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Interface Modification in Co/Cu Multilayers
Prepared by Ion-assisted Deposition

by

Neil D. Telling

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of
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April 1998
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The interfacial structure of Co/Cu multilayers deposited under energetic ion bombardment has been investigated using X-ray reflectivity techniques. An ion-assisted deposition system, based on unbalanced magnetron sputtering principles, has been developed in order to provide a method for the independent control of ion flux and energy. Using this system ion current densities measured at the substrate could be varied from \( \sim 30 \ \mu \text{A cm}^{-2} \) to \( \sim 100 \ \mu \text{A cm}^{-2} \) and average ion energies of \( \sim 50-200 \ \text{eV} \) could be selected. It was therefore possible to prepare Co/Cu multilayers under a variety of ion bombardment conditions and thus study the effect of this energetic particle bombardment on the evolution of interface structure.

Samples were characterised by measuring the specular and diffuse X-ray reflectivity, using anomalous scattering effects to enhance the contrast between the cobalt and copper layers. Quantitative analysis of the specular reflection revealed the existence of variations of the interface roughness in multilayers deposited under \( \sim 200 \ \text{eV} \) ion bombardment, such that the interfaces became smoother towards the free surface. Films deposited with the highest available levels of ion flux were found to display the greatest interface smoothing effect. However, no such variation was observed when ion energies of \( \sim 50 \ \text{eV} \) were applied, although differences in the large lateral scale correlated roughness were observed between \( \sim 50 \ \text{eV} \) ion-assisted and non ion-assisted samples. The sensitivity of the interface structure to energetic bombardment during growth is thus demonstrated and the results are discussed in terms of resputtering and ion bombardment induced reordering of the growing surface. It is shown that these effects can be exploited to obtain multilayers with atomically smooth interfaces.
Acknowledgements

There are many people who were involved in the work presented here and of whom I am greatly indebted. I have been extremely fortunate in having the pleasure of their company and friendship.

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Chapter 1

Introduction

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1.1 Introduction
1.2 The Importance of Interface Structure in Magnetic Multilayers
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1.1 INTRODUCTION

Magnetic multilayers are thin films consisting of a stack of alternate magnetic and nonmagnetic metallic layers. The magnetic and magnetotransport properties of these films depend not only on the properties of the individual layers, but also on the interactions between the layers. The bulk film properties are not therefore merely the collective behaviour of the stack. Both the magnetisation of individual layers and the interlayer interactions are extremely sensitive to the structure of the interfaces between layers. This is particularly true in the case of multilayers that display antiferromagnetic (AF) coupling [1-21] and the associated giant magnetoresistance (GMR) effect [22-63]. Multilayers consisting of ultrathin cobalt layers (∼ 10-20 Å thick) separated by copper layers (∼ 10-50 Å thick) repeated in a periodic fashion, are one of several systems that exhibit AF coupling and GMR behaviour. Understanding the evolution of interface structure in Co/Cu multilayers and consequently the ability to control interface growth is therefore of extreme importance in the continuing study of this multilayer system.

Before considering the structural modification of interfaces in Co/Cu multilayers by energetic particle bombardment, an outline of the origin of AF coupling and GMR effects, their sensitivity to interface structure and consequently the growth environment, will be given (section 1.2). Following this (section 1.3) the original aims of the project will be briefly discussed. The layout of the remainder of the thesis is also presented in this section.
1.2 THE IMPORTANCE OF INTERFACE STRUCTURE IN MAGNETIC MULTILAYERS

1.2.1 Magnetic Coupling and Giant Magnetoresistance in Magnetic Multilayers

Long range magnetic coupling between the magnetic layers in transition metal multilayers was first observed in Fe/Cr layered films [1-3]. It has since been studied in a range of different magnetic multilayers systems [4-17]. The sign of the coupling was found to oscillate between AF coupling and ferromagnetic (FM) coupling as a function of the thickness of the nonmagnetic (spacer) layer with a period of ~10 Å [3,4,6-8,14]. To explain this oscillatory coupling a mechanism based on the indirect exchange coupling, RKKY interaction [18,19] was proposed.

The RKKY interaction was developed to treat the indirect coupling of the spins of two (or more) remote magnetic moments via the s-d exchange interaction (for transition metals) with spin moments of the surrounding conduction electrons. This indirect coupling occurs because the first magnetic moment generates an oscillatory spin polarisation in the conduction electrons that is sensed by the second moment via the exchange interaction. For two moments separated by a distance \( R \), the interaction energy between them caused by the spin polarisation (the RKKY interaction) is [64]

\[
E_{\text{RKKY}} = -2J(R)S.S'
\]

where \( S \) and \( S' \) are the spins of the two moments and \( J(R) \) is the oscillatory exchange interaction and is dependent upon the band structure and the shape of the Fermi surface. The relative alignment and strength of the RKKY interaction between the two moments therefore depends on the sign and magnitude of \( J(R) \) and is thus a function of the separation \( R \).
For magnetic multilayers this interaction can be extended to consider the exchange coupling per unit area between two FM layers [65],

\[ E_{1,2} = A_{1,2} \mathbf{m}_1 \cdot \mathbf{m}_2 = A_{1,2} \cos \phi_{1,2} \]  

where \( \mathbf{m}_1 \) and \( \mathbf{m}_2 \) are the unit magnetisation vectors of each layer, \( A_{1,2} \) is the coupling constant per unit area and \( \cos \phi_{1,2} \) is the angle between the magnetisation vectors. For this expression the sign of \( A_{1,2} \) is defined as negative (positive) for FM (AF) coupling. Hence \( E_{1,2} \) is minimised when \( \mathbf{m}_1 \) and \( \mathbf{m}_2 \) are aligned parallel (antiparallel) for FM (AF) coupling.

The problem with using an RKKY interaction to explain oscillatory magnetic coupling in multilayers is that the oscillation period predicted (half the Fermi wavelength) is not nearly as long as the observed period (~10 Å). This apparent contradiction can be explained by considering the difference between the continuous medium for the electrons assumed in the RKKY theory, and the reality of a discrete spacer layer thickness as determined by the separation between atomic planes in the growth direction (perpendicular to the layers). The oscillation period obtained by ‘sampling’ the RKKY curve at discrete values is much larger than the wavelength in the medium, and can be shown to give an effective period consistent with observation [20].

Fluctuations in the short period oscillation caused by spatial fluctuations of the spacer layer [21] were found to lead to an additional coupling such that the total coupling energy is given by [66],

\[ E_{1,2} = A_{1,2} \mathbf{m}_1 \cdot \mathbf{m}_2 - 2B_{1,2} (\mathbf{m}_1 \cdot \mathbf{m}_2)^2 \]  

with \( B_{1,2} < 0 \)  

where \( B_{1,2} \) is known as the biquadratic coupling term. The coupling energy is dominated by the bilinear coupling \( (A_{1,2}) \) except when \( A_{1,2} \to 0 \). For these
thicknesses of the spacer layer the energy is minimised when the magnetisation vectors are aligned perpendicularly. This 90° coupling has been observed in a variety of magnetic multilayer systems [4,14,21] and has recently been found to have a strength that decays in an oscillatory fashion as a function of the spacer layer in Fe/Cr trilayers [14].

The giant magnetoresistance (GMR) effect is found to occur in magnetic multilayers when the thickness of the spacer layer is such that the magnetic layers are AF coupled [see for example references 6,23-25]. The origin of GMR is spin-dependent electron scattering that results in a different film resistivity for the AF and FM alignment of the magnetic layers. Experimentally this can be realised by measuring the change in resistance of an AF coupled multilayer when a magnetic field is applied of sufficient strength to overcome the AF coupling and align the magnetic layers parallel to each other. It is not the existence of magnetic coupling itself that is responsible for GMR, however, merely the change in alignment of the magnetic layers from antiparallel to parallel. The magnetoresistance is defined as

\[ \Delta R / R = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} \]  

where \( \Delta R \) is the change in resistance upon applying a magnetic field, \( R \) is the resistance in the magnetic field and \( R_{\uparrow\downarrow}, R_{\uparrow\uparrow} \) are the resistance of the antiparallel and parallel configurations respectively.

Spin-dependent scattering occurs in ferromagnetic metals because the conduction electrons in the s and p bands are predominantly scattered into the d band via the Mott scattering mechanism [67]. Provided the conduction electron
spins are conserved over distances of the order of or greater than the multilayer thickness, conduction can be considered to occur in two parallel spin channels for the up and down spin electrons. The strength of the spin-dependent scattering and hence the resistivity of each spin channel is proportional to the density of states (DOS) at the Fermi level in the d band. For FM metals such as cobalt and iron, there exists a spin asymmetry in the d band DOS at the Fermi level. Hence the resistivity of each spin channel at a given layer depends on the relative alignment of the electron spins and magnetisation of the layer.

In order to explain why there is a difference in the resistance for the FM and AF configuration, it is instructive to consider a simple resistor network model of GMR proposed by Edwards et al [68]. Note that by considering two parallel spin channels, the resistances $R_{\uparrow\uparrow}$ and $R_{\downarrow\downarrow}$ are derived as $1/R_{\uparrow\uparrow} = [1/R_{\uparrow} + 1/R_{\downarrow}]_{\uparrow\uparrow}$ and $1/R_{\downarrow\downarrow} = [1/R_{\uparrow} + 1/R_{\downarrow}]_{\downarrow\downarrow}$ for the two configurations, where $R_{\uparrow}(R_{\downarrow})$ are the resistances of the spin up (spin down) channel. The resistivities in each layer for the two configurations is illustrated schematically in figure 1.1. In the spacer layer the d band is symmetric at the Fermi level, producing an equal DOS for electron scattering of each spin state. Thus the resistivity, $\rho_n$ of these layers is the same for each spin channel.

In order to determine the magnetoresistance (MR) as defined in equation 1.4, the total resistance of each spin channel for each configuration must be determined. If the mean free path of the electrons was much shorter than an individual layer thickness, the electrons would be confined to each layer and all resistances should be added in parallel. Since there would be an equal number of each type of resistor for both configurations, the total resistance in each
configuration would be equal, $R_{\uparrow\uparrow} = R_{\downarrow\downarrow}$ and the MR = 0. Clearly this is not the case in a magnetic multilayer, where the mean free path in each layer is much larger than the layer thickness. Instead, the resistivity of a bilayer can be considered as the layer thickness weighted average of the resistivity of each layer. Since the geometrical factors of the length and cross-sectional areas of the multilayer are the same for both configurations, these will cancel in expression 1.4. It is therefore sufficient to consider the reduced resistance (per unit length and area) in calculating the MR.

$$\begin{align*}
&\text{Ferromagnetic} \\
&M N M N M N \\
&\rho_m^H \rho_s \rho_m^H \\
&\rho_m^L \rho_s \rho_m^L \rho_s
\end{align*}$$

$$\begin{align*}
&\text{Antiferromagnetic} \\
&M N M N \\
&\rho_m^H \rho_s \rho_m^L \\
&\rho_m^L \rho_s \rho_m^H \\
&\rho_s \rho_s \rho_s
\end{align*}$$

$R_L$ $R_H$

*Figure 1.1: Schematic illustration of the spin-dependent resistivities for the two coupling configurations.*

It is clear from figure 1.1 that there are two possible average bilayer resistances that depend on the resistivity of the magnetic layer. The higher bilayer resistance is thus given by the weighted averages of the resistivities according to [68],
and similarly the lower bilayer resistance is

\[ R_L = \frac{M\rho_{mL}^H + N\rho_s}{M + N} \]  \hspace{1cm} \text{(1.6)}

where \( \rho_m^H, \rho_m^L \) are, respectively, the high and low resistivities in the magnetic layer as illustrated in figure 1.1, and M(N) are the thicknesses of the magnetic (nonmagnetic) layers. It is therefore straightforward to see that the total resistance in each spin channel for the double bilayer shown in figure 1.1 in the FM configuration is \( R_\uparrow = 2R_H \) and \( R_\downarrow = 2R_L \). Whereas the total resistance of each channel in the AFM configuration is the same, \( R_\uparrow = R_\downarrow = R_H + R_L \). Substituting these values into expression 1.4 then yields a general expression for the MR,

\[ \Delta R / R = \frac{(R_H - R_L)^2}{4R_H R_L} \]  \hspace{1cm} \text{(1.7)}

Further substitution for \( R_H \) and \( R_L \) (from equations 1.5 and 1.6) into expression 1.7, then gives a simple model for the MR that depends only on the parameters \( \alpha = \rho_m^H / \rho_s \) and \( \beta = \rho_m^L / \rho_s \) and the ratio of the layer thicknesses, \( N/M \) thus,

\[ \Delta R / R = \frac{(\alpha - \beta)^2}{4(\alpha + N/M)(\beta + N/M)} \]  \hspace{1cm} \text{(1.8)}

This simple model therefore suggests that for given thicknesses \( N \) and \( M \), the MR depends on the relative sizes of \( \rho_m^H \) and \( \rho_m^L \) and thus on the degree of d band spin splitting at the Fermi edge. Thus it is the spin dependent scattering of electrons that results in the GMR in the magnetic multilayer. If the spin asymmetry is removed, and hence the electron scattering made spin independent, \( \alpha = \beta \) and from equation 1.8 the MR is zero. Example values of \( \alpha \) and \( \beta \) estimated from the
calculated DOS for cobalt and copper [68] are $\alpha = 8$ and $\beta = 1$. Substituting these values into equation 1.8 gives a MR of 68% for equal thickness layers which is of the order of largest experimentally measured values [33,34,44,61]. The model does not, however, take into account the strength of the magnetic coupling as a function of the spacer thickness. In fact, it assumes perfect antiparallel alignment in zero magnetic field at all thicknesses of the spacer layer, in contrast to the decaying oscillating nature of the coupling discussed earlier.

Another feature of the model is that only electron scattering in the bulk of the layers is considered. In recent years a debate has ensued over what proportion of the electron scattering occurs in the bulk and at the interfaces between layers. Interface scattering can be included in the model discussed here by adding additional resistors between the layers. The nature of the interface scattering can be either spin-dependent or spin-independent by suitable selection of the high and low resistivity terms.

1.2.2 Growth, Interface Structure and Giant Magnetoresistance

Regardless of whether spin-dependent scattering originates predominantly at the interface or in bulk layers, there is a weight of experimental evidence to suggest that GMR is extremely sensitive to the structure of the interfaces. Numerous studies have been conducted to explore the role of interface roughness in determining the magnitude of the measured GMR [27-44]. It now seems likely that the effect of interface roughness is different for Fe/Cr than for Co/Cu multilayers. An enhancement in GMR in Fe/Cr multilayers has been found when some intermixing of the Fe/Cr interfaces is present [27]. A similar enhancement
was also observed when the interface roughness was increased by sputter-deposition at higher argon partial pressures [28]. This would suggest spin-dependent interface scattering may play a role in the GMR in Fe/Cr multilayers. Additionally, neutron diffraction measurements have shown the presence of magnetic disorder at the Fe/Cr interface that appears to be correlated with the GMR effect [69,70]. However, a similar study [29] to that carried out in reference 28, found that the GMR decreased with increased interface roughness due to a greater saturation resistance, and possibly a reduction in the strength of the antiferromagnetic coupling. Similarly, Co/Cu multilayers deposited with intentionally mixed interfaces have been shown to have a GMR that decreased with the thickness of the mixed interface region [30]. Attempts at correlating the GMR in sputtered Co/Cu multilayers with interface structure for different sputtering conditions have also shown a decrease in the effect for greater interface roughness [31,32]. In one such study, the application of a negative substrate bias was shown to restore a layered morphology and GMR in Co/Cu multilayers deposited by RF/DC sputtering at high argon pressures [32]. The effect of sputtering conditions on multilayer structure will be discussed in some detail in Chapter 2.

Many techniques have been employed in order to attempt to control the interface structure and hence the GMR in magnetic multilayers. These fall broadly into the categories of controlling the interface evolution during growth by, for example, altering the substrate temperature [33-35] and post-deposition modification, such as annealing [31,36-41]. There have also been studies on GMR in multilayers prepared by ion-assisted deposition [43,44], although these did not include a characterisation of interface structure and so could not correlate the changes in GMR observed with interface roughness. In general, optimum substrate
temperatures could be found for which the interface roughness was minimised and consequently GMR maximised. In contrast, annealing of the multilayer was found to result in a decreased GMR in almost all cases. Although it seems likely that the reduction in GMR in annealed samples is caused by a greater proportion of spin independent scattering in the multilayer, it is not obvious where this additional scattering occurs, and in particular which interfaces roughen under annealing.

Much of the early apparently contradictory literature on GMR arose because of the lack of a definition of exactly what was meant by interface roughness. Comparison between the changes in GMR in samples deposited under different conditions and annealed samples is not strictly valid as the changes in roughness are unlikely to be the same. In particular, misconceptions about the interface structure in sputtered and MBE grown multilayers led to early speculation that GMR must be enhanced by interface roughness as the largest effects were observed in the supposedly rougher sputtered samples. In fact sputtered samples are generally smooth on a large lateral length scale but can posses short scale disorder such as grading between layers. MBE grown multilayers on the other hand, generally have a sharp composition modulation although the larger lateral scale roughness can be much greater than in the sputtered samples. Some recent studies have illustrated this difference and shown that, under optimum conditions, sputtered samples can be obtained with a similar layering quality to MBE grown films [71,72].

The above discussion contains the implicit misconception that sputter-deposition is in itself a fundamental growth technique for which a given multilayer structure can be expected. In fact, given the vast variations in deposition conditions that can be applied, sputter-deposition is probably better considered as an umbrella
term for all sputtering processes that include a degree of energetic particle bombardment at the substrate. Given this, it is somewhat surprising that many authors investigating GMR multilayers consider their films to be deposited from a 'black box' style source.

In order to gain a better understanding of the origin of the GMR effect it would first seem necessary to try to understand the influence of the growth environment on the interface structure realised. Part of the problem in characterising interface structure in GMR multilayers is that the component elements are frequently adjacent or nearly adjacent in the periodic table, thus providing little contrast for transmission electron microscopy (TEM) [35,45-47] or standard X-ray reflectivity (XRR) analysis [34,35,48,73,74]. However, recently the use of anomalous scattering to enhance XRR contrast [71,75,76], and other techniques such as polarised neutron reflectivity (PNR) [40,75,77,78] and nuclear magnetic resonance (NMR) [72,49,50,79], have been increasingly utilised to study interfaces in the GMR multilayers. This is leading to a better understanding of the nature of interface roughness, its correlation and its variation throughout the multilayer. In the light of these developments, the systematic study of interface evolution in Co/Cu multilayers deposited under controlled and variable levels of energetic particle bombardment has been undertaken and is presented in this thesis.

1.3 AIMS OF THE PROJECT AND THESIS STRUCTURE

The project was designed to be both an investigation of the growth of Co/Cu magnetic multilayers under energetic particle bombardment, and the
development of a simple ion-assisted deposition system. Based on unbalanced magnetron sputtering principles, such a system would enable the controlled growth of interfaces. It was envisaged that the effects of large lateral scale roughness and short scale disorder could be better investigated if the energy and flux of the ion bombardment were independently variable.

The project draws on previous work from many different areas of thin film research and development. Some of these, such as unbalanced magnetron sputtering, are frequently employed in thin film coating industries but have not before been utilised in ultrathin film and multilayer preparation. In fact, at present there is little available structural characterisation data on magnetic multilayers deposited under ion bombardment. Much of the previous work reviewed is therefore taken from related research areas, such as semiconductor films and multilayers, and X-ray mirrors. The growth and characterisation of these materials by various ion-assisted deposition techniques is discussed in Chapter 2. A discussion of the background of film growth by sputtering and the influence of the sputtering plasma is also given in this chapter.

The principal technique used to characterise interfacial structure in this project is X-ray reflectivity. An overview of the theory of X-ray reflection and diffuse scattering in multilayers is given in Chapter 3. Methods for calculating the reflectivity from a model multilayer are also discussed in this chapter, and some simple examples considered.

A review of the experimental techniques and procedures used for both the preparation of samples and their subsequent characterisation is given in Chapter 4. Following this an experimental investigation of the performance of a variable ion flux deposition system is discussed in Chapter 5. Alternatives to the main method
for ion flux control are also described in this chapter, and the procedure used to calibrate the atomic growth rates is demonstrated.

In Chapter 6 the detailed characterisation by X-ray reflectivity of the Co/Cu multilayers is examined. The evolution of interface structure as a function of ion energy and ion flux was investigated using specular and diffuse measurements and the results are discussed in this chapter. Additionally the surface structure probed by X-ray fluorescence and the effect of anomalous scattering around the K-absorption edge of cobalt and copper are considered. Preliminary results of recent spin-polarised neutron reflectivity measurements and X-ray reciprocal space mapping are also briefly presented at the end of the chapter. A final summary and concluding remarks are given in Chapter 7.
Chapter 2

Thin Film Growth Under Energetic Particle Bombardment

Contents

2.1 Introduction
2.2 Film Growth by Sputtering
2.3 Plasmas as Sources of Energetic Particle Bombardment
2.4 Ion-assisted Deposition and Microstructural Evolution
2.1 INTRODUCTION

It is becoming increasingly understood that the microstructure and morphology of thin films and multilayers depends sensitively on the growth conditions under which they are deposited. This realisation has fuelled research into both the effect of deposition conditions on film microstructure and methods of controlling the growth evolution. Many of these methods involve some form of additional substrate particle bombardment during film growth. Variations on sputterdeposition techniques make use of the sputtering plasma as a source of this additional bombardment.

The purpose of this chapter is to outline the way in which sputtering can be utilised as an ion-assisted deposition technique, and how such energetic particle bombardment affects the growth of thin films and multilayers. In the following section (2.2) the sputter-deposition process is described with particular reference to the operation of magnetron sputtering sources. Comparisons are made between growth by sputtering and growth by evaporation techniques. The sputtering plasma and its application to modified film growth is then discussed in section 2.3. Finally some recent experiments that make use of ion-assisted deposition to control thin film and multilayer growth are reviewed in section 2.4.

2.2 FILM GROWTH BY SPUTTERING

2.2.1 The Sputter-deposition Process

Sputter-deposition is one of the principal techniques employed in the growth of thin and ultrathin films. Sputtering is the process whereby an incident
particle colliding with a target surface initiates a collision cascade that results in the ejection of an atom of the target material. In general, the incident particle is an ion since it is relatively simpler to control the energy of a charged particle than that of a neutral particle. Apart from the ejection of target atoms there are also the possibilities of reflection of the incident ion by the target surface, implantation into the target and secondary electron emission. These processes are summarised in figure 2.1.

![Diagram of sputtering processes](image)

**Figure 2.1: Summary of the sputtering processes at the target**

Since the sputtering process results in the removal of material from the target one of the most common applications of sputtering that has been utilised is sputter-etching. This has been used to generate specific topographic patterns on surfaces [80] or to clean the surface of a material under vacuum conditions [81,82]. Sputtering is probably more widely used for deposition processes since the sputtered atoms can be condensed onto a substrate to form a thin film of the target material. This application of sputtering is more correctly termed sputter-deposition. However in the field of thin film physics the terms 'sputtering' and 'sputter-deposition' are often used interchangeably. Unless otherwise stated the term
sputtering shall be used to refer to sputter-deposition processes throughout this work.

There are many different sputtering techniques used in the fabrication of thin films. Most of these require the presence of a plasma in the growth chamber to provide ions for sputtering. Typical examples are DC/RF diode and triode sputtering and DC/RF magnetron sputtering. The main plasma-free sputtering process generally used is ion beam sputtering (IBS) where a separate ion beam source is used to bombard the target [83]. Although IBS still requires a plasma as a source of ions, in this case the plasma is contained within the boundaries of the ion gun and the ions extracted from it. The main sputtering process discussed here is DC magnetron sputtering. The other sputtering processes mentioned above have been reviewed previously by Chapman [84].

2.2.2 Magnetron Sputtering

In DC sputtering the electrons and ions in the plasma are subject to the electric field generated between the cathode (target), to which a negative dc bias is applied, and the anode (chamber wall) which is typically grounded. The electric field accelerates ions towards the target, which then induces sputtering, and electrons towards the chamber wall. The kinetic processes occurring in the sputtering plasma will be discussed in more detail in section 2.3. To sustain the discharge the electrons must undergo ionising collisions with the sputtering gas, typically argon. The greater the degree of ionisation that occurs the more efficient the sputtering process will be. Hence it is important to maintain the electrons within the target vicinity for as long as possible before they escape to the chamber.
wall. In addition the probability of ionising collisions can be increased by lengthening the path the electrons must travel before they reach the chamber wall.

A convenient method for controlling the electron motion in a sputtering plasma is to apply a magnetic field. The force on the electron charge is given by the familiar expression \( \mathbf{F} = q(\mathbf{v} \times \mathbf{B}) \) and acts along an axis orthogonal to the plane containing \( \mathbf{v} \) and \( \mathbf{B} \). Hence there will be an acceleration along this axis, as depicted in figure 2.2, that is inversely proportional to the mass of the charge. The field strengths used (typically ~ 100G) will not therefore directly affect the motion of the ions in the plasma.

![Diagram of electron motion in a magnetic field](image)

**Figure 2.2 : Motion of an electron in a magnetic field.**

When the velocity of the electron is parallel to \( \mathbf{B} \) the term \( \mathbf{v} \times \mathbf{B} \) vanishes and the electron is unaffected by the magnetic field. For the more general case shown in figure 2.2, the electron moves in a helical path about an axis parallel to the magnetic field. The radius of the circular motion is given by

\[
\frac{m_e (v \sin \theta)^2}{r} = Be(v \sin \theta)
\]

and hence
where $m_e$ is the electron mass and $\theta$ is the angle between $v$ and $B$ in the plane containing both vectors. It can be seen from the expression (2.1) that the radius is proportional to $\sin\theta$ and will be maximum when the velocity of the electron is perpendicular to $B$. For the case of an electron ejected along the normal to a surface with the magnetic field parallel to this surface, the electron will follow a circular path that returns it to the surface. The effect of the magnetic field is thus to trap the electron near the surface. The addition of an electric field along the surface normal distorts the circular electron path to that of a cycloidal path, although the entrapment effect is the same.

In a conventional magnetron the magnetic field shape is designed to trap as many electrons near the target surface as possible. A typical arrangement for a circular planar magnetron is shown in figure 2.3. The flux from the rear poles of the magnetron is contained within a mild steel yoke. Electrons emitted from the cathode (target) are initially accelerated towards the anode, executing a helical motion around the field lines. However, once these electrons encounter the magnetic field lines that are parallel to the surface they are bent in an orbit back to the target surface. The most efficient entrapment of electrons occurs in the areas where the magnetic field is parallel to the surface. Hence the ionisation is greatest in these areas, resulting in enhanced sputtering of the target region directly beneath. When the arrangement of the magnets in the magnetron is such that the magnetic circuit is closed around the target, the magnetron is said to be balanced. The advantage of this type of magnetron is that the plasma is contained near the target resulting in much higher deposition rates for thin film growth than can be
obtained using standard diode sputtering. Additionally the bombardment of the film/substrate by energetic particles from the sputtering plasma is minimised.

![Diagram of magnetron source](image)

**Figure 2.3 : Schematic illustration of a conventional magnetron source showing the magnetic field configuration.**

There are, however, cases when a controlled amount of bombardment of the film is desirable. The unbalanced magnetron allows part of the sputtering plasma to extend towards the substrate. This is achieved by 'unbalancing' the magnetic field configuration around the sputtering target by using outer poles that are slightly stronger than the central pole. The excess field lines from the outer poles form an extended magnetic 'bottle' towards the substrate as depicted in figure 2.4. Electrons that escape from the target area follow helical paths around these extended field lines. The tendency for plasmas to remain electrically neutral results in part of the plasma from the magnetic trap forming a plasma beam directed towards the substrate. The way in which this plasma can be used to control substrate bombardment will be discussed in section 2.3. Unbalanced magnetrons can be designed so that the target magnetic trap is nearly as strong as...
that in a conventional balanced source. The deposition rates are therefore similar to those obtained from a conventional magnetron.

![Diagram](https://via.placeholder.com/150)

**Figure 2.4**: Schematic illustration of an unbalanced magnetron source showing the extended magnetic field lines.

2.2.3 The Growth Environment and Film Microstructure

The evolution of microstructure in thin films deposited by evaporation techniques is fairly well understood. The main factors that influence the film growth are the chemical nature and surface integrity of the substrate, the substrate temperature and the energy of the evaporated atomic flux. Three highly generalised growth modes have been suggested to explain numerous observations on the early stages of growth. These are illustrated schematically in figure 2.5. The island growth mode occurs when the impinging atomic or molecular particles are more strongly bound to each other than to the substrate. Small stable clusters then nucleate on the substrate and grow to form three dimensional islands. Layer
growth occurs when the depositing particles are more strongly bound to the substrate and results in the formation of two dimensional sheets of the deposited material. The final growth mode, Stranski-Krastanov growth, is a combination of the former two modes. In this case the first few monolayers will grow in a layer fashion until this mode becomes energetically unfavourable and island growth occurs.

![Diagram of Modes of Thin Film Growth](image)

*Figure 2.5: Modes of thin film growth by evaporation.*

Although the atomic flux produced during sputtering can, under certain conditions, have a similar energy to evaporated material, there are many additional particles that can bombard the substrate during sputtering and hence influence the way in which film growth occurs. Most of these particles come either directly from the sputtering plasmas or are formed subsequently in collisions at the target. Owing to the high accelerating potentials typically employed (~ 2-3 kV) these additional particles have energies several orders of magnitude greater than the depositing material. Such high energy substrate bombardment is in general undesirable as it can lead to increased impurity and defective density within the film. Magnetron sputtering reduces the amount of high energy substrate bombardment by...
containing the plasma around the target to enable more efficient sputtering. Magnetrons can therefore be used at much lower operating voltages (~300 - 500 V) and lower argon pressures (1-10 mTorr as opposed to ~100 mTorr for standard sputtering).

Despite the lower target voltages used in magnetron sputtering, neutral argon atoms from the target area, with energies of several hundred eV can still bombard the substrate. The proportion and energy of the particles that reach the substrate will depend upon the argon pressure used since this determines the collision mean free path. At first sight it would seem that an obvious method for varying the energetic bombardment of the substrate would be to vary the argon pressure. However, this would alter many parameters simultaneously since the target voltage, ion and electron current, deposition rates and energy of the atomic flux all depend on the argon pressure. It is possible to minimise the energetic neutral Ar bombardment by increasing the argon pressure and thus leaving predominantly charged particle bombardment at the substrate. This is generally more useful since the charged particles can be controlled using electric and magnetic fields. The equilibrium state of the plasma will then dominate the film growth.
2.3 PLASMAS AS SOURCES OF ENERGETIC PARTICLE BOMBARDMENT

2.3.1 The Glow Discharge Environment and Sheath Formation

The glow discharges that are utilised in sputtering can be understood in terms of plasma concepts. A glow discharge is formed in the sputtering chamber by applying a large negative potential to the target (cathode) in the presence of an argon partial pressure. Impact ionisation of the neutral argon atoms and ion collisions with the cathode results in rapid charge multiplication. A steady state is reached when the degree of ionisation is such that there is a numerically equal generation of electron / ion pairs and thus the discharge becomes self-sustaining. The current then rises to a limiting value defined by the impedance of the power supply and the voltage drops to a minimum. This is the glow discharge operating regime.

Luminous regions are observed in the discharge due to electron impact induced excitation and subsequent relaxation of argon atoms accompanied by photon emission. Most of the ionising collisions are thought to occur in these regions. The discharge is essentially a partially ionised gas composed of ions, electrons and neutral atoms. The charged particle separation is small enough to allow coulomb interactions resulting in the fluid like behaviour of the plasma.

One of the fundamental properties of such a plasma that affect its behaviour is the difference in the velocity of the electrons and ions. Since the particles in the plasma perform quasi-random motion, their speeds can be well represented by the Maxwell-Boltzmann distribution,
\[ \frac{dn}{dc} = \frac{4n}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{3/2} c^2 \exp \left( \frac{-mc^2}{2kT} \right) \quad 2.2 \]

where \( dn \) is the number of particles out of a total, \( n \), that have speeds between \( c \) and \( c + dc \), and all other symbols have their usual meaning. The mean speed is given by

\[ \bar{c} = \frac{1}{n} \int cdn = \left( \frac{8kT}{\pi m} \right)^{1/2} \quad 2.3 \]

and the random current density is

\[ j = \frac{1}{4} n \bar{c} e = \frac{ne}{9} \left( \frac{3kT}{2\pi m} \right)^{1/2} \quad 2.4 \]

where the substitution for \( \bar{c} \) from equation 2.3 has been made. Measurements of glow discharges have indicated typical electron energies (equal to \( 3/2kT \)) of about 2 eV whereas ion energies are typically \( \sim 0.04 \) eV. The number of electrons and ions in the plasma, \( n \), is equal. Thus it can be seen from the expression in 2.4 that the ratio of the current densities for electrons, \( j_e \), and ions, \( j_i \), is

\[ \frac{j_e}{j_i} \approx \left[ 50 \frac{m_i}{m_e} \right]^{1/2} \approx 10^3 \]

where the ion mass, \( m_i \), is taken to be \( 6.6 \times 10^{-23} \) g and the electron mass, \( m_e \), is \( 9.1 \times 10^{-28} \) g.

One of the consequences of the much greater electron motion compared to that of the ions is that an isolated planar substrate placed in the discharge will initially be more heavily bombarded by electrons than ions. It will thus acquire a negative potential with respect to the plasma and begin to repel further electrons whilst attracting the positive ions. Eventually the substrate will acquire a negative floating potential, \( V_f \), that repels enough of the electrons that the ion flux is exactly
balanced. The plasma potential, $V_p$, is positive with respect to the substrate and for most magnetron sputtering plasmas is typically of the order of a few volts.

![Diagram of plasma potential and sheath](image)

**Figure 2.6**: Variation of electrical potential (upper) and potential energy for electrons and ions incident at a substrate sheath.

With the substrate negatively charged, only the more energetic electrons in the plasma have sufficient energy to cross the potential barrier $e(V_p-V_i)$ and balance the ion flux. Most of the electrons will not have sufficient energy to reach the substrate and so a positive space charge can develop in front of the substrate. This space charge is known as a sheath and, since it contains relatively few electrons to cause ionising collisions, is darker than the surrounding glow discharge. Sheaths of this type will form around any object placed in the plasma that has a negative potential with respect to $V_p$. Whereas only energetic electrons can cross the substrate sheath, losing kinetic energy in the process, ions will gain kinetic energy in being accelerated across the sheath region and thus bombard the substrate with energies of the order of $e(V_p - V_i)$. These processes are illustrated
schematically in figure 2.6. The arrival rate of ions at the substrate is thus determined by the random current density of ions incident at the substrate sheath/plasma interface.

2.3.2 Application of a substrate bias

Although the ion flux incident at the substrate is unaffected by the negative potential of the substrate, the energy of these ions is. The ions in the plasma may only have average energies of $<0.5$ eV but the ions bombarding the substrate have average energies given by $e(V_p - V_b)$ of typically ~ 15-20eV. This figure can be increased still further by applying a negative bias, $V_b$, to the substrate.

The ion current density to a biased substrate can be measured by inserting a small planar probe of 1 cm$^2$ area into the substrate table as illustrated schematically in figure 2.7. The probe is biased at the same potential as the substrate table but is electrically isolated from it by a small vacuum space. The current density characteristic of the probe is shown in figure 2.7(b). The floating potential measured by the probe is the point at which the net current flow is zero, as indicated in the figure. As the substrate bias is increased, a smaller proportion of the electron flux incident at the sheath/plasma interface will have sufficient energy to cross to the substrate. The net current density measured by the probe therefore increases (negatively) as the electron flux is repelled until virtually all the substrate bombardment is caused by ions. This saturated ion bombardment region can be seen in the probe characteristic as the plateau region indicated in figure 2.7(b).
Figure 2.7: Schematic illustration of a typical planar probe arrangement (a) and the probe characteristic curve (b).

When the probe is biased positively with respect to $V_b$, the electron repulsion is rapidly reduced and the electron current to the probe dominates the measured current density. This can be seen in the characteristic as the sharp (positive) rise in the current density. Hence, the current density of ions hitting a biased substrate can be measured and their average energy determined from the relation $e(V_p - V_b)$, where $V_b$ is the bias voltage. It will be shown in the next section (2.4) that the ion flux and energy are the two important parameters that affect microstructural evolution under ion bombardment. It should be noted that for magnetron sputtering, $V_b \gg V_p$ and hence the average ion energy can be approximated by $e|V_b|$.

The previous discussion assumes that the ions do not lose any significant energy due to collisions whilst crossing the substrate sheath. This is generally true for magnetron sputtering, but less so for higher argon pressure diode sputtering. A
typical collision that may occur, resulting in a symmetric charge exchange, is that of a fast (energetic) argon ion colliding with a neutral argon atom to give a fast neutral atom and slow argon ion:

\[ \text{Ar}^+_{\text{fast}} + \text{Ar}_{\text{slow}} \rightarrow \text{Ar}^+_{\text{slow}} + \text{Ar}_{\text{fast}} \]

Johan et al [85] have measured the ion energy distribution at a negatively biased electrode in a d.c. diode sputtering discharge. Their results obtained using an argon partial pressure of 19 Pa (more than an order of magnitude greater than typical magnetron partial pressures) for several values of substrate bias are shown in figure 2.8(a).

![Energy distribution N(E) for different bias voltages (a) and at a bias of -100 V for different argon discharge pressures (b) (from ref. [85]).](image)

\[ \text{Energy (eV)} \]

\[ \text{N(E)} \]
By calculating the sheath width and mean free path for argon ions, the authors estimated that one or two collisions were possible in the sheath. The energy distribution in figure 2.8(a) shows sharp maxima at the expected positions of \(-e|V_b|\) and lower energy tails that correspond to energy loses due to the predicted charge exchange collisions. The lower energy tail becomes less pronounced at lower argon pressures as shown for \(V_b = -100\) V in figure 2.8(b). This is due to the reduced probability of collisions as the pressure decreases and hence the mean free path for argon ions increases. Unfortunately no similar data are available for ion energy distributions from a magnetron plasma, although the expected distribution would be even sharper than that shown in figure 2.8.

2.3.3 The Unbalanced Magnetron as a Plasma Source

The use of magnetic fields to confine the discharge in magnetron sputtering has two important effects. The first is that the erosion of the target can be controlled by designing a suitable field configuration. This gives great flexibility in the range of materials that can be sputtered. The second is that the unbalanced magnetic flux guides part of the sputtering plasma to the substrate vicinity. Referring to figure 2.4, the plasma confined about the target is usually much more intense than that extending to the substrate due to the larger magnetic field strength at the target. These two regions are essentially separated for fixed operating conditions and thus the unbalanced magnetron can be thought of as a separate sputtering and plasma beam source. This enables the unbalanced magnetron to be used for ion assisted deposition processes. Additionally, the substrate current density can be controlled by altering the strength of the
unbalanced magnetic field. As this field is increased a greater fraction of electrons that escape the trap can be channelled toward the substrate, thus increasing the plasma density in this region. A greater plasma density affords a larger ion and electron current density at the plasma / substrate sheath interface resulting in a higher current density at the substrate.

The main advantage in using unbalanced magnetrons as ion sources rather than separate broad beam ion sources is that relatively high ion current densities ($\geq 1 \text{ mA/cm}^2$) can be obtained down to very low energies ($\leq 50 \text{ eV}$). Thus unbalanced magnetrons work well for low energy ion-assisted deposition processes when a high ion current is required. For this reason many of the earlier applications of unbalanced magnetron sputtering were for industrial related processes where the high deposition rates employed required that the ion current density at the substrate also be high to achieve the correct ion/atom arrival ratio at the substrate [86,87]. Another feature of unbalanced magnetrons that generated industrial interest was that several magnetrons could be coupled together by alternating the polarity of the unbalanced magnetic flux so that the field lines linked [87]. In this arrangement the ion current densities could be even higher ($>5 \text{ mA/cm}^2$) and the positioning of the magnetrons could be arranged for coating three dimensional substrates with microstructural control. To date, little use has been made of unbalanced magnetrons for depositing ultrathin films and multilayers despite the fact that the ability to control low energy bombardment is even more important when the deposited layers are at most a few nanometers thick.
2.4 ION-ASSISTED DEPOSITION AND MICROSTRUCTURAL EVOLUTION

2.4.1 Modelling film growth under ion bombardment

In order to try to understand the effect of low energy ion bombardment on a growing film it is useful to establish a realistic model of the process. This model can then be driven computationally to illustrate the result of the various ion-atom and atom-atom interactions that occur. A great deal of the work published in this area has been produced by Müller [88-91]. Two approaches were considered in this work, a collision cascade model [88,90] and molecular dynamics simulations [89,91].

The collision cascade model considers the time evolution of the atomic density at a given depth in the growing film. The basis of the model is that an ion with an energy of a few hundred eV, striking the surface of a porous film, causes knock on collisions with the surrounding film atoms. This process continues until the initial energy has been dissipated, either by the ejection of a film atom from the surface, or by absorption within the film. Since the energy of the impacting ion is low the collision cascade and corresponding atomic rearrangements occur in a region not far below the film surface. The inwardly recoiled surface atoms become trapped in microvoids below the film surface and the evolving microstructure consists of a depleted surface region and a more dense subsurface region. Refilling then occurs at the surface as deposition continues. In addition to the densification caused by recoil implantation, the ions themselves have sufficient energy to implant into the film and thus alter the stoichiometry of the film.
An example of a mass density distribution calculated for oxygen ion-assisted growth of ZrO$_2$ films using 600 eV bombardment is shown in figure 2.9 [90]. It can be seen that as film growth proceeds the denser region beneath the surface is extended. The resulting film produced after a given deposition time is thus denser than the more porous structure that would be produced in the absence of ion bombardment.

![Mass density distribution calculated for oxygen ion-assisted growth of ZrO$_2$ using 600 eV bombardment](image)

*Figure 2.9: Mass density distribution calculated for oxygen ion-assisted growth of ZrO$_2$ using 600 eV bombardment (from ref.[11]).*

For a more complete picture of the effects of ion bombardment on film growth, molecular dynamics calculations can be applied. These are classical calculations that consider the interactions between particles in a simulation cell of given dimensions. Müller has used molecular dynamics calculations to simulate the effect of ion bombardment on the growth of nickel atoms on a nickel substrate[89,91]. The calculation starts by considering the position, $x_i$, and velocity, $v_i$, of a particle $i$ after a given time, $\Delta t$, under the influence of a force determined by pairwise interactions with the surrounding particles,
where $\phi$ is the interaction potential. For the interaction of ions with film atoms, $\phi$ is assumed to be of a repulsive form given by \[91\]

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \left(0.35e^{-0.3r/a} + 0.55e^{-1.2r/a} + 0.1e^{-6.0r/a}\right)$$

where $a = 0.4683(z_1^{1/2} + z_2^{1/2})^{1/2}$ and $z_1$ and $z_2$ are the atomic numbers of ion and film atoms respectively. The attractive interaction between ions and atoms is considered to be negligible. The attractive part of the interaction between condensing Ni atoms is taken to be a Lennard-Jones function,

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where $\sigma$ corresponds to the (111) plane lattice spacing of fcc Ni and $\varepsilon$ is the strength parameter that determines the depth of the potential well. For the repulsive part of the interaction the potential given in equation 2.6 is assumed.

Given the form of the interaction potential $\phi$, the position and velocity of a particle at a time interval $\Delta t$ are given by

$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \mathbf{v}_i(t)\Delta t + \langle \mathbf{F}_i \rangle \Delta t^2 / 2m_i$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \langle \mathbf{F}_i \rangle \Delta t / m_i$$

where $\langle \mathbf{F}_i \rangle$ is the average force on the particle over the time interval,

$$\langle \mathbf{F}_i \rangle = \frac{1}{2} \left[ \mathbf{F}_i(x_i(t + \Delta t)) + \mathbf{F}_i(x_i(t)) \right]$$

The use of an average force in equations 2.8 and 2.9 means that these equations are exact expressions even though the determination of $\langle \mathbf{F}_i \rangle$ can be an
approximation [92]. The integration time step, $\Delta t$, is readjusted before each calculation and is subject to the constraints that the maximum atomic displacement does not exceed 0.025 times the lattice distance during each calculation.

The simulation cell is taken to be a (two dimensional) rectangle open at one end to allow the incoming particle flux. Two substrate layers are present initially and these are made to act as a perfect heat sink at zero temperature by resetting the velocities of all atoms that reach these layers to zero. Nickel vapour atoms are then introduced sequentially at random into the simulation cell and impinge upon the growing film. In Müller's calculation [91] the deposition rate is assumed to be sufficiently low that impact induced vibrations have time to relax and hence any heat generated can be dissipated through the substrate. The film temperature does not increase during growth and the model is not therefore a particularly realistic description of sputtering processes where an increase of $>20$ K is common (although much of this heat is generated by electron and ion bombardment).

After $v$ impinging vapour atoms, each with an energy of 0.1 eV, have arrived and the system has relaxed, a 100 eV argon ion is introduced into the simulation cell. The corresponding ion / vapour flux ratio is thus $j_i/j_v = 1/v$. This situation is shown in figure 2.10(a). The film structure produced by the low energy vapour is mobility limited such that a highly porous structure develops containing microvoids and columns. When the ion strikes the surface, part of its kinetic energy is transferred to the surrounding surface atoms. These in turn strike other atoms and so a collision sequence evolves. The resulting configuration obtained 0.82 ps after the initial impact is shown in figure 2.10(b). The entire relaxation process takes about 15 ps after which further vapour atoms are added to the simulation cell. It can be seen from figure 2.10(b) that the ion impact causes some of the
atoms to be displaced to lower lying positions and removes some of the
overhanging atoms that initiate void formation.

The microstructure that evolves following a series of such ion
bombardment induced cascades and vapour deposition, is shown for various ion
energies and ion/vapour flux ratios in figure 2.11. It can be seen that the atomic
displacements caused by the ion impacts lead to a breakdown in the porous
columnar structure (figure 2.11(a)) due to the filling of microvoids that are left
open by the reordering of surface atoms.

Figure 2.10: (a) Film structure resulting from condensing Ni vapour atoms
on a prefect Ni substrate and (b) the collision sequence 0.82
ps after a 100 eV Ar ion strikes the film (after ref.[89]).

The denser microstructure produced under ion bombardment is sensitive to
the flux ratio $J_i/J$, and the ion energy. The density can be increased either by
increasing the flux ratio (figure 2.11(b) and (c)) or by using higher energy ions
(figure 2.11(d) and (e)). As the ion energy increases, however, the depth of the
collision sequence will also increase as more atoms must become involved in order
to dissipate the initial energy. Thus at higher energies the reordering of atoms at a
greater depth below the surface would be expected. Ion energies $>100$ eV could
not be treated in Müller's calculations [91] due to limitations in computing time available. The effect of higher energy bombardment becomes important when more than one element is present in the film as ion mixing of the elements can occur. Some experimental cases that illustrate this are included in the following discussion.

Figure 2.11: Typical microstructure evolved for condensing Ni atoms with (a) no bombardment, (b) ion energy 50 eV, flux ratio 0.04, (c) ion energy 50 eV, flux ratio 0.16, (d) ion energy 10 eV, flux ratio 0.16 and (e) ion energy 75 eV, flux ratio 0.16 (after ref. [91]).
2.4.2 Ion-assisted growth of single layer films

The interest in ion-assisted deposition as a method of film growth has been generated by the realisation that the microstructure has a profound influence on the bulk properties of the film. The ability to control the microstructure thus implies a control over the film properties. A simple example of this is the effect of microstructure on the resistivity of thin metal films. Several studies have attempted to establish the effect of ion energy and ion flux on the resistivity and microstructure of films grown by ion assisted deposition [93-95]. Typical of these is the work by Kao et al [95] where a dual ion beam assisted deposition technique was applied to the growth of tungsten films. The experimental set-up used in this work is shown in figure 2.12.

![Dual ion beam deposition apparatus](image)

*Fig 2.12: Dual ion beam deposition apparatus (from ref. [16]).*

Two Kaufman ion beam sources [96-98] were utilised, the first as a source of ions for sputtering the target and the other for providing ions for ion-assisted growth. Owing to the low argon pressure in the chamber during deposition,
sputtering $\text{Ar}^+$ ions reflected from the target also bombarded the growing film. This complication was considered by measuring the resistivity as a function of sputtering $\text{Ar}^+$ energy and current, as well as ion-assisting energies and fluxes. Part of the resistivity data obtained is shown in figure 2.13. The resistivity was found to increase for larger sputtering ion energies, but decrease for higher fluxes of low energy (100 eV) assisting ions (figure 2.13(a)). It was suggested that the high energy bombardment from the reflected sputtering ions caused significant sputter-etching of the film resulting in a roughened surface containing defects. Evidence for this was found from SEM micrographs of the surface topography and cross-sectional TEM analysis. Ion bombardment induced defects disturbed the nucleation process and resulted in films with a finer grain microstructure. Since the grain size was much smaller than the conductive electron mean free path, electron scattering was dominated by grain boundaries and microdefects in the film. This would account for the increase in resistivity for high energy bombardment.

Further to this it was found that an additional low energy bombardment increased the mobility of film atoms and so smoothed the surface texture induced by the high energy bombardment, and also increased the packing density. This could explain the reduction in resistivity as the low energy ion flux was increased (figure 2.13(a)). A similar reduction in resistivity was found initially as the assisting ion energy was increased as shown in figure 2.13(b). The gradual rise in resistivity above 200 eV indicates the transition from increased adatom mobility and smoothing to higher energy bombardment processes such as sputter-removal of atoms.
Fig 2.13: Film resistivity as a function of (a) 100 eV assisting Ar⁺ flux and (b) assisting Ar⁺ energy at a flux of 0.017 mA/cm² (after ref.[95]).

As discussed in the previous section (2.3), unbalanced magnetron sources can be used in a similar fashion to Kaufman ion beam sources for ion-assisted deposition processes. Petrov et al [99,100] developed a reactive unbalanced magnetron sputtering technique for the deposition of polycrystalline T₉₅A₀₅N films. An external pair of Helmholtz coils were used in this work to vary the...
unbalanced magnetic flux and hence the ion current density at the substrate. The ion energy was then controlled by the application of a dc substrate bias.

It was found that the microstructure developed in a different manner depending on which parameter, either the ion energy or ion/atom flux ratio, was varied. As the ion energy was increased from 20-100 eV, evidence of ion induced damage accompanied by a decrease in average grain size and partial densification were observed. These processes are reminiscent of the high energy bombardment effect studied by Kao et al [95], although the energies involved in this case were much lower. In contrast, the microstructure observed when the ion/atom flux ratio was increased at a constant ion energy of ≅ 20 eV showed no evidence of ion damage and consisted of a coarser grain, more densely packed structure, reminiscent of that produced with an elevated (>400°C) substrate temperature. A collision enhanced surface adatom mobility was proposed to account for these changes, since the low ion energy constrained collision events to the near surface region. Additional evidence for this mechanism was suggested by considering the change in the preferred orientation of the films as a function of increased ion / atom flux ratio. It was suggested that an increased surface mobility should enable low energy crystal planes to develop during nucleation and coalescence. For TiN the lowest surface energy face is the (002) [101] which is consistent with the observed change in preferred orientation from TiN(111) to TiN(002) in the Ti_{10.5}Al_{9.5}N films.

The range of deposition techniques that include ion bombardment for microstructural modification has been extended in recent years to include ion-assisted molecular beam epitaxy (IAMBE) [102-107]. A novel IAMBE system using a triode discharge as a source of low energy ions was developed by Rohde et al [106] and used to study the nucleation and growth of GaAs films on Si(100)
This low energy, mobility limited growth follows the mechanisms typical of evaporation processes discussed earlier in section 2.2.3. Their findings suggested that the nucleation process could be changed from a Stranski-Krastanov growth mode (initial layer growth followed by three dimensional island formation) to layer-by-layer growth, by depositing under low energy (~30 eV) ion bombardment.

Fig 2.14: XTEM micrograph of an 18 monolayer GaAs film on Si(100), as-deposited (top) and grown with an additional 28 eV ion bombardment (from ref[107]).

In this case the ion bombardment appeared to be affecting the nucleation process directly since the ion energy was too low for effects such as preferential sputtering and ion induced mixing to contribute significantly. Furthermore, an ion bombardment enhanced mobility of the adatoms would be expected to promote island nucleation. Instead it was proposed that the critical process in determining the growth mechanism was the removal of atoms from barely stable nuclei forming on the substrate, by low energy ion collisions. If this rate of removal exceeded the rate of adatom addition then island nucleation was suppressed. This proposal was supported by the fact that the transition to layer-by-layer growth was only observed above a threshold ion current density (~ 0.2 mA/cm²). The importance of
this suppression of island growth is that planar, flat surfaces and interfaces can be formed. This is demonstrated in figure 2.14 taken from reference 107 that shows an 18 monolayer thick GaAs film on Si(100), grown with and without 28 eV ion bombardment.

2.4.3 Interface formation in multilayers deposited under ion bombardment

In principle, the surface smoothing effect of ion-assisted deposition could be used to reduce interface roughness in multilayers. However, in a multilayer film the possibility of ion bombardment induced mixing of the layers must be taken into account. Hence, there is an inherent problem, not only in producing interface smoothing without intermixing, but in being able to measure the interface roughness intrinsic to the multilayer microstructure separately from that caused by intermixing.

The mean penetration depth of bombarding ions increases as a function of ion energy and thus a more significant mixing effect would be expected at higher ion energies. Puik et al [108] have studied the effect of ion bombardment on the growth of Ni/C multilayers deposited by electron beam evaporation. A 200 eV Ar⁺ ion beam incident on the sample at 45° was used to provide ion fluxes during deposition (ion-assisted deposition) and between each deposited layer (ion etching). The mean penetration depth of the Ar⁺ ions for this configuration was calculated to be 4Å. The surface roughness during growth was monitored in-situ by measuring the reflected X-ray intensity at a glancing angle, θ, of 35° from an X-ray beam incident at the same angle and with a wavelength, λ, of 31.6Å.
Oscillations in the reflectivity intensity were measured as the film thickness, 
\( d \), increased with maxima at values of \( d \) determined from Bragg's law as integer 
multiples of \( 2\pi/Q \) where \( Q = (4\pi/\lambda)\sin\theta \). (X-ray reflectivity is discussed in chapter 3). The reflectivity oscillation period for this experiment was thus 28Å. This was 
used to fix the multilayer period at 28Å by first depositing carbon until a minimum 
in reflectivity was obtained and then depositing nickel until the corresponding 
maximum was measured. Thus each layer had a thickness of half a period (14Å). 
At the X-ray wavelength used the amplitude of the carbon reflectivity oscillation 
was much lower than that of nickel. Hence, a net increase in the reflectivity 
occurred as the number of multilayer periods increased.

The reflectivity maxima measured for a series of Ni/C multilayers is shown 
in figure 2.15. Two of the ion-assisted films, labelled ml II (ml III) were deposited 
normally for the first 9Å (6Å) of nickel growth and with ion-assistance for the 
remaining 5Å (8Å). The third ion-assisted film (ml IV) was deposited with ion-
assistance throughout nickel growth. Multilayers deposited without ion 
bombardment and with ion etched layers are also shown in figure 2.15 for 
comparison. It can be seen from the figure that the ion etched sample showed the 
strongest enhancement in reflectivity compared to the as-deposited film, and hence 
the largest surface smoothing effect. The ion-assisted films (ml II and ml III) also 
showed an enhancement but not as pronounced as for the ion etched film. The 
reason for this was that a greater thickness of nickel was exposed to the ion beam 
during ion etching thus minimising ion penetration through into the carbon layer. In 
the ion-assisted films, some ion induced mixing of the Ni/C layers was likely as the 
calculated ion energy distribution allowed penetration depths up to 15Å. As 
expected the intermixing effect was greater for thinner as-deposited nickel layers.
This intermixing reduced the reflectivity from the Ni/C interface which can be seen as a drop in the measured reflectivity (figure 2.15) for films ml II and ml III. The intermixing in the completely ion-assisted film was so pronounced that the reflectivity was destroyed after three periods. The degree of intermixing observed might be expected to depend on the porosity of the underlying carbon layer which is in turn influenced by the deposition process. Multilayers deposited by techniques other than evaporation may therefore show a different interface stability under ion bombardment.

![Graph](image)

*Figure 2.15: Reflectivity maxima measured as function of period for a series of Ni/C multilayers under different ion bombardment conditions (after ref.[108]).*

Vernon et al [109] and Stearns et al [110] have examined the effect of energetic particle bombardment during growth on the layer morphology in magnetron sputtered Mo/Si multilayers. In initial experiments [110] it was found that the multilayer structure degraded as the sputtering gas (argon) pressure was increased. Similar effects have been observed in magnetron sputtered Nb/Si multilayers [111]. In both cases a thermalisation of energetic particles such as reflected argon ions and sputtered atoms was suggested to account for the
observed changes in microstructure. In the absence of thermalisation these energetic particles could bombard the film and increase the surface mobility of adatoms, leading to surface smoothing and columnar growth suppression. The degree of thermalisation depends on the sputtering gas pressure and the target to substrate distance. Hence, with fixed target and substrate positions thermalisation effects become more pronounced as the sputtering pressure is increased.

Figure 2.16: Cumulative thickness errors, $\sigma_t$, as a function of argon pressure measured from a series of Nb/Si multilayers (after ref.[111]).

Fullerton et al [111] observed the onset of cumulative roughness and columnar growth as a function of sputtering pressure using cross-sectional transmission electron microscopy (XTEM) and X-ray reflectivity. To quantify the problem they introduced a cumulative thickness fluctuation parameter, $\sigma_t$, into a model for fitting the X-ray reflection data (a similar model is discussed later in Chapter 3). The values of $\sigma_t$ determined as a function of pressure for Nb/Si multilayers are shown in figure 2.16. The initial gradual increase in $\sigma_t$ can be seen to change to a sharp rise as the argon pressure exceeds 9 mTorr. This was found to
coincide roughly with the expected pressure for thermalisation of the sputtered atoms. It therefore seems likely that, in this case, the surface mobility of electrons was largely governed by the energy of the sputtered atomic flux.

Vernon et al [109] found that energetic neutral Ar atoms reflected at the magnetron target played a dominant role in determining the layer structure in Mo/Si multilayers. The probability of reflection depended upon the relative masses of the argon and target atoms. Since Mo is 2.4 times more massive than argon, but Si is only 0.7 times the mass of argon, the proportion and energy of reflected neutrals bombarding the substrate was much higher during Mo deposition than during Si deposition. Estimates of the average energy deposited per adatom during molybdenum deposition suggested that this value remained \( \geq 100 \text{ eV/adatom} \), up to argon pressures of 10 mTorr. In contrast, the same estimates for silicon deposition yielded values of 12 eV/adatom at 1.75 mTorr down to only 5 eV/adatom at 10 mTorr. The contribution due to the kinetic energies of both Si and Mo adatoms was given as \(<10 \text{ eV/adatom}\). Hence during silicon deposition the surface mobility of adatoms was dominated by the adatom energies whereas this had a negligible influence during molybdenum deposition.

In order to increase the average energy deposited per adatom at a higher argon pressure (10 mTorr), the substrate was biased during growth. This provided substrate bombardment by ions from the sputtering plasma with average energies of the order of the applied bias, as discussed earlier (section 2.3.2). XTEM and soft X-ray normal incidence reflectivity (NIR) were used to characterise a set of Mo/Si multilayers deposited with applied negative substrate biases of up to 300 V. It was found that, although a smooth layer structure evolved at all applied negative biases greater than zero, intermixing of the layers was observed for biases \( >\)
200V. This is illustrated in figure 2.17 which shows the measured NIR as a function of applied bias. The increase in reflection suggests a decrease in interface roughness for the -100 V and -200 V biased films. Intermixing that occurs at more negative biases accounts for the decrease in the reflectance at -300 V bias.

![Graph showing NIR as a function of applied bias.](image)

*Figure 2.17: Normal incidence X-ray reflectivity measured from a set of Mo/Si multilayers deposited at different substrate biases (after ref.[109]).*

XTEM micrographs obtained when a substrate bias of -100 V was applied selectively during the deposition of silicon and/or molybdenum deposition are shown in figure 2.18. It can be seen that the ion bombardment had little effect on suppressing interface roughness when applied only during molybdenum deposition. A smooth layered structure was, however, observed when the bias was applied during silicon deposition. It was estimated that the application of a -100 V bias increased the average energy deposited per adatom only slightly for Mo deposition (from 99 to 108 eV). During silicon deposition, however, this value was estimated to be more than four times greater than the corresponding value for unbiased growth. Hence, while the application of a negative bias had little effect on the
growth of molybdenum layers at high argon pressure, it restored the energy to the film lost by thermalisation of the silicon adatoms. Thus the layer structure observed in films deposited at 10 mTorr with a -100 V bias, was found to be qualitatively similar to unbiased films prepared at a lower argon pressure of 1.75 mTorr.

The results reviewed here [108-111] illustrate the dramatic role of energetic particle bombardment on interface structure in multilayers. Without sufficient surface mobility, adatoms cannot diffuse to low points on rough surfaces and a porous, columnar microstructure develops. This is characterised by a rough layer morphology in multilayer films that accumulates towards the film surface. Energetic particle bombardment during growth can provide surface smoothing and suppress columnar growth by: preferential sputtering of the high points on the
growth surface; increasing adatom mobility; re-ordering the surface layer atoms. Higher energy bombardment can also cause intermixing of the layers. The ability to control the energy of the bombarding particles is therefore crucial in optimising interface roughness.
Chapter 3

X-ray Scattering at Grazing Incidence in Layered Films

Contents

3.1 Introduction
3.2 Reflection of X-rays at an Interface
3.3 Optical Modelling of Specular Reflectivity
3.4 Interface Roughness and Diffuse Scattering
3.1 INTRODUCTION

In recent years the use of X-ray scattering techniques for the measurement of thin film surface and interface structure has increased considerably. This is partly due to improvements in the resolution of reflectometry instruments, but also partly due to the significant advancements in film growth techniques such that more sensitive characterisation techniques must be applied.

This chapter treats the basic theory covering the reflection of X-rays at surfaces and interfaces. In the following section (3.2) the idea of a complex refractive index for metals at X-ray wavelengths is developed. It will be shown how the reflection of X-rays at interfaces is dependent upon the contrast between the refractive index of the materials bounding the interface. The use of an optical model to calculate the reflected intensity for a layered material is then discussed in section 3.3. Finally the effect of various forms of roughness on the specular and diffusely scattered intensity is described in section 3.4.

3.2 REFLECTION OF X-RAYS AT AN INTERFACE

3.2.1 Diffraction at low Q: The Continuum Limit

In scattering processes a medium can be regarded as a continuum if the wavelength of the incident particle is larger than the interatomic distances involved. For a particle with wavelength $\lambda$, incident on a superlattice surface at an angle $\theta_i$ as shown in figure 3.1, the corresponding reciprocal space wavevector $k_i$ has a magnitude $2\pi/\lambda$. For elastic specular scattering the exiting particle has a
wavevector $k_r$, where $\theta_i = \theta_f$ and $k_i = k_f$. The scattering vector $Q$ is defined as the momentum transfer and is thus given by

$$Q = k_f - k_i$$

3.1

Hence for specular scattering processes, $Q$ points along the normal to the interface as indicated in the figure.

![Figure 3.1: Specular scattering at a surface](image)

In reciprocal space terms the medium can be regarded as a continuum provided that $Q < 2\pi/d$ where $d$ is the interatomic distance involved. Hence at grazing incidence reflection, diffraction effects from atomic periodicity do not occur. However, the superlattice period, $\Lambda_s$, is significantly longer than $d$ and hence Bragg diffraction will occur and 001 reflections will be observed whenever $Q = t \Lambda_s^*$ where $\Lambda_s^* = 2\pi/\Lambda$ is the reciprocal space period of the superlattice.

It is convenient to consider the positions of the Bragg peaks in terms of $Q$ rather than the scattering angle $\theta_f$. $Q$ is a quantity inherent in the superlattice structure rather than the scattering process and is thus independent of the type and energy of the scattered particle. At high $Q$ values both the long and short periodicities are probed and the observed diffraction pattern is a superposition of Bragg reflections resulting in the appearance of satellite peaks in the high angle superlattice diffraction pattern[112,113].
3.2.2 Total External Reflection

As in conventional optics, reflection and transmission of X-rays at an interface can be described by considering the change in refractive index in traversing the interface. From Snell's well known law, the refractive index of a film, \( n \), is related to the grazing incidence and refracted beam angles according to

\[
\frac{n}{n_o} = \frac{k_i}{k_o} = \frac{\cos \theta_o}{\cos \theta_i}
\]

where \( n_o \) in this case is the refractive index of air (\( n_o = 1 \)) and \( \theta_o \) and \( \theta_i \) are the grazing angles as indicated in figure 3.2.

For X-rays the refractive index is given by the expression

\[
n = 1 - \frac{N r_e \lambda^2}{2\pi f}
\]

where \( f \) is the atomic scattering factor, \( N \) is the atomic density, \( r_e \) is the classical electron radius \( e^2/mc^2 = 2.818 \times 10^{-13} \) cm and \( \lambda \) is the X-ray wavelength. Total external reflection from the film surface will occur when the refracted angle \( \theta_i = 0 \). From equation 3.2 this is only possible when \( n/n_o \) (equal to \( \cos \theta_o \)) is less than unity.
for $\theta_e > 0$. Provided that the photon energy is sufficiently distant from the critical absorption edges of the film atoms, $f$ is real and positive. Thus the refractive index of the film is less than unity by an amount, $\delta = \text{Re}\{N_r \lambda^2 \text{d}/2\pi\}$, which is typically of the order of $10^{-6}$ for most substances at hard X-ray wavelengths. From equations 3.2 and 3.3, the critical incidence angle, $\theta_e$, below which total external reflection occurs is given by

$$\cos\theta_e = 1 - \delta$$

3.4

and applying small angle approximations

$$\theta_e \approx \sqrt{2\delta}.$$ 3.5

In the neighbourhood of an absorption edge, however, this last simple expression is no longer valid.

3.2.3 Anomalous Dispersion

The atomic scattering factor, $f$, given in equation 3.3 is modified by anomalous dispersion of the X-rays in the scattering medium. The size of this effect is photon energy dependent and is enhanced in the vicinity of an absorption edge. The scattering and absorption of X-rays in the medium is described by the total (complex) scattering factor as function of photon energy, $E$, given by

$$f(E) = Z + f'(E) + if''(E)$$ 3.6

where $Z$ is the atomic number of the scatterer (i.e. the total number of electrons available for Thomson scattering), $f'$ and $f''$ are the resonance and absorption corrections to $f$, respectively.
The refractive index is thus in general a complex quantity of the form

\[ n = 1 - \delta - i\beta \]  \hspace{1cm} (3.7)

where

\[ \delta = \frac{N_r \lambda^2}{2\pi} (Z + f') \]  \hspace{1cm} (3.8)

and

\[ \beta = \frac{N_r \lambda^2}{2\pi} f''. \]  \hspace{1cm} (3.9)

The amplitude of X-rays after passing a distance, \( t \), through the scattering medium is proportional to \( \exp(-i2\pi nt/\lambda) \). Denoting the amplitude, \( A(t) \), then

\[ A(t) = A_0 \exp\left(-i \frac{2\pi}{\lambda} (1 - \delta)t\right) \exp\left(-\frac{2\pi}{\lambda} \beta t\right) \]  \hspace{1cm} (3.10)

and the corresponding intensity is

\[ I(t) = |A(t)|^2 = I_0 \exp\left(-\frac{4\pi}{\lambda} \beta t\right) \]  \hspace{1cm} (3.11)

where \( A_0 \) and \( I_0 \) are the incident X-ray amplitude and intensity respectively. Hence the real part of the refractive index, \((1-\delta)\), gives the phase change of the X-rays, whereas the imaginary part, \( \beta \), determines the attenuation according to

\[ I(t) = I_0 \exp(-\mu t) \]  \hspace{1cm} (3.12)

where \( \mu \) is the linear absorption coefficient and is thus given by

\[ \mu = \frac{4\pi\beta}{\lambda}. \]  \hspace{1cm} (3.13)

The anomalous dispersion factors, \( f' \) and \( f'' \), strongly affect the scattering amplitude near an X-ray absorption edge of the material. Consequently the refractive index changes markedly near an absorption edge. Calculated values
of the anomalous dispersion factors as a function of energy for cobalt and copper are shown in figure 3.3. From equations 3.9 - 3.13 it can be seen that the $f''(E)$ term is responsible for absorption and this is reflected by the sharp drop in $f''$ at the K-absorption edge of each element (7.709 keV for cobalt and 8.979 keV for copper). The $f'$ factors also show a sharp minimum near the absorption edges. This is because the anomalous dispersion factors are not independent quantities but are related by the dispersion relation [115]

$$f'(\omega) = \frac{2}{\pi} \int_0^\omega \frac{f''(\omega')\omega'}{\omega^2 - \omega'^2} d\omega'$$

where $\omega$ has been used to denote the photon energy.

Away from the absorption edge region, the anomalous dispersion factors of cobalt and copper become similar and have a less significant effect on the scattering amplitude. This, combined with the similarities in atomic number ($Z(\text{Co}) = 27$, $Z(\text{Cu}) = 29$) means that the refractive index of cobalt and copper calculated from equations 3.7 - 3.9 at energies away from an absorption edge, are very similar. The X-ray scattering contrast at a Co/Cu interface is thus very poor at these energies. However, just below the copper K-edge the dispersion factors for copper vary considerably with respect to the equivalent cobalt factors. Thus for energies in this region, the refractive index of copper is significantly different to that of cobalt despite the similar atomic numbers of the two elements. A similar contrast between the refractive indices can be found just below the cobalt K-edge, although in this case it is the $f'$ factor which is largely responsible for the change. Anomalous scattering can thus be used to enhance the scattering contrast between elements with similar atomic numbers. The experimental implications of this in terms of X-ray reflectivity measurements are demonstrated later in chapter 6.
Figure 3.3: Anomalous dispersion factors for cobalt and copper. The data were obtained from Henke et al [114].

This expression 3.5 given earlier implies that the critical angle for total external reflection, $\theta_c$, depends upon the anomalous dispersion terms and hence will also be radically altered when the incident photon energy is in the vicinity of an absorption edge. Nakayama et al. [116] have observed this behaviour for Fe/Mn multilayers by measuring the specular X-ray reflectivity as a function of photon energy (wavelength).
3.3 OPTICAL METHODS FOR MODELLING SPECULAR REFLECTIVITY

3.3.1 Parratt’s recursion relation

The algorithms frequently used for calculating the specular X-ray reflectivity from layered films were originally developed by Parratt as a method for studying surface compounds on homogenous media [117]. Parratt used these algorithms to calculate the reflectivity around the critical angle for total external reflection. By comparing his calculated curves with grazing incidence X-ray reflectivity data, he was able to determine the optical constants (\(\epsilon, \beta\)) for various surface layers and measure density gradients at surfaces caused by contaminant layers on metal films. His treatment of X-ray reflection and transmission at interfaces includes absorption within the layer and is therefore applicable to reflectivity near the critical edge where these effects are stronger. The basic theory can be extended to a computational rather than analytical form [118] and is outlined below.

A layered microstructure consisting of two materials, A and B with layer thicknesses \(d_A\) and \(d_B\) respectively, is shown in figure 3.4. The microstructure could be a synthetic multilayer film or representative of contaminant layers on a surface, as treated by Parratt [117]. The structure shown in fig 3.4 is periodic in the direction normal to the interfaces with a period \(d = d_A + d_B\), although this need not be the case. The total number of media involved in the scattering process, \(n\), is the number of repeating bilayers, \(N\), plus the vacuum and substrate, i.e. \(n = N + 2\).
The Fresnel coefficients for reflection at each interface are derived by imposing the boundary condition that the tangential components of the electric field vectors at each interface are continuous. As shown in figure 3.4, $E_j$ is the amplitude of the electric vector of the incident wave at the interface between the $j$th and $(j+1)$th layers and $E_j^R$ is the reflected amplitude from this interface. The Fresnel coefficient for reflection at this interface is given by

$$F_{j,j+1}^\sigma = \left(\frac{E_j^R}{E_j}\right)^\sigma = \frac{f_j - f_{j+1}}{f_j + f_{j+1}}$$

$$F_{j,j+1}^\pi = \left(\frac{E_j^R}{E_j}\right)^\pi = \frac{f_j/n_j^2 - f_{j+1}/n_{j+1}^2}{f_j/n_j^2 + f_{j+1}/n_{j+1}^2}$$

for the $\sigma$ and $\pi$ components of polarisation. The $f_j$ coefficients relate the $z$ component of the wavevectors across the interface and are given by

$$f_j = \left(n_j^2 - \cos^2 \theta\right)^{1/2}$$
where \( n_j \) is the complex refractive index of the \( j \)th layer as given by equation 3.7, and \( \theta \) is the glancing angle of incidence. Since \( \theta \), \( \delta \) and \( \beta \) are small, equation 3.17 can be written as

\[
f_j = \left( \theta^2 - 2\delta_j - 2i\beta_j \right)^{1/2}
\]

where \( \delta_j \) and \( \beta_j \) are the optical constants given by equations 3.8 and 3.9, for the material of the \( j \)th layer.

The reflectivity at the interface between the \( j \)th and \((j+1)\)th layers is defined as

\[
R_{j,j+1} = a_j \left( \frac{E_j^R}{E_j} \right)
\]

where \( E_j \) and \( E_j^R \) refers to the values of the vector amplitudes midway through the \( j \)th layer and \( a_j \) is the amplitude factor for half the perpendicular distance \( d_j \) and is given by

\[
a_j = \exp \left( -1 - \frac{\pi}{\lambda} f_j d_j \right).
\]

Using the boundary condition that the tangential components of \( E \) and \( H \) are continuous across the interface, expressions relating the amplitude of the electric vectors in the \( j \)th layer to those in the \((j+1)\)th layer can be obtained. From these expressions a solution to equation 3.19 can be obtained in the form of the recursion relation

\[
R_{j,j+1} = a_j \left[ \frac{R_{j+2,j+2} + F_{j+1}}{F_{j+1}} \right].
\]
At the substrate (layer n) the reflectivity, $R_{n,n+1} = 0$ since the substrate is considered infinitely thick. This provides a starting point for the calculation of the reflectivity and hence

$$R_{n-1,n} = a_{n-1}^4 F_{n-1,n}.$$  \hspace{2cm} 3.22

The expression 3.22 is then substituted back into the recursion relation 3.21 and the process is repeated back to the first interface. Analytically this would produce an extremely cumbersome expression for the reflectivity at the first interface if more than one or two layers were involved. However, by adopting a computational approach, the value of the reflectivity at the vacuum/multilayer interface, $R_{1,2}$ can be readily obtained. This is related to the intensity $I(\theta)$ reflected from the multilayer by

$$I(\theta) = I_o \left( R_{1,2} \right)^2 = I_o \left( \frac{E_R}{E_i} \right)^2$$ \hspace{2cm} 3.23

where $I_o$ is the incident beam intensity, and noting that $a_1$ is unity. These formulae therefore provide a method for calculating the specular intensity $I(\theta)$ for any medium that can be divided into discrete layers with different refractive indices.

3.3.2 XREALM Computational Code

Using the recursion relation 3.21 a computer code was developed by the author for calculating the specular reflectivity from layered media. The program, named XREALM, was written in Microsoft Qbasic and a listing of the code is given in Appendix A. It was designed to be as versatile as possible and allow calculations for model structures with any number of different layer thicknesses.
The program contains a user-defined database of the optical constants, $\delta$ and $\beta$ at different wavelengths for a range of materials. This enables buffer layers, capping layers and oxide layers to be included in models of multilayer structures. It also allows the program to be tailored to any system involving layered media.

![Graph showing reflected intensity versus $q_z$]

*Figure 3.5: Comparison of the reflected intensity calculated for a Co/Cu multilayer with the structure Si / [Co(21.8 Å)/Cu(28 Å)]$_{20}$ at a wavelength of 1.38 Å using the XREALM code and a program available on the Internet[119].*

In order to test the accuracy of the program, simulations of the specular reflectivity for a variety of different multilayer systems were produced and compared with the result of an equivalent model using a reflectivity routine available via the Internet at the Lawrence Berkely Laboratory [119]. This routine can only be used to calculate the reflectivity from periodic structures and is thus not suitable for simulating the multilayer structures developed in this work which generally contain additional capping layers. A comparison of the outputs of each
program using a model Co/Cu multilayer structure without additional buffer or
capping layers is shown in figure 3.5. It can be seen that the two programs produce
identical outputs at all values of $q_z$ from zero onwards.

3.3.3 Specular Reflectivity Curves

Using the XREALM program some general features of specular reflectivity
curves from layered films are now discussed.

A) Critical edge region

It was shown in section 3.2 that the critical angle for total external
reflection, $\theta_c$, can be related to the $\delta$ optical constant (equation 3.5) and that
absorption is related to the $\beta$ optical constant (equation 3.13). It is therefore
expected that the reflected intensity near the critical angle should depend upon
these constants.

In figure 3.6 the normalised reflected intensity calculated for several
materials at a wavelength of 1.54 Å is shown. The optical constants for these
materials at this wavelength are given in table 3.1. Copper, Cu$_2$O and GaAs have
relatively similar values of $\beta$ at this wavelength but differing values of $\delta$. From the
figure it can be seen that the reflected intensity decays at approximately the same
rate for these materials, but the position of the critical angle (the position at which
the reflected intensity drops sharply) is shifted to lower grazing angles as expected
from equation 3.5. In particular, comparing the Cu and Cu$_2$O curves it would seem
that the presence of an oxide on the film surface will shift the position of the
critical edge. This oxide must therefore be included in a simulation of the specular
reflectivity from such a sample in order to correctly fit the position of the critical edge.

![Graph showing reflected intensity as a function of glancing angle for different materials.](image)

**Figure 3.6**: Calculated reflected intensity at the critical edge region for the materials listed in table 3.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta \times 10^5$</th>
<th>$\beta \times 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>2.44</td>
<td>5.49</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>1.67</td>
<td>3.35</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.46</td>
<td>4.35</td>
</tr>
<tr>
<td>Co</td>
<td>2.38</td>
<td>34.45</td>
</tr>
</tbody>
</table>

**Table 3.1**: Optical constants calculated at a wavelength of 1.54 A [114].
The decay of the reflected intensity in the Co curve at $\lambda = 1.54$ Å, shown in figure 3.6, is much more pronounced than that of the other curves. This is because the energy (8051 eV) involved is above the cobalt $K$-absorption edge but below the copper $K$-absorption edge, as shown in figure 3.3. Thus the $f''$ dispersion term and hence the absorption term, $\beta$, is large for cobalt at this wavelength compared to the other materials. It can therefore be seen that as absorption increases, the critical edge becomes less well defined.

B) Effect of Film Thickness

The specular reflectivity calculated for a series of cobalt films of different thicknesses on a silicon substrate is shown in figure 3.7. The oscillations seen are a function of the film thickness and are caused by interference between the reflected amplitude of the electric field vector at the vacuum/surface interface and the film/substrate interface. These oscillations are known as Kiessig fringes and have maxima that satisfy Bragg's law modified for refraction

$$\sin^2 \theta = \left( \frac{n\lambda}{2d} \right)^2 + 2\delta$$ \hspace{1cm} 3.24

where

$$\sin^2 \theta = \sin^2 \theta_b + 2\delta$$ \hspace{1cm} 3.25

or for small angles

$$\theta^2 = \theta_b^2 + \theta_c^2$$ \hspace{1cm} 3.26

where $\theta$ is the measured position of the peak, $\theta_b$ is the position calculated from the simple Bragg's law neglecting refraction, $\sin \theta_b = n\lambda/2d$ and $d$ is the film thickness. The effect of refraction as shown in equation 3.26 is thus to modify the period of
the Kiessig fringes near the critical edge. At higher angles the refraction correction becomes negligible.

![Graph showing reflectivity for different cobalt film thicknesses](image)

**Figure 3.7**: Calculated reflectivity from a series of cobalt films of different thicknesses.

Another feature of the curves shown in figure 3.7 is that the envelope of the oscillation amplitude decreases as the film thickness increases. This is due to the attenuation of the X-ray beam caused by absorption within the film. As the path length through the film is shortened by increasing the glancing angle, $\theta$, attenuation of the beam is reduced. This can be seen in the figure as an increase in the amplitude of the Kiessig fringes in each curve as a function of $\theta$. If the absorption term is suppressed, neither of the above effects will be observed. For neutron reflectivity the absorption term for cobalt is negligible with respect to the film dimension. The specular reflectivity calculated at a neutron wavelength of 2.37Å for the same four cobalt films using neutron parameters for the $\delta$ and $\beta$ optical
constants [77], is shown in figure 3.8. The oscillation amplitude for each curve is now identical and does not vary as a function of $\theta$.

![Figure 3.8](image)

*Figure 3.8 : Calculated neutron reflectivity from a series of cobalt films of different thicknesses.*

C) Periodic Features

The reflected specular intensity from a periodic medium exhibits Bragg diffraction peaks according to equation 3.24. In a multilayer the period is defined by the repeating bilayer. Measurement of the Bragg peak positions therefore enables the bilayer thickness of the multilayer to be accurately determined. The specular reflectivity calculated for three model Co/Ti multilayer structures is presented in figure 3.9. Five orders of Bragg peaks can be seen added phase dependently to the Kiessig fringes from the finite film thickness. Each model structure was given the same bilayer period, however certain orders are missing in curves a) and b). This is due to the phase dependent superposition of the electric field vectors from different interfaces. For example, multilayer a) has equal
thickness layers. When the diffraction order, \( m \), is a multiple of 2, Bragg diffraction can occur for a bilayer period \( d_B + d_A \) phase shifted by \( \pi \) due to the wavevector traversing half the bilayer period \( d_A + d_B \). These wavevector amplitudes therefore interfere destructively and since there are an almost equal number of bilayers of the type \( d_B + d_A \) as there are \( d_A + d_B \), a null Bragg diffraction order results. This can be seen quite clearly in curve a) in the figure, where the 2\(^{nd} \) and 4\(^{th} \) orders are missing.

Figure 3.9: Calculated X-ray reflectivity at a wavelength of 1.54 Å for model Co/Ti multilayers with the structure; (a) \( \text{Si/Co}(40\text{Å})/\text{Ti}(40\text{Å}) \), (b) \( \text{Si/Co}(45\text{Å})/\text{Ti}(35\text{Å}) \), (c) \( \text{Si/Co}(53.3\text{Å})/\text{Ti}(26.7 \text{Å}) \).

The same effect will occur whenever the layer thicknesses result in two possible bilayer periodicities phase shifted by \( \pi \). For this to be true the number of orders, \( m \), of the \( \lambda/2 \) path difference, must be such that the fraction of each layer...
thickness to the bilayer period, i.e. $\frac{d_A}{d_A + d_B}$ and $\frac{d_B}{d_A + d_B}$, multiplied by the number of orders must yield an integer. For curve c) the ratio of the layer thicknesses $d_A/d_B$ is 2:1. Hence diffraction orders that are multiples of 3 will produce a null Bragg peak.

Between these extreme cases of Bragg order extinction, the relative intensities of the Bragg peaks will vary according to the layer thicknesses. Thus it is possible to determine not only the bilayer period but also each layer thickness by fitting the positions and relative intensities of the Bragg peaks. Non-periodic layers such as capping and oxide layers will distort the position and intensity of the Bragg peaks and must therefore be included in the fit.

3.4 INTERFACE ROUGHNESS AND DIFFUSE SCATTERING

3.4.1 Gaussian Distribution of the Interface Profile

Wide angle X-ray diffraction is sensitive to crystal structure on an atomic scale. At low angles, X-ray reflectivity is sensitive to fluctuations on an atomic scale even though it is insensitive to atomic structure. It is the distribution of the atomic structure that determines the scattering of the electric field vectors at the interfaces. In the direction normal to the interfaces (z direction), the fluctuations of the interface profile can be limited to a few monolayers of the medium. However, in the lateral direction (along the interface) the length scale involved, $\xi$, can be considerable larger. Specular reflectivity is sensitive to the rms amplitude of the roughness in the $z$ direction, described by the standard deviation, $\sigma$, of the Gaussian probability density distribution,
as illustrated in figure 3.10.

\[
P(z) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{z^2}{2\sigma^2} \right] \tag{3.27}
\]

The variance of the interface profile function is given by

\[
V[z(x)] = \left( z(x) - \langle z(x) \rangle \right)^2 = \langle z(x)^2 \rangle - \langle z(x) \rangle^2 \tag{3.28}
\]

If the origin of the function is defined to be the mean interface position, \( \langle z(x) \rangle = 0 \), the variance is simply the square of the rms roughness of the interface profile function, i.e. \( V = \langle z(x)^2 \rangle = \sigma^2 \).

Wave propagation in a rough multilayer has been treated in terms of a phase perturbation to waves travelling through the film due to fluctuations of the local interface position relative to the mean position [120]. The interface profile is implicitly included in the amplitude reflection coefficient calculated using this
method. In an ideal multilayer (without interface imperfections), the amplitude reflection coefficients have constant values. However, a non zero variance of the interface profile function leads to a non zero variance in the amplitude reflection coefficients resulting in diffuse scattering. The diffuse scattering removes intensity from the specular reflection according to the pseudo Debye-Waller damping term exp \([-Q_z^2 \sigma^2]\) [120-122]. This factor is statistically analogous to the Debye-Waller factor used to treat dynamic disorder due to thermal vibrations in crystals. The reflectivity at an interface is then given by

\[ R'_j = R_j \exp \left[ -\frac{16\pi^2 \sigma^2}{\lambda^2} \sin^2 \theta \right] \] (3.29)

where \( R_j \) is the reflection coefficient for the interface without roughness and substitution for \( Q_z = (4\pi/\lambda) \sin \theta \) has been made. From equation 3.29 it can be seen that interface roughness reduces the reflectivity more severely as \( Q_z \) is increased. This leads to the damping of higher order Bragg reflections and Kiessig fringes.

3.4.2 Specular Reflectivity from Rough Multilayers

The specular reflectivity from a multilayer with interfacial roughness present is relatively simple to quantify as the specular reflection follows a one dimensional path through reciprocal space. It is therefore possible to determine the total roughness present at each interface by calculating the intensity removed from the specular direction (equation 3.29) without knowledge of the spread of this intensity in reciprocal space. However, part of the intensity removed from the specular beam and spread throughout reciprocal space can actually fall along the
specular direction. In order to compare the calculated specular reflectivity with measured data this component of the diffuse intensity must first be removed.

To illustrate the effect of interface roughness on the specular reflectivity, the intensity was calculated for a series of Fe/Au multilayers using the XREALM computer code mentioned earlier. The total rms interfacial roughness at the interfaces for each model was varied from 0 to 8 Å. The resulting spectra calculated at a wavelength of 1.54 Å are shown in figure 3.11.

There is a pronounced difference in the scattering densities of iron and gold at the wavelength used and this leads to strong Bragg reflections and Kiessig fringes as seen in figure 3.11. Increasing the interface roughness reduces the reflection at the interfaces as a function of \( \theta \) according to equation 3.29. This leads to a damping of the Kiessig oscillation and the gradual suppression of the Bragg peak as seen in the figure. In addition the presence of roughness at the near surface interface reduces the intensity reflected near the critical edge, \( \theta_c \), as a greater portion is transmitted into the bulk of the film. It can be seen from the figure that the critical edge is less well defined at higher values of sigma as intensity is removed from this region in a similar manner to the effect of absorption discussed earlier (see for example figure 3.6). It will be shown later (Chapter 6) how the observation of these effects can be used to qualitatively and quantitatively compare multilayer films prepared under different conditions.
3.4.3 Diffuse Scattering and Correlated Roughness

Measurements of the intensity removed from the specular reflection enable the total rms roughness at each interface to be determined. The spread of this diffuse intensity in reciprocal space, however, reveals the nature of the roughness present. By 'nature' is meant the length scale of the roughness and whether the roughness is a smoothly varying profile such as that depicted in figure 3.10, or a
jagged stepped profile. Additionally the degree of replication of the roughness profile across successive interfaces can be seen in the diffuse intensity. These concepts are described by considering the correlation of various types of roughness. For a single surface a lateral correlation exists. The lateral correlation length is typically defined as the separation of two points on the surface required to make the heights of these points statistically uncorrelated. The lateral length scale of the roughness that induces diffuse scattering is measured as a function of the lateral momentum transfer, $q_x$. Hence, the measurement of the diffuse intensity along the $q_x$ axis, appropriately corrected for geometrical factors, can reveal the statistical distribution of the surface roughness$^{[121,122]}$.

In a multilayer the vertical (or interlayer) correlation of the roughness will also affect the diffuse scatter. For perfect vertical correlation (exact replication of the interface profile for all interfaces), the total intensity measured along $q_z$ is identical to that obtained for a perfect multilayer with no interface roughness present. The specular intensity, however, exhibits a pseudo Debye-Waller attenuation as discussed in the previous section. As each interface profile is identical there exists a constant phase relation between the diffusely scattered intensity at each interface. Thus, the diffuse intensity is a coherent sum of the interfacial diffuse scatter and will be peaked at the Bragg condition analogously to the specular reflectivity. The case of perfectly correlated roughness is illustrated in figure 3.12 (a). The combination of lateral and vertical roughness correlations form the diffuse intensity into well defined 'sheets' in reciprocal space passing through the specular superlattice points.
For vertically uncorrelated roughness there is a random phase relation between the intensity diffusely scattered at each interface. Thus the diffuse intensity in this case is spread into all regions of reciprocal space as shown in figure 3.12 (b). However, individual interfaces can still contain laterally correlated roughness that will produce a well defined distribution of the diffuse intensity in the $q_xq_y$ plane (normal to the plane of the page in figure 3.12). As the diffuse intensity is not peaked at the Bragg condition for vertically uncorrelated roughness, the total intensity measured along $q_z$ follows a pseudo Debye-Waller attenuation in the same fashion as the specular reflectivity.

In order to include lateral and vertical roughness correlations in the calculation of the diffuse scattering from rough multilayers, a correlation function is typically introduced. This parameter describes the correlation between height fluctuations on interfaces $i$ and $j$ respectively, and is given by[123]
where

\[ C_0(r) = \sigma_i \sigma_j \exp\left[-\left(r/\xi_{11}\right)^2h\right] \]  

is the in-plane correlation function. The term \( \delta Z_i(r) \) is the height fluctuation at a distance, \( r \), from an arbitrary origin. \( Z_i \) is the mean position of interface \( i \), \( \xi_\perp \) and \( \xi_{11} \) are the vertical and lateral correlation lengths respectively, \( \sigma_i \) is the rms roughness of the \( i \)-th interface and \( h \) is a texture coefficient. The magnitude of the correlation function increases as the degree of correlated roughness in the multilayer increases.

It can be seen from equation 3.30 that for perfect vertical correlation (\( \xi_\perp \to \infty \)) the correlation function is identical for all interfaces and depends only on the lateral correlation \( C_0(r) \). Conversely when \( \xi_\perp \) is much less than the interface spacing (\( |Z_i - Z_j| \)) the correlation function vanishes for different interfaces (\( i \neq j \)). This case is representative of vertically uncorrelated roughness.

Most real multilayer films exhibit vertical roughness correlations between these two extremes. For this partially correlated roughness the total rms interface roughness, \( \sigma_i \), can be divided into the correlated, \( \sigma_c \), and uncorrelated, \( \sigma_u \), components according to the expression

\[ \sigma_i^2 = \sigma_c^2 + \sigma_u^2 \]  

The specular reflectivity is sensitive only to the total rms interface roughness. The degree of vertically correlated roughness can be gauged by performing non-specular measurements quasi-parallel to \( q_\perp \) in order to measure the diffuse Bragg
peaks. As the vertical correlation length, $\varepsilon_\perp$, is increased a greater number of interfaces contribute to the diffuse Bragg peak and its breadth decreases. For perfect vertical correlation the diffuse intensity measured in this way is identical to the specular intensity. The experimental techniques used in order to measure the specular and non-specular reflectivity will be discussed in the next chapter.
Chapter 4

Experimental Techniques

Contents

4.1 Introduction
4.2 Sample Preparation
4.3 X-ray Reflectivity and Fluorescence
4.1 INTRODUCTION

In this chapter the experimental techniques used in the completion of the work are described. The standard sample preparation procedures employed in the fabrication of Co/Cu multilayers are discussed in section 4.2. The use of station 2.3 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory for X-ray reflectivity measurements is discussed in section 4.3. Details of the reflectivity scans and sample alignment procedures are described in this section. In particular it will be shown how the reflectivity techniques were used to probe the sample microstructure.

4.2 SAMPLE PREPARATION

4.2.1 Preparation of substrates

A scheme for preparing the silicon substrates was devised and repeated for all the samples discussed in this work. The substrates were cut from 3 inch Si(111) wafers into squares measuring 20 x 20 mm. The target and substrate materials used in the deposition of Co/Cu multilayers are listed in table 4.1. Once cut, each substrate was ultrasonically cleaned in acetone for 5 minutes. It was then rinsed with propanol and immediately blown dry with nitrogen. It was found that acetone was a more effective solvent for degreasing the silicon than propanol. Rinsing immediately with propanol removed any residues left by the acetone solvent. The clean substrate was then quickly mounted on the sample holder using a silver conducting paint and immediately inserted into the vacuum chamber. The purpose of the silver paint was both to maintain the growing film at the substrate table.
potential and to hold the substrate in place. Electrical continuity between the deposited film and sample holder was confirmed for each finished sample.

<table>
<thead>
<tr>
<th>Target / Substrate</th>
<th>Dimensions / mm</th>
<th>Purity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co Target</td>
<td>0.5 x 50 (diameter)</td>
<td>99.99+</td>
</tr>
<tr>
<td>Cu Target</td>
<td>2.0 x 50 (diameter)</td>
<td>99.99+</td>
</tr>
<tr>
<td>Si Substrate</td>
<td>0.38 x (20 x 20)</td>
<td>99.999</td>
</tr>
</tbody>
</table>

Table 4.1: Target and substrate materials used in for depositing Co/Cu multilayers.

4.2.2 Growth Chamber Configuration

The growth chamber used in this work was part of a modified Nordiko NM2000 sputtering system. The original system contained three deposition sources that could be rotated under a fixed water cooled substrate table. In order to deposit multilayered films, one of the original sources was replaced with a fixed plate containing two unbalanced magnetron sources facing a central position on the substrate table. The two sources were individually shuttered using electro-pneumatic actuators. The shuttering system was controlled by a separate computer. A schematic illustration of the chamber arranged for multilayer deposition is shown in figure 4.1. Substrates were mounted on the removable sample holder which was then fixed into the water cooled substrate table prior to evacuating the chamber. The magnetrons were also water cooled in order to reduce target heating from the plasma.
4.2.3 Growth Procedure

A photograph of the sputtering system together with an outline illustration showing the principal components, is shown in figure 4.2. The deposition chamber was mounted on top of a diffusion pump backed by a rotary pump. Unfortunately, there was no sample air lock on the system and so the entire chamber had to be vented in order to change samples. It was found that contamination of the chamber wall by water vapour was considerably reduced by venting the chamber to an inert gas such as Argon, rather than simply venting to air.
Figure 4.2: Photograph and labelled outline of the Nordiko Sputtering system.
This reduced the pumping time of the system. In addition, a liquid nitrogen trap mounted just above the diffusion pump was used to increase the pumping speed of water from the chamber.

Before depositing each film the chamber was evacuated to a background pressure of $\sim 10^{-7}$ Torr. This pressure was initially monitored using an ion gauge mounted on the side of the chamber. Subsequently the ion gauge was replaced with the quadrapole mass spectrometer shown in figure 4.2. The pressure readings obtained using each instrument were found to be equivalent. Additionally the residual gas levels before deposition were monitored using the mass spectrometer. A typical example of the mass spectrum obtained after pumping the system for approximately three hours is shown in figure 4.3. It can be seen that the main gas contributing to the background is water vapour. Water vapour is known to dissociate in a magnetron plasma into oxygen and hydrogen [61]. In order to limit film oxidation it was therefore important to maintain the water vapour at as low a level as possible. The oxygen contribution from residual air in the system can be seen to be appreciably lower than the water vapour level.

Once the required base pressure was achieved the argon gas line was repeatedly evacuated using a rotary pump and then refilled with argon several times. This was done in order to remove any residues left in the line that might contaminate the growing film. A controlled flow of argon was then allowed into the chamber and the magnetron plasmas ignited. The magnetrons were allowed to run for several minutes with the shutters closed before commencing film deposition in order to remove any contaminants on the target surfaces. The multilayer deposition was then performed by alternately shuttering each source.
4.3 X-RAY REFLECTIVITY AND FLUORESCENCE

4.3.1 Reflectometer configuration

The reflectometer used was a high resolution powder diffractometer that had been modified for reflectivity measurements. A photograph of the interior of the diffractometer hutch showing part of the beamline is shown in figure 4.4. The station is situated approximately 15m, tangentially from a 1.2 T dipole magnet in the 2 GeV electron storage ring at Daresbury Laboratory. It receives X-ray wavelengths in the range 0.7 - 2.5 Å. This polychromatic beam was monochromated using a monolithic Si(111) channel-cut single crystal. This can
Figure 4.4: Photograph of part of the beamline on station 2.3 at Daresbury Laboratory showing the Si(111) monochromator.
be seen inside the cylindrical steel chamber in figure 4.4. The crystal temperature was maintained at $303.0 \pm 0.1$K in order to maintain a constant lattice parameter.

The monochromatic X-ray beam was then defined by a centre opening Huber slits with an aperture adjustable from 0.01 - 2 mm vertically and 0.01 - 10 mm horizontally. For all the experiments reported in this work the slits were set to 0.1 mm vertically and 10 mm horizontally. This gave a well defined beam incident at the centre of the two circle diffractometer. The incident beam was monitored using a scintillation counter in order to normalise the reflected intensity and thus account for the decay of the beam with time. A schematic illustration of the diffractometer is given in figure 4.5.

![Schematic illustration of the diffractometer beamline on station 2.3 at the SRS, Daresbury Laboratory.](image)

*Figure 4.5: Schematic illustration of the diffractometer beamline on station 2.3 at the SRS, Daresbury Laboratory.*
The \( \theta \) and \( 2\theta \) circles of the diffractometer were independently controlled by a servo drive system with a resolution of 0.2 and 0.1 mdeg respectively. This high resolution is necessary in reflectivity work in order to measure features with a very narrow angular distribution, as will be seen in the next section. An additional goniometer stage was mounted horizontally on the \( \omega \) (sample) circle in order to facilitate sample alignment. This can be seen in the figure 4.6 which shows a close up view of the sample stage and diffractometer. A silicon wafer sample positioned on a glass plate holder and mounted on the goniometer, can be seen in the figure. The goniometer provided a vertical translation and two axes of rotation; one in the reflectometer plane (allied to the \( \theta \) circle) and the other in the orthogonal plane (around the beam axis).

Two pairs of adjustable centre-opening slits were positioned on the \( 2\theta \) arm to define the resolution of the reflected beam, as shown in figure 4.5. Both slits were set to 0.1 mm vertically and 10 mm horizontally. The scatter slits (labelled \( S \) in figure 4.5) placed 200 mm away from the centre of the \( \theta \) and \( 2\theta \) circles, were used to reduce background and improve the collimation of the beam. The slits labelled \( R \) in figure 4.5, defined the angular resolution and were placed 70 cm from the \( \theta/2\theta \) centre. The reflected beam was detected using the enhanced dynamic range detector (EDR). A remotely controlled attenuator was positioned in front of the incident beam in order to enable measurements of the straight through beam and to reduce very intense sample reflections.

With the slits correctly aligned, the beam had an approximately Gaussian angular distribution, as can be seen in the measured intensity of the straight through beam recorded at a wavelength of 1.0 Å, shown in figure 4.7. The full
Figure 4.6: Photograph of the diffractometer on station 2.3 at Daresbury Laboratory showing the sample goniometer stage.
width at half maximum of the Gaussian fit is $8.1 \pm 0.4$ mdeg which is an order of magnitude better than a conventional diffractometer. In addition to the EDR detector, a fluorescence detector with a wide aperture was positioned directly above the sample as shown in figure 4.7. This detector was used to record the fluorescence intensity from the sample as a function of X-ray energy.

![Graph showing peak shape with fitted Gaussian function](Image)

*Figure 4.7: Measured peak shape of the straight through beam profile (closed squares) and fitted Gaussian function (solid line) of FWHM = $0.0081 \pm 0.0004^\circ$*

4.3.2 Sample Alignment

The diffractometer was positioned so that the beam passed through the centre of rotation of the 0/2θ circle. The sample holder was then mounted at this position. It was important to ensure that the sample was also positioned at the centre of rotation in order to stop the beam moving around on the sample surface.
during a scan. In order to do this the sample was dropped below the beam with the
detector set to receive the straight through beam. The sample was then rocked
about the straight through beam so that each sample edge cut the beam. This
produced a 'top hat' intensity profile, a typical example of which is shown in figure
4.8. The centroid of this profile was used as the zero angle of the sample circle. It
should be noted that when the two diffraction circles (sample and detector) can be
driven separately as in this case, the sample angle is referred to as $\omega$ and the
detector angle as $2\theta$. The angle $\omega$ only becomes $\theta$ for coupled $\theta$-$2\theta$ scans in which
$\omega$ is fixed to half the detector angle.

![Graph](image)

**Figure 4.8**: 'Top hat' intensity profile obtained by rocking the sample
about the straight through beam position.

Once the zero $\omega$ angle had been set to coincide with the centroid of the 'top
hat' profile, all subsequent movement of $\omega$ rotated the sample symmetrically
through the beam and about the centre of rotation. The sample was then slowly
raised until it half cut the straight through beam.
The next stage in the alignment procedure was to accurately set \( \omega \) to exactly half of the \( 2\theta \) angle in order to record the specularly reflected intensity from the sample. This was done by moving the detector angle \( (2\theta) \) to a position at which the specular reflection was of significant intensity (typically \( 1^\circ \)). The sample angle \( (\omega) \) was then rocked about this position. At the specular condition (i.e. when \( \omega=\theta \)) the intensity increases by several orders of magnitude. The sample angle could therefore be defined as being equal to half the detector angle at this position. Once the sample had been aligned in this way, the reflectivity scans outlined in the subsequent section could be performed.

4.3.3 Reflectivity Scan Geometry

The principal reflectivity scan employed in this work was the specular \( \theta-2\theta \) reflectivity scan. In this type of scan the momentum transfer vector, \( q \), was varied in the direction normal to the sample surface. This was measured experimentally by moving the sample at exactly half the angular rate of the detector such that \( \omega=\theta \), as illustrated in figure 4.9 (a). The co-ordinates system \((x,z)\) used in the figure rotates with the sample about as axis normal to the plane of the page, such that the \( z \) direction remains normal to the sample surface. The component of \( q \) along the \( z \) direction is \( \frac{2\pi}{\lambda \sin \theta} - (-\frac{2\pi}{\lambda \sin \omega}) \) and since \( \omega=\theta \), \( q_z = \frac{4\pi}{\lambda \sin \theta} \). The component of \( q \) along the transverse \((x)\) direction is \( \frac{2\pi}{\lambda \cos \theta} - \frac{2\pi}{\lambda \cos \omega} = 0 \). Hence it can be seen that for a \( \theta-2\theta \) scan with \( \omega=\theta \), the momentum transfer is measured along \( q_z \) as illustrated on the right hand side in figure 4.9 (a).
Figure 4.9: Schematic illustration of the scan geometry and the corresponding scan trajectory in reciprocal space for a) specular scans and b) offspecular scans. The x and z components of the momentum transfer vector $\mathbf{q}$ are also given.
The second type of reflectivity scan employed was the transverse scan or rocking curve, so called because the sample is rocked about the $\omega=\theta$ position. This scan is depicted in the figure 4.9(b). It can be seen that with the detection position ($2\theta$) fixed, the momentum transfer is non-parallel to the $z$ direction when $\omega\neq\theta$. This gives a component of $q$ in the $x$ direction as indicated in figure 4.9(b). For small angles the expression for $q_z$ is approximately given by $2\pi / \lambda \left[(2\theta - \omega) + \omega\right] = 4\pi / \lambda \theta$. Hence at small angles the $q_x$ component is constant (since the detection angle $2\theta$ is fixed) and the scan trajectory is parallel to $q_x$, as shown on the right hand side of the figure. At the specular condition ($\omega=\theta$) the expressions for $q_x$ and $q_z$ reduce those given in figure 4.9 (a) as expected.

The final type of reflectivity scan used was the offset $\theta-2\theta$ or longitudinal scan. In this scan the sample angle was deliberately offset from the specular condition by a constant angle $\Delta \omega$. A coupled $\theta-2\theta$ scan was then performed. The value of $\omega$ used in the expressions in figure 4.9 (b) is then given by $\omega=\theta + \Delta \omega$. Thus the components of $q_x$ and $q_z$ are varied simultaneously. The trajectory of this scan is thus a diagonal cut through the $q_xq_z$ reciprocal plane as shown on the right of figure 4.9 (b).

4.3.4 Geometric Corrections to Reflectivity Scans

In order to compare the measured reflectivity data with calculated values, the raw data was first corrected for various features of the experimental geometry. One such feature was the effect of the finite size beam width. Calculated reflectivity data are based on the assumption that the incident beam has an infinitely
small vertical width. As mentioned earlier the beam width in the experiments discussed here was defined to be 0.1mm in the vertical direction. This meant that due to the finite sample length there was an angle, \( \omega_{\text{lim}} \), below which the beam split over the edges of the sample. The reflected intensity below this angle was proportional to the percentage of the incident beam that hit the sample rather than the total incident beam intensity. The measured reflectivity was therefore be less than the real value.

This problem can be accounted for by considering an effective beam width as illustrated in figure 4.10. For a sample of length 20 mm as shown, the beam overfill angle, \( \omega_{\text{lim}} \), is given by \( \sin^{-1}(0.1/20) = 0.29^\circ \). The effective beam width as a function of the sample angle (\( \omega \)) is thus simply \( 20 \sin \omega \) mm. The effective incident intensity, \( I_{\text{eff}} \), can thus be approximated by

\[
I_{\text{eff}} = I_0 \left( \frac{20 \sin \omega}{0.1} \right)
\]

where \( I_0 \) is the incident beam intensity. Since the reflected intensity is directly proportional to the incident intensity (see section 3.3.1) the true reflected intensity for values of \( \omega \) below \( \omega_{\text{lim}} \) is thus

\[
I_{\text{true}} = I_{\text{det}} \left( \frac{0.1}{20 \sin \omega} \right)
\]

where \( I_{\text{det}} \) is the detected intensity. Hence, the raw data obtained below \( \omega_{\text{lim}} \) can be corrected by multiplying the detected intensity by the above factor. This correction was applied to all reflectivity scans that involved movement of \( \omega \) below \( \omega_{\text{lim}} \).
The second correction was applied only to transverse scans (rocking curves). This was used to account for the changing beam ‘footprint’ on the sample as a function of the grazing sample angle, \( \omega \). At values of \( \omega \) below \( \theta \), the sample volume being probed was greater than that at the specular condition (\( \omega=\theta \)). Hence, the intensity measured at low angles was greater, resulting in an asymmetry in the rocking curve profile. The beam ‘footprint’ is proportional to \( \frac{1}{\sin \omega} \). Hence to remove the asymmetry in the rocking curves the raw data was multiplied by the factor \( \frac{\sin \omega}{\sin \theta} \). This had the effect of normalising the data to the sample volume at the specular condition (since \( \omega=\theta \) and hence \( \frac{\sin \omega}{\sin \theta}=1 \)). This correction was applied after the rocking curve data had first been corrected for beam overfilling as detailed earlier.
Chapter 5

Control of Ion Bombardment and Multilayer Growth

Contents

5.1 Introduction
5.2 Ion Bombardment using Modified Unbalanced Magnetrons
5.3 Alternative Methods for Controlling Ion Fluxes from Magnetrons
5.4 Calibration of Deposition Rates
5.5 Summary and Conclusions
5.1 INTRODUCTION

It is relatively straightforward to vary the average energy of ions bombarding a growing film during magnetron sputtering by the application of a suitable substrate bias. Provided that the applied negative bias is significantly greater than the floating potential of the isolated substrate, saturated ion bombardment will occur at the substrate. As mentioned earlier, the average energy of the ions is then determined by the difference between the plasma sheath potential just in front of the substrate and the applied bias. Varying the ion flux to the substrate is however somewhat more difficult.

In unbalanced magnetron sputtering the ion flux is delivered to the substrate via the unbalanced magnetic field lines that extend from the magnetron target area to the substrate vicinity. Variation of the ion flux can therefore be achieved by altering the strength of this unbalanced magnetic flux. This has been accomplished previously by the use of external magnetic fields [99] or simply by changing the magnet configuration in the magnetron [86]. Positioning additional magnets behind the substrate in order to repel or attract the unbalanced magnetic flux has also been used [124]. In this chapter the principal method described is the use of a magnetic keeper attachment to the magnetrons. Alternative methods using an electromagnetic coil and a broad beam ion source type grid are discussed in section 5.3.

Using the techniques for varying the ion bombardment discussed here, a system for the ion-assisted deposition of magnetic multilayers was developed. One of the requirements of this system was that it should be capable of producing
multilayers with a well defined period. In order to do this the deposition rates of each metal used had to be precisely known. Experiments designed for the calibration of the deposition rates from the magnetron sources are discussed in section 5.4.

5.2 ION BOMBARDMENT USING MODIFIED UNBALANCED MAGNETRONS

5.2.1 Altering the unbalanced magnetron field

In order to control the unbalanced magnetic flux lines from the magnetron a cylindrical mild steel keeper attachment was placed over the existing magnetron. The keeper was designed to redirect some of the unbalanced field lines by providing a low reluctance path to the rear poles of the magnetron. A reduction in the magnetic flux to the substrate would reduce the plasma density in the vicinity of the substrate and hence diminish the ion flux to the substrate. In effect the keeper would change the configuration of the magnetron to that of a conventional balanced source. This modification alone would allow the magnetron to be operated in either balanced or unbalanced modes. However, in order to provide levels of ion bombardment between these two extremes part of the keeper was made detachable.

Two possibilities were investigated as methods for varying the magnetron mode. The first was to replace the top half of the keeper with a replica made from a nonmagnetic material (in this case stainless steel). The second method involved making a detachable annulus to fit into the top half of the keeper. Different thicknesses, $d$, of the annulus could then be used to vary the reluctance of the
keeper and hence the magnetic flux to the substrate. These two methods of magnetic flux control are illustrated schematically in figure 5.1. The purpose of using nonmagnetic replicas rather than merely removing part of the keeper was to ensure that any shadowing of the atomic or ionic flux was consistent throughout the experiments.

5.2.2 Measurements of Ion Current Density

Experiments were performed in order to test the feasibility of the mild steel keeper system for varying the ion flux to the substrate. In each experiment the deposition chamber was evacuated to below $3 \times 10^{-7}$ Torr prior to any measurements being performed. The magnetron power was limited to less than 100 W in order to reduce the build up of deposited material. Measurements of the ion current density (proportional to the ion flux) delivered to the substrate were made by positioning a planar Langmuir probe of 1 cm$^2$ area at the substrate position, as shown in figure 5.1. The probe was electrically isolated from the substrate table, although the negative bias was applied to both the probe and table to ensure equipotential field lines over the substrate area. Two magnetrons positioned adjacently, as described in section 4.3, were used in these experiments. However, owing to the divergence of the magnetic field lines from the two sources a mild steel keeper was always positioned over the magnetron containing the cobalt target, whilst the keeper on the other (copper) source was altered.
Figure 5.1: Schematic illustration of the different magnetic keeper arrangements used in the experiments. The configuration with a non-magnetic keeper section is shown in (a) and with the magnetic section in (b). The variable annulus is shown in (c).
In the first experiment the ion current density was measured at the probe position as a function of applied probe and substrate table bias. An Argon sputtering gas pressure of 8 mTorr was used and measurements were obtained from both the cobalt and copper magnetrons with either the mild steel keeper section or stainless steel replica positioned over the copper magnetron as illustrated in figures 5.1 (a) and (b). The measured data for these two configurations are shown in figure 5.2. It can be seen that the effect of replacing the mild steel keeper section with the stainless steel replica was to increase the ion current from the copper magnetron measured with an applied bias of -50 V, by a factor of approximately three from ≈35 $\mu$Acm$^{-2}$ to ≈100 $\mu$Acm$^{-2}$. There was also a slight

\[\text{Figure 5.2: Current density measured at the substrate position as a function of applied substrate bias from the copper magnetron source (circles) and cobalt magnetron source (squares). Open (closed) symbols are values measured with the mild steel (stainless steel) keeper section positioned over the copper magnetron.}\]
change in the ion flux from the cobalt magnetron which was probably due to the close proximity of the two magnetrons enabling some of the magnetic flux from the cobalt magnetron to pass though the keeper positioned over the copper source. However, clearly the dominant effect of the detachable keeper section was to alter the ion flux from the copper magnetron.

In the second experiment the ion current density was recorded with the detachable magnetic annulus depicted in figure 5.1 (c) positioned over the copper magnetron and the cobalt magnetron left unchanged. The results obtained using several thicknesses, d, of the annulus with an Argon pressure of 7 mTorr are shown in figure 5.3. It can be seen from the figure that as the thickness of the mild steel annulus was increased (from 0 to 0.9 mm), the saturation ion current density (measured at a bias of -60 V) decreased from 0.1 mAcm\(^{-2}\) to 0.05 mAcm\(^{-2}\). This effect was due to a greater portion of the magnetic flux being diverted through the annulus and keeper, and hence away from the substrate, as the thickness of mild steel was increased. The reduction in magnetic flux at the substrate reduced the plasma density and hence ionic current density measured at the substrate position.

The floating potential of the substrate, given by the applied bias required to achieve a net current density of zero, is sensitive to the average energy of the electrons hitting the substrate. A slightly more negative floating potential for smaller d thicknesses can be seen in figure 5.3 suggesting a small increase in the energy of the electrons reaching the probe, although this effect was not as pronounced as the change in saturation ion current density.
Figure 5.3: Current density measured at a small planar probe of 1cm² area as a function of the applied negative bias, for a series of annulus thicknesses, at an Argon partial pressure of 7mTorr.

5.2.3 The Effect of Sputtering Gas Pressure on Ion Current Density

The ion current density measured at an applied bias of -60 V for different thicknesses of the annulus is shown as a function of Argon partial pressure in figure 5.4. The floating potentials recorded as a function of pressure (not shown) displayed similar trends, but with less variation for different annulus thicknesses. At the lowest pressure recorded, the ion current densities measured using the
Figure 5.4: Saturation ion current density measured at an applied bias of -60V as a function of Argon partial pressure, for a series of annulus thicknesses.

stainless steel annulus and thickest mild steel annulus, differed by a factor of almost 3. The increase in ion current with decreasing pressure was a consequence of the lengthening mean free path of the electrons resulting in a higher proportion reaching the probe area. However, at very low pressures (< 3 mTorr) the reduction in Argon atoms available for ionising collisions with the electrons limits the maximum ion current, as can be seen by the levelling of the curves.

The most striking feature of this figure is the consistency of the shape of the curves for different annulus thicknesses. Other authors [86] have found that the ion current measured as a function of pressure, displayed different trends for
different configurations of the magnetic trap. The similarity in the shape of the curves shown in figure 5.4 may therefore suggest that the mild steel annulus did not significantly affect the magnetic trap at the target. Further evidence to support this is given in figure 5.5 which shows the magnetron operating voltage as a function of pressure. Any improvement in the efficiency of the magnetic trap caused by increasing the thickness of the annulus, would be seen as a reduction in the operating voltage. Although there is a slight trend in the position of the curves for different thicknesses of annulus, this reflects the order in which the measurements were made rather than the thickness of the annulus, and is most likely to arise from a change in the thickness of the magnetron target with time (i.e. as material is sputtered from the target).

Figure 5.5: Magnetron operating voltage measured as a function of Argon partial pressure, for a series of annulus thicknesses.
It should be noted that a change in the magnetic trap around the target is undesirable as it is likely to alter the deposition rate of material sputtered from the magnetron. A quartz oscillator positioned near the substrate in order to monitor the atomic flux from the magnetrons, did not show a significant change for different configurations of the keeper suggesting that the deposition rate was unaffected by changes to the keeper. It was later found that multilayers deposited at a -50 V bias with the mild steel and stainless steel keeper sections in place, had an almost identical bilayer period as indicated by the nearly concurrent position of their X-ray reflectivity Bragg peaks (see figure 6.12 curves (a) and (b), section 6.3).

The advantage of using a keeper attachment to control the ion flux from the magnetron is that no additional current supply is required to the magnetron. This is particularly important when practical considerations such as the base pressure of the vacuum system are taken into account. It is also extremely easy to change the keeper configuration on each magnetron without removing the magnetrons from the chamber and therefore relatively straightforward to produce a set of samples deposited under differing levels of ion bombardment. However, using this system it is not possible to alter the ion flux in situ, that is with the chamber evacuated and the magnetrons operating. In the next section some alternative methods of controlling the ion flux in situ are discussed.
5.3 ALTERNATIVE METHODS FOR CONTROLLING ION FLUXES FROM MAGNETRONS

5.3.1 Electromagnetic Coil

The strength of the unbalanced magnetic field from the magnetrons used in this work was relatively weak (<100 G). Therefore only moderate additional magnetic fields were required to significantly alter the strength of this unbalanced flux and hence affect the extended region of plasma. A 12 cm diameter coil was used for this purpose consisting of 1000 turns of 0.5 mm wire. The field measured at the centre of the coil was 200 G with a current through the coil of 0.8 A.

Initially the coil was positioned around the substrate position as shown in figure 5.6. The substrate table was biased at -60 V and the ion current to the table recorded. Utilising the substrate table area as a probe in this way is a crude but convenient method for obtaining qualitative information on the effects of the coil on the plasma density at the substrate.

The ion current measured from the magnetron containing the copper target (with the shutter closed on the other magnetron) is shown in figure 5.7. Negative values of the coil current indicate that the current is flowing so as to produce a field opposing that from the magnetron. With the coil current flowing in this direction, the unbalanced magnetic flux is repelled away from the substrate area.

The increase in ion current associated with the increase in plasma density at the substrate for larger positive coil currents, can clearly be seen in the figure. However, the initial drop in ion current for the opposing magnetic field (negative coil current) is followed by a slow rise for more negative currents. In fact the
Figure 5.6: Schematic illustration showing the two unbalanced magnetrons with the electromagnetic coil positioned around the substrate table.

Figure 5.7: Ion current measured from the magnetron containing the copper target as a function of coil current. Negative currents indicate an opposing field generated to the unbalanced magnetic field.
effect of the repelling magnetic field was to distort the unbalanced magnetic field from the magnetron to the extent where plasma could leak around the coil to the back of the substrate table. It was this effect that caused the increase in ion current at larger negative values of the coil current seen in the figure.

The same coil was then positioned directly over the magnetron containing the copper target as shown in figure 5.8. In this configuration the coil directly controls the unbalanced magnetic field from the magnetron and is thus similar to the magnetic keeper approach discussed in section 5.2. However, with a coil the 'mode' of the unbalanced magnetron is continuously variable. Applying an opposing field (negative coil current) suppresses the unbalanced magnetic flux, and is thus analogous to the use of a thicker magnetic keeper, discussed earlier. However, when a positive coil current is used, the magnetic field strengthens the unbalanced magnetic flux. This is not possible with the magnetic keeper system.

Figure 5.8: Schematic illustration showing the coil positioned around the unbalanced magnetron contained the copper target.
The ion current to the substrate as a function of the coil current is shown in figure 5.9. It should be noted that the substrate table area was partially obscured by the coil when the data in figure 5.7 were recorded and hence the absolute values of ion current measured are lower in this figure than in figure 5.9.

![Graph showing ion current as a function of coil current.](image)

*Figure 5.9: Ion current measured at the substrate table as a function of coil current, from the magnetron containing the copper target.*

The approximately linear response of the ion current to changes in the coil current, seen in figure 5.9, is in contrast to the curve shown in figure 5.7. It can be seen that as the unbalanced magnetic field was strengthened by the field from the coil (positive coil current) the plasma density in the substrate vicinity was enhanced and hence the ion flux to the substrate table increased. Conversely the plasma density diminished as the opposing magnetic field from the coil was increased.
(negative coil current). This figure clearly demonstrates how unbalanced magnetrons are used to provide ion bombardment at the substrate.

Comparing figures 5.9 and 5.7, it is evident that positioning the coil directly over the magnetron is the more suitable of the two methods for controlling the ion flux to the substrate. The main disadvantage of using a coil in the vacuum chamber is the problem of outgassing from the large surface area of the wire. In addition, if large coil currents are sustained for long periods of time there is also the possibility that the coil will get significantly hot causing further outgassing problems. Petrov et al [99] have bypassed this problem by positioning coils outside of the vacuum chamber. However the geometry of the chamber used in the work discussed here made this approach impractical.

5.3.2. Gridded Ion Source Technique

In the final part of this section a trial experiment for controlling the ion flux to the substrate using an ion source type grid is briefly reported. The method employed used a combination of the magnetic keeper discussed in section 5.2, and a wire mesh grid. The grid was positioned over the aperture in the top of the cylindrical keeper as shown in figure 5.10. The purpose of the keeper in this case was to contain the plasma between the target and the grid, both by providing an anode for the magnetron plasma and by redirecting the unbalanced magnetic flux as described previously.

The principle of a gridded broad beam ion source is the extraction of ions from an enclosed plasma through a grid by applying a negative potential to the grid [96-98]. This should also be possible using the arrangement shown here. However,
in this case an alternative approach was considered. Rather than using the magnetron as a broad beam ion source, a positive potential was applied to the grid in order to extract electrons from the magnetron. These electrons would then induce further ionising collisions in the weak plasma around the substrate area, and hence increase

![Diagram of Magnetron and keeper assembly with additional grid.](image)

**Figure 5.10**: Magnetron and keeper assembly with additional grid.

the plasma density in this region. The magnetron would thus act as an electron source to the plasma. Altering the plasma density in this way is only possible because of the higher argon pressures used in magnetron sputtering compared to broad beam ion source operating pressures (typically ~ 0.01 mTorr).

The ion current to the substrate table measured at an argon pressure of 20 mTorr as a function of the applied grid bias is shown in figure 5.11. The increase in ion current for more positive applied grid biases suggests that the plasma density
near the substrate has increased. Visual observation tended to confirm this with a visible glow discharge appearing between the grid and the substrate table as a positive potential was applied to the grid.

![Graph showing ion current to the substrate table measured as a function of applied grid bias]

*Figure 5.11: Ion current to the substrate table measured as a function of applied grid bias*

Although the results of this short trial experiment are encouraging, a great deal of further work is required to ascertain the effect of the grid on the uniformity of the atomic flux and the consistency of the deposition rate in order to assess if the technique is viable for producing films by ion assisted deposition. In addition, the effect of argon pressure on the operating parameters of the 'gridded' magnetron source will need to be investigated.
5.4 CALIBRATION OF DEPOSITION RATES

5.4.1 Principles of the Calibration Technique

There are many methods available for the measurement of the thickness of a deposited film. Frequently used techniques include stylus methods and direct measurement of the film thickness using electron microscopy. X-ray reflectivity can also be used to determine the film thickness by measuring the period of the Kiessig fringe oscillations (see section 3.3.3). However, when depositing a multilayer film it is important to establish the rate at which a layer of each material grows within the structure of the multilayer film. The bilayer period of the multilayer can be readily measured using X-ray or neutron reflectivity as shown in section 3.3.3. A very simple method for directly obtaining the deposition rate of each metal layer from a series of Co/Cu multilayers using X-ray reflectivity is discussed here.

The bilayer period, $d$, of a multilayer is given very simply by the expression

$$d = (\gamma_{Cu}) t_{Cu} + (\gamma_{Co}) t_{Co}$$

where $\gamma_{Cu}$ and $\gamma_{Co}$ are the deposition rates of copper and cobalt respectively and $t_{Cu}$ and $t_{Co}$ are the deposition times used for a given sample. If a set of multilayer samples is prepared with the deposition time of one metal, for example $t_{Co}$, fixed whilst varying the other deposition time, $t_{Cu}$, the deposition rates of each metal can be obtained by plotting the bilayer period, $d$, measured in the X-ray reflectivity curve against $t_{Cu}$ (in this case). The plotted data will then obviously be a straight line crossing the $y$-axis at the value corresponding to the thickness of copper layers in the multilayer, $\gamma_{Cu} t_{Cu}$, having a gradient equal to the cobalt deposition rate $\gamma_{Co}$.

As several samples are required for an accurate calibration using this technique, it is probably better suited to relatively fast deposition techniques such
as magnetron sputtering. It is of course necessary to maintain the same deposition conditions for the entire calibration sample series in order to obtain accurate values of $\gamma_{Cb}$ and $\gamma_{Cb}$. Conversely a set of samples that yield anything other than a straight line plot would imply that the deposition rates are varying between sample depositions. A random scattering of the points could be caused by, for example, a failure to maintain constant deposition conditions. Alternatively a curve would indicate a gradual change in the deposition rates such as may occur just after a magnetron target is replaced.

5.4.2. Calibration Example using Co/Cu Multilayers

In order to calibrate the deposition rates from the cobalt and copper sources at an Argon sputtering gas pressure of 8 mTorr and at given magnetron operating conditions, a series of samples was prepared with a fixed copper layer deposition time of 4 s and with the cobalt layer deposition time varied from 4 s to 18 s. The bilayer period of each multilayer was then determined from X-ray reflectivity measurements by fitting the position of the first order Bragg peaks using the modelling techniques described in chapter 3.

The measurements of the bilayer period are plotted against the cobalt layer deposition time in figure 5.12. A linear regression fit to the data is also shown. From the fitted line the gradient and y-axis intercept were obtained. These values, together with the subsequently calculated deposition rates are shown in table 5.1. The close fit to the data suggests that the deposition rates were unchanged between sample depositions. This is an important result because between each sample deposition the vacuum chamber was vented and then re-evacuated and
argon gas introduced for sputtering. This stability in the deposition rates therefore implies that the sputtering condition were accurately reproduced each time.

![Graph showing the relationship between deposition time and bilayer period.](image)

**Figure 5.12**: Measured bilayer period plotted as a function of cobalt layer deposition time (points) and linear regression fit (line).

<table>
<thead>
<tr>
<th>Gradient / Ås(^{-1})</th>
<th>Intercept / Å</th>
<th>(\gamma_{\text{Cu}}) / Å</th>
<th>(\gamma_{\text{Co}}) / Ås(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>18.0</td>
<td>4.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**Table 5.1**: Parameters calculated from the linear regression fit.
5.5 SUMMARY AND CONCLUSIONS

In this chapter several methods for the control of ion fluxes during ion-assisted deposition have been discussed. It was shown that the largest variation in the ion flux was obtained when the unbalanced magnetic field from the magnetron was altered. This was done both by positioning an electromagnetic coil over the magnetron and by placing a magnetic keeper over the magnetron. Although both methods proved effective in controlling the ion flux, the magnetic keeper approach was found to be simpler to adapt to the magnetron system and provided fewer practical problems.

In order to vary the ion flux using the magnetic keeper method, part of the keeper was made detachable. The ion flux could then be altered by varying the thickness and material of the detachable section. It was shown that the variation in ion flux achieved using this method was independent of the argon sputtering pressure and did not significantly affect the deposition rate from the magnetron.

For multilayer deposition, calibration of the deposition rates from the two magnetrons was achieved by measuring the bilayer spacing in a series of samples. By fixing the deposition time for one layer and altering the deposition time for the other layer, the deposition rates could thus be determined. It was shown how this was done for Co/Cu multilayers under specific sputtering conditions.

It has been shown in this chapter how the ion flux to the substrate and deposition rates from two magnetron sources can be calibrated. For given sputtering conditions the deposition rates can be determined and the ion flux varied as a separate parameter. This enables the preparation of multilayers under different levels of concurrent ion bombardment. Thus it can be seen that the unbalanced
magnetron can be utilised as both a deposition source and independent ion source. The main disadvantage of using the unbalanced magnetron for this purpose compared to a separate broad beam ion source, is that ion irradiation of the substrate cannot be attained without concurrent deposition. Ion etching of a multilayer between deposited layers is not therefore possible. Nevertheless, as an ion-assisted deposition source the unbalanced magnetron is extremely versatile.
Chapter 6

X-ray Reflectivity Studies of Co/Cu Multilayers Grown by Ion-Assisted Deposition

Contents

6.1 Introduction
6.2 Anomalous Dispersion and Fluorescence Measurements
6.3 Growth Under Low Level Ion Bombardment
6.4 Interface Roughness and Energetic Particle Bombardment
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6.6 Summary and Conclusions
6.1 INTRODUCTION

In this chapter the structure of Co/Cu multilayers deposited under concurrent ion bombardment is investigated. The use of ion bombardment in this way allows the study of energetic particle bombardment on the film microstructure. In chapter 5, methods for controlling the ion bombardment of the growing film were discussed. This controlled use of ion-assisted deposition was used to deposit a series of Co/Cu multilayers for investigation.

X-ray reflectivity is an ideal tool for the microstructural characterisation of multilayer films and in particular for the analysis of interface structure. Real-space techniques for the characterisation of the interface structure, such as transmission electron microscopy (TEM), are difficult to apply to Co/Cu multilayers due to the lack of scattering contrast between the two elements. It is shown in this chapter that the use of a tuneable synchrotron X-ray source can overcome the scattering contrast problem in X-ray reflectivity. In addition, the combination of specular and diffuse scattering measurements enable the microstructure in the lateral direction (parallel to the interfaces) as well as perpendicular to the interfaces to be probed.

In the following section, the use of grazing incidence X-ray fluorescence and the anomalous dispersion effect are demonstrated with respect to Co/Cu multilayers. Following this (section 6.3) the effect on interface structure of applying a modest bias at a low ion flux level is discussed. More extreme variations in the ion bombardment conditions are examined in section 6.4. Finally some preliminary neutron reflectivity measurements and reciprocal space mapping techniques are presented.
6.2 ANOMALOUS DISPERSION AND FLUORESCENCE MEASUREMENTS

6.2.1 Fluorescence Measurements near the K-absorption Edge

The fluorescence intensity at grazing incidence was recorded using station 2.3 at the Daresbury Laboratory using the equipment illustrated earlier in Chapter 4. These measurements are particularly interesting when the incident photon energy is near an absorption edge of the sample material and allow the chemical nature of the sample to be investigated.

As discussed in section 3.2, the X-ray absorption spectrum for a given material is related to the $f'$ component of the atomic scattering factor. The absorption spectrum can be measured simply by detecting the transmitted X-ray intensity through the material as a function of X-ray energy. This has been done by Bonse et al [125] for the case of a copper foil, as shown in figure 6.1. An alternative approach used here, is to measure the X-ray fluorescence intensity from the sample as a function of X-ray energy. By exploiting the tunability of the synchrotron radiation source at Daresbury Laboratory, the absorption spectrum around the copper and cobalt K-edges was obtained from Co/Cu multilayer samples.

In addition to revealing the K-absorption edge, the near edge structure is also characteristic of the local environment of the atoms. A recent paper by Prieto et al [126] demonstrated how this characteristic ‘fingerprint’ of the local atomic environment can be used to determine the crystal phase of the cobalt layers in ion beam sputtered Co/Cu multilayers. Interestingly they found that the cobalt layers
were predominantly of an fcc phase (and so displayed a near-edge structure similar to the copper foil shown in figure 6.1) for copper layer thicknesses greater than 20Å.

![Absorption spectrum](image)

**Figure 6.1**: Absorption spectrum measured from a pure copper foil using a transmission technique. Data taken from Bonse et al [125].

In a reflectivity experiment, the penetration depth of the X-rays into the sample can be varied by changing the angle of incidence of the X-ray beam. For typical Co/Cu multilayers, such as those discussed later in sections 6.3 and 6.4, the critical angle ($\theta_c$) for total external reflection of X-rays at $\lambda=1.3814$ Å was found to be $\approx 0.3^\circ$. Hence, if the sample is positioned at an incident angle below $0.3^\circ$, the X-rays are reflected from the surface layer with very little penetration into the bulk of the sample. By scanning the X-ray energy with the sample at this position, the near-edge structure of the surface layer atoms can be observed. Repeating the scan with the sample rotated to a larger incidence angle enables a greater depth into the sample to be probed. This was done for a Co/Cu multilayer with the nominal structure Si(111)/Co(38Å)/[Cu(28Å)/Co(21Å)]$_{20}$/Cu(25Å), which is referred to as sample 1B in section 6.4 later. Scans around the copper K-edge for this sample at
incident angles of 0.2° and 0.5° are shown in figure 6.2 curves (a) and (b) respectively. The expected position of the copper K-edge [127] is indicated in the figure and coincides well with the measured data. It should be noted that although the critical angle, $\theta_c$, is a function of X-ray energy, for the highest energy used in these scans, ($E=9060$ eV), $\theta_c$ is still significantly greater than 0.2° and hence the fluorescence intensity measured throughout the scan was always due to total externally reflected X-rays.

Figure 6.2: Fluorescence spectrum from a Co/Cu multilayer (sample 1B) recorded around the copper K-absorption edge at grazing incidence angles of (a) 0.2° and (b) 0.5°.

Comparing the two curves in figure 6.2 it would seem that the local environment of the copper atoms in the surface layer of the film is significantly
different to that of atoms in the bulk of the film. Curve (b) shows a characteristic fcc phase for the bulk copper layers as seen by comparison with the copper foil spectrum in figure 6.1. Curve (a) however, shows a near-edge structure more reminiscent of a bcc phase (see for example reference 126) which may be the result of the formation of a surface oxide.

![Fluorescence spectrum](image.png)

**Figure 6.3**: Fluorescence spectrum from a Co/Cu multilayer (sample 1B) recorded around the cobalt K-absorption edge at grazing incidence angles of (a) 0.2° and (b) 0.5°.

Scans measured around the cobalt K-edge for the same sample at incident angles of 0.2° and 0.5° are shown in figure 6.3 curves (a) and (b) respectively. The expected position of the cobalt K-edge [127] is indicated in the figure and is in reasonable agreement with the measured data. The surface sensitivity of the
fluorescence technique used at grazing incidence is exemplified in this figure. In the region of total external reflection (curve (a)), the cobalt K-edge cannot be resolved. This suggests that there is insufficient cobalt in the surface layer of the film to be detected. For this sample the uppermost cobalt layer is buried beneath a copper capping layer that may have oxidised and expanded. It is therefore not surprising that the cobalt edge could not be detected. However, when the sample was rotated to 0.5°, allowing X-rays to penetrate the layers beneath the surface, the cobalt edge was clearly visible (curve (b)). The shape of curve (b) in figure 6.3 is similar to that of figure 6.2 (b) implying that the cobalt layers in the film are predominantly fcc for the layer thicknesses in this sample.

![Fluorescence spectrum from a Co/Cu multilayer (sample 2B)](image)

**Figure 6.4**: Fluorescence spectrum from a Co/Cu multilayer (sample 2B) recorded around the copper K-absorption edge at grazing incidence angles of (a) 0.2° and (b) 1.1°. The absorption spectrum of a copper foil taken from [125] is also shown (solid line) for comparison.
For comparison, fluorescence measurements were performed on a different Co/Cu multilayer (referred to as sample 2B in section 6.4), that was prepared under identical conditions to the previous sample but was finished in a cobalt layer without an additional capping layer. The near-edge structure around the copper K-edge at incident angles of 0.2° and 1.1° is shown in figure 6.4 curves (a) and (b) respectively. By using an incident angle of 1.1° instead of 0.5° as in the previous sample, a larger number of layers were probed due to the greater path length of X-rays into the sample. This enabled the near-edge structure of bulk copper layers (curve (b)) to be more clearly resolved than for the previous sample. The similarity of the data in curve (b) to that obtained from a pure copper foil [125] (solid line in the figure) can be seen. A weak copper K-edge can also be seen at an incident angle of 0.2° (curve (a)) indicating that the uppermost cobalt layer is sufficiently thin to allow some penetration of the incident beam into the copper layer below.

![Fluorescence spectrum from a Co/Cu multilayer (sample 2B) recorded around the cobalt K-absorption edge at grazing incidence angles of (a) 0.2° and (b) 1.1°.](image)

*Figure 6.5: Fluorescence spectrum from a Co/Cu multilayer (sample 2B) recorded around the cobalt K-absorption edge at grazing incidence angles of (a) 0.2° and (b) 1.1°.*
The near-edge structure around the cobalt K-edge is shown in figure 6.5 at incident angles of 0.2° (curve (a)) and 1.1° (curve (b)). The surface layer (curve (a)) is very similar to that obtained for the previous sample (figure 6.2 (a)) and again implies the presence of a surface oxide on the film. However, in this case the oxide is seen in the cobalt edge spectrum which is expected as the film was finished with a cobalt layer at the surface. As for the previous sample the bulk cobalt layers can be seen to have an fcc structure (curve (b)) very similar to that of the copper layers.

6.2.2 Anomalous Scattering in Reflectivity Experiments

As discussed in Chapter 3 the X-ray absorption of a given material is contained in the imaginary component of the complex refractive index, \( n = 1 - \delta - i\beta \) where \( \beta = \lambda\mu / 4\pi \), \( \mu \) is the linear absorption coefficient and \( \delta \) is related to the real components of the scattering factor. For a multilayer consisting of alternating layers of elements that are very close to each other in the periodic table, the change in refractive index, \( n \), in passing from one element to the next at energies away from an absorption edge, is negligible. This lack of scattering contrast between the two elements makes it very difficult to observe the superlattice Bragg peaks. However, as discussed earlier in Chapter 3, by tuning the X-ray energy to just below the absorption edge of one of the elements, a significant difference in the refractive indices of the elements can be obtained and thus the scattering contrast between layers can be greatly enhanced.
Multilayers of cobalt (atomic number 27) and copper (atomic number 29) suffer a lack of scattering contrast due to the similar electron densities of the two metals. An enhancement in the scattering contrast can be obtained by using an X-ray energy just below the cobalt K-edge or just below the copper K-edge. In the experiments discussed in this chapter, the energy was tuned to just below the copper K-edge with $\lambda=1.3814$ Å. The dramatic effect of the anomalous dispersion terms on the scattering contrast can be demonstrated by taking a series of specular reflectivity scans at energies around the K-edge. This was done for a typical Co/Cu multilayer sample at energies around the copper K-edge, as shown in figure 6.6.

![Specular X-ray reflectivity measured for a series of X-ray wavelengths from a Co/Cu multilayer showing the enhancement in the first order Bragg peak near the Cu K-absorption edge.](image)

Figure 6.6: Specular X-ray reflectivity measured for a series of X-ray wavelengths from a Co/Cu multilayer showing the enhancement in the first order Bragg peak near the Cu K-absorption edge.
At energies above the absorption edge (\(\lambda < 1.3814 \, \text{Å} \)) only a weak Bragg peak can be seen in the figure. This region corresponds to the maximum absorption plateau just above the K-edge (see for example figure 6.2(b)). As soon as the energy was decreased so as to drop over the absorption edge (\(\lambda = 1.3814 \, \text{Å} \)) a sharp rise in the intensity of the Bragg peak can be seen. As the wavelength was increased still further, the absorption term slowly increases again as the energy moves away from the K-edge, and the intensity of the Bragg peak can be seen to slowly diminish (\(\lambda > 1.3814 \, \text{Å} \)). The 'spikey' appearance of the Kiessig fringes and Bragg peaks in the scans taken at wavelengths greater than 1.3814 Å may be due to interference effects resulting from slight changes in the surface height across the beam area on the sample. In what follows the X-ray wavelength was set at 1.3814 Å in order to provide the best possible contrast for determining the layer structure in the Co/Cu multilayers investigated.

6.3 GROWTH UNDER LOW LEVEL ION BOMBARDMENT

6.3.1 Introduction and Experimental Details

Initial experiments on the effect of ion bombardment on the growth of Co/Cu multilayers were performed using only subtle changes in the ion bombardment conditions. As little information on the effect of any form of energetic bombardment during growth of this system was available, it was not known exactly how dramatic the differences between samples deposited with and without an applied substrate bias would be. Measurements of the magnetron plasma discussed earlier in section (5.2) suggested a floating potential for unbiased
samples of around -15 V. Saturated ion bombardment was only observed for applied biases of >-30V. Multilayer samples were therefore deposited with the substrate electrically floating or with an applied bias of -50V in order to observe the effect of low energy saturated ion bombardment. In order to reduce possible mixing of the individual layers in each film, the ion flux was minimised by using the thickest mild steel keeper configuration on each magnetron as detailed earlier.

The two samples discussed here were deposited onto Si(111) substrates prepared by the standard method (Section 4.2.1) with a nominal structure of Si(111)/Co(60Å)/[Cu(25Å)/Co(23Å)]19/Cu(75Å). Details of the deposition conditions are summarised in table 6.1. The use of the magnetic (cobalt) target on one magnetron reduced the strength of the magnetic trap around this target and resulted in a much lower cobalt deposition rate compared to the equivalent copper rate. Although this could be compensated by increasing the target voltage, it was chosen not to do this in order to minimise the possibility of substrate bombardment by energetic Ar neutrals reflected from the target. A lower cobalt deposition rate increases the possibility of contamination from gaseous impurities. However this was not found to significantly effect the structural integrity of the multilayer.

<table>
<thead>
<tr>
<th>Argon Partial Pressure</th>
<th>8.0 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber Background Pressure</td>
<td>2 x 10^{-7} Torr</td>
</tr>
<tr>
<td>Deposition Rates</td>
<td>Copper 5.3 Å/s</td>
</tr>
<tr>
<td></td>
<td>Cobalt 1.6 Å/s</td>
</tr>
</tbody>
</table>

Table 6.1 : Summary of Deposition Conditions
X-ray reflectivity measurements were performed using the experimental set-up and techniques discussed in section 4.3. The samples were characterised using specular 0-20 scans, offset 0-20 scans, and transverse scans (grazing incidence rocking curves). All reflectivity data shown were normalised to the incident beam and the true specular reflectivity obtained by subtracting the diffuse background measured just off the specular position, from the normalised intensity measured in the 0-20 scans. The latter correction made only very subtle alteration to the intensity measured in the 0-20 scans due to the relatively small contribution of the diffuse scatter to the apparent specular signal. Although the diffuse component becomes a larger fraction of the total intensity measured with increasing values of $q_z$, in all Co/Cu multilayers investigated to date the diffuse contribution was found to be a negligible fraction of the total intensity even at high $q_z$. Indeed for typical counting times used in the 0-20 scans, at high $q_z$ the diffuse component was undetectable above background levels.

In addition to the diffuse signal, the data were corrected for overfilling of the sample volume at very low angles due to the finite sample size. Transverse scans were also corrected for the changing sample volume probed by multiplying the corrected normalised data by $\sin \omega / \sin \theta$. This has the effect of normalising the data to a constant sample volume.

6.3.2 Layer Structure in Biased and Unbiased Films

Specular reflectivity measurements obtained from the unbiased and biased films, hereafter referred to as sample A and B respectively, are shown in figures 6.7(a) and 6.7(b). Best-fit simulations of the specular profiles are shown under
each experimental curve. The simulations were performed using the recursive formulae detailed in section 3.3. A 60 Å cobalt buffer layer was included in the simulations. The low frequency oscillation seen in the experimental curves was modelled by assuming partial oxidation of the surface copper layer. The best-fit to this low frequency curve was obtained by modelling the oxidised capping layer as a bilayer consisting of a 56 Å copper layer and 14 Å copper (I) oxide layer for each sample. Interfacial roughness was included in the simulations by multiplying the Fresnel reflection coefficients at each interface by a Debye-Waller factor (see the earlier discussion in section 3.4 for details).

The best-fit simulation curves for each sample were obtained using an rms roughness of 5 ± 1 Å for the interfaces in the bulk of the film and 7 ± 1 Å rms for the interface between the silicon substrate and buffer layer. The fit was improved by adding an additional 8 ± 1 Å and 9 ± 1 Å rms roughness between the capping layer and film interface and the oxide and capping layer respectively. An rms surface roughness of 2.0 ± 0.5 Å was also included in the simulations. The clear visibility of the Bragg peaks and Kiessig fringes in both samples suggests well ordered layers have formed during growth. From the simulations, sample A was found to have a bilayer period of 47.6 Å and a cobalt to copper thickness ratio of 0.943. Sample B was found to have a bilayer period of 46.2 Å and a thickness ratio of 0.925. Suppression of the second order Bragg peak, clearly seen in both sample curves and simulations, is expected for layer thickness ratios approaching unity.

The most notable difference between the two samples is the reduction in the bilayer period of sample B. This reduction is outside any experimental error we have observed previously in the control of deposited thicknesses. It is possible, therefore, that some kind of densification of the microstructure has occurred.
Figure 6.7: Experimental (bold curves) and best-fit simulation (fine curves) specular reflectivity profiles obtained for the unbiased sample (a) and biased sample (b). The simulations have been vertically displaced for clarity and the fit parameters are given in the text.
The origin of this densification could be the suppression of void formation and surface roughening. This suppression is expected for films deposited under energetic particle bombardment [91,113]. Another possibility is that the ions bombarding the film when the -50 V bias was applied were sufficiently energetic to cause resputtering of the deposited layers, thus reducing the net deposition rate. In order to gain an insight into the nature of the interface roughness present and how it may relate to the microstructure, it was necessary to examine the diffusely scattered intensity.

6.3.3 Interface Structure and Roughness Correlation

The longitudinal diffuse scatter measured in the offset 0-2θ scans from sample A is compared with the specular curve in figure 6.8(a). The reproduction of the first order Bragg peak for all offset angles, indicates the presence of vertically correlated roughness in the samples. In addition there is clear reproduction of the Kiessig fringes for offset angles out to 0.06°. This implies partial correlation of the roughness through the entire thickness of the film for the lateral length scale of roughness probed (~1 μm). The correlation of roughness on this length scale is common for sputtered multilayer films [113]. The higher frequency roughness probed at larger offset angles is less well correlated as can be seen in the gradual damping of the Kiessig fringes and broadening of the diffuse Bragg peaks. The exact nature of the roughness in this sample is unclear but could be due to the presence of defects on the substrate surface, such as terraces, that are replicated at the multilayer interfaces. The critical dependence of interface roughness on the substrate surface microstructure has been documented elsewhere [128].
Figure 6.8: Specular and off-specular intensity measured for increasing offset angles, $\Delta\omega$, for (a) sample A and (b) sample B. The off-specular scans have been shifted for clarity.
The same series of scans for sample B is shown in figure 6.8(b). The reproduction of the Kiessig fringes for small offset angles is very much weaker than for sample A and the diffuse Bragg peaks are significantly broader. This indicates that the low frequency roughness component is less well correlated. This could be due to ion bombardment induced damping of the roughness from the substrate by the removal of low co-ordination number atoms at the edges of terraces and other defects on the growing surface.

Figure 6.9: Transverse scan intensities measured through the first order Bragg peak for sample A (solid line) and sample B (dotted line).
The transverse diffuse scattering scans for the two samples taken with the detector set at the first order Bragg reflection, are shown in figure 6.9. The limited range in $q_x$ restricts the measurement of diffuse scatter to that from low frequency roughness ($<2 \mu m^{-1}$). Sample A shows a specular spike at $q_x=0$ Å$^{-1}$ on top of a broad diffuse base that decays with increasing $q_x$. This is characteristic of a multilayer with a greater degree of roughness conformality at longer length scales. By contrast sample B shows a much less intense diffuse component that is nearly constant down to the in-plane length probed in these scans (~6000Å), suggesting that the larger lateral scale roughness conformality is not present in this sample. In addition, the ratio of the intensity at $q_x=0$ Å$^{-1}$ to the diffuse intensity just off the central spike (~10$^3$) is greater than that of sample A. These observations support the idea of the suppression of correlated low frequency roughness by energetic ion bombardment during growth. The ratio given above compares well with that obtained from high quality multilayers reported elsewhere [128].

6.3.4 Conclusions

Multilayers with compositionally sharp interfaces were obtained by low energy ion-assisted deposition using unbalanced magnetron sputtering techniques. The roughness at the multilayer interfaces was found to be partially correlated throughout the film. For the sample deposited without an applied substrate bias, the larger scale roughness probed was nearly conformal and is thought to originate from the microstructure of the substrate surface. The application of a -50V d.c. substrate bias during growth appeared to suppress the replication of large lateral
scale roughness on the substrate surface. This resulted in a multilayer with smoother and possibly slightly denser layers than are otherwise obtained.

The slightly shorter bilayer period measured in the sample deposited with the applied substrate bias, implies some form of preferential sputtering of the growing surface has occurred. This could provide a mechanism for surface smoothing by the removal of loosely bound atoms at the edges of terraces on the growing film. Since the limiting factor in determining the quality of multilayers is the substrate surface roughness, any method that produces a smooth starting surface should enable the growth of multilayers with extremely flat interfaces. In order to investigate the changes in multilayer structure due to ion bombardment further, samples were deposited with larger substrate biases and different levels of ion flux.

6.4 INTERFACE ROUGHNESS AND ENERGETIC PARTICLE BOMBARDMENT

6.4.1 Introduction and Experimental Details

In order to investigate the effect on multilayer structure of the average energy of the bombarding ions during film growth, samples were prepared using a range of different applied biases. In addition, by using two different configurations of the mild steel keeper arrangement on the copper magnetron source (see section 5.2), the effect on multilayer structure of both the average ion energy and ion flux was investigated. There are two motivating objectives for using ion-assisted deposition in this way; to test the suitability of the process for controlled interface
growth, and as a tool for studying the effects of intrinsic energetic particle bombardment in sputter-deposited Co/Cu multilayers.

Three sets of Co/Cu multilayer samples with different layer thicknesses were deposited using either of the two mild steel keeper configurations described in section 5.2. With the mild steel section in place, the ion current density recorded with an applied bias of -50 V was \(~35 \mu\text{Acm}^{-2}\) and is hereafter referred to as the low flux level. With the stainless steel section in place the ion current density at -50 V bias was \(~100 \mu\text{Acm}^{-2}\), hereafter referred to as high flux. At low argon pressures, neutral particles with energies of several hundred eV can bombard the growing film. The effect of this neutral bombardment would dominate the eventual film structure with ion bombardment being only of secondary importance. Therefore, in order to observe the effect of applying a modest bias of between -50 V and -200 V, a relatively high sputtering gas pressure of 8 mTorr was used, thus thermalising most of the energetic neutral flux before it reached the film.

As before the substrates were prepared by the standard method (see section 4.2.1) and a silver conducting paint was used to ensure a good electrical conductance between the growing film and substrate. The preparation details for all three sample sets are summarised in table 6.2. X-ray reflectivity measurements were performed on station 2.3 at the SRS, Daresbury Laboratory using a wavelength of 1.3814 Å as before.
Table 6.2: Ion bombardment conditions and nominal structures of the three sample series showing ion flux levels and applied substrate biases used during deposition.

The following discussion is divided up into three parts. In the first (section 6.4.2) the specular and diffusely scattered intensity measured from a sample deposited at a low substrate bias (-50 V) but with high ion flux is discussed. In the second part (section 6.4.3) the effect of varying the applied substrate bias up to -200 V is considered and comparisons made with the low bias sample. Finally, measurements made on samples deposited with different levels of ion flux are presented (section 6.4.4).

The samples were characterised using specular θ-2θ scans, offset θ-2θ scans and transverse scans. All reflectivity curves were normalised to the incident
beam intensity and the corrections detailed in section 6.3.1 were applied. Simulations of the specular reflectivity were obtained as discussed earlier. Interfacial roughness was included by multiplying the Fresnel coefficients for the interfaces by a Debye-Waller factor.

6.4.2 Interface Structure in Low Biased (≤ 50V) Samples

The specular reflectivity profile obtained from sample 1B together with a best fit simulation is shown in figure 6.10. Bragg peaks up to the third order can be seen in both curves. The relative peak intensities depend on the ratio of the thickness of cobalt and copper layers. From the simulation, a bilayer periodicity of 48.1 Å and a cobalt bilayer fraction of 0.43 were obtained, which are in good agreement with the expected values.

In addition to the Bragg peaks, a strong low frequency oscillation can also be seen. This oscillation is similar to that observed in figure 6.7 and can be modelled by a capping layer on the sample surface that has partially oxidised and expanded. A reasonable reproduction of this oscillation was obtained in the simulation curve by simplifying the structure of the oxidised capping layer to that of a bilayer consisting of a 65 Å copper layer and 21 Å copper(I) oxide layer. From repeated simulations it was found that the thickness of the capping/oxide layer not only affects the position of the Bragg peaks as has been previously observed [129], but also has a profound effect on the intensity of the Bragg peaks and the minima occurring near these peaks. Interference between the phase and antiphase amplitude reflections from the multilayer and surface layer is responsible for the enhancement in maxima and minima near the Bragg peaks. The observation of such
effects depends on the degree of surface roughness of the sample. As the intensity reflected from the surface is weakened due to surface roughness, the effect of the surface layer on the reflectivity profile is reduced.

The intensity of the surface layer oscillation depends upon the reflected amplitude from the multilayer interfaces and as such is sensitive to the rms interfacial width. As this width is increased, the reflectivity from the multilayer interfaces is weakened causing a subsequent reduction in the intensity of the surface layer oscillation. A reliable measure of the interfacial width of the multilayer could therefore be obtained by fitting not only the intensities of the Bragg peaks but also the intensity of the surface oscillation. From the simulated

![Figure 6.10](image)

*Figure 6.10: Specular reflectivity intensity measured from sample 1B [high ion flux, -50V bias] (top curve) and best-fit simulation curve. The simulation has been offset vertically for clarity and the fit parameters are given in the text.*
curve shown, values of $5 \pm 1$ Å rms roughness for the multilayer interfaces, $10 \pm 2$ Å for the interface between the capping layer and oxide, and $6 \pm 1$ Å for the interface between the silicon substrate and film were obtained. Although strictly speaking a native silicon oxide layer should be included in the simulation, only very subtle changes in the reflectivity were found if this was done.

Another feature of the reflectivity curve from this sample is the lack of observable broadening in the Bragg peaks up to the third order. This implies that the rms interfacial width is constant throughout the sample. This assumption is validated in the simulated data as the width of the Bragg peaks are comparable to the experimental curve. A lack of any variation in this parameter suggests that it is unlikely that any significant cumulative roughness exists in this sample. This would explain the lack of surface roughness and hence the clear visibility of the surface layer oscillation.

Diffuse scattering from the multilayer was used to determine the nature of the interfacial roughness between layers. Transverse scans with the detector position set at $2\theta=1^\circ$, and the first and second Bragg peaks are shown in figures 6.11 (a), (b) and (c) respectively. The same vertical scale is used in each case for comparison. The scans show a two-component function consisting of an instrument resolution limited specular peak at $q_x=0$, on top of a broad diffuse base. The diffuse component is a measure of the interfacial roughness present in the sample. As the detector angle is increased a wider range in $q_x$ can be probed. Hence a broader envelope function of the diffuse intensity is measured as can be seen by comparing the different curves in figure 6.11. Both the specular and diffuse intensity decay as a function of increasing $q_x$.  

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The scan shown in figure 6.11(a) was taken with the detector positioned away from the Bragg condition and the diffuse component is therefore a measure of the intensity scattered by roughness that is not vertically correlated throughout the multilayer. The clear visibility of the specular peak in this curve indicates that a fairly low level of laterally correlated interfacial roughness is present in this sample. The satellite peaks either side of the specular peak are known as Yoneda wings and are caused by multiple diffraction in the multilayer that occurs when either the sample or detector position are equal to the critical angle for total external reflection [121].

The diffuse component measured at the first Bragg peak, shown in the transverse scan in figure 6.11(b), is dominated by roughness that is at least partially correlated across successive layers. Evidence for this can be seen in the offset 0-20 scans shown in figure 6.12. For both offset angles the diffuse intensity is peaked at the Bragg condition indicating the presence of diffuse streaks in reciprocal space running parallel to \( q_x \) through the Bragg lattice points. These streaks, caused by vertically correlated roughness in the multilayer, were found in the earlier samples (section 6.3) and have been seen previously in sputtered [113,121,130] and evaporated [131] multilayers. The lateral length of the roughness probed in the off-specular scans is smaller for larger offset angles, \( \Delta \omega \). Hence the lack of observable broadening between the Bragg-like peaks in the two offset scans shown in figure 6.12 implies that the roughness is equally well correlated for both lateral lengths probed; \( \sim 2.5 \, \mu m \) at \( \Delta \omega = 0.1 \) and \( \sim 5000 \, \AA \) at \( \Delta \omega = 0.5^\circ \). This seems to be a feature of samples deposited with an applied bias of \(-50V\) as was found earlier (section 6.3).
Figure 6.11: Diffuse intensity measured in the transverse scans for sample 1B [high ion flux, -50V bias] with the detector position set at (a) 2θ=1°, (b) the first order Bragg peak and (c) the second order Bragg peak.

The ratio of the specular intensity to the diffuse intensity close to the specular position at the Bragg peak, gives an indication of the degree of correlated roughness present in the sample. The ratio at the first Bragg peak, seen in the transverse scan in figure 6.11(b) and in the offset curve at Δω=0.1° in figure 6.12, is more than three orders of magnitude. The transverse scan for the second order Bragg peak shown in figure 6.11(c) gives a value for this ratio that is still several hundred. It is therefore unlikely that the interfacial width of 5 ± 1 Å measured in the specular θ-2θ scan is due solely to correlated roughness, although a full quantitative analysis of the transverse scans is required to confirm this assumption.
Figure 6.12: Specular (top curve) and offset θ-2θ scans measured from sample 1B [high ion flux, -50 V bias]. The curve with $\Delta \omega = 0.5^\circ$ has been shifted vertically downwards for clarity.

Sample 1B is typical of Co/Cu multilayers studied that were deposited under very low energy (<50 eV) bombardment. Sample 1A, for which no additional bias was applied but which would still be subject to ionic and electronic bombardment, was found to be both qualitatively and quantitatively similar to sample 1B. A simulation fit obtained for this sample (not shown) gave a total rms roughness of $5 \pm 1 \, \text{Å}$ for the multilayer interfaces as found for 1B.

6.4.3 Application of Larger Substrate Biases

Dramatic changes in multilayer structure were not seen until higher bias values of -100 V (sample 1C) and -200 V (sample 1D) were applied. All four samples in this set are shown for comparison in figure 6.13. Despite the fact that
the deposition times, magnetron powers and sputtering gas pressures used for all four samples were identical, the Bragg peaks from consecutive samples are displaced to higher angles and hence the bilayer period shortens as a function of increasing applied bias. This is consistent with a greater degree of resputtering of material from the growing film as the average energy of ionic bombardment is increased by the application of larger substrate biases, although there may also be the possibility of a contribution from ion bombardment induced densification.

In addition to the shift in Bragg peak position, the lower two curves in figure 6.13 have significantly broader features than the -50 V and unbiased samples. Broadening of this type has been predicted from theoretical model superlattices where the rms interface roughness parameters, $\sigma_i$, are not constant.

Figure 6.13 : Specular intensity measured from the samples in series 1. The top curve is from the unbiased sample and the bias increases as -50 V, -100 V and -200 V for respective curves from the top.
for all interfaces, j, but vary about an average value $\langle \sigma \rangle$ [120]. In order to model the specular reflectivity curve from the -200 V biased sample (1D) a linear variation in the rms interface roughness was assumed with the form $\sigma_j = \langle \sigma \rangle + \Delta \sigma/(m - \frac{1}{2})$ where $\Delta \sigma$ is the breadth of the distribution and $m$ is the total number of layers in the sample. The experimental and best fit simulation curve for this sample are shown in figure 6.14. From the simulation it was found that this sample had a similar surface layer structure to the previous sample with a Cu capping and oxide layer of 36 Å and 21 Å respectively. By fitting the Bragg peak positions and relative intensities the bilayer structure was found to be [Cu(24 Å)/Co(16 Å)], which corresponds to a 12% reduction in the Cu layer thickness and a 23% reduction in the Co layer thickness with respect to sample 1B. The average rms interface roughness, $\langle \sigma \rangle$, was found to be 6.0 ± 0.5 Å with a distribution breadth, $\Delta \sigma = 8.0 \pm 0.5$ Å. The simulation fits the data well and adequately reproduces the peak broadening and loss of Kiessig fringe intensity.

The calculated interface roughness distribution for this sample is compared graphically to that obtained for the previous sample in figure 6.15. The linear variation in rms interface roughness found is particularly interesting because the interfaces appear to become more ordered as the film grows. Although linear variations in the opposite sense have been shown to produce broadened features in reflectivity curves [113, 120], such distributions would produce neither the intensity of the Bragg peaks shown nor the surface oscillation that is still clearly visible in this sample. In effect the surface sensitivity of the reflected intensity would be reduced with only the layers nearest to the substrate contributing.
Figure 6.14: Specular intensity measured from sample 1D [high ion flux, -200 V bias] (top) and best-fit simulation curve. The simulation has been vertically displaced for clarity and the fit parameters are given in the text.

Figure 6.15: Interface roughness distributions determined from the simulation fits for sample 1B (circles) and sample 1D (triangles). Consecutive layers are numbered from the surface (j=1).
The direction of improved interface growth in this sample leads us to conclude that the peak broadening seen here is not caused by the cumulative interface roughness that has been observed elsewhere in multilayer films [113]. Another possibility might therefore be that the ion bombardment gradually reduces roughness from the substrate as the film grows. However it is not immediately obvious why the interface roughness near the substrate, found here, should be so much larger than that measured for the previous sample. The replication of substrate roughness has been attributed to one of the causes of vertically correlated roughness in multilayers grown on silicon [128]. Any variation in

\[ q_x (\text{Å}^{-1}) \]

*Figure 6.16: Diffuse intensity measured in the transverse scan taken at the first order Bragg maxima for sample 1B (dotted curve) and sample 1D (solid curve).*
the roughness replicated from the substrate should therefore be detectable by
measuring the diffuse scatter from the vertically correlated roughness such as that
shown earlier in figure 6.11(b). When the transverse scans taken at the first Bragg
peak from samples 1B and 1D are compared (figure 6.16) the magnitude of the
diffuse intensities is found to be fairly similar. It is possible, therefore that the
variation in interface roughness found in sample 1D may be at least partly due to a
variation in the laterally correlated and uncorrelated interface roughness. There is
some evidence for a difference in the laterally correlated roughness when the
transverse scans taken at $2\theta=1^\circ$ are compared for the two samples (figure 6.17).
The additional diffuse scatter near the specular peak present in the curve from
sample 1D but absent in the other sample, suggests a slightly greater level of lateral
correlation of the roughness in the sample deposited with the higher substrate bias.

![Graph showing diffuse intensity vs. q_x(A^-1)](image)

Figure 6.17: Diffuse intensity measured in the transverse scans taken with
the detector positioned at $2\theta=1^\circ$ for sample 1B (dotted curve)
and sample 1D (solid curve).
The larger values of interface roughness for the initial deposited layers in the higher biased sample may be due to a greater degree of interfacial mixing (zero length scale correlation). This might be expected because as the substrate bias is increased, the average energy of the bombarding ions and hence their penetration depth into the growing film also increase. It is not immediately obvious why the interface roughness should improve as further layers are deposited. One possible explanation is that the energy flux to the growing film is sufficient to gradually densify the film to the point where the average energy of the ions is no longer great enough to penetrate a significant depth into the film. At this point the ion bombardment would serve only to remove loosely bound material from the film surface and as such decrease interface roughness rather than inducing intermixing. The stage during growth when this improvement in interface structure begins could be interpreted as the point at which the two curves in figure 6.15 cross.

6.4.4 Variations in Ion Flux

Up until now evidence has been presented for a change in the growth mechanism when the average energy deposited per atom was varied by changing the average energy of the bombarding ions. In sample series 2 and 3 the deposition process was taken one step further by altering the ion flux as well as the average ion energy. By using a shorter bilayer period for these samples the reflectivity was effectively made more sensitive to the interfacial structure. These multilayers are structurally similar to those found to display the magnetic coupling and magnetotransport effects described in Chapter 1.
The specular reflectivity curves obtained from the samples in series 2 are shown in figure 6.18. As before there is a significant change in the reflectivity profiles as the ion bombardment conditions are altered and in a shift in the Bragg peak as the substrate bias was increased. These samples differ to the previous set in that there was no additional capping layer deposited on the multilayer. The surface structure is therefore likely to contain some cobalt oxide and indeed there is evidence of a surface layer oscillation in all four curves.

The higher biased samples, curves (c) and (d) in the figure, show broad Bragg peaks as seen for the previous sample set. However, these curves are by no means identical and a more significant rise in the intensity of the Bragg peaks is seen in curve (d). Additionally, the presence of Bragg peaks out to the third order in curve (d) suggests that at least a portion of the interfaces in this multilayer are significantly smoother than those in the other samples. This would imply that both high ion energy and high flux are required to produce the interface smoothing effects observed. If only the ion flux is increased and the substrate bias is maintained at -50 V (curves (a) and (b)) a drop in the intensity of the Bragg peak is seen without observable broadening. It would seem therefore that at low energies the ionic bombardment is not sufficiently energetic to induce interface smoothing. Increasing the flux merely increases the degree of interface disorder without variation in the roughness at different interfaces.

A similar dependence on the ion bombardment conditions was found for the third sample series with the shortest bilayer period. Again the most intense Bragg peak was observed for the sample deposited with both a -200 V substrate bias and high ion flux (sample 3D). The specular reflectivity profile obtained
Figure 6.18: Specular intensities measured from the samples in series 2. Curves (a) - (d) correspond to samples 2A - 2D respectively. The bottom graph shows the same four curves normalised to the region of total external reflection.
Figure 6.19: Specular intensity measured for sample 3D [high ion flux, -200 V bias] (top) and best-fit simulation curve (middle). The bottom curve is a simulation for the equivalent perfect superlattice. The simulations have been vertically displaced for clarity and the parameters are given in the text.

from this sample, together with a best fit simulation curve, is shown in figure 6.19. The simulated reflectivity for the ideal multilayer structure without surface layer contamination or interfacial roughness is also included in this figure for comparison. As before the Bragg peak position is shifted to a higher angle for this sample compared to the low bias samples (not shown). From this simulation the repeating unit was found to be [Cu(9.2 Å)/Co(13.5 Å)]. It can be seen that the Bragg peak in the experimental and best-fit simulation curve is considerably broader than that of the theoretical perfect multilayer. The broadening of the Bragg peak was reproduced in the best-fit simulation using the linear variation in interface roughness described previously. In addition it was found that larger values of roughness were required for the near surface interfaces in order to obtain a
reasonable fit to the data. This additional roughness may be due to partial internal oxidation of the multilayer that has occurred in the absence of a capping layer. Surprisingly the best fit was obtained when a pure Co surface layer of 42 Å thickness was used in the simulation although the reason for this is unclear at present.

The chemical composition as a function of depth has been investigated for a similar sample to 3D (finished with a cobalt layer) by sputter depth-profiling Auger Electron Spectroscopy (AES). The composition profile for this sample is shown in figure 6.20.

Figure 6.20: AES profile of a Co/Cu multilayer finished with a cobalt surface layer, showing atomic species as a function of depth.
The resolution of the depth profiling AES technique is not generally sufficient to resolve the individual layers of the multilayers obtained in this work. However, several other features of the film can be discerned. At the surface the cobalt concentration is about half its value in the bulk of the film. Oxygen levels greater than 20% can be seen to persist several nanometres into the film. It is not unreasonable to assume that oxidation leads to roughening of the uppermost few layers of the multilayer. Further into the film the cobalt and copper concentrations assume approximately constant values as expected. The presence of a cobalt buffer layer can be seen as a peak in the cobalt intensity just before the substrate. The substrate position is given approximately by the point at which the silicon concentration rises to half its maximum.

Figure 6.21: Interface roughness distribution determined from the best-fit simulation curve for sample 3D [high ion flux, -200 V bias]. Consecutive layers are numbered from the surface (j=1).
The interface roughness distribution calculated for sample 3D is shown graphically in figure 6.21. The roughness of the upper surface layers can be seen to approximately coincide with the partial internal oxidation seen in figure 6.20 (pale blue curve). With the exception of the near surface layers the roughness distribution is similar to that found for sample 1D but with a smaller breadth, \( \Delta \sigma = 4.0 \pm 0.5 \text{ Å} \), and lower average roughness, \( \langle \sigma \rangle = 3.0 \pm 0.5 \text{ Å} \). The differences in these values compared to the earlier sample (1D) may be related to the different layer thicknesses of the two samples. More importantly the trend for a decrease in interfacial roughness as a function of film growth is the same for these two different samples deposited under the same ion bombardment conditions of high substrate bias and high ion flux. From figure 6.21 it can be seen that the interface smoothing leads to eventual interface widths of less than one monolayer thickness for this sample.

6.4.5 Summary and Conclusions

Samples deposited with a low applied substrate bias of \(-50 \text{ V}\) produced specular reflectivity profiles that showed several orders of sharp Bragg peaks, indicating a static interfacial roughness distribution throughout the film. No evidence of cumulative roughness was seen in these films, although measurements of diffusely scattered intensity suggested a degree of partially correlated roughness was present. At higher biases of \(-100 \text{ V}\) and \(-200 \text{ V}\) the specular intensity contained broad Bragg peaks that can be explained in terms of a linear variation in the interfacial roughness such that interfaces are progressively smoother towards the film surface. The diffuse intensity measured at the first Bragg peak for the \(-200 \text{ V} \)
A biased sample was similar to that measured from the -50 V biased samples, although qualitative comparisons are difficult to interpret due to the shift in Bragg peak position to higher qz. However, it would seem likely that the differences in the specular intensity must be at least partly due to changes in the uncorrelated roughness component.

By examining samples deposited with a range of different ion flux levels as well as substrate bias values, it was found that the greatest improvement in interface smoothness was achieved when both the largest bias (-200 V) and highest level of ion flux were applied. In all samples of this type the variation in interface roughness resulted in very smooth interfaces for the uppermost portion of the multilayer. This suggests that if the densification process could be separated from the multilayer growth stage, near perfect interfaces could be realised. This hypothesis could be tested by attempting to deposit multilayers onto thick buffer layers using the ion bombardment conditions discussed here.

6.5 FUTURE DIRECTIONS

6.5.1 Reciprocal Space Mapping

It has been shown that a wealth of information concerning the distribution of roughness in multilayers can be obtained by measuring the spread of scattered X-ray intensity in reciprocal space. Modern diffractometers such as the reflectivity facility on station 2.3 at Daresbury Laboratory are now automated to the extent where a series of scans can be collected with a continuous variation in one or more of the scan parameters. This is particularly useful for obtaining maps of the
scattered intensity in reciprocal space. One method for obtaining such a map is to collect a series of offset $\theta$-2$\theta$ scans with the offset angle $\Delta\omega$, varied so as to obtain a sweep through the reciprocal space as illustrated in figure 6.22.

![Diagram](image)

*Figure 6.22: Schematic illustration of the sweep through reciprocal space measured in a series of offset scans.*

Preliminary measurements of the scattered intensity from a Co/Cu multilayer collected in this way are shown in figure 6.23. The data was taken for part of the measurable reciprocal space region. The reciprocal space map depicts an overview of the microstructure of the film. The first and second order Bragg peaks can be clearly seen along the specular region. The resolution of the map shown in the figure is limited in the $q_x$ direction by the step size of the offset angle, $\Delta\omega$, taken between $\theta$-2$\theta$ scans. For this reason the specular region appears to be broader in $q_x$ than is normally observed.

The so called diffuse Bragg streaks referred to earlier can be seen extending outwards across the reciprocal plane from both the first and second orders. Transverse scans taken at the Bragg orders probe the intensity approximately parallel to the lateral axis ($q_x$). Although it is not immediately clear from figure 6.23, the first order Bragg peak is positioned at $q_x \approx 0.16\AA^{-1}$. However, it can be seen that contrary to the direction of the transverse scan, the diffuse Bragg
Figure 6.23: Reciprocal space map of the scattered X-ray intensity from a Co/Cu multilayer obtained from a series of offset 0-20 reflectivity scans.
streak from the first order extends to roughly \( q_z \approx 0.2 \text{Å}^{-1} \). The diffuse streak is in fact bent into a 'banana' shape by refraction effects. This characteristic shape of the diffuse Bragg streaks has been predicted theoretically [132,133] and observed previously [134] in multilayers in which there exists some interlayer correlation of the roughness. The curvature is strongest near to the total external reflection region.

Diffuse Bragg peaks are one form of resonant diffuse scattering that can occur in a multilayer. The 'Yoneda wings' mentioned in section 6.3.2 are another form. These are found in transverse scans as satellite peaks on either side of the specular peak. They are caused by resonant scattering occurring whenever either the sample or detector angle are equal to the critical angle for total external reflection, \( \theta_c \). In a reciprocal space map the full extent of Yoneda wings can be seen as a diffuse sheet similar to the Bragg peaks. A Yoneda wing can be identified in figure 6.23 extending from \( \sim 0.0005 \text{Å}^{-1} \) to \( 0.0015 \text{Å}^{-1} \) in \( q_x \) and \( \sim 0.05 \text{Å}^{-1} \) to \( \sim 0.12 \text{Å}^{-1} \) in \( q_z \). It is interesting to note that the intensity of the Yoneda wing decays with increasing \( q_z \) in a similar fashion to the specular intensity. In both cases this is due to the greater penetration of the X-rays through the sample surface as \( q_z \) is increased beyond the region of total reflection.

It can be seen that even with the preliminary data presented here, an overall qualitative description of the multilayer microstructure can be obtained by reciprocal space mapping. Once this overview has been established potentially interesting features of the data can be identified and quantitative data obtained using specular and transverse scans in the conventional fashion.
6.5.2 Spin Polarised Neutron Reflectivity

The Co/Cu multilayer sample characterised by reciprocal space mapping was deposited using the highest available ion flux level and a -200 V substrate bias. As with all previous samples prepared in this way, the rms interface roughness was found to decrease towards the film surface. The specular X-ray reflectivity data for this sample is shown together with a best fit simulated curve in figure 6.24 (a). From the simulation the composition was found to be Si(111) / Cu (50 Å) / [Co(24 Å) / Cu(17 Å)]20 / Co(7 Å) / CoO(22 Å). The rms interface roughness profile is shown in figure 6.24(b).

![Graph (a)](image1)

![Graph (b)](image2)

Figure 6.24: (a) X-ray reflectivity profile of a Co/Cu multilayer (top curve) and best fit simulation. Details are given in the text. (b) Interface roughness profile used in the best fit simulation.

In chapter 3 it was shown that the reflection of particles at an interface depends upon the scattering density of the medium. For neutrons this is given by
the product $Nb$ where $N$ is the atomic density and $b$ is the neutron scattering length. For spin polarised neutrons the scattering length is modified by the magnetic polarisation of the medium such that the effective scattering length is $b_{\text{eff}} = b \pm A \mu_p$ where $A$ is a constant and $\mu_p$ is the inplane component of the average magnetic moment per atom that is either parallel (+) or antiparallel (−) to the neutron polarisation axis. Hence the effective scattering density of a given layer can be split as $Nb \pm Np$ where $Nb$ and $Np$ are the respective nuclear and magnetic scattering density. The scattering contrast between layers in a magnetic / nonmagnetic multilayer will therefore depend on the spin polarisation of the neutrons.

The spin polarised specular neutron reflectivity curves measured for the Co/Cu sample are shown in figure 6.25. These preliminary measurements from this sample were obtained using the CRISP reflectometer at the ISIS neutron source based at the Rutherford Appleton Laboratory. The data collected for both spin polarisations at a temperature of 5 K and in an applied field of 3 kG are shown in the figure. Spin up (down) in this case refers to the parallel (antiparallel) alignment with respect to the applied field direction. At high magnetic fields it can be assumed that the inplane component of the magnetic polarisation of the cobalt layers is parallel to the applied field. Thus spin flip scattering, sensitive to the orthogonal inplane magnetic component, can be neglected.

A strong asymmetry in the two spin states can be seen in figure 6.25. This is caused by the different scattering length densities of the two spin states. The size of the spin splitting depends on the strength of the average moment on the cobalt atoms. The severe splitting of the spin states at the critical edge, shown in the figure, is indicative of a strong moment in the near surface cobalt layers. The
difference in the scattering lengths results in a spin-dependent refractive index and thus a different critical angle for each spin state. The suppression of the Bragg peak in the spin up data is due to the fact that for this spin state the cobalt scattering length is approximately equal to the scattering length for copper, that is \((Nb + Np)_{Co} \approx Nb_{Cu}\). This effect has been observed previously in Co/Cu multilayers [77] and leads to a reduced scattering contrast at the Co/Cu interfaces for this spin state. Conversely for the other spin state, \((Nb - Np)_{Co}\), the scattering contrast between cobalt and copper layers is enhanced.

\[\text{Figure 6.25 : Spin polarised neutron reflectivity obtained from a Co/Cu multilayer. The sample details are given in the text.}\]

In order to obtain quantitative information from the reflectivity profile it is necessary to fit the data using a suitable model. Neutron scattering densities differ from the X-ray counterpart only in terms of the additional magnetic component.
and a negligible absorption coefficient. The XREALM modelling code developed as part of this work for calculating the specular X-ray reflectivity, could therefore be used to simulate the neutron data. Such a model will need to contain the surface oxide compound determined from the X-ray measurements, as this is likely to affect the critical angle of each spin state. In principle it should be possible to determine the scattering length densities of each layer and thus obtain the average moments in each cobalt layer. This is of particular interest when the variation in interface roughness shown in figure 6.24 (b) is considered. It is possible that there may be a variation in the magnetisation of each layer associated with the variation in interface widths. However, as the results shown in figure 6.25 are very recent, much of the analysis is still in progress and will be reported later elsewhere.

6.6 SUMMARY AND CONCLUSIONS

The structural characterisation of Co/Cu multilayers prepared using ion-assisted sputter-deposition has been discussed. Quantitative information regarding the surface and interface roughness was obtained by fitting simulations to the specular reflectivity data. The fitting procedure was complicated by the presence of surface oxides on the films that were found to affect the position and intensities of the Bragg features. The oxidised surface layer added a low frequency phase-dependent oscillation to the specular curve, that was seen as broad hump between the main Bragg peaks. This additional oscillation sometimes leads to the appearance of a dip in the reflectivity curve where a peak would normally be expected.
Evidence for the presence of these oxides was seen in the X-ray fluorescence intensity measured at grazing incidence. When the angle of incidence on the sample was set below the critical edge, so as to minimise the penetration of X-rays into the sample, a broad peak was observed at the K-absorption edge of the surface layer element. This broad feature in the fluorescence scan is reminiscent of a bcc structure such as copper (I) oxide. As the sample was rotated to larger angles to allow the buried layers to be probed, a more typical fcc structure was observed.

Simulations that do not include surface oxides are likely to underestimate the degree of surface and interface roughness in the sample. By assuming a simplified form of the oxidised surface layer, the broader features in the specular reflectivity curves were reproduced and a more reliable determination of the roughness parameters were obtained. Additionally it was found that larger values of the roughness parameters were required for the near surface interfaces in order to fit the data from samples deposited without a protective capping layer. A chemical depth profile obtained using Auger Electron Spectroscopy showed the presence of oxygen several nanometres below the film surface. The roughness of the surface layers may therefore be caused by partial internal oxidation of the uncapped multilayer.

From the X-ray reflectivity data it was found that, in general, multilayers deposited under some form of ion bombardment possess minimal vertically correlated roughness. Slightly higher levels of low frequency correlated roughness were observed in a sample deposited without an additional substrate bias and under the lowest level of ion flux available. It was suggested that this may be due to a low surface mobility of the adatoms resulting in the replication of substrate defects
throughout the multilayer stack. The application of a -50 V bias was found to suppress this low frequency roughness component, possibly by preferential sputtering of loosely bound material on the growing surface. It is not unreasonable to assume that the crucial parameter in determining the extent to which such resputtering occurs is the average energy deposited per atom. When this parameter is greater than the sputtering threshold for the material there is a high probability that resputtering will occur. For copper the sputtering threshold is \(-50 \text{ eV}\). It is not surprising, therefore, that resputtering was observed when a -50 V bias was applied as this corresponds to an average ion energy of \(-50 \text{ eV}\).

A greater degree of resputtering was in fact observed as both the substrate bias and ion flux were increased as evidenced by a reduction in the bilayer period. Smoother interfaces were observed in samples deposited under higher energy (-200 eV) bombardment although diffuse scattering measurements showed little difference in the correlated roughness component for high and low energy bombardment. It was therefore suggested that ion bombardment induced intermixing may be responsible for the differences in interface structure. Most surprising of all it was found that, whereas a constant interface roughness was found in the low energy bombardment samples, the interface roughness varied in the high energy samples. This roughness distribution was simplified in model simulations by introducing a linear variation such that the roughness decreased from the substrate to the film surface. At present the reason for this gradual smoothing is unclear. However one possible explanation given was that the sensitivity of the film microstructure to ion bombardment reduced as growth proceeded. This effect might be caused by an ion bombardment induced densification of the microstructure. Unfortunately the sensitivity of X-ray
reflectivity to the surface oxide makes it difficult to fit additional parameters such density gradients in the model simulations. For the same reason, it is therefore difficult to separate the effects of resputtering and densification using X-ray reflectivity alone, although other techniques such as ion scattering could prove useful in resolving this problem.

Another important result presented in this chapter was the significance of both ion energy and ion flux in determining the evolution of interface structure. It was shown how, although both high and low ion flux bombardment at higher energies lead to a roughness distribution (indicated by broad Bragg peaks in the specular reflectivity profile), significantly smoother interfaces were found in samples deposited under both high energy and high flux bombardment. This result was repeatedly obtained for samples deposited under these conditions, regardless of the thickness of the bilayer period.

Finally the use of related techniques for the characterisation of Co/Cu multilayers deposited under ion bombardment was discussed. The use of offset θ-2θ scans to obtain a reciprocal space map of the microstructure was demonstrated. In addition, preliminary spin polarised neutron reflectivity measurements were presented to highlight the powerful combination of this technique together with X-ray reflectivity for relating the interface microstructure to the magnetic properties of these materials.
Chapter 7

Final Conclusions

Contents

7.1 Ion-assisted Deposition System
7.2 Interface Modification in Co/Cu Multilayers
7.3 Further Work
7.1 ION-ASSISTED DEPOSITION SYSTEM

The ability to control the flux and energy of substrate particle bombardment using a modified magnetron sputtering process has been demonstrated. This control was achieved without variation of the deposition parameters or sputtering operating conditions. The independent control of the energy and flux of ion bombardment in this way enables a move away from more generalised theories of thin film growth by sputtering to allow consideration of the effect of charged particle bombardment on interface evolution.

Several methods of ion flux variation were considered. The most promising of these made use of the ability to alter the strength of the unbalanced magnetic flux that reached the substrate. This method effectively allowed each unbalanced magnetron to be controlled as a separate plasma and deposition source. It is thus suitable for multilayer deposition where different ion/atom substrate flux ratios may be required for different materials.

An original but extremely simple method for varying the unbalanced magnetic field strength was investigated. This made use of a mild steel keeper attachment to the magnetron that was used to guide part of the magnetic flux away from the substrate. The appeal of this simple approach is that it can readily be adapted to existing magnetron sputtering systems in order to reduce the ion flux to the substrate. In the context of this work it enables the magnetic field from an unbalanced magnetron source to be controlled, allowing several discrete levels of ion flux to be selected. Together with the application of a substrate bias, samples can be prepared under a range of different levels of ion flux and energy.
7.2 INTERFACE MODIFICATION IN Co/Cu MULTILAYERS

By making use of the unique ion-assisted deposition system developed in this work, Co/Cu multilayers were prepared under a variety of different ion bombardment conditions. The interface structure in the samples was probed using X-ray reflectivity techniques by measuring the specular and diffusely scattered intensity.

No evidence was found for the presence of cumulative interface roughness in these multilayers, although this effect may have occurred if a larger number of bilayers (>20) were deposited. Cumulative roughness is undesirable in multilayers as it limits the total number of coherent interfaces that can be deposited. This is important when considering the interface sensitive effects of GMR and magnetic coupling discussed in Chapter 1. The lack of such cumulative roughness in the films discussed here, however, hindered the quantitative analysis of interface roughness as the specular reflectivity was sensitised to the surface structure of the films. In particular, the oxidation of the capping layer led to a low frequency oscillation that was added phase-dependently to the multilayer reflectivity. It was found that a reasonable fit to the specular reflectivity curves could be obtained if an oxidised capping layer was included in the simulation model. Auger electron spectroscopy and X-ray fluorescence measurements tended to confirm the presence of this surface oxide although its depth into the film seemed to depend on the thickness of the capping layer.

The roughness of the interfaces was found to depend on both the ion energy and flux applied during growth. At low fluxes a difference in the size of large lateral length scale roughness was found for as-deposited samples and ~50
eV ion-assisted samples. This was attributed to preferential sputtering of deposited atoms in the ion-assisted samples resulting in a suppression of roughness replication from the substrate. A slight shortening of the bilayer period in the ion-assisted sample was also observed.

Resputtering and consequently bilayer period shortening, were found to be more dramatic at higher substrate biases and hence greater average ion energies. As detailed in Chapter 2, intermixing of the layers and microstructural densification were expected at higher ion energies. It is possible that part of the reduction in bilayer period observed here is due to such densification processes. However, it was not possible to quantify this effect in the experiments performed. A roughening of the initial interfaces, consistent with ion bombardment induces intermixing, was observed in ~200 eV ion-assisted samples. Unexpectedly, the interface structure was subsequently found to improve for additional interfaces towards the film surface. It would seem, therefore, that the initial damage to the interface structure was overcome as the film microstructure stabilised during growth. Smoothing of the upper interfaces was observed compared to the lower energy (~50 eV) ion-assisted samples. The degree of interface smoothing was found to be dependent on the ion flux and was greatest for samples deposited under the highest available levels of ion flux and energy.

It can be concluded, therefore, that the interface roughness in Co/Cu multilayers can be significantly reduced by controlled ion bombardment during growth. The magnitude, correlation and variation of the interface roughness all depend on the ion flux and energy applied. As the GMR and magnetic coupling depend sensitively on the interface roughness it is not surprising that such a large range of different values have been reported in sputtered samples. The results
presented here go some way towards demonstrating the sensitivity of the interface structure in Co/Cu multilayers to substrate particle bombardment during growth. Under optimum ion bombardment conditions it should be possible to prepare samples with structures approaching an ideal model.

7.3 FURTHER WORK

The obvious continuation of this work is to attempt to correlate the magnetic and magnetotransport properties of ion-assisted Co/Cu samples with the interface structure produced. To some extent this has already been initiated by performing the spin polarised neutron reflectivity measurements that were briefly mentioned in Chapter 6. The allied use of X-ray reflectivity to characterise samples simplifies the extraction of the magnetic structural information from the neutron data. For a full characterisation of magnetisation and magnetic coupling in these samples, a polarisation analysis of the reflected neutron beam is required. The main limitation in using this technique is the low intensity of the reflected beam at higher \( Q_z \) values. Samples with little interfacial roughness are therefore desirable in order to maximise the Bragg peak intensity.

Further questions regarding the evolution of the interfaces under \(-200\, \text{eV}\) bombardment remain unanswered. In particular the roughness variation as a function of the number of bilayer periods has not yet been measured. It would be extremely important if Co/Cu multilayers could be prepared with low levels of interface roughness for a large number of bilayers, for example several hundred. At present, cumulative roughness limits the number of layers that can be coherently deposited. The magnitude of the GMR in these films could be significantly larger.
than presently obtainable due to the greater number of interfaces present for spin-dependent scattering. This would have huge implications for devices incorporating magnetic multilayer systems where such large GMR effects are highly desirable.
References


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Appendix A

XREALM Program Code

DECLARE SUB templinvar()
DECLARE SUB replotted (lastpoint!)
DECLARE SUB checkerrors (errorcode AS INTEGER)
DECLARE SUB abouttext()
DECLARE SUB inuse()
DECLARE SUB notinuse()
DECLARE SUB plotinterface()
DECLARE SUB deletelayers (pointer AS INTEGER, markerpos AS INTEGER)
DECLARE SUB interfacedata()
DECLARE SUB startup()
DECLARE SUB displayscan()
DECLARE SUB scandata()
DECLARE SUB teststack (b AS INTEGER)
DECLARE SUB beigincalc()
DECLARE SUB repeatlayers (pointer AS INTEGER, repeatpos AS INTEGER)
DECLARE SUB newsample()
DECLARE SUB addlayer (pointer AS INTEGER)
DECLARE SUB sampline (temp AS INTEGER, tempy AS INTEGER, column AS INTEGER, colour AS INTEGER)
DECLARE SUB samplle (temp AS INTEGER, tempy AS INTEGER, column AS INTEGER, colour AS INTEGER)
DECLARE SUB sampledata()
DECLARE SUB printlayers (startlayer AS INTEGER, endlayer AS INTEGER, pagenum AS INTEGER)
DECLARE SUB optline (temp AS INTEGER, tempy AS INTEGER, colour AS INTEGER)
DECLARE SUB outputsdata()
DECLARE SUB deletemat (pointer AS INTEGER)
DECLARE SUB printmats (xlim!, ylim AS INTEGER)
DECLARE SUB inputkeys (length AS INTEGER, x AS INTEGER, y AS INTEGER, text$)
DECLARE SUB helptxtl()
DECLARE SUB openmainwindow (colour AS INTEGER)
DECLARE SUB closemainwindow()
DECLARE SUB opticalcnssts (pointer AS INTEGER)
DECLARE SUB selectmat()
DECLARE SUB inputdata()
DECLARE SUB clearhelpwindow()
DECLARE SUB saveplotdata (endofdata AS INTEGER)
DECLARE SUB Rcoeff (j AS INTEGER, b AS ANY)
DECLARE SUB adval (j AS INTEGER, b AS ANY)
DECLARE SUB Fcoeff (j AS INTEGER, b AS ANY)
DECLARE SUB gval (j AS INTEGER, b AS ANY)
DECLARE SUB multiplycomplex (A AS ANY, b AS ANY, c AS ANY)
DECLARE SUB divcomplex (A AS ANY, b AS ANY, c AS ANY)
DECLARE SUB addcomplex (A AS ANY, b AS ANY, sign AS INTEGER, c AS ANY)
DECLARE SUB sgtntcomplex (A AS ANY, b AS ANY)
DECLARE SUB menuposoff (current AS INTEGER)
DECLARE SUB menuposon (current AS INTEGER)
DECLARE SUB menubar()

TYPE complex

realpart AS DOUBLE
imaginary AS DOUBLE

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END TYPE

TYPE fourdimen
  x AS DOUBLE
  y AS DOUBLE
  real AS DOUBLE
  imag AS DOUBLE
END TYPE

TYPE opt
  delta AS DOUBLE
  beta AS DOUBLE
END TYPE

DIM SHARED delta(200) AS DOUBLE
DIM SHARED beta(200) AS DOUBLE
DIM SHARED dlayer(200) AS DOUBLE
DIM SHARED sigma(200) AS SINGLE
DIM SHARED plotdata(1200) AS fourdimen
DIM SHARED theta AS DOUBLE
DIM SHARED m AS INTEGER  ' m is substrate layer no.
DIM A(10) AS complex
DIM b(10) AS complex
DIM c(10) AS complex
DIM d(10) AS complex
DIM SHARED g(100) AS complex
DIM temp AS complex
DIM j AS INTEGER
DIM refl AS complex
DIM pn AS INTEGER
DIM intensity AS DOUBLE
DIM SHARED optcnst(2400) AS opt 'stores delta and beta vals in blocks of 20 per material, i.e. 0-19 belong to material 1 etc.
DIM SHARED lambdalib(2400) AS SINGLE 'stores lambda vals. in blocks of 20 per material corresponding to delta and beta values above
DIM SHARED matname$(120) 'stores names of materials
DIM SHARED lastmat AS INTEGER  'number of materials stored
DIM SHARED layertype(200) AS INTEGER ' stores pointer to matname$ for layers no.
  ' 1 (surface) to m (substrate)

CONST pi = 3.1415926535897#

DIM SHARED lambda AS SINGLE
DIM SHARED startheta AS DOUBLE
DIM SHARED endtheta AS DOUBLE
DIM SHARED steptheta AS DOUBLE

DIM SHARED menu$(2, 7)
DIM SHARED dir$
DIM SHARED usererror AS INTEGER  'set by program to flag user error

menu$(1, 0) = " Scan": menu$(2, 0) = " param's"
menu$(1, 1) = " Optical": menu$(2, 1) = " const's"
menu$(1, 2) = " Sample": menu$(2, 2) = " param's"
menu$(1, 3) = " Interface": menu$(2, 3) = " param's"
menu$(1, 4) = " Begin": menu$(2, 4) = " calc."
menu$(1, 5) = " Replot": menu$(2, 5) = " curve"
menu$(1, 6) = " Save": menu$(2, 6) = " curve"
matname$(0) = "******"

CALL startup
'CALL teststack(0)

CALL inputdata
'CALL newsample

KEY(8) ON
CALL notinuse

ON KEY(1) GOSUB 10
ON KEY(2) GOSUB 20
ON KEY(3) GOSUB 30
ON KEY(4) GOSUB 40
ON KEY(5) GOSUB 50
ON KEY(6) GOSUB 60
ON KEY(7) GOSUB 70
ON KEY(8) GOSUB 80

5 GOTO 5

10 "FUNCTION KEY 1 PRESSED"
CALL inuse
CALL scandata
CALL notinuse
CALL abouttext
RETURN

20 "FUNCTION KEY 2 PRESSED"
CALL inuse
CALL selectmat
CALL notinuse
CALL abouttext
RETURN

30 "FUNCTION KEY 3 PRESSED"
CALL inuse
CALL sampledata
CALL notinuse
CALL abouttext
RETURN

40 "FUNCTION KEY 4 PRESSED"
CALL inuse
CALL interfacedata
CALL notinuse
CALL abouttext
RETURN

60 "FUNCTION KEY 6 PRESSED"
CALL inuse
CALL replotdata(pn - 1)
CALL notinuse
CALL abouttext
RETURN

70 "FUNCTION KEY 7 PRESSED"
CALL inuse
CALL saveplotdata(pn - 1)
CALL notinuse
CALL abouttext
RETURN

80 "FUNCTION KEY 12 PRESSED"
CALL outputdata
VIEW (0, 0)-(639, 349), 1
END

50 "FUNCTION KEY 5 PRESSED"
CALL iinuse
IF layertype(1) <> 0 THEN CALL begincalc 'check sample data entered
IF layertype(1) = 0 THEN usererror = 2

IF usererror <> 0 THEN CALL checkerrors(usererror): RETURN

CALL outputdata
CALL menuposon(4)
CALL clearhelpwindow
VIEW (1, 65)-(492, 340), 10, 15

'**** MAIN LOOP (calculate reflectivity as function of theta)****

lambda = lambda * 1E-08 'set lambda in cm for calculation
pn = 0 ' pointer to store position in array plotdata
CALL displayscan
COLOR 2, 1
LOCATE 9, 68: PRINT USING "##.####"; lambda * 1E+08
COLOR 15, 1
LOCATE 14, 66: PRINT "[current]"

' initial x position, xpnt2
xpnt2 = 0
theta = starttheta
tmpkey$ = ""

DO WHILE tmpkey$ <> CHR$(27) AND theta < endtheta
  tmpkey$ = INKEY$
  LOCATE 15, 68: PRINT USING "##.####"; 2 * theta * (180 / pi)

  CALL Rcoeff(O, refl)
  intensity = (refl.realpart * refl.realpart + refl.imaginary * refl.imaginary)

  pnt = -30 * (LOG(intensity) * .434294)
  pnt = INT(pnt)
  IF theta = starttheta THEN pnt2 = pnt
  xpnt = INT(theta * xscale) - INT(starttheta * xscale)

  plotdata(pn).x = 2 * (theta * 180 / pi)
  plotdata(pn).y = intensity
  plotdata(pn).real = refl.realpart
  plotdata(pn).imag = refl.imaginary

  LINE (xpnt - 1, pnt - 1)-(xpnt + 1, pnt + 1), 12, B
  LINE (xpnt2, pnt2)-(xpnt, pnt), 11

  xpnt2 = xpnt: pnt2 = pnt
  pn = pn + 1
  theta = theta + steptheta

LOOP ' **end of loop

CALL menuposoff(4)

lambda = lambda * 1E+08

pnt2 = 0: xpnt2 = 0
CALL clearhelpwindow
CALL notinuse
CALL abouttext
RETURN

SUB a4val (j AS INTEGER, b AS complex)
' Derives the value of a(j) to the 4th power

STATIC temp AS DOUBLE

temp = (4 * pi * dlayer(j)) / lambda
CALL gval(j, g(j))
b.realpart = (EXP(temp * g(j).imaginary)) * COS(temp * g(j).realpart)
b.imaginary = -1 * (EXP(temp * g(j).imaginary)) * SIN(temp * g(j).realpart)

END SUB

SUB abouttext

CALL clearhelpwindow

COLOR 15, 1
LOCATE 8, 66: PRINT " XREALM"
LOCATE 10, 66: PRINT " Ver 1.2"
LOCATE 12, 66: PRINT "(c) 1997 NDT"
LOCATE 20, 66: PRINT " F 8 - Exit"

END SUB

SUB addcomplex (A AS complex, b AS complex, sign AS INTEGER, c AS complex)

' Adds or subtracts the complex numbers a and b depending on
' whether sign is -1 (for subtraction) or +1 (for addition)
' setting sign to integer other than 1, gives e.g. a-2b etc.

STATIC tempb AS complex

tempb.realpart = b.realpart * sign
tempb.imaginary = b.imaginary * sign

c.realpart = A.realpart + tempb.realpart
    c.imaginary = A.imaginary + tempb.imaginary

END SUB

SUB addlayer (pointer AS INTEGER)

' Add new layer to sample

STATIC temp AS INTEGER

FOR temp = m + 1 TO pointer + 1 STEP -1
    layertype(temp) = layertype(temp - 1)
NEXT temp

m = m + 1

END SUB

SUB begincalc

STATIC templp AS INTEGER
STATIC findlam AS INTEGER
STATIC range AS INTEGER

' first clear previous delta and beta values

FOR templp = 1 TO m
    delta(templp) = 0
    beta(templp) = 0
NEXT templp

' now search each layertype at position templp for constants
' at set value of lambda using range to search correct part
' of optcnsst array

FOR templp = 1 TO m
    range = 20 * (layertype(templp) - 1)

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FOR findlam = 0 TO 19
IF lambdalib(findlam + range) = lambda THEN
    delta(templp) = optcnst(findlam + range).delta
    beta(templp) = optcnst(findlam + range).beta
END IF
NEXT findlam
IF delta(templp) = 0 AND usererror = 0 THEN usererror = 1
NEXT templp
END SUB

SUB checkerrors (errorcode AS INTEGER)
' Checks errorcode sent by program against list of actions.
' If errorcode sent is zero, checkerrors assumes no errors
IF errorcode <> 0 THEN
    CALL clearmainwindow(10)
    LINE (100, 140)-(400, 240), 1, BF
END IF
IF errorcode = 2 THEN
    LOCATE 13, 17: PRINT "No sample data has been entered"
END IF
IF errorcode = 1 THEN
    LOCATE 12, 17: PRINT "Constant missing for selected lambda. Use F2 to edit values"
    LOCATE 14, 17: PRINT "lambda.
END IF
IF errorcode <> 0 THEN
    LOCATE 16, 17: PRINT "anykey$ = anykey$ = anykey$ = INKEY$
    LOOP
END IF
CALL clearmainwindow(10)
CALL notinuse
errorcode = 0
END SUB
SUB clearhelpwindow
VIEW SCREEN (500, 65)-(638, 340), 1, 15
END SUB
SUB clearmainwindow (colour AS INTEGER)
VIEW SCREEN (1, 65)-(492, 340), colour, 15
END SUB
SUB closemainwindow
STATIC A, c AS INTEGER
VIEW SCREEN (1, 65)-(492, 340), 10, 15
c = 330
'FOR a = 300 TO 60 STEP -6
'c = c - 3
'LINE (480 - a / 6, c / 3)-(a + a / 6, c - c / 3), 15, B
'LINE (480 - (a + 6) / 6, (c + 3) / 3)-((a + 6) - (a + 6) / 6, (c + 3) - (c + 3) / 3), 10, B
'NEXT a
VIEW SCREEN (1, 65)-(492, 340), 10, 15
SUB deletelayers (pointer AS INTEGER, markerpos AS INTEGER)

STATIC A$
STATIC temp AS INTEGER
clearhelpwindow
COLOR 15, 1
LOCATE 7, 67: PRINT "***DELETE***"
LOCATE 9, 66: PRINT "Press '"(del)"'
LOCATE 11, 66: PRINT "to clear all"
LOCATE 14, 66: PRINT "any other key"
LOCATE 16, 66: PRINT "to remove only"
LOCATE 18, 66: PRINT "highlighted"
LOCATE 20, 66: PRINT "layers"
A$ = ""
DO WHILE A$ = ""
A$ = INKEY$
END IF
clearhelpwindow
END SUB

SUB deletemat (pointer AS INTEGER)
' Deletes material from list and shifts all others up to compensate
STATIC temp AS INTEGER
FOR temp = pointer TO lastmat
  matname$(temp) = matname$(temp + 1)
NEXT temp
lastmat = lastmat - 1
END SUB

SUB displayscan
COLOR 15, 1
LOCATE 7, 66: PRINT "Lambda (angs)"
LOCATE 12, 66: PRINT "2-theta (deg)"
LOCATE 14, 66: PRINT "[start]"
LOCATE 17, 66: PRINT "[finish]"
LOCATE 20, 66: PRINT "[step size]"

COLOR 3, 1

LOCATE 9, 68: PRINT USING "##.###"; lambda
LOCATE 15, 68: PRINT USING "##.##"; 2 * starttheta * (180 / pi)
LOCATE 18, 68: PRINT USING "##.##"; 2 * endtheta * (180 / pi)
LOCATE 21, 68: PRINT USING "##.##"; 2 * steptheta * (180 / pi)

END SUB

SUB divcomplex (A AS complex, b AS complex, c AS complex)
' Divides complex numbers a and b and returns c=a/b

STATIC denom AS DOUBLE

denom = b.realpart * b.realpart + b.imaginary * b.imaginary

c.realpart = (A.realpart * b.realpart + A.imaginary * b.imaginary) / denom

c.imaginary = (b.realpart * A.imaginary - A.realpart * b.imaginary) / denom

END SUB

SUB Fcoeff (j AS INTEGER, b AS complex)
' Derives the Fresnel reflection co-eff. between layers j and j+1
' (in doing so, uses gval to set g(j) and g(j+1) )

STATIC top AS complex
STATIC bottom AS complex
STATIC temp AS DOUBLE

CALL gval(j, g(j))
CALL gval(j + 1, g(j + 1))
CALL addcomplex(g(j), g(j + 1), -1, top)
CALL addcomplex(g(j), g(j + 1), 1, bottom)
CALL divcomplex(top, bottom, b)

var temp = (pi * sigma(j) * SIN(theta)) / lambda

b.realpart = b.realpart * EXP(-16 * temp * temp)
b.imaginary = b.imaginary * EXP(-16 * temp * temp)

END SUB

SUB gval (j AS INTEGER, b AS complex)
' Derives the value of g(j) and returns it as complex number b

STATIC A AS complex

A.realpart = theta * theta - 2 * delta(j)
A.imaginary = -2 * beta(j)
CALL sqrtcomplex(A, b)

END SUB

SUB helptxt1
' Help text message 1 in help window

COLOR 15, 1

LOCATE 7, 67: PRINT "Use keys ;"
LOCATE 9, 67: PRINT " 8 
" LOCATE 11, 67: PRINT " 4 6"
LOCATE 13, 67: PRINT " 2"
LOCATE 15, 67: PRINT " to move"
LOCATE 18, 67: PRINT "'Enter' to "
LOCATE 19, 67: PRINT "'edit"'
LOCATE 22, 67: PRINT "'+/-' to"
LOCATE 23, 67: PRINT "'add/delete"
SUB inputdata
' loads data from disk

STATIC f AS INTEGER
STATIC h AS INTEGER

CHDIR "c:/xrealm"

OPEN "optdata.dat" FOR INPUT AS #1

INPUT #1, lastmat
FOR f = 1 TO lastmat
   INPUT #1, matname$(f)
   FOR h = 0 TO 19
      INPUT #1, optcnst(h + (f - 1) * 20).delta, optcnst(h + (f - 1) * 20).beta
   NEXT h
NEXT f
CLOSE

OPEN "sample.dat" FOR INPUT AS #2

INPUT #2, m
FOR f = 1 TO m
   INPUT #2, dlayer(f)
   INPUT #2, layertype(f)
   INPUT #2, sigma(f)
NEXT f
CLOSE

IF dir$ <> "" THEN CHDIR dir$

END SUB

SUB inputkeys (length AS INTEGER, x AS INTEGER, y AS INTEGER, text$)
' reads data from keyboard and returns string text$ of 'length'

STATIC temp$ STATIC textpos AS INTEGER 'position of text cursor

temp$ = "" text$ = ""
FOR textpos = 1 TO length 'this loop is required for MID$
   text$ = text$ + " "
   NEXT textpos

COLOR 15, 1

textpos = 1
LOCATE y, x: PRINT "*"

DO UNTIL temp$ = CHR$(13)
   COLOR 12, 1: LOCATE y, x + (textpos - 1): PRINT CHR$(219): COLOR 15, 1
   temp$ = ""
   DO WHILE temp$ = "".
      temp$ = INKEY$
   LOOP
   IF temp$ = CHR$(8) AND textpos > 1 THEN
      textpos = textpos - 1
      MID$(text$, textpos) = " "
      LOCATE y, x: PRINT text$; " "
   END IF
   IF temp$ <> CHR$(8) AND textpos < length + 1 AND temp$ <> CHR$(13) THEN
      MID$(text$, textpos, 1) = temp$
      LOCATE y, x: PRINT text$; " "
      textpos = textpos + 1
   END IF
END IF

LOOP
LOCATE y, x + (textpos - 1): PRINT " " 'remove '*' text$ = MID$(text$, 1, textpos - 1) 'remove extra trailing spaces END SUB

SUB interfacedata

STATIC temp$
STATIC tmplp
CALL clearmainwindow(1)
CALL menuposon(3)

LOCATE 8, 5: PRINT "Enter rms surface roughness value (angs)"
CALL inputkeys(5, 5, 10, temp$)

CALL clearmainwindow(1)

IF UCASE$(temp$) = "LIN" THEN CALL templinvar
sigma(0) = VAL(temp$) * 1E-08

'FOR tmplp = 1 TO m - 1
'sigma(tmplp) = VAL(temp$) * 1E-08
'NEXT tmplp

CALL plotinterface

A$ = ""
DO WHILE A$ <> CHR$(27)
A$ = ""
DO WHILE A$ = "n"
A$ = INKEY$
LOOP

CALL clearmainwindow(10)
CALL menuposoff(3)

END SUB

SUB inuse

' Sets all functions keys other than current to OFF

STATIC templp AS INTEGER

FOR templp = 1 TO 7
KEY(templp) OFF
NEXT templp

END SUB

SUB menubar

' Draws the menubar at the top of the screen

STATIC temp AS INTEGER

FOR temp = 2 TO 9
PALETTE temp, 63
NEXT temp

PALETTE 10, 0
VIEW SCREEN (0, 0)-(639, 349), 10, 10

FOR f = 0 TO 6
COLOR f + 2, 1
LINE (6 + f * 88, 9)-(88 + f * 88, 60), f + 2, B
PAINT (10 + f * 88, 10), 1, f + 2
LOCATE 2, 2 + f * 11: PRINT menu$(1, f)
LOCATE 3, 2 + f * 11: PRINT menu$(2, f)
'LOCATE 2, 2 + f * 11: PRINT "text tests"
'LOCATE 3, 2 + f * 11: PRINT "like these"
LOCATE 4, 5 + f * 11: PRINT "f"; f + 1

NEXT f
END SUB

SUB menuposoff (current AS INTEGER)

STATIC temp AS INTEGER
FOR temp = 0 TO 6
PALETTE temp + 2, 63
NEXT temp
END SUB

SUB menuposon (current AS INTEGER)

STATIC temp AS INTEGER
FOR temp = 0 TO 6
IF temp <> current THEN PALETTE temp + 2, 7 ELSE PALETTE temp + 2, 63
NEXT temp
END SUB

SUB multiplycomplex (A AS complex, b AS complex, c AS complex)
'Multiplies complex numbers a and b and returns c = a/b

c.realpart = A.realpart * b.realpart - A.imaginary * b.imaginary
C.imaginary = A.realpart * b.imaginary + b.realpart * A.imaginary
END SUB

SUB newsample
'clears all sample parameters and sets to initial values

STATIC temp AS INTEGER
FOR temp = 0 TO 200
layertype(temp) = 0
dlayer(temp) = 0
sigma(temp) = 0
NEXT temp
m = 1
END SUB

SUB notinuse
' sets all function keys on

STATIC temp1p AS INTEGER
FOR temp1p = 1 TO 7
KEY(temp1p) ON
NEXT temp1p
END SUB

SUB openmainwindow (colour AS INTEGER)

STATIC A, c AS INTEGER
VIEW SCREEN (1, 65)-(492, 340), 10, 15
c = 90
FOR A = 60 TO 300 STEP 6
C = c + 3
LINE (-80 + A / 6, c / 3)-(A + A / 6, c + c / 3), 15, B
LINE (-80 + (A - 6) / 6, (c - 3) / 3)-(A - 6) / 6, (c - 3) + (c - 3) / 3), 10, B
NEXT A

VIEW SCREEN (1, 65)-(492, 340), colour, 15
END SUB

SUB opticalcnsts (pointer AS INTEGER)
' Edit/add optical constants
STATIC A$, temp$
STATIC tmp AS INTEGER, tempy AS INTEGER, lastwav AS INTEGER
STATIC deloop, firstwav AS INTEGER
CALL printopts(pointer, lastwav)
tmp = (pointer - 1) * 20
temy = 10
CALL optline(tmp, tempy, 15)
A$ = ""
DO WHILE A$ <> CHR$(27)
A$ = ""
DO WHILE A$ = ""
A$ = INKEY$
LOOP
IF A$ = "8" AND tempy > 10 THEN
CALL optline(tmp, tempy, 2)
temy = tempy - 1: tmp = tmp - 1
CALL optline(tmp, tempy, 15)
END IF
IF A$ = "2" AND tempy < (10 + (lastwav - ((pointer - 1) * 20))) THEN
CALL optline(tmp, tempy, 2)
temy = tempy + 1: tmp = tmp + 1
CALL optline(tmp, tempy, 15)
END IF
IF (lastwav - ((pointer - 1) * 20)) < 14 THEN firstwav = 1
IF lambdalib((pointer - 1) * 20) = 0 THEN firstwav = 0
IF A$ = "0" THEN
CALL optline(tmp, tempy, 2)
lastwav = lastwav + firstwav
tempy = 10 + (lastwav - ((pointer - 1) * 20))
tmp = lastwav
CALL inputkeys(6, 5, tempy, temp$
> lambdalib(lastwav) = VAL(temp$
> CALL inputkeys(11, 25, tempy, temp$
> optcnst(lastwav).delta = VAL(temp$
> CALL inputkeys(11, 44, tempy, temp$
> optcnst(lastwav).beta = VAL(temp$
> CALL printopts(pointer, lastwav)
temy = 10
tmp = (pointer - 1) * 20
CALL optline(tmp, tempy, 15)
END IF
IF A$ = "." AND lastwav > 0 THEN
FOR deloop = tmp TO lastwav - 1
lambdalib(deloop) = lambdalib(deloop + 1)
optcnst(deloop) = optcnst(deloop + 1)
NEXT deloop
lambdalib(lastwav) = 0
optcnst(lastwav).delta = 0
optcnst(lastwav).beta = 0
tmp = (pointer - 1) * 20
temy = 10
CALL printopts(pointer, lastwav)
CALL optline(tmp, tempy, 15)
END IF
LOOP
END SUB

SUB optline (temp AS INTEGER, tempy AS INTEGER, colour AS INTEGER)
'print line of optical cnsts data in colour
COLOR colour, 1
LOCATE tempy, 4: PRINT USING "##.#####"; lambdalib(temp)
LOCATE tempy, 24: PRINT USING "##.#####"; optcnst(temp).delta
LOCATE tempy, 43: PRINT USING "##.#####"; optcnst(temp).beta
END SUB

SUB outputdata
' saves data to disk
STATIC f AS INTEGER
STATIC h AS INTEGER
CHDIR "c:\xrealm"
OPEN "optdata.dat" FOR OUTPUT AS #1
WRITE #1, lastmat
FOR f = 1 TO lastmat
    WRITE #1, matname$(f)
    FOR h = 0 TO 19
        WRITE #1, optcnst(h + (f - 1) * 20).delta,
        WRITE #1, optcnst(h + (f - 1) * 20).beta
    NEXT h
NEXT f
CLOSE

OPEN "sample.dat" FOR OUTPUT AS #2
WRITE #2, m
FOR f = 1 TO m
    WRITE #2, dlayer(f)
    WRITE #2, layertype(f)
    WRITE #2, sigma(f)
NEXT f
WRITE #2, dir$
CLOSE
IF dir$ <> "" THEN CHDIR dir$
END SUB

SUB plotinterface
STATIC plotx AS INTEGER
LINE (40, 180)-(40, 301), 12
LINE (40, 301)-(450, 301), 12
FOR plotx = 1 TO m - 1
    LINE (plotx * 10 + 40, 300 - (1.2E+09 * sigma(plotx)))-(plotx * 10 + 45, 300), 2, BF
NEXT plotx
COLOR 12, 1
LOCATE 13, 2: PRINT "rms roughness"
LOCATE 23, 50: PRINT "interface"
END SUB
SUB printlayers (startlayer AS INTEGER, endlayer AS INTEGER, pagenum AS INTEGER)

CALL clearmainwindow(1)
STATIC temp AS INTEGER

' calc. current page number (pagenum) from startlayer
pagenum = FIX(startlayer / 17) 'pagenum has first page = 0

IF (m − startlayer) < 17 THEN
  endlayer = (m − startlayer) + 1 'last layer to be displayed
ELSE endlayer = 17
END IF

COLOR 15, 1
LOCATE 6, 4: PRINT "Layer"
LOCATE 6, 15: PRINT "Material"
LOCATE 6, 27: PRINT "Thickness (angs)"
LOCATE 6, 47: PRINT "D\textsuperscript{2}rms (angs)"
COLOR 2, 1
FOR temp = 1 TO endlayer
  IF (temp + startlayer) − 1 <> m THEN
    CALL sampline(temp + (17 * pagenum), temp + 7, 0, 2)
  END IF
NEXT temp

IF (endlayer + startlayer) − 1 = m THEN
  CALL sampline(m, endlayer + 7, 0, 2)
  LOCATE endlayer + 7, 28: PRINT "SUBSTRATE"
  LOCATE endlayer + 7, 49: PRINT " "
END IF

END SUB

SUB printmats (xlim, ylim AS INTEGER)
' Prints materials list and defines x and y limits to columns and rows
STATIC tempx, tempy, pointer AS INTEGER

CALL clearmainwindow(1)
COLOR 15, 1
LOCATE 6, 14: PRINT "Materials / library spaces available"
LINE (100, 85) − (395, 85), 15
COLOR 2, 1

' first determine limits of grid data with lastmat entries
IF lastmat / 17 <> FIX(lastmat / 17) THEN
  xlim = FIX(lastmat / 17) + 1 '17 entries in each column
ELSE xlim = INT(lastmat / 17)
END IF

ylim = (lastmat) − (17 * (xlim − 1))
' having calc. no. of rows and columns, now calc. co-ords

xlim = ((xlim − 1) * 8) + 4 'columns start at 4, and are 8 wide
ylim = ylim + 7 'rows start at 8

' xlim, ylim is now the co-ord. of the lastmat entered

' print grid data
pointer = 1
FOR tempx = 4 TO 52 STEP 8
  FOR tempy = 8 TO 24
    LOCATE tempy, tempx: PRINT matname$(pointer)
    pointer = pointer + 1
  NEXT tempy
NEXT tempx

END SUB
SUB printopts (pointer AS INTEGER, lastwav AS INTEGER)

STATIC temp, f AS INTEGER

CALL clearmainwindow(1)

' Calc. position of last wavelength entered for this material
lastwav = 20 * (pointer - 1)
DO UNTIL lambdaLib(lastwav + 1) = 0 AND lambdaLib(lastwav + 2) = 0
  lastwav = lastwav + 1
LOOP

CALL sortoptdata((pointer - 1) * 20, lastwav)

' Print optical constants for current material
COLOR 15, 1
LOCATE 6, 4: PRINT "Optical constants for "; matname$(pointer); ":";
LOCATE 8, 4: PRINT "Wavelength(A) "; delta "; beta"
COLOR 2, 1
f = 10
FOR temp = (pointer - 1) * 20 TO lastwav
  LOCATE f, 4: PRINT USING "##.####"; lambdaLib(temp)
  LOCATE f, 24: PRINT USING "##.####"; optcnst(temp).delta
  LOCATE f, 43: PRINT USING "##.####"; optcnst(temp).beta
  f = f + 1
NEXT

END SUB

SUB Rcoeff (j AS INTEGER, b AS complex)

' Calculates the reflectivity co-effs. recursively
STATIC templ AS complex
STATIC temp2 AS complex
STATIC temp3 AS complex
STATIC top AS complex
STATIC bottom AS complex
STATIC quotient AS complex
STATIC a4 AS complex

IF j + 1 = m THEN temp2.realpart = 0; temp2.imaginary = 0

IF j + 1 < m THEN CALL Rcoeff(j + 1, temp2)
CALL Pcoeff(j, templ)
CALL multiplycomplex(templ, temp2, temp3)
CALL addcomplex(templ, temp2, 1, top)
bottom.realpart = temp3.realpart + 1
bottom.imaginary = temp3.imaginary
CALL divcomplex(top, bottom, quotient)
CALL a4val(j, a4)
CALL multiplycomplex(a4, quotient, b)

END SUB

SUB repeatlayers (pointer AS INTEGER, repeatpos AS INTEGER)

STATIC temp$ STATIC tmplpl AS INTEGER
STATIC temppl2 AS INTEGER
STATIC numnew AS INTEGER

CALL clearhelpwindow

COLOR 15, 1
LOCATE 7, 66: PRINT "Repeat how"
LOCATE 8, 66: PRINT "many times?"
CALL inputkeys(4, 66, 10, temp$)

numnew = (repeatpos - pointer + 1) * (VAL(temp$) - 1)
FOR tmplp1 = m TO pointer STEP -1         'first move existing layers
layertype(tmplp1 + numnew) = layertype(tmplp1)
dlayer(tmplp1 + numnew) = dlayer(tmplp1)
sigma(tmplp1 + numnew) = sigma(tmplp1)
NEXT tmplp1
FOR tmplp2 = 0 TO numnew - 1 STEP (repeatpos - pointer + 1)
FOR tmplp1 = pointer TO repeatpos
layertype(tmplp2 + tmplp1) = layertype(numnew + tmplp1)
dlayer(tmplp2 + tmplp1) = dlayer(numnew + tmplp1)
sigma(tmplp2 + tmplp1) = sigma(numnew + tmplp1)
NEXT tmplp1
NEXT tmplp2
m = m + numnew
CALL clearhelpwindow
END SUB

SUB replotdata (lastpoint)
' Replots current curve within scan parameters set by F1

STATIC tmplp AS INTEGER
STATIC xpnt AS DOUBLE
STATIC xpntprev AS DOUBLE
STATIC ypnt AS DOUBLE
STATIC ypntprev AS DOUBLE
STATIC tempx AS DOUBLE
STATIC tempxprev AS DOUBLE
STATIC range AS DOUBLE
STATIC A$;

CALL clearhelpwindow
CALL displayscan
VIEW (1, 65)-(492, 340), 10, 15
CALL menuposon(5)

COLOR 2, 1
LOCATE 9, 68: PRINT USING "###.###": lambda
COLOR 15, 1

FOR tmplp = 1 TO lastpoint
    ypnt = INT(-30 * (LOG(plotdata(tmplp).y) * .434294))
    ypntprev = INT(-30 * (LOG(plotdata(tmplp - 1).y) * .434294))
    tempx = plotdata(tmplp).x - (starttheta * 360 / pi)
    tempxprev = plotdata(tmplp - 1).x - (starttheta * 360 / pi)
    range = (245 / ((endtheta - starttheta) * 180 / pi))
    xpnt = range * tempx
    xpntprev = range * tempxprev
    LINE (xpnt - 1, ypnt - 1)-(xpnt + 1, ypnt + 1), 12, B
    LINE (xpntprev, ypntprev)-(xpnt, ypnt), 11
NEXT tmplp

A$ = ""
DO WHILE A$ <> CHR$(27)
    A$ = INKEY$
LOOP
clearhelpwindow
menuposoff (5)
END SUB

SUB sampledata
' Edit/Add sample parameters

CALL menuposon(2)
CALL openmainwindow(1)
CALL clearhelpwindow

STATIC lastlayer AS INTEGER
STATIC pointer AS INTEGER
STATIC markerpos AS INTEGER
STATIC ypos AS INTEGER
STATIC pagenum AS INTEGER
STATIC column AS INTEGER
STATIC temp AS INTEGER
STATIC A$
STATIC tmp$

CALL printlayers(1, lastlayer, pagenum) 'print first 17 layers (or less if m+1<17)

column = 1; ypos = 8; pointer = 1; markerpos = 0
CALL sampline(pointer, ypos, column, 15)
A$ = ""
DO WHILE A$ <> CHR$(27)
A$ = ""
DO WHILE A$ = ""
A$ = INKEY$
LOOP

IF A$ <> "1" AND A$ <> "7" AND A$ <> "*" AND A$ <> "." AND markerpos > pointer - 1 THEN
CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
pointer = markerpos
ypos = (pointer - (pagenum * 17)) + 7
CALL sampline(pointer, ypos, column, 15)
markerpos = 0
END IF

IF A$ = "6" AND column < 3 AND pointer <> m THEN
CALL sampline(pointer, ypos, column, 2)
column = column + 1
CALL sampline(pointer, ypos, column, 15)
A$ = ""
END IF

IF A$ = "4" AND column > 1 AND pointer <> m THEN
CALL sampline(pointer, ypos, column, 2)
column = column - 1
'CALL sampline(pointer, ypos, column, 15)
A$ = ""
END IF

IF A$ = "2" AND pointer + 1 = m THEN
'force to column 1 before
CALL sampline(pointer, ypos, column, 2)
'moving down to layer m
' in next 'if' statement
column = 1
END IF

IF A$ = "2" AND ypos < lastlayer + 7 THEN
CALL sampline(pointer, ypos, column, 2)
pointer = pointer + 1
ypos = ypos + 1
CALL sampline(pointer, ypos, column, 15)
A$ = ""
END IF

IF A$ = "2" AND ypos = lastlayer + 7 AND pointer <> m THEN
pointer = pointer + 1
ypos = 8
CALL printlayers(pointer, lastlayer, pagenum)
CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "8" AND ypos > 8 THEN
CALL sampline(pointer, ypos, column, 2)
pointer = pointer - 1

ypos = ypos - 1
CALL sampline(pointer, ypos, column, 15)
A$ = ""

END IF

IF A$ = "8" AND ypos = 8 AND pointer > 17 THEN
    pointer = pointer - 1
    ypos = 24
    CALL printlayers(pointer - 16, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "3" AND (pagenum * 17) + 18 = m THEN
    'force to column 1 before
    'moving down to next page
    column = 1
    pointer = ((pagenum - 1) * 17) + 1
    ypos = 8
    CALL printlayers(pointer, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "3" AND pointer > 17 THEN
    pointer = ((pagenum + 1) * 17) + 1
    ypos = 8
    CALL printlayers(pointer, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "9" AND m < 500 AND layertype(pointer) <> 0 THEN
    CALL addlayer(pointer)
    layer(pointer) = 0
    layertype(pointer) = 0
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    DO WHILE layertype(pointer) = 0
        LOCATE ypos, 16: PRINT " 
        CALL inputkeys(6, 16, ypos, tmp$)
        FOR temp = 1 TO lastmat
            IF UCASE$(matname$(temp)) = UCASE$(tmp$) THEN
                layertype(pointer) = temp
            END IF
        NEXT temp
    LOOP
    DO WHILE VAL(tmp$) = 0
        LOCATE ypos, 30: PRINT ..
        CALL inputkeys(6, 30, ypos, tmp$)
        layer(pointer) = VAL(tmp$) * 1E-08
    LOOP
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "9" AND m = 1 THEN
    DO WHILE layertype(pointer) = 0
        LOCATE ypos, 16: PRINT " 
        CALL inputkeys(6, 16, ypos, tmp$)
        FOR temp = 1 TO lastmat
            IF UCASE$(matname$(temp)) = UCASE$(tmp$) THEN
                layertype(pointer) = temp
            END IF
        NEXT temp
    LOOP
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = CHR$(13) AND column = 1 THEN
    tmp$ = ""
    DO WHILE tmp$ = ""
        LOCATE ypos, 16: PRINT " 
        CALL inputkeys(6, 16, ypos, tmp$)
        FOR temp = 1 TO lastmat
            IF UCASE$(matname$(temp)) = UCASE$(tmp$) THEN
                layertype(pointer) = temp
            END IF
        NEXT temp
    LOOP
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF
IF UCASE$(matname$(temp)) = UCASE$(tmp$) THEN
    layertype(pointer) = temp
    NEXT temp
END IF

IF A$ = CHR$(13) AND column = 2 THEN
    tmp$ = ""
    DO WHILE VAL(tmp$) = 0
        LOCATE ypos, 30: PRINT " "
        CALL inputkeys(6, 30, ypos, tmp$)
        dlayer(pointer) = VAL(tmp$) * 1E-08
        LOOP
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = CHR$(13) AND column = 3 THEN
    tmp$ = ""
    DO WHILE VAL(tmp$) = 0
        LOCATE ypos, 48: PRINT " "
        CALL inputkeys(6, 51, ypos, tmp$)
        sigma(pointer) = VAL(tmp$) * 1E-08
        LOOP
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "1" AND pointer <> m AND markerpos < m - 1 AND markerpos < (pagenum + 1) * 17 THEN
    markerpos = markerpos + 1
    CALL sampline(pointer, ypos, 0, 15)
    CALL sampline(markerpos, ypos + (markerpos - pointer), 0, 15)
END IF

IF A$ = "7" AND markerpos > pointer THEN
    CALL sampline(pointer, ypos, 0, 15)
    CALL sampline(markerpos, ypos + (markerpos - pointer), 0, 2)
    markerpos = markerpos - 1
END IF

IF A$ = "*" AND markerpos > 0 THEN
    CALL repeatlayers(pointer, markerpos)
    pointer = 1: ypos = 8: markerpos = 0
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
END IF

IF A$ = "." THEN
    CALL deletelayers(pointer, markerpos)
    ypos = (pointer + 7) - (pagenum * 17): column = 1
    CALL printlayers((pagenum * 17) + 1, lastlayer, pagenum)
    CALL sampline(pointer, ypos, column, 15)
    markerpos = pointer - 1
END IF

IF A$ <> "1" AND A$ <> "7" THEN markerpos = pointer - 1
LOOP
    CALL menuposoff(2)
    CALL clearmainwindow(10)
END SUB

SUB sampline (temp AS INTEGER, tempy AS INTEGER, column AS INTEGER, colour AS INTEGER)
    ' prints line in sample data with 'colour'
    COLOR colour, 1
LOCATE tempy, 5: PRINT temp

IF column = 2 OR column = 0 THEN
   LOCATE tempy, 28: PRINT USING "####.###": dlayer(temp) * 1E+08
END IF

IF column = 1 OR column = 0 THEN
   LOCATE tempy, 16: PRINT matname$(layertype(temp))
END IF

IF column = 3 OR column = 0 THEN
   LOCATE tempy, 48: PRINT USING "####.###": sigma(temp) * 1E+08
END IF
END SUB

SUB saveplotdata (endofdata AS INTEGER)
   ' Saves plot data to file, file$ in directory c:\simulate
   STATIC temp AS INTEGER
   CALL clearmainwindow(l)
   CALL menuposon(6)
   IF dir$ <> "" THEN CHDIR dir$
   tempdir$ = "": file$ = ""
   LOCATE 7, 4: PRINT "Current directory: ": dir$
   LOCATE 9, 4: PRINT "Enter directory: "
   LOCATE 11, 2: PRINT "(return for current)"
   DO WHILE tempdir$ = ""
      CALL inputkeys(40, 22, 9, tempdir$)
      IF tempdir$ <> "" THEN dir$ = tempdir$
      IF tempdir$ = "" AND dir$ <> "" THEN tempdir$ = "previous"
   LOOP
   LOCATE 13, 4: PRINT "Enter file name: "
   CALL inputkeys(8, 22, 13, file$)
   IF file$ = "" THEN CALL clearmainwindow(10): CALL menuposoff(6): EXIT SUB
   file$ = file$ + ".xrm"
   OPEN file$ FOR OUTPUT AS #2
   PRINT #2, "Two-theta", "Retl.", "Realpart", "Imaginary"
   PRINT #2, ""
   FOR temp = 0 TO endofdata
      WRITE #2, plotdata(temp).x, plotdata(temp).y, plotdata(temp).real, plotdata(temp).imag
   NEXT temp
   CLOSE
   CALL clearmainwindow(10)
   CALL menuposoff(6)
END SUB

SUB scandata
   STATIC postmp AS INTEGER
   STATIC temp$
   DIM colpos(5) AS INTEGER
   CALL menuposon(0)
   CALL clearhelpwindow
   CALL displayscan
   postmp = 1: colpos(2) = 3: colpos(3) = 3: colpos(4) = 3
   colpos(postmp) = 15
   205
COLOR 15, 1: LOCATE 9, 68: PRINT USING "###.#####": lambda
A$ = ""
DO WHILE A$ <> CHR$(27)
A$ = ""
    DO WHILE A$ <> "2" AND A$ <> "8" AND A$ <> CHR$(13) AND A$ <> CHR$(27)
    A$ = INKEY$
    LOOP
    colpos(postmp) 3
COLOR colpos(1), 1: LOCATE 9, 68: PRINT USING "###.#####": lambda
COLOR colpos(2), 1: LOCATE 15, 68: PRINT USING "###.#####": 2 * starttheta * (180 / pi)
COLOR colpos(3), 1: LOCATE 18, 68: PRINT USING "###.#####": 2 * endtheta * (180 / pi)
COLOR colpos(4), 1: LOCATE 21, 69: PRINT USING "###.#####": 2 * steptheta * (180 / pi)
    IF A$ = "2" AND postmp < 4 THEN postmp = postmp + 1: colpos(postmp) = 15
    IF A$ = "2" AND postmp = 4 THEN colpos(postmp) = 15
    IF A$ = "8" AND postmp > 1 THEN postmp = postmp - 1: colpos(postmp) = 15
    IF A$ = "8" AND postmp = 1 THEN colpos(postmp) = 15
COLOR colpos(1), 1: LOCATE 9, 68: PRINT USING "###.#####": lambda
COLOR colpos(2), 1: LOCATE 15, 68: PRINT USING "###.#####": 2 * starttheta * (180 / pi)
COLOR colpos(3), 1: LOCATE 18, 68: PRINT USING "###.#####": 2 * endtheta * (180 / pi)
COLOR colpos(4), 1: LOCATE 21, 69: PRINT USING "###.#####": 2 * steptheta * (180 / pi)
    IF A$ = CHR$(13) AND postmp = 1 THEN
        LOCATE 9, 68: PRINT "    "
        temp$ = ""
        DO WHILE VAL(temp$) = 0
            CALL inputkeys(7, 69, 9, temp$)
        LOOP
        lambda = VAL(temp$)
        CALL displayscan
        COLOR 15, 1: LOCATE 9, 68: PRINT USING "###.#####": lambda
        END IF
    IF A$ = CHR$(13) AND postmp = 2 THEN
        LOCATE 15, 68: PRINT "    "
        temp$ = ""
        DO WHILE VAL(temp$) = 0
            CALL inputkeys(7, 70, 15, temp$)
        LOOP
        starttheta = (VAL(temp$) / 2) * (pi / 180)
        CALL displayscan
        COLOR 15, 1: LOCATE 15, 68: PRINT USING "###.#####": 2 * starttheta * (180 / pi)
        END IF
    IF A$ = CHR$(13) AND postmp = 3 THEN
        LOCATE 18, 68: PRINT "    "
        temp$ = ""
        DO WHILE VAL(temp$) = 0
            CALL inputkeys(7, 70, 18, temp$)
        LOOP
        endtheta = (VAL(temp$) / 2) * (pi / 180)
        CALL displayscan
        COLOR 15, 1: LOCATE 18, 68: PRINT USING "###.#####": 2 * endtheta * (180 / pi)
        END IF
    IF A$ = CHR$(13) AND postmp = 4 THEN
        LOCATE 21, 69: PRINT "    "
        temp$ = ""
        DO WHILE VAL(temp$) = 0
            CALL inputkeys(7, 70, 21, temp$)
            steptheta = (VAL(temp$) / 2) * (pi / 180)
        END IF
LOOP
CALL displayscan
COLOR 15, 1: LOCATE 21, 68: PRINT USING "###.###"; 2 * steptheta
(180 / pi)
END IF

LOOP
CALL menuposoff(0)
CALL clearhelpwindow
END SUB

SUB selectmat
menuposon (1)
openmainwindow (1)
clearhelpwindow
CALL helptxt1

STATIC A$
STATIC tempx, tempy, pointer AS INTEGER
STATIC xlim, ylim AS INTEGER ' define limits of data in row/columns
STATIC temp$
STATIC up, down, left, right AS INTEGER

CALL printmats(xlim, ylim)

tempx = 4: tempy = 8: pointer = 1
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
A$ = ""
DO WHILE A$ <> CHR$(27)
A$ = ""
DO WHILE A$ = ""
A$ = INKEY$
LOOP

down = 0
up = 0
left = 0
right = 0
IF tempy = 24 AND tempy <> ylim THEN down = 1
IF tempx = xlim AND tempy = ylim THEN down = 2
IF tempy = 8 THEN up = 1
IF tempx = 4 THEN left = 1
IF tempx = xlim AND right = 0 THEN right = 1
IF tempy > ylim AND tempy + 1 <= ylim AND tempx = xlim - 8 AND right = 0 THEN right = 2
'LOCATE 20, 20: PRINT down, up, left, right, pointer

IF A$ = "2" AND down = 0 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempy = tempy + 1: pointer = pointer + 1
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "2" AND down = 1 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempy = 8: tempx = tempy + 8: pointer = pointer + 1
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "8" AND up = 0 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempx = tempx - 1: pointer = pointer - 1
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "8" AND up = 1 AND left = 0 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempx = 24: tempx = tempx - 8: pointer = pointer - 1
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "4" AND left = 0 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempx = tempx - 8: pointer = pointer - 17
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "6" AND right = 0 THEN
COLOR 2, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
tempx = tempx + 8: pointer = pointer + 17
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = "." AND lastmat > 1 THEN
CALL deletemat(pointer)
CALL printmats(xlim, ylim)
pointer = 1: tempx = 4: tempy = 8
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

IF A$ = CHR$(13) THEN
CALL opticalcnsts(pointer)
CALL printmats(xlim, ylim)
CALL helptxtl
COLOR 15, 1: LOCATE tempy, tempx: PRINT matname$(pointer)
END IF

CALL closemainwindow
CALL clearhelpwindow
CALL menuposoff(l)
END

SUB sortoptdata (start AS INTEGER, finish AS INTEGER)
  ' Sorts optical constants into order of increasing wavelength
  ' start defines start position in array lambdalib
  ' finish defines end position.

  STATIC temp, flag AS INTEGER
  STATIC swaplam, swapdel, swapbet AS SINGLE

  flag = 1   'flag is set=1 if any swaps in list are needed, 0 otherwise

  DO WHILE flag = 1
    flag = 0
    FOR temp = start TO finish - 1
      IF lambdalib(temp + 1) < lambdalib(temp) THEN
        swaplam = lambdalib(temp + 1)
lambdalib(temp + 1) = lambdalib(temp)
lambdalib(temp) = swaplam
        swapdel = optcnst(temp + 1).delta
        swapbet = optcnst(temp + 1).beta
      END IF
  END DO
END SUB
optcnst(temp + l).delta = optcnst(temp).delta
optcnst(temp + l).beta = optcnst(temp).beta
optcnst(temp).delta = swapdel
optcnst(temp).beta = swapbet
flag = 1
END IF
NEXT temp
LOOP
END SUB

SUB sqrtcomplex (A AS complex, b AS complex)
' Derives the square root of a complex number, and returns
' the positive vals for real and imaginary parts (n.b. -ve
' values are equally valid, but not mixtures of the two :
' i.e. a + ib or -a -ib are roots but not a - ib or -a +ib)
'alpha and beta are local variables
alpha = A.realpart
beta = A.imaginary * A.imaginary
b.realpart = 1 / SQR(2) * SQR((alpha + SQR(alpha * alpha + beta)))
b.imaginary = A.imaginary / (2 * b.realpart)
END SUB

SUB startup
' Setups program menus, layout etc.
SCREEN 9
lambda = 1.38
starttheta = (.2 / 360) * pi
endtheta = (6 / 360) * pi
steptheta = (.02 / 360) * pi
CALL menubar
VIEW PRINT 6 TO 25
CALL clearmainwindow(10)
CALL abouttext
PALETTE 14, 26
PALETTE 11, 27
END SUB

SUB templinvar
'Temporary version of liner rms roughness variation
STATIC jtemp AS INTEGER
FOR jtemp = 1 TO m
sigma(jtemp) = (4 + 5 * (jtemp / m - .5)) * 1E-08
NEXT jtemp
END SUB

SUB teststack (b AS INTEGER)
DO WHILE b < 100
PRINT b;
CALL teststack(b + 1)
LOOP
END SUB
Appendix B

Publications

“Evidence of roughness distributions and interface smoothing in Co/Cu multilayers deposited under energetic particle bombardment”

“Microstructural modification in Co/Cu multilayers prepared by low energy ion-assisted deposition”

“Simple method for the control of substrate ion fluxes using an unbalanced magnetron”