well. I like to think that we should never underestimate the importance of non-important matters, a friendly working environment is vital to a satisfying output.

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Chapter 1

Introduction

1.1 Background

Neutron scattering is a versatile non-destructive experimental technique to study the structure and dynamics of materials. The technique is used by over 5000 researchers over the world [1] spanning over an increasingly large range of disciplines, including physics, chemistry, biology, ceramics and metallurgy [2]. Neutron scattering differentiates itself from X-ray scattering due to the interaction with the investigated material. While X-rays interact with the electron cloud, neutrons interact with the nucleus of the atom. This gives several distinct advantages for neutron scattering. As the nucleus of an atom is only a tiny portion of the atom, most of the material will be empty space to a neutron. Because of this, neutrons have a very large penetration depth [3], making it possible to study bulk materials. Moreover, the wavelength of neutrons is similar to the atomic spacing in solids, making it ideal for structural studies [4]. Another advantage of neutron scattering arises from the fact that neutrons carry a magnetic dipole moment, the interaction of the neutron's spin with unpaired electrons in ferro- and paramagnetic materials gives rise to magnetic scattering [5]. The scattering properties for neutrons vary seemingly randomly across the periodic table, even different isotopes of the same element can have completely different properties for neutrons. This makes the combination X-ray and neutron scattering a very powerful technique, as the scattering properties for X-rays are dependent on the atomic number. By combining these two techniques, it is possible to obtain two completely independent data sets with the same structural information. This latter advantage is exploited in this report, where a combination of neutron and X-ray scattering is used to find the structural properties of deposited multilayers.

The dawn of neutron scattering began in the first half of the twentieth century. The first experiments on Bragg reflection using neutrons were performed as early as 1936, however it wasn't until the second half of the 1940s that the invention of the nuclear reactor made the first proper neutron experiments possible [6]. As free neutrons have a mean lifetime of 15 minutes [4], they need to be produced while running the experiment. Traditionally, free neutrons for scientific experiments are produced at fission reactors. In this process, a neutron collides with uranium-235, forming the following nuclear reaction:

releasing two or three free neutrons carrying an energy of 1.29 MeV [4], averaging to 2.52 free neutrons after each collision. Each emitted neutron can undergo

a fission reaction with another ^{235}U particle forming a chain reaction where even more free neutrons are emitted. This technique has however reached its technological limits in terms of neutron flux due to power density problems in the reactor core [7][8], but also the risk of nuclear proliferation has made the enrichment of ^{235}U a politically difficult matter [8]. A slightly newer technique that does not have this disadvantage is the use of spallation sources. In these sources, proton pulses are accelerated to high energies, typically in the range of GeV, and directed onto a target. The resulting spallation reaction could be described as

In this reaction, ST describes the spallation target, which releases several different spallation fragments as well as a total of k neutrons per spallation event. Depending on the target material, the total amount of neutrons for each spallation event could be as high as 50 [4], making an extremely high peak flux of neutrons possible. For both of these techniques, the energy of the neutrons is too high to be used for experiments, with energies that correspond to a wavelength in the order of $\lambda = 10^{-5}$ Å [4]. In order to reduce the energy of the neutron beam, the neutrons are transferred through a moderator material such as H_2O . This slows the neutrons down, and thereby reduces their energy such that they can be used for neutron scattering experiments. Finally, neutrons need to be brought from the source to experiments. As neutrons do not have any charge, they cannot be bend by any electromagnetic field. Instead, neutron mirrors are used that enclose the flight path of neutrons [9].

1.2 European Spallation Source

As this project is part of the SwedNess neutron graduate school, it should be seen in context of the construction of the European Spallation Source (ESS), which is being built in Lund. An overarching goal of SwedNess in general is to develop an understanding of neutron scattering in particular and thereby increasing the expertise that is needed with planned operations of ESS in the future. The spallation source is designed to deliver 5 MW of 2.5 GeV protons to a single target, which corresponds to an increase in average and peak neutron flux by a factor of 30 compared to the currently most powerful pulsed spallation source at ISIS in the UK [10]. The aim of ESS is to deliver a time average flux of neutrons that is comparable to the brightest continuous source in existence at ILL, using a low enough pulse repetition rate such in order to avoid loss of efficiency at high flux even for cold neutrons applications [11]. Construction started at 2014, with full operational performance planned in 2025 [11].

1.3 Neutron multilayers

Neutron multilayers are used in many different neutron optical instruments. A common example is that of neutron guides, which are necessary to guide a

neutron beam from source to experiment. In a neutron guide, different neutron supermirrors are used to enclose the beam trajectory, these neutron supermirrors consist of multilayers with many different periods. Multilayers are also used for monochromators, which are used to select specific wavelengths of a beam. By choosing a certain period at a specified angle, only one wavelength fulfils the Bragg condition at reflection. Therefore, only a certain wavelength will be reflected at the specified angle. This technique is commonly used to filter specific wavelengths. Multilayers with one magnetic material can be used to create neutron polarisers, filtering a certain spin direction of the neutron beam. The total neutron scattering potential has a contribution from the nuclear and magnetic scattering length, whether the magnetic scattering length subtracts or adds to the total scattering length depends on the polarisation state of the incoming neutron beam [5]. Using the right set of materials, the scattering contrast will disappear for one spin-state only, making the multilayer transparent for that spin-state while the other spin-state is reflected. Cold neutron beams may also be polarized using ^3He filters, but a better performance can be achieved when the required angular acceptance of the beam is narrow [12]. Polarized neutron beams can be used to investigate magnetic properties of materials. The performance of multilayer components in terms of reflected intensity is highly dependent on both the scattering contrast and the interface width between the layers. The scattering contrast is limited by the materials of choice, while the interface width can be reduced using the correct deposition techniques. Reducing this interface width offers great possibilities in terms of performance for multilayer components. The obtained reflectivity depends exponentially on the achieved interface width. Meaning even a small improvement will lead to a drastic increase in reflectivity performance. This means that the total flux at experiment can be increased very significantly by improving the instrumentation, without the need of more power-intensive neutron sources. Another advantage of a reduced interface width is that the minimum thickness that can be achieved is reduced as well. The total thickness of a layer can not meaningfully be less than the width of the interfaces. If the interfaces can be made flatter and more abrupt, the layers can be made thinner as well. This makes it possible for instance to deposit monochromators that can be applied for higher wavelengths and lower energies, such as cold neutron beams.

1.4 Research aims

The essential goal of this work is to enhance the performance of neutron multilayers by reducing the interface width between the layers. The biggest improvement in terms of neutron flux at experiment is not expected to come from more brilliant neutron sources, but instead from the improvement of different neutron optical components [13]. As multilayers are such essential and crucial elements in any of the intended neutron instrumentation, even the slightest improvements of the performance will have an immediate and large impact on

all research conducted using those instruments. The work presented is mainly focused on the simulation and modeling of neutron multilayers. The underlying goal here is to develop an understanding of the interface evolution of the samples, and how their reflectivity performance is affected by different parameters.

1.5 Outline of the thesis

This thesis will start with a theoretical background behind this work. Starting with chapter 2, the general scattering theory will be described. In this chapter, the underlying concepts will be explained in a general way. The optical theory that is used for the scattering experiments is described in chapter 3, where diffraction for different multilayers are explained. The deposition of the multilayers in this work is covered in chapter 4. This chapter will also describe the sputtering techniques, and how these are used to minimize the interface width between the individual layers. The instrumental aspects for the reflectivity are described in chapter 5, where both neutron and X-ray reflectometry will be described. The theory behind the reflectivity simulations that are used for the characterization of structural parameters is described in chapter 6. The other techniques that have been used for multilayer characterizations are covered in chapter 7. A summary of the results will be given in chapter 8, followed by an outlook in chapter 9. The summary of the papers in this work is covered in chapter 10, while the papers themselves can be found after the bibliography.

Chapter 2

Scattering theory

2.1 Neutron scattering

For a proper understanding of neutron scattering, it is important to consider that the Schrödinger wave equation can be applied to particles as well. Intuitively, neutrons are usually considered real particles with a very small but finite radius, but also neutrons can either be described as a wave or as a particle. In fact, the wavelength of a neutron can in principle have any arbitrary size. From this realization of neutrons as a wave, it follows that the same principles of diffraction apply for neutrons as for X-rays. The underlying concepts that are described in this chapter are therefore applicable for both neutrons and X-rays. In order to fully understand what happens when a neutron beam scatters from an interface, we consider an incoming neutron beam towards a surface with a certain scattering potential V_0 , as illustrated in figure 2.1. The neutron wave can be described by Schrödingers equation as usual:

$$\left(\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}). \quad (2.1)$$

The energy of the neutron is denoted by E , while V describes the potential to which the neutron is subject to, which may be described by the following expression [14]:

$$V(\mathbf{r}) = \frac{2\pi\hbar}{m} N_b. \quad (2.2)$$

The factor N_b denotes the scattering length density (SLD) and can be seen as a measure of the scattering power for a certain material. This quantity will be elaborated upon in subsection 2.2.2. For pedagogical reasons we assume that the scattering interface is perfectly flat and abrupt. The potential barrier that is present at the interface is therefore strictly perpendicular to the surface. Hence only the normal component of the wave vector is affected by the potential barrier and it is therefore the normal component of the neutron's kinetic energy that determines whether total reflection will occur at the barrier. The perpendicular component of the wave vector $\mathbf{k}_i$ can be expressed as usual:

$$\mathbf{k}_{i\perp} = \frac{\sqrt{2mE_{i\perp}}}{\hbar} = \mathbf{k}_i \sin \theta. \quad (2.3)$$

Rewriting for the kinetic energy gives us:

$$E_{i\perp} = \frac{(\hbar \mathbf{k}_i \sin \theta_i)^2}{8\pi^2 m}. \quad (2.4)$$

Figure 2.1: The neutron beam is subject to a potential barrier upon reflection at an interface. Part of the beam, while another part of the beam will be reflected.

If the perpendicular component of the kinetic energy, $E_{i\perp} < V$, then total reflection will occur, the critical angle is then given by $E_{i\perp} = V$. We can express the critical angle in terms of the scattering vector $\mathbf{q}$. The wave vector $\mathbf{k}$ can simply be expressed as $\mathbf{k} = \frac{2\pi}{\lambda}$, and since $\mathbf{q} = 2\mathbf{k}_i \sin \theta_i$ we get:

$$\mathbf{q} = \frac{4\pi}{\lambda} \sin \theta. \quad (2.5)$$

Using this result in combination with equations 2.2 and 2.4 gives us:

$$\mathbf{q}_c = \sqrt{16\pi N_b}. \quad (2.6)$$

This interaction is generally considered elastic, meaning the normal part of the beam will be fully reflected with the same reflected angle as the incident beam, just as one would expect from a perfect mirror. This part of the reflection where $\theta_i = \theta_r$ is commonly referred to as specular reflection.

If $E_{i\perp} > V$, total reflection will not occur and part of the neutron beam will be transmitted through the interface. The transmitted beam will have its kinetic energy reduced by the potential barrier, giving us $E_t = E_i - V$. So using this energy with the potential given in equation 2.2 we get:

$$\mathbf{k}_{t\perp}^2 = \frac{2m(E - V)}{\hbar^2} = \frac{2mE}{\hbar^2} - 4\pi N_b, \quad (2.7)$$

$$\mathbf{k}_{t\perp}^2 = \mathbf{k}_{i\perp}^2 - 4\pi N_b. \quad (2.8)$$

It follows from this relation that the potential barrier needs to be as large as possible to maximize total reflection, since a lower potential barrier leads to a larger portion of the neutron wave being transmitted. We can also define our refractive index:

$$n^2 = \frac{\mathbf{k}_t^2}{\mathbf{k}_i^2} = \frac{\mathbf{k}_{t\parallel}^2 + (\mathbf{k}_{i\perp}^2 - 4\pi N_b)}{\mathbf{k}_i^2} = \frac{\mathbf{k}_{i\parallel}^2 + (\mathbf{k}_{i\perp}^2 - 4\pi N_b)}{\mathbf{k}_i^2}. \quad (2.9)$$

Where we used $\mathbf{k}_{i\parallel} = \mathbf{k}_{t\parallel}$, as there's no potential barrier in the parallel direction. This part of the neutron wave is therefore unchanged at reflection. Solving equation 2.9 further then finally gives us:

$$n^2 = 1 - \frac{4\pi N_b}{k_i^2} = 1 - \frac{\lambda^2 N_b}{2\pi}. \quad (2.10)$$

For neutrons, $n \approx 1$, so the refractive index for neutrons is often approximated by:

$$n = 1 - \frac{\lambda^2 N_b}{2\pi}. \quad (2.11)$$

2.1.1 Fresnel reflection

To obtain an expression for the intensity after reflection, we start with an incoming neutron wave Ψ_i hitting an interface with refractive index n . This results in a partially reflected, and transmitted wave denoted by Ψ_r and Ψ_t respectively. If we consider the the vertical component of the wave, that is in the z -direction, we can apply the boundary condition to get the following expression:

$$\Psi_0 = A_i \cdot e^{i \cdot \mathbf{k}_i z} + A_r \cdot e^{-i \cdot \mathbf{k}_r z}, \quad (2.12)$$

$$\Psi_1 = A_t \cdot e^{i \cdot \mathbf{k}_t z}. \quad (2.13)$$

From the boundary conditions at $z = 0$, we get:

$$A_i + A_r = A_t, \quad (2.14)$$

$$A_i \cdot \mathbf{k}_i + A_r \cdot \mathbf{k}_r = A_t \cdot \mathbf{k}_t. \quad (2.15)$$

For elastic scattering the wave vector is conserved, it does change direction however giving us $\mathbf{k}_r = -\mathbf{k}_i$ from the reflected wave. Leaving us with the following condition:

$$(A_i - A_r) \cdot \mathbf{k}_i = A_t \cdot \mathbf{k}_t. \quad (2.16)$$

Combining equations 2.14 and 2.16, we get:

$$\frac{A_i - A_r}{A_i + A_r} = \frac{\mathbf{k}_t}{\mathbf{k}_i}. \quad (2.17)$$

Which we can rewrite using basic standard algebra as:

$$r = \frac{A_r}{A_i} = \frac{\mathbf{k}_i - \mathbf{k}_t}{\mathbf{k}_i + \mathbf{k}_t}. \quad (2.18)$$

Where r represents the fraction of the incident beam that is reflected. Note that the intensity, which is what is actually being measured during an experiment, is given by r^2 . Using equations 2.6, 2.8 and 2.18, we can re-write this in terms of q and q_c :

$$I = |r^2| = \left[\frac{q - \sqrt{q^2 - q_c^2}}{q + \sqrt{q^2 - q_c^2}} \right]^2. \quad (2.19)$$

During experiments, one often uses the incident angle θ_i instead of $\mathbf{q}$. To get to the intensity in terms of the incidence angle θ_i one can simply use equation 2.5 and put it into equation 2.19. At high angles of incidence, when $\mathbf{q} \gg \mathbf{q}_c$, equation 2.19 reduces to:

$$I = \frac{16\pi}{\mathbf{q}^4} N_b^2. \quad (2.20)$$

From which it follows that the intensity for a single layer falls off with $\mathbf{q}^4$ at higher angles, even for perfectly smooth interfaces. This expression is also used for the Born approximation, which will be covered later in subsection 6.2.

2.2 Neutron scattering length

While X-ray scattering comes from interaction with the electron cloud, neutron scattering can occur in two ways; nuclear scattering and magnetic scattering. Magnetic scattering occurs when unpaired electrons in a material interact with the magnetic moment of the neutron, while nuclear scattering occurs due to interaction with the nucleus. In this work we will focus on nuclear scattering. The scattering of neutrons depends directly on the scattering potential between the nucleus and the neutron, denoted by $V(\mathbf{r})$. This interaction potential acts on an extremely short range and falls to zero in the order of 10^{-15} m. Since this is orders of magnitudes shorter than the typical wavelength of neutrons, which is in the order of 10^{-10} m, we can essentially describe the nucleus as a pure point scatterer. The incoming wave of neutrons can be described by a planar wave:

$$\Psi_i = e^{i\mathbf{k}x}. \quad (2.21)$$

where $\mathbf{k}$ is the wavenumber $\frac{2\pi}{\lambda}$, and x is the distance from the nucleus in the propagation direction. The scattered wave will be spherically symmetrical and can be described as:

$$\Psi_s = \frac{b}{r} e^{i\mathbf{k}\mathbf{r}}, \quad (2.22)$$

where $\mathbf{r}$ is the radial distance to the nucleus, and b is the scattering length of the nucleus. The scattering length differs for each isotope in the periodic table and represents the strength of the neutron-nucleus interaction, the scattering length can basically be seen as the radius of the nucleus as experienced by the neutron. This gets intuitively clear when one thinks of the scattering length in the scattering cross section. The total scattering cross section is simply defined as the amount of neutrons scattered per second divided by the neutron flux:

$$\sigma_s = \frac{\text{Neutrons scattered per second}}{\Phi}. \quad (2.23)$$

Where Φ is the neutron flux, which describes the incident neutrons per unit area per second. As suggested by the name, the scattering cross section represents an area, and can be interpreted as a measure of the size of the nucleus as experienced

by the neutron. We can calculate the scattering cross section by starting from the differential scattering cross section [1]:

$$\sigma_s = \frac{\text{Neutrons scattered per second into solid angle } \Omega}{\Phi}. \quad (2.24)$$

The total scattering cross section is related to the differential cross section by:

$$\sigma_s = \int \frac{d\sigma}{d\Omega} d\Omega. \quad (2.25)$$

We can calculate the neutron flux by multiplying the probability density function of the neutron wave $|\Psi_i|^2$ by its velocity. For the incident neutron beam, this will simply be:

$$\Phi = \mathbf{v}|\Psi_i|^2 = \mathbf{v}. \quad (2.26)$$

While the scattered neutron flux can be expressed by:

$$\Phi_s = \mathbf{v}|\Psi_s|^2 = \mathbf{v} \frac{b^2}{r^2}. \quad (2.27)$$

To get to the amount of scattered neutrons per second that pass through an area dA we simply have to integrate over this area. Which leads to [15]:

$$v \frac{b^2}{r^2} dA = \mathbf{v} b^2 d\Omega. \quad (2.28)$$

As this quantity describes the amount of neutrons scattered per second into a solid angle, it is exactly equal to the numerator in the differential cross section as seen in equation 2.24 so plugging this in we get:

$$\frac{d\sigma}{d\Omega} d\Omega = \frac{\mathbf{v} b^2 d\Omega}{\Phi d\Omega} = b^2. \quad (2.29)$$

Where we used the fact that the magnitude of the neutron velocity is equal to that of the neutron flux as seen in equation 2.26. To get to the total scattering cross section we have to integrate over all space in terms of the solid angle. As there are exactly 4π steradians in a circle, we obtain:

$$\sigma_s = \int b^2 d\Omega = 4\pi b^2. \quad (2.30)$$

From which it follows that the scattering cross section forms circular area with a radius equal to the scattering length. In a sense, the scattering cross section describes the size of the nucleus as seen by the neutron, where the scattering length is the effective radius of the nucleus in this case. Note how the scattering length varies unsystematically across the periodic table and is not a single function of the mass number of the element.

2.2.1 Origin of neutron scattering lengths [16]

The neutron scattering length is often considered to vary randomly for each isotope. It is however possible to make a rough estimation of the neutron scattering length. We consider a neutron with an energy E_i being scattered from an attractive square well potential at $-V_0$. The well has a width of $2R$, and a potential of $V_0 \gg E_i$. Starting from the Schrödinger equation we've got:

$$\left(\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}). \quad (2.31)$$

Outside of the square well, the potential $V(\mathbf{r}) = 0$, and therefore the solution to the equation becomes:

$$\Psi_{s,\text{out}} = \frac{\sin \mathbf{k}\mathbf{r}}{\mathbf{k}\mathbf{r}} - b \frac{e^{i\mathbf{k}\mathbf{r}}}{\mathbf{r}}, \quad (2.32)$$

where $\mathbf{k} = \sqrt{2mE_i}\hbar$. Inside the square well, the solution becomes:

$$\Psi_{s,\text{in}} = A \frac{\sin \mathbf{q}\mathbf{r}}{\mathbf{q}\mathbf{r}}, \quad (2.33)$$

where the wave number $\mathbf{q}$ is described as $\mathbf{q} = \sqrt{2m(E_i + V_0)}\hbar$. Note that the factor $\mathbf{k}\mathbf{r} \ll 1$ due to the very small neutron mass and we can therefore approximate equation 2.32 as:

$$\Psi_{s,\text{out}} \approx 1 - \frac{b}{\mathbf{r}}. \quad (2.34)$$

Since the wave function has to be completely continuous over all space, we can use the boundary condition $|\mathbf{r}| = R$ to get:

$$\Psi_{s,\text{out}} = \Psi_{s,\text{in}}, \quad (2.35)$$

at the boundary, which leads to:

$$1 - \frac{b}{R} = A \frac{\sin \mathbf{q}R}{\mathbf{q}R}, \quad (2.36)$$

which can be rewritten to:

$$R - b = A \frac{\sin \mathbf{q}R}{\mathbf{q}}. \quad (2.37)$$

Even at the derivative, these functions need to be continuous, which gives us:

$$\frac{d}{dR}(R - b) = \frac{d}{dR} A \frac{\sin \mathbf{q}R}{\mathbf{q}}. \quad (2.38)$$

$$1 = A \cos \mathbf{q}R, \quad (2.39)$$

Figure 2.2: The ratio b/R varies very sharply as a function of qR , meaning the scattering length b can move to a seemingly random value for each added nucleus.

$$A = \frac{1}{\cos \mathbf{q}R}. \quad (2.40)$$

Combining equation 2.37 and 2.40 gives us:

$$R - b = \frac{1}{\cos \mathbf{q}R} \frac{\sin \mathbf{q}R}{\mathbf{q}}, \quad (2.41)$$

Rewriting the sine and cosine into a tangent:

$$R - b = \frac{\tan \mathbf{q}R}{\mathbf{q}}, \quad (2.42)$$

And finally, we can express the ratio b/R as a function of $\mathbf{q}R$:

$$\frac{b}{R} = 1 - \frac{\tan(\mathbf{q}R)}{\mathbf{q}R}. \quad (2.43)$$

This equation gives a first order estimate of the scattering length b . As can be seen in figure 2.2, b/R varies extremely sharply as a function of $\mathbf{q}R$, which means that the scattering length can jump to a completely different value for each added nucleus. This is illustrated further by the highlight of hydrogen-1 (H) and deuterium (D) which have a large contrast in scattering length despite belonging to the same element. It can also be seen that the scattering length can be negative for certain isotopes, this corresponds to a negative phase shift

upon scattering. Note that this description is merely an approximation, apart from the mathematical simplifications we have ignored both absorption and the magnetic component of the neutron scattering length. The imaginary part of the scattering length, which describes the absorption, is generally very low for neutrons which is in many cases a reason to choose for neutrons over X-rays as this allows the penetration of much larger samples. The magnetic component of the scattering length can be used with polarised neutron reflectivity in order to investigate magnetic properties of a material.

2.2.2 Scattering length density

While the total scattering power of a single nucleus can be well described in terms of scattering length, in order to get a good measure of the total scattering power of a material we also need to take the physical density into account. If the nuclei are more tightly packed, there will be more nuclei per unit volume to scatter from, which inevitably leads to stronger scattering. The total scattering power of a material is therefore best described in terms of scattering length density (SLD), which can be calculated by summing the scattering lengths of each element in the material and dividing this by the volume of the unit cell [9]:

$$\text{SLD} = \frac{\sum_{i=1}^N b_i}{V_m}. \quad (2.44)$$

Where b_i is the scattering length of each element and V_m is the volume of the unit cell. Note how this does not need to be an actual unit cell as seen in crystallography, it is indeed a representative volume of the material which in principle can be completely amorphous. As an amorphous material does not have a well defined crystal to define a volume, it can be calculated using the bulk density of the unit cell and the molecular weight:

$$V_m = \frac{M}{\rho N_a}. \quad (2.45)$$

Where ρ is the density of the material, N_a is the Avogadro constant. The scattering density of a composite material can then be calculated by putting equation 2.45 into equation 2.44:

$$\text{SLD} = \frac{\rho N_a \sum_{i=1}^N b_i}{\sum_{i=1}^N b_i M_i}. \quad (2.46)$$

The scattering density relates directly to the refractive index of neutrons as provided in equation 2.11, rewritten here for clarity:

$$n = 1 - \frac{\lambda^2}{2\pi} \cdot \text{SLD}. \quad (2.47)$$

Because of this linear relationship between SLD and refractive index, the SLD is often considered to be a direct analogue to the refractive index.

2.3 Choice of materials

The materials of choice in a neutron multilayer depend largely on the SLD. The imaginary component of the SLD, which describes absorption, needs to be as low as possible while the contrast in SLD between the layers need to be as large as possible to maximize total reflection. To illustrate, the real and imaginary components of a set of materials are plotted in figure 2.3, where only a select number of materials with a low imaginary component are shown. To maximize reflection, a combination of materials needs to be chosen with a large difference in the real part of the SLD. A combination of Ti and Be seems reasonable at first glance, but Be is not chosen as it's toxic and undergoes nuclear reactions when radiated with neutrons. Therefore a combination of Ni and Ti, as highlighted in the figure, is usually the material system of choice. Note that some materials with intermediate values are omitted in order to increase readability.

Figure 2.3: A selection of materials with their scattering lengths are plotted for low imaginary values, a system with Ni/Ti offers a large contrast in the real SLD with low values for the imaginary part.

2.4 Neutron scattering in reciprocal space

It can be extremely convenient in neutron scattering to describe phenomena in reciprocal space instead of real space. This convenience arises from the fact that the diffraction pattern is directly related to the reciprocal space of the SLD-profile of the material, so by becoming familiar with this description, one can tell a lot about the structural properties of a given multilayer simply from a glance at the obtained diffraction pattern [17]. The reciprocal space corresponds to the Fourier transform of real space, and is often also referred to as q -space or Fourier space.

2.4.1 Reciprocal space

To understand the diffraction pattern in reciprocal space we can imagine an incoming neutron wave that scatters upon an interface as shown in figure 2.4a. The incident and scattered wave vector are denoted by $\mathbf{k}_i$ and $\mathbf{k}_f$ respectively. The scattering vector is described by the vector $\mathbf{q}$ and can be expressed as $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ [18]. From geometry, we can see that:

$$\sin \frac{2\theta}{2} = \frac{0.5\mathbf{q}}{k_i}. \quad (2.48)$$

Where we can use $k_i = 2\pi/\lambda$ to show:

$$\mathbf{q} = \frac{4\pi}{\lambda} \sin \theta. \quad (2.49)$$

a) Reflection from a single layer b) Ewald sphere construction

Figure 2.4: a) An incoming neutron wave with incident and refracted wave vector $\mathbf{k}_i$ and $\mathbf{k}_f$ scatters upon an interface. The scattering vector $\mathbf{q}$ is obtained by $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ and is in the q_z direction for specular scattering. b) The Ewald sphere construction can be used to illustrate for which incidence angles a diffraction peak can be found.

Which is the equation that is generally used to convert from q -space to θ . The points in q -space where diffraction peaks are found can be illustrated using an Ewald sphere construction, as shown in figure 2.4b. The incoming wave vector $\mathbf{k}_i$ is drawn with its tip drawn at the scattering site. A sphere is drawn around this vector, and a diffracted beam will be formed if the drawn sphere intersects with an interface in reciprocal space. From this, we can see how a diffraction peak can be observed at the given incidence angle 2θ , corresponding to the third peak in q -space. We can also note how the diffraction peaks are equidistant to each other with a distance of $2\pi/\lambda$. During a specular neutron reflectivity experiment, a scan is made in the $\mathbf{q}_z$ direction by varying the incidence angle θ .

2.4.2 Fourier expansion for an ideal multilayer

The intensity profile that is obtained by experiment is directly dependent on the SLD-profile in the probed direction, as explained in subchapter 2.1. For a perfect multilayer with abrupt interfaces, the SLD-profile in the depth direction will have the form of a square wave. The obtained intensity profile can then be explained by the Fourier transform of this profile. The SLD-profile can be written as an infinite series of cosines and sines [18]:

$$g(z) = a_0 + \sum_{n=1}^{\infty} \left[a_n \cos\left(\frac{2\pi}{\Lambda}nz\right) + b_n \sin\left(\frac{2\pi}{\Lambda}nz\right) \right]. \quad (2.50)$$

As an example, we take such an SLD profile for a multilayer where the bilayer consists of two distinct layers with a thickness of 1 nm each without any interface imperfections. The amplitude of the SLD is chosen to be equal to $1.0 \text{ \AA}^{-2}$ for this example, as can be seen from the square wave in figure 2.5. The first term a_0 can be easily found by evaluating the SLD-function over one period. The resulting integral can be found using basic geometry, as the integral simply equals the total area under the curve. For the first period, the total area evidently equals zero:

$$a_0 = \int_0^{\Lambda} g(z)dz = 0. \quad (2.51)$$

The terms for a_n can be found in a similar way:

$$a_n = \frac{1}{0.5\Lambda} \int_0^{\Lambda} g(z) \cos\left(\frac{2\pi}{\Lambda}nz\right)dz, \quad (2.52)$$

$$= \frac{2}{\Lambda} \int_0^{0.5\Lambda} \cos\left(\frac{2\pi}{\Lambda}nz\right)dz - \frac{2}{\Lambda} \int_{0.5\Lambda}^{\Lambda} \cos\left(\frac{2\pi}{\Lambda}nz\right)dz, \quad (2.53)$$

$$= \frac{4}{\Lambda} \int_0^{0.5\Lambda} \cos\left(\frac{2\pi}{\Lambda}nz\right)dz = 0. \quad (2.54)$$

Note how all even Fourier components disappear, this is a direct result from the fact that both layers in the multilayer have an equal thickness. The ratio between

the thicknesses of the individual layers in the bilayer is an important parameter and is usually denoted as $\Gamma = l_a/l_b$ where l_a and l_b denote the thickness of each layer in the bilayer. In general it follows from the Fourier composition that for a Γ -value of $1/m$, every m 'th component will disappear. In this example where the layers are equally thick we get $\Gamma = 0.5$, meaning every second component will disappear. This leaves us with a series of sines:

$$g(z) = \sum_{n=1}^{\infty} b_n \sin\left(\frac{2\pi}{\Lambda}nz\right). \quad (2.55)$$

Evaluating the sine gives us:

$$b_n = \frac{1}{0.5\Lambda} \int_0^{\Lambda} g(z) \sin\left(\frac{2\pi}{\Lambda}nz\right) dz, \quad (2.56)$$

$$= \frac{2}{\Lambda} \int_0^{0.5\Lambda} \sin\left(\frac{2\pi}{\Lambda}nz\right) dz - \frac{2}{\Lambda} \int_{0.5\Lambda}^{\Lambda} \sin\left(\frac{2\pi}{\Lambda}nz\right) dz, \quad (2.57)$$

$$= \frac{4}{\Lambda} \int_0^{0.5\Lambda} \sin\left(\frac{2\pi}{\Lambda}nz\right) dz, \quad (2.58)$$

$$= \frac{2}{n\pi} (1 - \cos n\pi). \quad (2.59)$$

Which can be reduced to:

$$b_n = \begin{cases} 0, & \text{if } n \text{ is even.} \\ \frac{4}{n\pi}, & \text{if } n \text{ is odd.} \end{cases} \quad (2.60)$$

This leaves us with our final Fourier series for a square wave:

$$g(z) = \sum_{n=1}^{\infty} \frac{4}{n\pi} \sin\left(\frac{2\pi}{\Lambda}nz\right). \quad (2.61)$$

This result is illustrated in figure 2.5. The square wave illustrates the actual SLD-profile, while the sinusoidal waves are the Fourier components as described in equation 2.61, in this illustration only the first three components are shown. The amplitudes of the peaks of the measured signal in a scattering experiment are directly proportional to the amplitudes of the Fourier components described here. This makes it clear how a higher contrast in scattering potential results in a stronger signal. A similar analysis is valid for interfaces with interface imperfections, where the transition from one layer to another is more gradual. While the resulting Fourier components will be different from equation 2.61, it can be seen from the described example in figure 2.5 that the first component of the Fourier series will be very sensitive to the contrast in SLD between the layers, while the other components will be more sensitive to the interface width.

Figure 2.5: The interface width can be described as an infinite series of a sine waves. The first three components of the Fourier series are shown in this figure, summing all Fourier components will eventually result in the sketched square wave.

Chapter 3

Multilayer and supermirror optics

3.1 Reflectivity from different interfaces

To get to the reflectivity for multilayer instruments, we will start with the simplest case of reflectivity from a substrate. After that, we will expand this to the case of a single layer on top of a substrate, followed by a multilayer.

3.1.1 Substrate

Reflectivity on a single substrate describes the simplest form of Fresnel reflectivity, which is covered in subsection 2.1.1. The measured intensity can then be expressed using the fraction of reflected intensity as given in equation 2.19, and multiplying it with the incident intensity I_0 :

$$I = I_0 \left[\frac{\mathbf{q} - \sqrt{\mathbf{q}^2 - \mathbf{q}_c^2}}{\mathbf{q} + \sqrt{\mathbf{q}^2 - \mathbf{q}_c^2}} \right]^2. \quad (3.1)$$

A simulated intensity profile resulting from this expression is shown in figure 3.1, where an incident neutron beam with a wavelength of 5.0 Å reflects upon a silicon substrate.

Figure 3.1: A simulation of the reflectance for a single layer of nickel with a thickness of 30 nm on a Si substrate and a neutron wavelength of 5 Å.

3.1.2 Single layer

If we add a single layer to the substrate, additional reflections will appear due to the finite thickness of this layer. The resulting reflection can most clearly be understood by tracing an incoming beam, as shown in figure 3.2. The incoming beam partly reflects at the surface, while another part gets transmitted through the top layer and reflected at the substrate interface. The phase difference between the two transmitted beams depend on the optical path, and it follows from the figure that this can be described by:

$$\Delta = (AB + BC)n - AD. \quad (3.2)$$

Where n is the refractive index of the layer. From simple geometry in the figure, it also follows that the path difference can be described as:

$$\Delta = 2d \sin(\theta_t) \approx 2d \sqrt{\theta^2 - \theta_c^2}. \quad (3.3)$$

From the left-hand side, we can see that this is analogue to the Bragg equation, where a maximum occurs whenever the phase difference is a multiple of the wavelength, or when $\Delta = m\lambda$. Filling this into the right-hand side, we can re-write this [19] to get the reflection angle for the m 'th top:

$$\theta_m^2 = \theta_c^2 + \left(\frac{\lambda}{2d}\right)m^2. \quad (3.4)$$

Such a reflection is simulated in figure 3.3, where a neutron-beam is reflected from a single layer of nickel with a thickness of 30 nm. It follows from equation 3.4, that the spacing between these maxima that can be observed are inversely dependent on the thickness of the layer. The distance between these fringes in reciprocal space is equidistant and can be expressed as

$$\Delta \mathbf{q} = \frac{2\pi}{d}, \quad (3.5)$$

where d is the layer thickness. A thick layer therefore leads to a closer spacing between the fringes while a very thin layer will have these fringes very far apart.

Figure 3.2: An incoming neutron beam hits a single thin film from the substrate.

Figure 3.3: A simulation of the reflectance for a single layer of nickel with a thickness of 30 nm on a Si substrate and a Neutron wavelength of 5 Å.

3.1.3 Multilayers

We can expand this concept as well to multilayers, which consist of a certain number of periods. One period is a set of two layers which is then repeated throughout the stack. A schematic drawing of such a multilayer is shown in figure 3.4. As can be observed in figure, the difference in optical path between the reflected beams depends on the total thickness of one period. The total thickness of one bilayer is known as the period, and is denoted with Λ . The position of the fringes that arise from the periodicities can be described in a similar way as equation 3.4, but where we use the bilayer thickness instead of the individual

Figure 3.4: A schematic overview showing reflection from a multilayer. For pedagogical purposes, only one reflected beam is drawn per period. In reality, reflection occurs at every layer in the sample.

layer thickness:

$$\theta_m^2 = \theta_c^2 + \left(\frac{\lambda}{2\Lambda} \right) m^2. \quad (3.6)$$

Where m is an integer number which now denotes a maximum as illustrated in figure 3.5. These maxima, which are known as Bragg peaks, are the result of the bilayer period. Apart from these Bragg peaks, we can also observe so-called Kiessig fringes between the 'peaks. These fringes arise from the total thickness of the multilayer, following the same principle as a single layer described in subchapter 3.1.2. Assuming there is no damping due to roughness for example, we can observe $N - 2$ of these Kiessig fringes between the maxima from the layer periodicity in a multilayer with N bilayers [19]. This is also shown in figure 3.5, where clear Kiessig are observed between the larger Bragg peaks. In reciprocal space, the distance between the Kiessig fringes and between the Bragg peak are both equidistant and can be expressed as:

$$\Delta q_{\text{Kiessig}} = \frac{2\pi}{N\Lambda}, \quad (3.7)$$

$$\Delta q_{\text{Bragg}} = \frac{2\pi}{\Lambda}, \quad (3.8)$$

for the Kiessig fringes and Bragg peaks respectively.

Figure 3.5: A simulation of the reflectance for a multilayer system consisting of 12 bilayers of Ni and Ti, with a total period of 50 nm.

3.1.4 Supermirror

While the total reflectivity for a perfect multilayer can in principle be near unity for a high enough number of periods, this is only at a very narrow angular range at the first Bragg peak. To extend the reflectivity to a broader angular range, so-called neutron supermirrors are used. These mirrors consist of a depth-graded periodicity as illustrated in figure 3.6. There are several algorithms that describe the optimal layer thicknesses for a material system of choice. For the graph in figure 3.6b, a Ni/Ti mirror has been simulated with 5000 bilayers. The thickness of both Ni and Ti in the j 'th bilayer follow a power-law according to:

$$d_j = \frac{168.17}{(j - 0.97)^{0.25}}, \quad (3.9)$$

Where $j = 1$ at the top of the sample. This power-law description is essentially equivalent to the first depth-graded function for neutron supermirrors as introduced in 1977 [20]. The most commonly used algorithm nowadays is the Hayter Mook algorithm [21], described elsewhere [22]. Supermirrors are often characterized in terms of m :

$$m = \frac{\theta_{\text{mirror}}}{\theta_{\text{Ni,c}}}, \quad (3.10)$$

where θ_{mirror} is the effective critical angle of the mirror and $\theta_{\text{Ni,c}}$ is the critical angle of Ni. Neutron supermirrors consisting of Ni/Ti are commonly used for neutron guides to transport neutrons from source to experiment and are therefore an important component within the neutron scattering field.

Figure 3.6: a) A schematic overview of a neutron supermirror with varying layer thicknesses. For clarity, only five periods are drawn and internal reflections are omitted. b) Simulated reflectivity performance of a Ni/Ti neutron supermirror with 5000 bilayers at a wavelength of $\lambda = 3 \text{ \AA}$.

3.2 Interface imperfections

So far, we have assumed reflection from ideal interfaces. In reality however, interfaces are not perfectly flat or abrupt. Meaning the interfaces themselves have a certain width in the normal direction, this width is called the interface width and is denoted by σ . The interface width arises from two different physical factors: the abruptness of the interface, which arise from factors such as interdiffusion and intermixing, and the interfacial roughness. These two physical factors behave independently, a perfectly flat sample can still contain intermixing while a rough sample still can be perfectly abrupt on a local level. The total interface width can therefore be considered as the sum of these effects, and can thus be expressed as:

$$\sigma^2 = \sigma_d^2 + \sigma_r^2. \quad (3.11)$$

Where σ_d describes the interface width due to the intermixing and interdiffusion and σ_r describes the interface width due to the roughness. Note how the exact deviation from a perfect interface varies on a local level, the interface width is therefore defined as a square root averaged value over the probed interface. If we consider the SLD-profile of such imperfect interfaces, it follows that the effects of intermixing and interfacial roughness are indistinguishable from each other in the normal direction. Both factors lead to a more gradual transition of SLD from one interface to the other, resulting in a reduction of specular reflectivity. In the case of interfacial roughness, part of the incident beam will be scattered into non-specular directions while intermixing leads to a higher portion of the beam being transmitted into the sample. These different sources of interface width can therefore be observed by performing non-specular scans, in specular reflectivity these effects are indistinguishable from each other however, as illustrated in figure 3.7.

A typical distribution of the interface profile in the normal direction is given by the error function:

$$g(z) = \text{erf}\left(\frac{z}{\sqrt{2}\sigma}\right). \quad (3.12)$$

The derivative of the error function shows how the profile depends on the probed

Figure 3.7: While intermixing and surface roughness are distinct phenomena, they are indistinguishable in the SLD profile normal to the interface.

z-direction, this turns out to be a Gaussian distribution [23]:

$$f(z) = \frac{dg}{dz} = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{1}{2}\left(\frac{z}{\sigma}\right)^2\right]. \quad (3.13)$$

The attenuation factor in the diffraction pattern follows from the Fourier transform, this is another Gaussian function. So the attenuation factor associated with our Fresnel equations can be described as

$$\tilde{f}(z) = \exp\left[-\frac{s^2\sigma^2}{2}\left(\frac{4\pi\sigma\sin\theta}{\lambda}\right)^2\right]. \quad (3.14)$$

This factor is known as the Debye-Waller factor and is commonly used to simulate imperfect interfaces [24]. From this factor and combining it with Fresnel equations, we find that the reflectivity of a multilayer can be described as:

$$R = R_0 \exp\left(-2\pi m \frac{\sigma}{\Lambda}\right). \quad (3.15)$$

Note that the reflectivity of a sample depends exponentially squared on the interface width. So even a modest improvement of the interface width has a large impact on the total reflectivity. The importance of the multilayer period can intuitively be explained by the fact that a multilayer with a smaller period has a larger fraction of the layer consisting of interfaces. The smaller the period, the more important the quality of the interface therefore becomes to obtain a good reflectivity performance.

3.3 Off-specular scattering

So far we have only considered the specular part of reflection where the angle of incidence is equal to the scattering angle. For an ideal interface the scattering potential will always be constant in the in-plane direction of the sample, meaning the incident beam the perpendicular component of the neutron beam is not subject to any potential barriers. All scattering will therefore only occur in the specular direction normal to the plane of incidence where such a potential barrier does exist. For a non-ideal sample with surface roughness however, local differences in scattering length density occur in the in-plane direction of the sample. The parallel component of the neutron beam is therefore subject to a potential barrier, leading to partial refraction into the in-plane direction. This phenomenon, where scattering occurs outside of the specular direction is called off-specular scattering. This is further illustrated in figure 3.8, where an incoming neutron beam reflects from the sample and reaches the detector, the specular signal can be found in the plane of incidence while the off-specular signal is perpendicular to the plane of incidence. Since off-specular scattering probes the in-plane direction of the interface, one can obtain a lot of information about the roughness profile at the interfaces. Interface roughness for instance gives

Figure 3.8: An incoming neutron beam reflects from the sample and reaches the detector, the specular signal can be found in the plane of incidence while the off-specular signal is perpendicular to the plane of incidence.

rise to sharp local scattering potential barriers in the off-specular direction, and therefore contributes to the off-specular signal. Intermixing however leads to a more gradual contrasts in the in-plane direction and contributes therefore much less to the off-specular signal. A strong off-specular signal is therefore often the result of surface roughness instead of intermixing, a distinction that cannot be made with specular scattering. For specular scattering, we found that the interface profile could be described by a Gaussian distribution as described by equation 3.13. For off-specular scattering, it turns out that the interface width can be described by a height-height correlation function, commonly described by [25]

$$C(\mathbf{r}) = \sigma^2 \exp \left[- \left(\frac{\mathbf{r}}{\xi_{\parallel}} \right)^{2h} \right]. \quad (3.16)$$

Two new parameters are introduced in this expression. The term $\xi_{\parallel}$ describes the lateral correlation length in the sample. The lateral correlation length, illustrated in figure 3.9e, is sometimes described as the cut-off for the length scale where an interface begins to look smooth. The absolute magnitude of the interface width can very well be low, but the interface still looks very rough if the lateral correlation length is low enough. A large correlation length increases the intensity in reciprocal space, and reduces the width of the signal. Because of this, a sample with large lateral correlation length will have its off-specular signal distributed close to the specular signal. The term h is the Hurst parameter and describes the jaggedness of the interfaces in the sample, as illustrated in figure 3.9f. A sample with a Hurst parameter of 1.0 looks relatively smooth, while interfaces get more jagged the closer the Hurst parameter gets to zero. By taking solving

the Fourier transform analytically, we can see that this provides a Lorentzian shaped off-specular signal around the specular peak for the special case of $h = 0.5$ and a Gaussian shaped signal for $h = 1.0$ [26]. Another important factor is how closely correlated the layers are to each other. The overall contribution from single uncorrelated layers are rather small, but can grow exponentially with an increasing amount of correlated layers. The corresponding correlation function in the normal direction can be given by [25]

$$G_{j,k}(z) = \sigma_j \sigma_k \exp\left(-\frac{z_j - z_k}{\xi_{\perp}}\right). \quad (3.17)$$

The term $\xi_{\perp}$, illustrated in figure 3.9e, describes the cross-correlation length and tells us how correlated the layers are. If cross-correlation length is much larger than the layer thickness, then the layers are perfectly correlated and this factor will be equal to one. If the cross-correlation length is very small however, then this factor will be equal to zero. The corresponding reciprocal signal will therefore disappear for completely uncorrelated layers. This parameter is particularly interesting for this work, as the presence of roughness correlation means that deviations from an ideal layer at the interface repeat themselves for subsequent layers, meaning that such deviations may increase with each newly deposited layer. This phenomenon, which is called accumulated roughness, is a particular challenge when depositing multilayers with a many periods, which are necessary when depositing supermirrors for instance. Correlated roughness in a multilayer can be detected from the appearance of so-called Bragg sheets in the off-specular signal. This is intuitively clarified in figure 3.10. When the interface profile is completely uncorrelated, the off-specular signal scatters into different directions for each layer within the sample, meaning the off-specular signal will be spread out over the entire reciprocal plane. For completely correlated layers, the off-specular signal is scattered into the same direction for each layer. As the periodicity of this interface profile is the same as the multilayer period, this signal will be focused on in perpendicular sheets around the Bragg peaks of the specular signal.

Figure 3.9: a) An ideal multilayer with flat and abrupt interfaces. b) Correlated roughness, the roughness profile for each interface is repeated throughout the layer. c) Uncorrelated roughness, the roughness profile is independent for each layer. d) Accumulating roughness, the interface width increases throughout the multilayer. e) The lateral correlation length and the vertical correlation length scale for a multilayer. f) Interfaces with increasing jaggedness throughout the multilayer. Note how a low Hurts parameter corresponds to a more jagged layer with high spatial frequency.

Figure 3.10: a) Reflection for very correlated layers. As the interface imperfections are similar for each layer, scattering will occur in the same direction for each layer. b) The off-specular mapping for neutron reflection with correlated roughness. As the rays are scattered in the same direction, very concentrated Bragg sheets arise around the same q_z values whenever the specular Bragg condition is fulfilled. c) Reflection for uncorrelated layers. As the interface imperfections are different for each layer, the resulting scattering direction will be different as well. d) The off-specular mapping for neutron reflection with uncorrelated roughness. The uncorrelated layers give rise to a spread-out diffuse signal over q -space.

3.4 Coherence length

The waves that are described in this work are assumed to be a perfect plane wave, this is however an idealization. In reality the wave is not perfectly monochromatic, meaning it carries different wavelengths. Over a certain horizontal distance the wave will therefore become out of phase, giving rise to a longitudinal coherence length. Simultaneously, the wave does not have a perfectly defined propagation direction, this gives rise to a transverse coherence length. These two effects are shown in figure 3.11. The magnitude of the coherence lengths restricts how sensitive the beam is to different features in the sample. If certain deviations in the interface are smaller than the relevant coherence length, then these features will not be visible in the resulting diffraction signal. It can therefore be important to be aware of the magnitude of these coherence lengths. The off-specular measurements in this work probe the horizontal plane of the sample interfaces and are therefore sensitive to the horizontal coherence length of the incident beam. Apart from the quality of the beam, the geometry plays an important role as well when it comes to the sensitivity of the different features in the sample profile. An incident beam at a low angle will dominantly probe the horizontal in-plane direction, and will therefore be more sensitive to the longitudinal coherence length. Subsequently, an incident beam of a higher angle will be more sensitive to the transverse coherence length.

3.4.1 Longitudinal coherence length

As illustrated in figure 3.11a, the beam will slowly become out of phase as it propagates due to the different wavelengths present in the beam. The total longitudinal coherence length is defined as the distance after which the wave is completely out of phase [23]. To calculate this, we can imagine that two waves with slightly different wavelengths λ and $\lambda - \Delta\lambda$ will slowly become out of phase as they propagate. After a distance of L_L , they are completely out of phase. After a distance of $2L_L$, the phase difference between the waves will be equal to exactly one period meaning they're back in phase again. This process is

Figure 3.11: a) The longitudinal coherence length. Phase information is lost as different wavelengths in the beam slowly drift out of phase. b) Transverse coherence length. Vertical phase information is lost due to deviations in the propagation direction.

a) Longitudinal coherence length b) Transverse coherence length

Figure 3.12: a) Two waves with slightly varying wavelengths will slowly get out of phase, after a distance $2L_L$ the waves are completely in phase again. b) Two waves with the same wavelength and a slightly different propagation direction are spatially separated by a distance D . Their phases will slowly shift during propagation. A full phase-shift of one wavelength is accomplished after a longitudinal distance of R . The transverse shift associated with this phase shift of 2λ is equal to $2L_T$.

illustrated in figure 3.12a. Leaving us with the following expression:

$$2L_L = N\lambda = (N + 1)(\lambda - \Delta\lambda). \quad (3.18)$$

Where we used the fact that the wave with wavelength $\lambda - \Delta$ will be exactly one period behind the wave with wavelength λ once they're back in phase again. We can re-write equation 3.18:

$$N\lambda = N\lambda - N\Delta\lambda + \lambda - \Delta\lambda, \quad (3.19)$$

subtracting $N\lambda$ from both sides:

$$0 = -N\Delta\lambda + \lambda - \Delta\lambda, \quad (3.20)$$

which we can rewrite as:

$$\frac{\lambda}{\Delta\lambda} = N + 1 \approx N, \quad (3.21)$$

where we used the fact that it takes a large number of periods for a beam to get back into phase again. We can now combine equation 3.18 with equation 3.21 to get to the equation for the longitudinal coherence length:

$$L_L = \frac{\lambda^2}{2\Delta\lambda}. \quad (3.22)$$

3.4.2 Transverse coherence length

Another imperfection of an actual beam arises from the fact that a beam generally does not have a perfectly well-defined direction. Different parts of the beam therefore travel in a slightly different propagation direction, as is illustrated in figure 3.11b. This gives rise to a transverse coherence length, which is defined as the lateral distance along a wave front after which two waves with the same wavelength, originating from two separate points in space, are out of phase. This is further illustrated in figure 3.12b. The spatial separation in the origin, denoted in the figure by D , is often defined by a slit. As the beams propagate further, they will slowly shift out of phase. After a longitudinal distance R , the waves will be in phase again. For an angular divergence of $\Delta\theta$ we get:

$$\tan(\Delta\theta) = \frac{R}{D}. \quad (3.23)$$

The associated transverse coherence length can then be expressed as:

$$\tan(\Delta\theta) = \frac{\lambda}{2L_t}. \quad (3.24)$$

Combining equation 3.23 and 3.24 gives us the transverse coherence length:

$$L_t = \frac{\lambda R}{2D}. \quad (3.25)$$

From which it becomes clear that the transverse coherence length is largely dependent on the slit size that is being used.

Chapter 4

Multilayer depositions

In order to create high quality multilayers a proper understanding of the growth technique is necessary. In this chapter we will explain the techniques used to grow the samples discussed in this work, starting by an introduction on magnetron sputter deposition itself.

4.1 Magnetron sputter deposition

One of the most popular techniques to grow multilayers is physical vapor deposition (PVD) [27]. Magnetron sputter deposition is a common type of PVD, which is used to grow the samples in this work. The basic working principle behind sputtering is intuitively quite simple. A steady flow of noble gas is led into a vacuum chamber. Meanwhile, a bias is applied to the sputtering target, which contains the material that will be deposited upon the substrate. Stray electrons near the target are accelerated towards the substrate due to the electric field that is present, colliding with neutral atoms from inlet sputtering gas on the way. If these electrons have gained sufficient energy upon collision, it may knock off an electron from the sputtering gas, converting it in to a positively charged ion [28]:

Note how two additional electrons are released during this ionization process, these too are accelerated by the electric field and can bombard additional gas atoms generating even more free electrons. Meanwhile the ionized atoms, which are positively charged, will be attracted to the negatively charged sputtering target. Upon collision, both target atoms as well as secondary electrons are ejected. The secondary electrons will be accelerated and ionize even more neutral gas atoms while part the ejected target atoms will land on the substrate surface, slowly creating a uniform layer of the target material. This state of ionized gas is known as a plasma, and is generally considered as an own state of matter. Upon the electron excitation of the sputtering gas, photons will be emitted which gives the visible plasma a visible glow. In order for the plasma to be sustained, there has to be a sufficient amount of collisions between electrons and sputtering atoms. The secondary electrons are therefore important to sustain the plasma [28].

In order to maximize the amount of secondary electrons that can be used for the ionization process magnets are placed behind the target material. The subsequent Lorentz force on the electron provides a path for the electrons to follow. A typical orientation of these magnets can be seen in figure 4.1, where the magnetic field is orientated radially above the target surface. The resulting path will follow a direction according to the cross-product $\mathbf{E} \times \mathbf{B}$, forming a

Figure 4.1: A simplified sketch of magnetron sputtering. Incoming Argon ions collide upon the sputtering target, knocking out target atoms which in their turn form a new layer of the material on the substrate.

circular trajectory above the target surface. Given the preferential status of this path for the electrons, the ionization rate will be higher in this region leading to a higher plasma density. It is for this reason that a circular erosion zone appears on used targets [29].

4.2 Ion assistance

In order to optimize the growth process and create smooth and abrupt layers, it is important to consider the energy of the incoming adatoms on the multilayer that is being deposited. When the adatom energy is too low, the surface mobility will be very limited meaning incoming adatoms will stick directly to their landing sites. Because of this, any deviation in the film surface will not be evened out but instead will be repeated. Such growth will therefore lead to rough surfaces with a lot of accumulated roughness [23].

Increasing the adatom energy will increase the surface mobility, adatoms that land on the surface can migrate to another spot, smoothening out the deposited layer. It is therefore important for a smooth film, to increase the adatom mobility. One way to do this, is to use the ions that are available in the plasma during film growth [30]. By applying a negative bias on the substrate, there will be a significant potential drop towards the substrate meaning the ions will be accelerated towards the film. By controlling the bias on the substrate, the ion-atom ratio can be controlled such that there is enough energy per adatom to enable surface migration at the landing sites. These different cases of film

Figure 4.2: a) Film growth with low adatom energy, adatoms stick directly to their landing sites leading to a rough surface. b) Ion-assistance during layer growth increases adatom mobility, making surface migration possible. Note how the ions are not part of deposited layer, instead they recoil in the form of neutral gas atoms [31].

growth are illustrated in figure 4.2. However, the high-energy bombardments of ions can lead to intermixing at the interfaces, meaning particles of the film will be displaced into the substrate. Using a too high energy therefore leads to an increase in intermixing, which essentially has the same effect as regular roughness. It is therefore important to find a good balance between the smoothening effect due to surface migration at high adatom energies, and the lack of intermixing that comes with low adatom energies. The plasma can be guided using a magnetic field near the substrate, such that a lower ion energy is required for surface migration, there will however still remain intermixing between the two layers.

While this intermixing effect is mainly limited to the first atomic layer, the multilayers in this work have an interface width that is roughly in the order of the atomic spacing. Such small displacements can therefore lead to a significant increase in the total interface width and should therefore be avoided.

In order to achieve this, a so called modulated ion assistance scheme is used during the growth of the deposited multilayers. In this set-up, an initial layer is grown with a low bias at the substrate. This layer initial layer is therefore grown with a very low adatom energy, leading to relative rough growth at a lower density, but without any intermixing. After an initial part of the layer is grown using this low-bias scheme, the bias is increased in order to allow for surface migration when the adatom reaches the surface, smoothening the rest of the layer. While there will be intermixing at this higher bias, the intermixing will be limited to the initially grown layer which is the same material. The initially grown layer therefore acts as a buffer layer, to protect the lower layer against intermixing. This process with an alternating bias scheme is repeated throughout the deposition of the entire multilayer, leading to smooth and abrupt surfaces [23]. This scheme is illustrated in figure 4.3

Figure 4.3: a) An initial buffer layer is grown with a low substrate bias. The leads to a very rough initial layer without intermixing. b) The rest of the layer is grown with a higher substrate bias, giving the adatoms enough energy to migrate. the buffer layer prevents intermixing into the layer beneath. The different colors for the initial and final layers are for the purpose of clarity, they are the same material.

4.3 $^{11}\text{B}_4\text{C}$ co-deposition

When growing multilayers using magnetron sputtering, nanocrystallites tend to form throughout the sample. These crystallites lead to faceted interfaces between the layers which can contribute to an increased interface width. Another contributing factor to the interface width is the formation of intermetallics between the layers, decreasing the abruptness between the layers. Furthermore, roughness patterns at the interface tend to be replicated leading to roughness accumulation. It would therefore be beneficial to eliminate the formation of crystallites by growing an amorphous multilayer instead. This can be established by co-depositing $^{11}\text{B}_4\text{C}$ during the growth process. The addition of boron to the layer inhibits the formation of crystallites, leading to amorphous layers throughout the entire multilayer. Using a continuous deposition of $^{11}\text{B}_4\text{C}$ during the growth process, boron is added through the entire multilayer. For neutron multilayers it is important to consider that the boron-10 isotope, which is present in natural boron, absorbs neutrons. The boron-11 isotope however is transparent to neutrons, it is for this reason that an isotope enriched $^{11}\text{B}_4\text{C}$ target is used during the deposition. The power to the $^{11}\text{B}_4\text{C}$ magnetron is constant during the entire deposition, resulting in a stable $^{11}\text{B}_4\text{C}$ -flux during film growth. Note that the addition of $^{11}\text{B}_4\text{C}$ leads to a dilution of the SLD-contrast between the interfaces, adding too much $^{11}\text{B}_4\text{C}$ therefore leads to a reduction in reflectivity. The power that is used for the $^{11}\text{B}_4\text{C}$ -target is therefore tweaked such that it is high enough to make the entire sample is amorphous, but not increased any further to prevent unnecessary dilution in SLD-contrast between the interfaces.

4.4 Reducing interface width

When designing high-performance neutron multilayers, it is essential to consider the interface width in the sample. A combination of the techniques above is used to minimize the total interface width as much as possible. The co-deposition of $^{11}\text{B}_4\text{C}$ removes all crystallinity of the multilayer. However, the adatom mobility during deposition is also significantly reduced leading to a strong accumulation of interface width throughout the layer. A high ion-assistance is therefore needed to increase the adatom mobility enough to allow for surface diffusion. These adatom energies however lead to a strong intermixing between the interfaces, making it essential to combine the $^{11}\text{B}_4\text{C}$ co-deposition with the modulated ion assistance technique. The resulting deposition scheme therefore incorporates the modulated ion assistance scheme as described in chapter 4.2. Where an initial buffer layer is grown with a low bias, followed by the rest of the layer grown with a higher substrate bias. During this entire process, $^{11}\text{B}_4\text{C}$ is co-deposited throughout the multilayer to inhibit the formation of crystallites. The bias used during the process needs to be fine-tuned, such that intermixing does not exceed the initial buffer layer, while being high enough to allow for surface diffusion.

4.5 Deposition system at PETRA III

The samples that are described in this thesis have been deposited at a ultra-high vacuum (UHV) magnetron sputtering chamber at PETRA III at the Deutsches Elektronen-Synchrotron in Hamburg, Germany [32]. The system is mounted on a 1-tonne ultra-high load, high resolution hexapod in the beamline allowing for fine alignment of the sample with respect to the synchrotron beam. In this setup, it is possible to do in-situ X-ray scattering measurements during film growth. The cylindrical deposition chamber has a diameter of 600 mm and four 75-mm diameter sputter sources tilted with an angle of 35° towards the substrate normal. Between the sputter sources, a μ -metal shielding is placed in order to extend the magnetic field closer to the substrate and minimise cross contamination. In front of the sputter sources, fast-acting shutters are mounted to control the sputtered flux. Enabling the growth of single layers, multilayers as well as the co-deposited samples grown in this work. The substrate is rotated during deposition, during this work at a constant rate of 7 rpm. The substrate table is electrically isolated in order to enable a negative substrate bias during film growth. The deposition chamber also allows for substrate heating during deposition, which has not been used during the depositions performed in this work.

Chapter 5

Instrumental aspects

5.1 Neutron reflectometry

Neutron reflectometry (NR) is a technique to investigate structural properties of thin film multilayers. The physical principles behind this technique are described in chapter 2. The instrument used for NR is able to measure both specular and off-specular diffraction patterns simultaneously. These diffraction patterns can be used to obtain structural information about the sample that has been measured. Narrow Bragg peaks in the specular diffraction pattern for a multilayer indicate a regular periodicity [17] for example, and the distance between the peak widths can be used to calculate the period of the sample. In order to obtain quantitative information about the sample structure, the diffraction patterns can be fitted to mathematical simulations as covered in chapter 6.

5.2 The beam overspill effect

The spot size of the neutron beam grows with decreasing incidence angles and becomes infinitely large when the incidence angle approaches zero. A large part of the incident beam therefore does not reach the sample, leading to a reduction of intensity at lower angles. This is often called the beam overspill effect, this is illustrated in figure 5.1. The region where the intensity is reduced due to this effect is usually called the footprint of the sample.

This effect needs to be calculated for using geometry and the beam profile. The experimentally measured curve can be expressed as:

$$E(\theta) = g(\theta)R(\theta). \quad (5.1)$$

Where $g(\theta)$ is the attenuation factor due to the beam overspill effect, and $R(\theta)$ describes the reflectivity curve in absence of this factor. The factor $g(\theta)$ can be determined by considering the geometry of the beam which then reduces to [33] [34]:

$$\frac{\int_{-(L/2)\sin\theta}^{(L/2)\sin\theta} P(z)dz}{\int_{-(L/2)\sin\theta_{so}}^{(L/2)\sin\theta_{so}} P(z)dz}. \quad (5.2)$$

where L is the size of the sample, θ the incidence angle and θ_{so} the angle where the beam spot size is exactly the same as the sample length. $P(z)$ is the beam profile and can be expressed as

$$P(z) = A \exp\left(-\frac{z^2}{2\sigma^2}\right). \quad (5.3)$$

Figure 5.1: Part of the beam will not be reflected at low angles as the beam size will be larger than the sample surface. This leads to a reduced intensity at lower angles.

The amplitude in this equation is described by A and σ describes the half-width at half-maximum (HWHM) of the beam. For the analysis done in this work, the beam-overspill effect has been calculated using PySared, the data reduction software available at the neutron beamline at ILL. The footprint effect for X-rays has been calculated using the GenX software [35]

5.2.1 Neutron instrument

The NR measurements in this work have been performed on the neutron reflectometer SuperADAM at Institut Laue-Langevin (ILL) [36]. The measurements have been performed at a neutron wavelength of 5.21 Å. A sketch of the instrument can be seen in figure 5.2. The monochromator consists of a beryllium filter which selects a single neutron wavelength. The slits collimate the beam, shaping the beam. The polarizer, magnetic field and the spin flipper are needed for polarised neutron reflectometry (PNR), which is not covered in this work. The mentioned polarizer, which is a solid state filter, can filter out unwanted wavelength harmonics as well [36]. The sample is kept in place at the sample holder, after which the reflected neutron beam travels through flight tubes towards the

Figure 5.2: A top-down sketch of the SuperAdam reflectometer located at ILL.

position sensitive detector (PSD) where off-specular and specular diffraction patterns can be measured simultaneously.

5.2.2 Alignment procedure

Depending on the relevant features in the diffraction pattern, a good alignment of the sample can be extremely important. In particular a proper correction of the beam overspill effect is highly dependent on the alignment of the sample [33]. The NR measurements in this work have all been aligned using the same procedure. Before mounting the sample, the instrument needs to be aligned to the direct beam. This is done by moving the 2θ angle until the direct beam is visible in the detector, after which a proper region of interest (ROI) can be chosen with the acquisition software that is used. When this is done, 2θ is set to zero and the sample is mounted physically at the sample holder. In the next step, the sample is translated perpendicular to the sample surface until it blocks half of the direct beam intensity. A rocking curve is performed by tilting the ω angle at this location, and the ω angle is aligned at maximum intensity meaning the sample surface is parallel to the direct beam. After this, 2θ can be set to a low diffraction angle of about 0.4° where ω is tuned such that the reflected beam is in the middle of the ROI window and the total intensity in the ROI is at a maximum. At this position, the sample is translated perpendicular to the sample surface again, the sample height is set to the centre of the resulting curve. If the resulting beam is not vertical in the ROI window, the sample can be rotated around the x-axis until it is. Finally, a beam-stop is used to absorb most of the direct beam intensity.

5.3 X-ray reflectometry

Like neutron reflectometry, X-ray reflectometry (XRR) is a non-destructive characterization technique that can be used to obtain structural properties of thin film multilayers. The physical principles follow the same formalisms as NR as described in chapter 2. While the underlying physics is very similar, NR does offer a few advantages over XRR. It is for example not possible to measure magnetic properties with XRR, and the short penetration length makes it much more difficult to measure bulk materials with this technique. Another useful property of neutrons is the fact that the scattering length for neutrons vary wildly per isotope as explained in section 2.2.1, making it possible to distinguish different isotopes of the same element. This also means that the scattering length for X-rays and neutrons are completely unrelated, this fact makes the combination of XRR and NR a very powerful technique as it gives two completely independent datasets with the same structural information. Combining these two techniques can therefore be an extremely powerful tool for mathematical simulations.

The XRR measurements in this work are performed on a Bragg-Brentano diffractometer, the corresponding geometric set-up can be seen in figure 5.3. The typically relevant angles are 2θ , which describes the angle between the direct beam and the reflected beam, and ω which is the angle between the incoming beam and the sample surface. In order to retrieve specular diffraction patterns, $\omega - 2\theta$ scans where done. In this setup, 2θ is measured from $0^\circ - 12^\circ$ while ω is kept at $2\theta/2$. The off-specular diffraction curves where measured by performing an ω scan at a constant value for 2θ , typically at the first Bragg peak. The resulting intensity pattern, where ω is varied at a constant angle for 2θ is often called a rocking curve. Off-specular diffraction gives quantitative information about the roughness profile in the multilayer.

Figure 5.3: A sketch showing a typical Bragg-Brentano diffractometer and the relevant geometry.

5.3.1 X-ray instrument

X-Ray reflectivity measurements were done using a Panalytical Empyrean diffractometer using a Cu-K α X-ray tube, giving rise to a wavelength of $\lambda = 1.54\text{\AA}$. On the incident side, a Ni filter was used to attenuate the K β radiation of the X-rays. A parallel beam mirror was used in order to create a parallel beam of X-rays followed by a divergence slit of $1/32^\circ$ to collimate the beam. On the diffracted side, a parallel plate collimator has been used in combination with a collimator slit. The used detector is a PIXcel detector in 0D mode.

5.3.2 Alignment procedure

A proper alignment is also essential for XRR measurements. For a typical alignment procedure in this work, 2θ has been aligned before doing any measurements on the sample. This is done by doing a 2θ scan on the diffractometer around $2\theta = 0^\circ$, and setting the resulting centre of the peak at zero degrees. Afterwards the sample can be aligned in the vertical z -direction by setting the direct beam at $2\theta = 0^\circ$ and moving the sample into the beam until it blocks half of the direct beam intensity. Once this is done, the sample is tilted by changing the ω angle such that the intensity reaches a maximum value. At this angle, the sample should be parallel to the beam. Since tilting the sample effectively changes the sample height, an additional alignment in the vertical z -direction is done until the sample blocks half of the sample beam. Finally, the 2θ is set to a low diffraction angle such that the detector measures the reflected beam. Usually this is done around the first Bragg peak of the multilayer. At this position the sample is tilted again around ω after which the peak position of the obtained reflectivity curve is set to $\omega = 2\theta/2$. After this procedure has been carefully followed, the sample should be aligned and the measurement can begin.

Chapter 6

Reflectivity simulations

In order to obtain structural parameters for the samples, the experimental reflectivity curves need to be fitted to mathematical simulations for each sample. There are several possible mathematical descriptions that can be used, within this work there are two different descriptions that are applied based on the software that has been used. Specular reflectivity is used described using the Parratt recursion formula, whilst the off-specular simulation is described using the Born-approximation. Both of these formalisms are described in this chapter. Fitting of the specular parameters using Parrat recursion is done with the GenX software [35]. Off-specular simulations in this work, which use the Distorted Wave Born Approximation, are done using the BornAgain software [37].

6.1 Parrat recursion

The specular reflectivity of the samples is simulated using the Parratt recursion formalism. This description recursively accounts for the reflection from each subsequent interface in order to simulate the total intensity at detector. For a multilayer with a certain amount of layers, the reflectivity for the j 'th layer in the sample can be calculated using [38]

$$\chi_j = \frac{R_j}{T_j} = \exp(-2i\mathbf{k}_{z,j}z_j) \frac{r_{j,j+1} + \chi_{j+1} \exp(2i\mathbf{k}_{z,j}z_j)}{1 + r_{j,j+1}\chi_{j+1} \exp(2i\mathbf{k}_{z,j+1}z_j)}. \quad (6.1)$$

R_j and T_j in this equation describe the reflected and transmitted amplitude for layer j . The fraction of these, χ_j therefore describes the normalised intensity from each layer. The factor $r_{j,j+1}$ is the Fresnel coefficient for the interface, and can be written as:

$$r_{j,j+1} = \frac{\mathbf{k}_{z,j} - \mathbf{k}_{z,j+1}}{\mathbf{k}_{z,j} + \mathbf{k}_{z,j+1}}. \quad (6.2)$$

It follows from this description that this formalism is recursive, the reflectivity of layer $j+1$ is required to calculate the reflectivity of the j 'th layer. Assuming the substrate is thick enough, there will be no reflection from the bottom of the substrate and the recursion therefore starts at $\chi_{N+1} = R_{N+1} = 0$. The incident wave is normalized to unity, giving $T_0 = 1$. Using these two known conditions as starting point, the total reflectivity for the entire multilayer can then be calculated recursively. This formalism is commonly used to simulate the specular reflection for neutrons and X-rays in reflectivity simulation software.

6.2 Born Approximation

The Born Approximation (BA) was proposed as early as 1926 by Max Born. To get to this approximation, we may first start with the general time-independent Schrödinger equation:

$$\left(\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}). \quad (6.3)$$

We can re-write this as:

$$(\nabla^2 + k^2) \Psi(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r}) \Psi(\mathbf{r}). \quad (6.4)$$

Where

$$k^2 = \frac{2mE}{\hbar^2}. \quad (6.5)$$

The general solution to this equation can be expressed as an integral:

$$\Psi(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}') d^3 \mathbf{r}'. \quad (6.6)$$

The factor G in this equation is known as Green's function, which can be obtained by solving the point source equation:

$$(\nabla^2 + k^2) G(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (6.7)$$

Solving this for the Green's function gives us the integral form for the Schrödinger equation.

$$\Psi(\mathbf{r}) = e^{i\mathbf{k}_0 \cdot \mathbf{r}} - \frac{m}{2\pi\hbar^2} \int \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') \Psi(\mathbf{r}') d^3 \mathbf{r}'. \quad (6.8)$$

This equation can be solved approximately using the so-called Born series. The zero'th order solution of the Born approximation is given by a planar wave:

$$\Psi_0(\mathbf{r}) = e^{i\mathbf{k}_0 \cdot \mathbf{r}}. \quad (6.9)$$

The first order solution is then given by inserting the solution for Ψ_0 into the integral of the general equation expressed in equation 6.8. This gives us:

$$\Psi_1(\mathbf{r}) = e^{i\mathbf{k}_0 \cdot \mathbf{r}} - \frac{m}{2\pi\hbar^2} \int \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r} - \mathbf{r}_1|} V(\mathbf{r}_1) \Psi_0(\mathbf{r}_1) d^3 \mathbf{r}_1, \quad (6.10)$$

$$= e^{i\mathbf{k}_0 \cdot \mathbf{r}} - \frac{m}{2\pi\hbar^2} \int \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r} - \mathbf{r}_1|} V(\mathbf{r}_1) e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} d^3 \mathbf{r}_1. \quad (6.11)$$

The second order can then be found by inserting this first order solution into equation 6.8. By continuing this way, any order can be obtained, but for most cases only the first order approximation is actually used.

6.2.1 The Distorted Wave Born Approximation

When the scattering intensity becomes very large, the assumption of a planar wave in the conventional BA no longer holds, scattering entities themselves can introduce perturbations into the field and the wave therefore needs to be described as a distorted wave, a superposition of a downwards and upwards traveling planar wave. This is the underlying principle of the Distorted Wave Born Approximation (DWBA), which is the formalism that is used to simulate off-specular scattering in this work. The described wave function has a distorted form that can be described as downward and upward travelling waves for both the scattered and incident waves [39]:

$$\psi_w(\mathbf{r}) = \psi_w^-(\mathbf{r}) + \psi_w^+(\mathbf{r}), w = i, f. \quad (6.12)$$

Where ψ_w^- describes the downwards wave while ψ_w^+ describes the upwards wave. The relevant scattering elements can then be described using Dirac notation as follows [39]:

$$\langle \psi_i | \delta v | \psi_f \rangle = \langle \psi_i^- | \delta v | \psi_f^+ \rangle + \langle \psi_i^- | \delta v | \psi_f^- \rangle + \langle \psi_i^+ | \delta v | \psi_f^+ \rangle + \langle \psi_i^+ | \delta v | \psi_f^- \rangle. \quad (6.13)$$

Where δv describes a perturbation on the scattering potential that the incident wave experiences. If we expand the left-hand side in the integral notation we get:

$$\langle \psi_i | \delta v | \psi_f \rangle = \int e^{i\mathbf{k}_i \cdot \mathbf{r}} \delta v e^{i\mathbf{k}_f \cdot \mathbf{r}} d^3\mathbf{r} = \int \delta v e^{i\mathbf{q} \cdot \mathbf{r}} d^3\mathbf{r}. \quad (6.14)$$

Which gives us the Fourier transform of the perturbed potential δv , which is what is being measured at the detector. Note how the first term on the right-hand side in equation 6.13 simply describes the interaction with the downwards and the upwards wave, which is the usual term as used by the conventional BA. The additional terms are added upon this in the DWBA, and these describe the additional scattering effects for intense scattering. These terms are all illustrated in figure 6.1.

Figure 6.1: A representation of different terms that are taken into account for the DWBA. The first term is identical to the conventional BA, while the other three terms describe scattering events from the scattering entities themselves.

6.3 Sample description

The samples are described in a physical model such that the experimental data can be fit to the described formalisms. In order to do this in a meaningful way, some approximations need to be made. It is easy to describe a sample in as much detail as possible with many fitting parameters, but this comes with a risk of overfitting, losing a physical meaning behind the result. It is therefore often better to make a robust and simple model, than to make a complicated model that fits better to the data. Mathematician George Box famously said, ‘all models are wrong, but some of them are useful’ [40]. The goal of the model description is not to find a model that gives a perfect fit to our data, but instead to find a model that gives useful information. In this work this means a model that reliably gives physically correct information about the structural parameters of the sample. All samples that are covered in this thesis are described using the same physical model. A stack of an N amount of periods consisting of Ni and Ti are deposited on top of a Si substrate with a thin layer of SiO_2 on top. Finally, a small oxide layer is assumed to be present on the top layer. A sketch describing this is shown in figure 6.2. While the initial interface width of the Ni and Ti layers are considered independent from each other, the accumulation of the interface width is assumed to be equal. The total interface width for a Ni and Ti layer in the stack, is therefore determined by:

$$\sigma_{\text{Ti}} = A \cdot j + \sigma_{\text{Ti},i}, \quad (6.15)$$

$$\sigma_{\text{Ni}} = A \cdot j + \sigma_{\text{Ni},i}. \quad (6.16)$$

Where A is the accumulated interface width per period, j indicates the position of the bilayer, and $\sigma_{\text{Ni},i}$ and $\sigma_{\text{Ti},i}$ describe the initial interface width of the Ni- and Ti layers respectively.

Figure 6.2: An illustration of the sample as described in the simulated model, not to scale. Each bilayer is given an index, dubbed j . For illustrative purposes, a limited amount of bilayers are drawn.

Chapter 7

Multilayer characterization

7.1 Elastic Recoil Detection Analysis

The elemental composition of the multilayers in this work have been determined using Elastic Recoil Detection Analysis (ERDA). In this work, the Tandem Laboratory at Uppsala University has been used to perform such analysis. For this technique, the sample is targeted by an ion beam with an energy in the order of tens of MeV. Atoms from the sample surface are ejected due to collision events between the energetic ions and the sample surface. Using the atomic number of the target elements and the energy of the backscattered ions, the recoil can be measured and analyzed to obtain compositional information. Such an obtained ERDA spectrum can be observed in figure 7.1. Upon collision, light elements are most likely to be ejected in the forward direction. This technique is less suitable for heavier elements as they do not recoil as easily and overlap with backscattered ions [31]. In this work, a primary $^{127}\text{I}^{8+}$ beam with an energy of 36 MeV has been used at an incident angle of 67.5° relative to the surface normal, the energy

Figure 7.1: An example of results as obtained by ERDA. The different elements that are present in the sample are observed as "banana peaks", the curved signals that are visible in the graph. Note how the iodine signal are backscattered ions from the target beam, there is no iodine present in the measured sample.

detector was placed at a recoil scattering angle of 45° . The system is described in more detail elsewhere [41], [42]. The measured spectrum has been analysed using the Potku software [43] in order to determine the elemental composition of the sample.

7.2 X-ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) has been used in this work to analyse the bonding of the boron and carbon atoms that are present in the film. XPS provides qualitative and quantitative information about the chemical composition of the sample near the surface. This technique is based on the photoelectric effect [44], electrons on the sample are ejected by an incident X-ray beam with a certain kinetic energy E_k that is measured at the detector. The binding energy E_b is related to this kinetic energy as:

$$E_b = E_{XPS} - (E_k + \phi). \quad (7.1)$$

Where term E_{XPS} represents the energy of the incident X-rays. The function ϕ is the work function for the instrument, this represents the minimum energy that is needed to remove an electron from the instrument [45]. Equation 7.1 can therefore be used to see which chemical bonds were present in the sample, what makes this particular powerful is that it does not just show the elemental composition of the sample but also how the elements were bonded.

Figure 7.2: The C1s XPS spectrum for two deposited samples. The left-hand side shows a Ni/Ti sample with a power of 0 W to the $^{11}\text{B}_4\text{C}$ magnetron, while the right-hand side shows a Ni/Ti sample with a power of 70 W to the $^{11}\text{B}_4\text{C}$ magnetron.

7.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) has been used to get a direct view of the structural characteristics, as well as the roughness propagation throughout the entire sample. TEM is an electron microscopy technique that is able to obtain structural information from samples that are thin enough to transmit electrons. In a simplistic sense, TEM can be compared to a slide projector, where the sample itself is used as the slide and the electron beam is the beam of light [28]. The interaction of the electrons with the sample form an image which is magnified by a lens. The high magnification that is obtainable with TEM is a result from the very small wavelengths that are used. There are different modes of operation that determine the beams reaching the objective lens are processed. The ones that are relevant to this work are further covered here, all discussed modes of operation are shown in figure 7.3.

7.3.1 Bright-field imaging

Bright-field (BF) imaging is known as the conventional TEM [28]. With this mode of operation the diffracted beam is excluded and only the central transmitted beam is allowed to pass through. This is done by placing an aperture in the back focal plane of the objective lens. For BF imaging, the obtained contrast in the resulting image is a result of mass-absorption and the interference from

Figure 7.3: A TEM measurement of one of the samples that has been deposited in this work. The modes of operations that have been discussed in this text are labeled in the figure.

transmitted electrons. As heavier elements absorb more, a multilayer with heavy/light elemental layers will respectively appear as dark/bright layers in the obtained image. Similarly, thicker layers will appear darker than thin layers [31].

7.3.2 Dark-field imaging

With dark-field (DF) imaging, one of the diffracted beams is chosen. In this case, an aperture is inserted that blocks both the transmitted central beam as well as the other diffracted beams. With this mode of operation, the obtained contrast is primarily a result of diffraction [31]. As this mode of operation is dependent on diffraction conditions, the resulting contrast will be dependent on the formation of crystallites.

7.3.3 High Resolution Transmission Electron Microscopy

To obtain images with an even higher magnification, high resolution transmission electron microscopy (HR-TEM) can be used. With this mode of operation, both the scattered and transmitted beams are used in order to form an interference image [31]. This technique is based on the phase shift that the electron wave experiences when interacting with the atoms in a sample. The interference pattern in the image plane gives rise to the contrast in HR-TEM images. Small features such as dislocations can be recorded with this technique due to the strong interaction between electrons and the atoms in the sample [46].

7.3.4 Selected Area Electron Diffraction

Selected Area Electron Diffraction (SAED) patterns are diffraction patterns of a selected area within one sample. To obtain such a pattern, a special aperture is inserted into the image plane to select an area of the sample. The diffraction pattern can be magnified and viewed by the TEM. Crystalline materials give rise to diffraction spots, while polycrystalline and amorphous materials give diffraction rings of varying sharpness and width, note how these rings can be observed as well in figure 7.3. In this mode of operation it is also possible to find strains and texture deviations for individual grains in the sample [28].

Chapter 8

Summary of the results

8.1 B₄C containing Ni/Ti multilayers

Ni/Ti layers were co-deposited with B₄C in order to eliminate the formation of nanocrystallites, this has been combined with a modulated ion assistance scheme to smoothen the interfaces. In this scheme, an initial layer with a thickness of 1 nm is grown using a substrate bias of -30 V, the remainder of the layer is grown with a substrate bias of -100 V. In situ high-energy synchrotron wide angle X-ray scattering (WAXS) showed an effective hindering of nanocrystallites during growth as a result of the B₄C co-deposition. After deposition, the B₄C containing films have been characterized using X-ray reflectivity, which showed a significant improvement compared to the pure Ni/Ti multilayers.

8.2 Pure Ni/Ti multilayers

Pure Ni/Ti multilayers were deposited at the magnetron sputter deposition at Petra III in Hamburg, described in subsection 4.5. During growth a split-bias scheme was used where an initial buffer layer of 1 nm was grown at a lower bias of -30 V, followed by a high bias of -100 V for the rest of each layer. The samples described in this work have a total of 104 bilayers with a period of 45.8 Å. The magnetron powers used during growth are 20 W and 60 W for the Ni- and Ti target respectively.

8.2.1 Structural parameters

Structural parameters of the samples were obtained by fitting the measured NR and XRR data to a model simulation of the multilayer. In this model, any accumulation of interface width is assumed to be linear and equal for both multilayers. The resulting fit shows an average initial width of 6.9 Å for the sample, with an increase of the interface width of 0.04 Å per bilayer, meaning the total averaged interface width has grown to 10 Å for the top bilayer. The specular diffraction pattern shows a slight broadening of the Bragg peaks, indicating an increase in layer thickness throughout the layer. The simulated fit to the experimental data shows an increase of 0.002 Å per bilayer. The obtained period was 45.8 Å. The sample has been measured with TEM microscopy as well. The TEM measurement confirms the findings from the model simulation, with abrupt interfaces and very limited roughness accumulation.

8.3 $^{11}\text{B}_4\text{C}$ containing Ni/Ti multilayers

The samples that have been co-deposited with $^{11}\text{B}_4\text{C}$ are grown at the deposition system at Petra III in Hamburg. The magnetron powers that were used are 20 W, 60 W and 35 W for the Ni, Ti, and $^{11}\text{B}_4\text{C}$ target respectively. These samples were grown with a split-bias scheme, using an initial bias at -30 V to grow a buffer layer followed by a high bias at -100 V for the rest of the layer. These samples were analysed using ERDA in order to obtain information about the elemental composition for the multilayer. These measurements indicate that the sample contains about 3.6% C and 22% ^{11}B . The sample also contains about 1% Ar, which comes from the sputtering gas that is used during deposition. The B to C ratio is slightly higher than expected from a pure $^{11}\text{B}_4\text{C}$ target. The reason behind this remains unknown, but these findings have been confirmed using Rutherford Backscattering Spectroscopy (RBS) as well. A possible explanation could be an unexpected elemental composition in the target that was used.

8.3.1 Structural parameters

Structural parameters of the samples that were co-deposited with $^{11}\text{B}_4\text{C}$ have been obtained by a combined fit of NR and XRR data on a model simulation of this multilayer. The same model has been used for these samples as for the pure Ni/Ti samples, any accumulation in interface width is assumed to be linear and equal throughout the multilayer. The SLD has been calculated using the elemental composition obtained by ERDA where the density for each layer has been calculated using a simple rule of mixtures for the bulk densities for each element. The resulting fit to this model does not show any roughness accumulation throughout the sample. The obtained interface width has an average value of 4.5 Å at the first bilayer with no signs of roughness accumulation, which is a clear improvement when compared to the pure Ni/Ti samples. The specular diffraction pattern shows a slight broadening of the Bragg peaks, indicating an increase in layer thickness throughout the layer. The simulated fit to the experimental data shows an increase of 0.002 Å per bilayer. The obtained period was 47.0 Å. These samples were measured with TEM as well, the TEM micrographs for this sample is shown in figure 7.3. These measurements are in line with the obtained fit to the simulated model, with very abrupt layers and no obvious sign of an increase in interface width throughout the layer. The resulting neutron and X-ray reflectivity measurements are shown in figure 8.1 for both pure Ni/Ti sample and the $^{11}\text{B}_4\text{C}$ containing sample. The inset shows the rocking curves for the NR measurements for both samples. Note how the sample that has been co-deposited with $^{11}\text{B}_4\text{C}$ has a higher diffuse signal. The exact reason behind this remains an open question, as the diffuse signal is actually lower for the $^{11}\text{B}_4\text{C}$ containing sample at the second Bragg peak. This could possibly be the result of lower intermixing, leading to sharper interfaces in the lateral direction and therefore increasing the contribution from correlated roughness at the interfaces in the sample.

Figure 8.1: a) The obtained neutron reflectivity signal for both samples. b) X-ray reflectivity data for both samples. The difference in background intensity for the X-ray reflectivity signal is due to the use of a mask for the $^{11}\text{B}_4\text{C}$ containing sample, decreasing the signal-to-noise ratio. The insets show the rocking curves for both samples at the first Bragg peak.

Chapter 9

Outlook

9.1 Ni/Ti multilayers

Initial results described in chapter 8 show a clear improvement in interface width for the samples that have been co-deposited with $^{11}\text{B}_4\text{C}$. There are however several aspects where this technique could be further improved. Initial depositions have been made using a magnetic coil in the deposition chamber to attract ions during layer growth. This also allows for a lower substrate bias during growth, which can limit the total intermixing. The resulting samples show a clear further improvement in reflectivity, both for neutron and X-ray reflectivity measurements.

These samples have been measured at the neutron beamline at ILL as well, and a clear improvement in neutron reflectivity can be observed. The simulated models do not show a straightforward fit to the experimental data however, this could partly be caused by misalignment during experiment. This analysis was not completed in time in order to be included in this thesis. Further experimental work needs to be done as well with regard to the growth process. A possible technique that needs to be investigated for instance is to limit the inclusion of $^{11}\text{B}_4\text{C}$ to the Ni-layer only. Due to the large difference in neutron SLD for Ti and $^{11}\text{B}_4\text{C}$, a lot of optical contrast is lost due to the $^{11}\text{B}_4\text{C}$ co-deposition. By limiting the co-deposition of $^{11}\text{B}_4\text{C}$ to the Ni-layer, this contrast can be significantly improved. This still needs to be tested experimentally.

Finally, a greater understanding is needed of the sample structure in the horizontal plane. Preliminary work has been done on off-specular simulations in order to get a qualitative understanding of the obtained rocking curve, but a proper off-specular fit to the experimental data has proven to be rather difficult due to the low amount of features in the rocking curve. Such an analysis would therefore probably require additional experimental analysis as well.

9.2 Polarizing multilayers

While these results show great potential for non-polarising neutron multilayers, the same techniques could be applied to polarizing multilayers as well. While a common material system for neutron polarising multilayers is Fe/Si, experimental work has been performed on Co/Ti multilayers as well by others [47]. Some preliminary work has been done within this thesis on such Co/Ti layers, but challenges still remain with regard to magnetization. Individual layers lose their magnetization when co-deposited with $^{11}\text{B}_4\text{C}$, which makes the addition of

$^{11}\text{B}_4\text{C}$ troublesome. Limiting the co-deposition of $^{11}\text{B}_4\text{C}$ to the non-magnetic layers could be an option, but makes it difficult to balance the SLD such that one polarization direction will be filtered out. A final concern is demagnetization effects for very thin magnetic layers, leading to depolarization [47]. Further experimental analysis on such samples is planned for the future.

Chapter 10

Summary of the papers

10.1 Paper I

Ni/Ti is the materials system of choice for broadband neutron multilayer supermirrors. The reflected absolute intensity as well as neutron energy range from state-of-the-art mirrors are hampered by a Ni/Ti interface width, typically 0.7 nm (caused by nanocrystallites, interdiffusion, and/or intermixing), limiting the optical contrast across the interface as well as limiting the minimum usable layer thickness in the mirror stack. In this work we explore elimination of nanocrystallites by amorphization through boron-carbon doping in combination with interface smoothening by modulation of ion-assistance during magnetron sputter deposition of individual Ni and Ti layers, ranging from 0.8 nm to 6.4 nm in thickness. In situ high-energy synchrotron wide angle X-ray scattering (WAXS) revealed an effective hindering of Ni/Ti crystallization through a minute concurrent B₄C flux during growth. Post-growth X-ray reflectivity (XRR) confirmed the incorporation of B₄C but also showed that interface widths deteriorated when a constant substrate bias of -30 V was used. However, XRR showed that interface widths in B₄C -doped multilayers improved significantly, compared to those in pure Ni/Ti multilayers, by employing a two-stage substrate bias, where the initial 1 nm of each layer was grown with -30 V substrate bias, followed by -100 V bias for the remaining part of the layer. The present results shows that B₄C doping of Ni/Ti multilayers leads to significantly smaller interface widths when combined with engineered interfaces through temporal control of the substrate bias. Consequently, a significant improvement of neutron supermirror performance can be expected by employing this technique using ¹¹B isotope-enriched ¹¹B₄C source material.

10.2 Paper II

In this work we investigated a novel magnetron sputter growth technique where ¹¹B₄C co-deposition has been combined with a split-bias scheme in order to reduce interface width at Ni/Ti multilayers. Combined fits to experimental XRR and NR data indicate average interface widths of 4.5 Å without any accumulated roughness when the sample is co-deposited with ¹¹B₄C. This is a significant reduction from the deposited sample with pure Ni/Ti, which shows an average initial interface width of 6.3 Å at the first period with an accumulation of 0.04 Å per period. This improved interface width offers very good prospects for high-performance supermirrors with high-m values, as well as for neutron instruments for thermal neutrons where thinner interface widths are required.

10. Summary of the papers

Since neutron multilayers are such essential and crucial elements in any intended instrumentation, even the slightest improvement of the performance will have an immediate and large impact on all research using those instruments.

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Publications

Papers included in the thesis:

- Paper I** **Layer Morphology Control in Ni/Ti Multilayer Mirrors by Ion-assisted Interface Engineering and B₄C Doping**
Fredrik Eriksson, Naureen Ghafoor, Sjoerd Broekhuijsen, Daniel Ostach, Grzegorz Greczynski, Norbert Schell, and Jens Birch
In Manuscript
- Paper II** **Synthesis of ¹¹B₄C containing Ni/Ti multilayers and characterization using combined X-ray and neutron reflectometry**
Sjoerd Broekhuijsen, Fredrik Eriksson, Naureen Ghafoor, Martin Wess, Alexei Vorobiev and Jens Birch
In Manuscript

Papers

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