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The Growth and Characterisation of Mn_2Au Thin Films and Heterostructures

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in partial fulfilment of the requirements for the degree of Doctor of
Philosophy

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Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work, with the exception of the assistance noted in the acknowledgements.

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Summary

The aims of this thesis were to first develop a method of growing high quality Mn_2Au thin films via molecular beam epitaxy and then to integrate those films into heterostructures which could be used to study the exchange coupling effect in Mn_2Au and FM bilayers, in an effort to further work towards achieving tunneling anisotropic magnetoresistance for Mn_2Au .

In Chapter 1 antiferromagnetism is introduced. A brief history of the first theoretical postulations of antiferromagnetism, antiferromagnetic materials, and the first direct experimental detection of antiferromagnetic order are described. The first applications of antiferromagnetic materials are covered, along with the modern field of antiferromagnetic spintronics and some of the primary phenomena of interest. The various types of magnetic order of interest are defined. The exchange coupling effect and various applicable models for exchange bias are reviewed and their role in the magnetoresistive effects necessary for understanding the tunneling anisotropic magnetoresistance effect are described, in relation to both ferromagnetic materials and antiferromagnetic materials.

Chapter 2 describes in detail the tools and techniques used in this work. Particular emphasis is given to the growth technique of molecular beam epitaxy, the method with which the stoichiometry of the Mn_2Au films was controlled and the *in-situ* characterisation technique reflection high energy electron diffraction. *Ex-situ* characterisation techniques such as X-ray diffraction and X-ray reflectometry are described along with the magnetic characterisation technique of vibrating sample magnetometry.

Chapter 3 describes, briefly, the growth of Mn_2Au thin films on substrates such as MgO (001) and Al_2O_3 ($1\bar{1}02$), before moving on to the growth of high crystalline quality Mn_2Au (110) thin films grown on a high quality, epitaxial Pt (111) seed layer using an Al_2O_3 (0001) substrate. It describes in detail the optimisation of the deposition temperature of each layer and investigates the structural and morphological characteristics of the films.

Chapter 4 describes the growth of both Co (111)/ Mn_2Au (110) and Fe (110)/ Mn_2Au (110) based heterostructures using a high quality Pt (111) seed layer on an Al_2O_3 (0001)

substrate. The heterostructures are structurally characterised in their as-deposited state before being subjected to vacuum annealing cycles in an applied magnetic field at various temperatures. The effects of annealing on the structure of the stack are investigated. The magnetic properties of the stack are characterised using room temperature vibrating sample magnetometry, both before and after the annealing cycles.

Chapter 5 investigates the exchange coupling effect in Mn_2Au (001)/Fe (001) and Mn_2Au (110)/Fe (110) stacks. The growth of each, on their respective substrates and seed layers, are described and the structural differences between these and the films grown in Chapters 3 & 4 are outlined. The exchange coupling effect is analysed at room temperature using vibrating sample magnetometry; azimuthal hysteresis loops are measured for the full range of in-plane stack orientations and the resulting anisotropy and coercivity profiles are analysed for each stack, both before and after a field cooling cycle in an applied magnetic field. The stacks are characterised further using low temperature magnetometry and the scope and limitations of the exchange coupling effect in each Mn_2Au orientation are elucidated. Finally, the Néel temperatures of each stack are estimated, by using a modified power law function to fit the temperature dependent coercive fields of each stack.

In Chapter 6 the results obtained were summarised and future experiments to continue this body of work are suggested.

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Abstract

In this thesis, Mn_2Au thin films and heterostructures are grown via molecular beam epitaxy. Mn_2Au thin films are investigated on MgO (001) and Al_2O_3 ($1\bar{1}02$) substrates, and on Pt (111) seed layer grown on an Al_2O_3 (0001) substrate. The MgO (001) and Al_2O_3 ($1\bar{1}02$) substrate resulted in polycrystalline films, while the Al_2O_3 (0001)/Pt (111) substrate and seed layer resulted in high crystalline quality Mn_2Au (110) films. The films were characterised *in-situ* via reflection high energy electron diffraction, low energy electron diffraction; and *ex-situ* via $\theta - 2\theta$ X-ray diffraction, azimuthal X-ray diffraction, reciprocal space maps, and X-ray reflectometry. The heterostructures used Al_2O_3 (0001)/Pt (111) seed layers to grow Co (111)/ Mn_2Au (110) bilayers and Fe (110)/ Mn_2Au (110) bilayers which were structurally analysed using reflection high energy electron diffraction and $\theta - 2\theta$ X-ray diffraction, as-deposited and after annealing at 350°C and 500°C in an 800 mT applied magnetic field. Magnetic characterisation of the stacks was performed using room temperature vibrating sample magnetometry, both as-deposited and after the annealing cycles. The heterostructures were found to demonstrate exchange coupling between the Co (111)/ Mn_2Au layers as deposited, and the field cooling was unable to induce room temperature exchange bias in any of these. Heterostructures of the form Mn_2Au (001)/Fe (001) was grown on an Al_2O_3 ($1\bar{1}02$)/Ta (001) substrate/seed layer along with one of the form Mn_2Au (110)/Fe (110) grown on an Al_2O_3 (0001)/Pt (111) seed layer. These heterostructures were characterised structurally using reflection high energy electron diffraction, $\theta - 2\theta$ X-ray diffraction, and azimuthal X-ray diffraction. The scope of the exchange coupling effect in these heterostructures was comprehensively investigated using room temperature vibrating sample magnetometry, both in their as-deposited state and after a field cooling cycle from 350°C to room temperature in an 800 mT applied magnetic field. The exchange coupling effect was also investigated using low temperature vibrating sample magnetometry measurements in the range of 5 K-270 K, after further field cooling in a 1 T applied field from 300 K-5 K.

List of Publications and Presentations

Publications

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Presentations

1. *The Growth and Characterisation of Anti-FerroMagnetic Mn_2Au based multilayers for Magnetic Applications*

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Chapter 1

Introduction & Literature Review

The existence of antiferromagnetic (AFM) materials were first postulated in the early 1930s by Louis Néel after a theoretical study of the remaining non-ferromagnetic (FM) 3d transition series elements such as Mn, Cr, V, and Ti. Néel thought that such elements may have a negative exchange interaction which would lead the microscopic magnetic moments to align antiparallel to each other [1]. Néel showed that such AFM systems have a critical temperature at which the exchange interaction breaks down, now known as the Néel temperature (T_N) [2]. It is now known that, of these 3d metals, only Cr orders antiferromagnetically. None of the 3d metals displays the simple type of antiferromagnetism that Néel originally considered but many alloys of these 3d transition metals mentioned do order antiferromagnetically. The first experimental evidence of AFM ordering was obtained via neutron diffraction measurements of transition metal oxides, such as MnO, in 1949 [3]. After this, many more AFM materials were discovered, but potential applications for the theoretically interesting AFM state remained elusive. This is best illustrated by a quote from Néel which was given during his 1970 Nobel laureate acceptance lecture: “A large number of AFM materials is now known: these are generally compounds of the transition metals containing oxygen or sulphur. They are extremely interesting from the theoretical viewpoint, but do not seem to have any applications.” [4].

At the point in time of Néel’s lecture, the exchange anisotropy between AFMs and FMs had been discovered [5] and Néel had contributed to its understanding [6]. However, it would be approximately another two decades before an application relying on this exchange anisotropy would emerge. This was in a spin valve type memory device based on the giant magnetoresistance (GMR) effect, which was loosely based on a previous design by Hunt [7]. This effect relies on the resistance change between two adjacent FM electrodes, separated by a thin non-magnetic (NM) layer, which is caused by a change in the direction of magnetisation of one of the FM layers such that they are

no longer parallel. One of the FM electrodes is exchange coupled to an adjacent AFM layer such that the magnetisation of one of the FM electrodes is pinned, while the other is free to rotate. This led to a thorough investigation into the utility of AFM materials as a passive element in many devices relying on the exchange bias (EB) effect over the subsequent decades.

Although previous theoretical work had considered the use of AFMs as the active element in GMR based effects [8–10], it was not until 2010 that promising theoretical use cases for AFMs as the active element emerged [11]. In 2011 one of these effects was experimentally confirmed, the tunneling anisotropic magnetoresistance (TAMR) effect, in the AFM IrMn_3 . The effect relied on exchange coupling (EC) between the AFM and FM layer, which upon magnetisation reversal of the FM layer by an external magnetic field, which causes partial rotation of the AFM moments through the EC effect. This effect displayed a much larger magnitude in the case of IrMn_3 than in any other previous works in FMs and was subsequently optimised for an IrMn_3 thickness of 4 nm to show a small signal stable up to 250 K [12], while another work showed a room temperature signal in a perpendicular exchange coupled junction [13]. Following this, other use cases of the AFM layer as the active element in devices were demonstrated [14–16], some of which also relied on the TAMR effect [14, 15]. These works, among many others, suggest that the future of spintronic applications will rely largely on AFMs, such that AFM spintronics has become its own sub-field of research. This is best demonstrated by the frequent review articles published over the last number of years [17–22].

Mn_2Au is one of the key metallic AFMs of interest for AFM spintronics due to its extremely high Néel temperature, in excess of 1300 K [23]; its composition of non-toxic elements and the large spin flop transition field it possesses, which is on the order of 30 T–50 T [24]. The crystal structure of Mn_2Au is body-centered tetragonal and the Mn sublattices lie collinearly in the basal plane along the $\langle 110 \rangle$ directions [25]. The two Mn spin sublattices are inversion partners—an applied current results in the induction of opposite spin galvanic effects on both sublattices, allowing for electrical switching of the Néel vector. This is better known as Néel-order spin-orbit torque (NSOT) [26]. The concept of spin-torque torque (SOT) is described as so; an unpolarised charge current passing through a magnetic material with large spin-orbit coupling will undergo spin dependent scattering upon interaction with the magnetisation, creating a spin current which exerts a torque on the individual magnetic moments; which, if the current density is large enough, will switch the direction of magnetisation of the material. In NSOT the spin current is generated in the material, while in other materials the spin current is created via the spin hall effect in a heavy metal, which is injected into the magnetic material to switch the magnetisation direction. The presence of NSOT in Mn_2Au [27–29], combined with the large spin-orbit coupling (SOC) [11] means that Mn_2Au is an ideal candidate for room temperature AFM spintronic applications.

Mn₂Au has been suggested as a material that may have a significant room temperature TAMR effect [11], and although TAMR for Mn₂Au has not been demonstrated to date, some works have shown large anisotropic magnetoresistance (AMR) effects in Mn₂Au [27, 30]. One of the limiting factors in this is that not much research has been done on the EB or EC effects in Mn₂Au [31, 32], and so the scope and limitations of EB in Mn₂Au are currently not fully understood. The aims of this thesis were to first develop a method of growing high quality Mn₂Au thin films via molecular beam epitaxy (MBE) and then to integrate those films into heterostructures which could be used to study the EC effect in Mn₂Au and FM bilayers, in an effort to further work towards achieving TAMR in Mn₂Au. Mn₂Au has been suggested as a material that may have a significant room temperature TAMR effect [11], and although TAMR for Mn₂Au has not been demonstrated to date, some works have shown large anisotropic magnetoresistance (AMR) effects in Mn₂Au [27, 30]. One of the limiting factors in this is that not much research has been done on the EB or EC effects in Mn₂Au [31, 32], and so the scope and limitations of EB in Mn₂Au required further study. The aims of this thesis were to first develop a method of growing high quality Mn₂Au thin films via molecular beam epitaxy (MBE) and then to integrate those films into heterostructures which could be used to study the EC effect in Mn₂Au and FM bilayers, in an effort to further work towards achieving TAMR in Mn₂Au.

1.1 Thesis Outline

The remainder of Chapter 1 will be devoted to providing a brief introduction to the relevant topics in magnetism necessary for a clear understanding of the experimental Chapters 3, 4, and 5. A comprehensive literature review of the recent research works on Mn₂Au will be given.

In Chapter 2 the techniques used to grow and characterise the AFM Mn₂Au films and heterostructures are discussed. There is a particular emphasis on the growth techniques used and how the stoichiometry of the films was controlled. The crystallographic and structural characterisation techniques used, such as high-resolution X-ray diffraction (XRD), X-ray reflection (XRR), and reflection high energy electron diffraction (RHEED) among others are discussed. The magnetic annealing furnace and magnetic characterisation tools such as vibrating sample magnetometry (VSM) are described also.

Chapter 3 is focused on the growth of high quality Mn₂Au thin films via MBE. Ubiquitous substrate choices such as MgO (100) and Al₂O₃ (1 $\bar{1}$ 02) are first investigated, before moving on to work using a high quality Pt (111) seed layer on an Al₂O₃ (0001) substrate. The growth of the Mn₂Au layers is optimised for substrate deposition temperature and the films are characterised using the techniques described in Chapter 2.

Chapter 4 centers on the integration of the Mn_2Au thin films into FM/ Mn_2Au heterostructures. Building on the work of Chapter 3, a high quality Pt (111) seed layer on an Al_2O_3 (0001) substrate is used for the growth of all the heterostructures. Two FM/ Mn_2Au combinations are investigated: Co/ Mn_2Au and Fe/ Mn_2Au . The thickness of the FM layers in both types of heterostructures are fixed, while the Mn_2Au thickness' are varied between 2.5 nm-10 nm and 2 nm-10 nm, for each respective heterostructure type. The growth of the heterostructures are comprehensively analysed using RHEED and XRD, before being vacuum annealed with an applied in-plane magnetic field in an effort to induce exchange bias in the heterostructures. The structural changes to the heterostructures after annealing are studied via XRD. The magnetic properties of the heterostructures are studied before and after the annealing procedures, via room temperature VSM.

Chapter 5 concentrates on the exchange coupling properties of Mn_2Au (001)/Fe (001) and Mn_2Au (110)/Fe (110) bilayers. The Mn_2Au (001) bilayers are grown on a Ta (001) buffer layer using Al_2O_3 ($1\bar{1}02$), which was previously shown in other works [32–34], while the Mn_2Au bilayers are grown on a Pt (111) seed layer using an Al_2O_3 (0001) substrate, as shown in Chapter 3. The structural properties of the bilayers are analysed using RHEED and XRD, before being subjected to a vacuum anneal in an applied in-plane magnetic field in an effort to induce exchange bias. The magnetic properties of the bilayers are comprehensively studied using a combination of room temperature VSM and low temperature VSM hysteresis loops between 5 K-270 K using low temperature magnetometry.

Chapter 6 summarises the key results of each chapter while discussing future experiments that can be performed to expand on this body of work.

1.2 Literature Review

1.2.1 Magnetism and Types of Magnetic Textures

The study of magnetism is both that of magnetic fields and of materials displaying magnetism. This includes the effects arising from varying electric fields and the intrinsic angular momentum associated with the magnetic moment of electrons, which is known as spin. Magnetic fields are produced either by the magnetic ‘dipole’ moments on electrons (i.e., spin) or by varying electric fields, one example of which can be seen by the production of a magnetic dipole moment by a current travelling in a looped wire. Similarly, an electron in an atomic orbital or elementary particle with spin, such as an electron, which orbits a nucleus will result in a magnetic moment. At the microscopic level, the origin of magnetism and magnetic moments have been described quantum mechanically since the 1930s and are related to the spin angular momentum of an electron, the electron’s orbital motion, and how its motion changes in an external

magnetic field. More comprehensive explanations of the fundamental principles of magnetism can be found in [1, 35, 36]. Only a brief overview of the quantities and notation necessary for this work will be discussed here.

Generally, materials that display magnetism, outside the presence of an external magnetic field, are made up of relatively large arrays of these magnetic moments. One category of materials, in which the magnetic moments all align in the same orientation leading to a net externally detectable magnetisation in the material are known as ferromagnetic materials. The sum of these magnetic moments per unit volume is defined as the magnetisation ($\mathbf{M}$). It is a vector quantity that points in the average direction of the sum of all the directions of the microscopic moments. Similarly, materials can have multiple arrays of these magnetic moments, where the magnetic moments from different arrays can oppose each other. In the case where the magnetic moments on opposite arrays are equal in magnitude, the magnetisation in the material sums to zero, meaning that materials like this generally produce no stray magnetic fields. These materials are known as antiferromagnetic materials. Additionally, the two arrays of magnetic moments can also have unequal magnitudes while aligned oppositely, and materials such as these are termed ferrimagnetic.

Even materials that have no net magnetic moment can display a magnetic response when subjected to an external magnetic field. A diamagnetic response is the most common of these. As a magnetic field is applied to the material, induced magnetic dipole currents occur opposite to the direction of the applied magnetic field, and as the magnitude of the applied field is increased the magnitude of the induced moments also increases. This results in a net magnetisation opposing the direction of the applied magnetic field. A paramagnetic response is the result of an induced magnetic dipole moment in the presence of an applied magnetic field. The key difference being, that the magnetic moments align in the same direction as the applied field, increasing linearly with the magnitude of the field but with a very weak net magnetisation.

The response of the materials described in the previous paragraphs to an applied magnetic field is described as the magnetic susceptibility χ of that material and is defined by the following equation:

$$\hat{\chi} = \frac{\vec{M}}{\vec{H}} \quad (1)$$

where $\mathbf{M}$ and $\mathbf{H}$ are the vector magnetisation and external applied field.

Table 1.1 shows examples of the magnetic susceptibility for diamagnets, paramagnets, and FMs. Antiferromagnets and ferrimagnets are not represented in the table, along with more complex spin textures given as they can be broadly classed with FMs in this case as they are all ordered textures, unlike diamagnets and paramagnets.

Table 1.1: A table describing the typical magnetic susceptibility (χ) response for diamagnetic, paramagnetic and ferromagnetic materials and examples of each [35, 36].

Magnetism Type	χ	Material Examples
Diamagnet	$\approx -10^{-5}$	Bi, Be, Cu, Ag, Au
Paramagnet	$\approx 10^{-3} - 10^{-5}$	Al, Pt, Mn
Ferromagnet	$\approx 50 - 10000$	Co, Fe, Ni

The energy of an electron in an external magnetic field ($\mathbf{H}$), which has spin angular momentum (m_s) and magnetic moment ($\mathbf{m}$) is given by the following equation:

$$E = -\mu_0 \mathbf{m} \cdot \mathbf{H} = g \mu_B \mu_0 H m_s \quad (2)$$

where μ_0 is the permittivity of free space, g is the g-factor and the μ_B is the Bohr magneton which is defined as:

$$\mu_B = \frac{e\hbar}{2m_e} \quad (3)$$

A torque ($\mathbf{T}$) acting on a magnetic moment ($\mathbf{m}$) is given by the following:

$$\mathbf{T} = \mu_0 \mathbf{m} \times \mathbf{H} \quad (4)$$

The main types of magnetism briefly mentioned already are discussed in further detail below.

1.2.1.1 Diamagnetism

As previously mentioned diamagnetic materials have a negative susceptibility and display a small net negative magnetisation for a positive applied field. The susceptibility response for diamagnetic materials was first explained by Langevin in 1905 [37]. In diamagnetic materials, each of the electrons is paired, with the pair consisting of a spin-up and a spin-down, which results in a zero net magnetic moment for each atom. When a diamagnetic material is subjected to an external magnetic field, there is a change in the orbital motion of the electrons at the atomic level, which gives rise to the diamagnetic response. Langevin considered the orbital motion of the electrons around the nucleus to be analogous to that of a current carrying loop. At zero field the moment generated by the electron pair cancels out, but in an applied field, there will be an induced magnetic moment in the opposite direction to the applied field caused by the changing in the magnetic flux through electrons orbits or “loops”. According

to the Langevin model, the diamagnetic susceptibility is dependent on the number of electrons Z and the number of atoms N in volume V :

$$\chi = \frac{M}{H} = -\frac{N}{V} \frac{e^2 \mu_0}{6m_e} \sum_i^Z \langle R_i^2 \rangle \quad (5)$$

where e is the charge of the electron, m_e is the mass of the electron, and R_i is the radius of the electron orbital. This equation shows that the diamagnetic response is temperature independent and negative in sign.

1.2.1.2 Paramagnetism

In contrast to diamagnetic materials, the origin of paramagnetic properties is a result of unpaired electrons in a material. In paramagnets the unpaired electrons have magnetic moments, which consist of contributions of the spin and orbital angular momentum of the electron, however, the moments are randomly oriented such that there is net zero magnetisation in the absence of an applied field. In an applied field, some fraction of the moments will tend to align along the direction of the applied field creating a weak net magnetisation along the direction of the applied field. An exceptionally high magnetic field would be needed to directly align all of the magnetic moments along the same direction and once the applied field is removed the moments return to their randomly oriented state. The susceptibility of paramagnetic materials is given by the Curie Law:

$$\chi = \frac{C}{T} \quad (6)$$

where C is the Curie constant of the material in question, which is dependent on temperature, the number density of the magnetic moments, and the magnitude of the magnetic moments. C is defined by the following equation:

$$C = \frac{n \mu_0 \mu_B^2}{k_B} \quad (7)$$

where n is the number of unpaired electrons per unit volume.

Ordered magnetic materials, such as materials displaying ferromagnetism and antiferromagnetism can also undergo a transition to become paramagnetic. This occurs at a temperature where the thermal energy is strong enough to overcome the exchange energy which keeps the magnetic moments in an ordered state. The critical temperature at which this occurs is known as the Curie temperature (T_C) in FMs and the Néel temperature (T_N) for AFMs. In this case, there is a more general form of the previous equation which describes the susceptibility in the case of materials that undergo a

magnetic-paramagnetic transition:

$$\chi = \frac{C}{T - \theta} \quad (8)$$

where θ is a positive constant equal to T_C for FMs and is a negative constant for AFM materials with a PM transition at T_N .

1.2.1.3 Ferromagnetism

Ferromagnetic materials are similar to PM materials in the sense that they both have magnetic moments arising from unpaired electrons. In the case of FM materials, the magnetic moments associated with these unpaired electrons are ordered at zero field such that FM materials retain a net magnetisation. There are strong interactions between all the magnetic moments which leads to this ordered array. This was first explained phenomenologically by Weiss in 1907, with what was dubbed the Weiss molecular field [38]. Weiss postulated that there was a very large internal magnetic field which aligned the internal magnetic moments along a particular direction, but it was quickly realised that such an internal magnetic field, which was typically on the order 10 T-100 T, could not be explained by the magnetic effects due to dipole fields solely.

It was only thirty years later that the origin of the ordered array of FM moments in zero applied magnetic field was understood through quantum mechanics when the spin degree of freedom was included in the wave function of an electron. The spin dependent Hamiltonian of a many electron system with electron spins of $\mathbf{S}_i$ and $\mathbf{S}_j$, leads to a Heisenberg exchange energy of:

$$E_{ex} = -J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (9)$$

where J is the exchange constant describing the type of magnetic ordering in a system. In the case of FMs $J > 0$ and for AFMs $J < 0$.

The Stoner model for band theory of magnetism describes ferromagnetism in terms of the competing electron-electron repulsion and exchange energies leading to a split in the density of states (DOS). From this theory emerges the Stoner Criterion which determines if a material will be PM or FM. For a material to be FM:

$$JD(E_F) \geq 1 \quad (10)$$

Where $D(E_F)$ represents the density of states at the Fermi level. Only three elemental materials fulfil the Stoner Criterion: Co, Fe, and Ni.

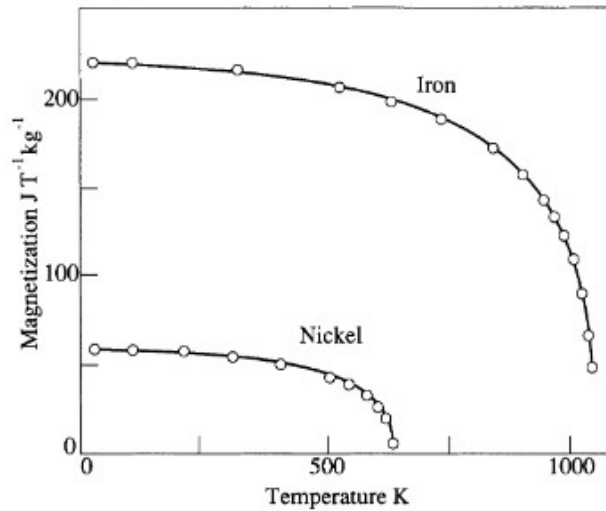


Figure 1.1: An example of Curie temperature determination in Fe and Ni. As the temperature increases the magnetisation decreases until it reaches zero magnetisation, which is at the transition temperature T_C . The Curie temperatures of Fe and Ni are 1044 K and 628 K respectively. Adapted from [1].

The Curie temperature of FM materials is essentially determined by the temperature at which the magnetisation of the material becomes zero and the material become paramagnetic. Figure 1.1 shows an example of the evolution of the spontaneous magnetisation of Fe and Ni as a function of temperature. The magnetisation of both materials approaches zero at their respective Curie temperatures of 1044 K and 628 K [39].

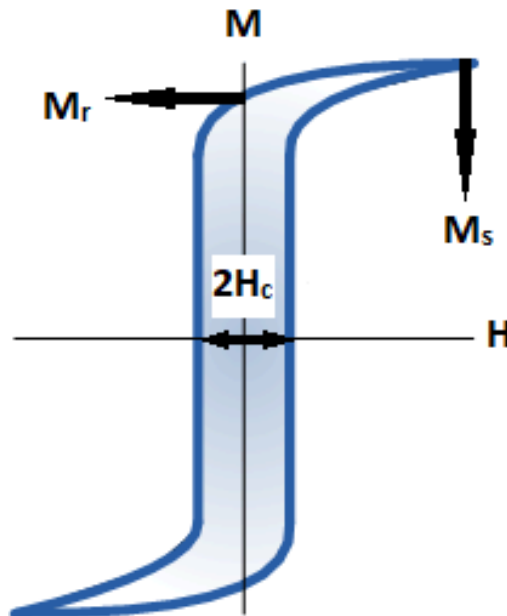


Figure 1.2: An example of a FM hysteresis loop with the key parameters noted. The saturation magnetisation, the remanent magnetisation, and the coercivity of the loop are noted in the figure.¹

¹Image adapted from <https://www.electronics-tutorials.ws/wp-content/uploads/2018/05/electromagnetism-mag20.gif>

Figure 1.2 shows an example of a magnetisation loop of a FM material. There are several important features on the graph as follows: (1) The saturation magnetisation (M_s), occurs when a sufficiently high magnetic field is applied to a sample to align all of the magnetic moments and the magnetisation of the material becomes saturated. This is a characteristic property of FM materials and for example, Fe has a saturation magnetisation of 1700 kA m^{-1} [39]. (2) The remanent magnetisation (M_r) is the magnetisation of the material, which remains when there is zero applied magnetic field. (3) The coercive field (H_c) which is broadly defined as the total width of the loops at zero magnetisation divided by two. It is a measure of how resistant the FM material is to an external magnetic field without reversing magnetisation.

1.2.1.4 Antiferromagnetism

As previously defined, AFM materials are those in which there are two or more FM arrays of moments that are anti-aligned in a manner, in which there is no net magnetisation. Previously the direction of magnetisation in AFMs was mentioned, but not defined: It is known as the Néel vector ($\mathbf{L}$) in AFMs and is similar to $\mathbf{M}$ in FMs. In the case of two spin sublattice AFMs, each with sublattice magnetisation of $\mathbf{M}_a$ and $\mathbf{M}_b$ respectively; the Néel vector is parallel to the orientation of the AFM moments, with the vector being described in equation form as:

$$\mathbf{L} = \frac{\mathbf{M}_a - \mathbf{M}_b}{2} \quad (11)$$

where $\mathbf{M}_a$ is equal to $-\mathbf{M}_b$, and the magnitude of the antiferromagnetic magnetisation is given by $\mathbf{M}_{AFM}$:

$$\mathbf{M}_{AFM} = \frac{\mathbf{M}_a + \mathbf{M}_b}{2} \quad (12)$$

AFMs were for a long time considered to be PMs until the 1930s when Néel postulated the existence of AFMs, followed shortly after by Landau [40]. The existence of AFM order was confirmed via neutron diffraction of MnO in 1949 [3]. Some studies on materials that displayed no net magnetic moment, exhibited a temperature dependent magnetic susceptibility which deviated from what was expected for PM and FM materials [41]. The susceptibility is characterised by a maximum at a particular temperature, which was explained theoretically as the transition from the magnetically ordered AFM state to the magnetically disordered PM state [42]. An example of the magnetic susceptibility of AFM MnF_2 as a function of temperature can be seen in Figure 1.3 [43]. The peak in the susceptibility corresponds to the Néel temperature which is 68 K. Above the Néel temperature the material is PM and follows the Curie Law for PM susceptibility. The Curie Weiss law described above in Equation 8, describes the susceptibility behaviour of materials which undergo an AFM-PM transition when $\theta < 0$.

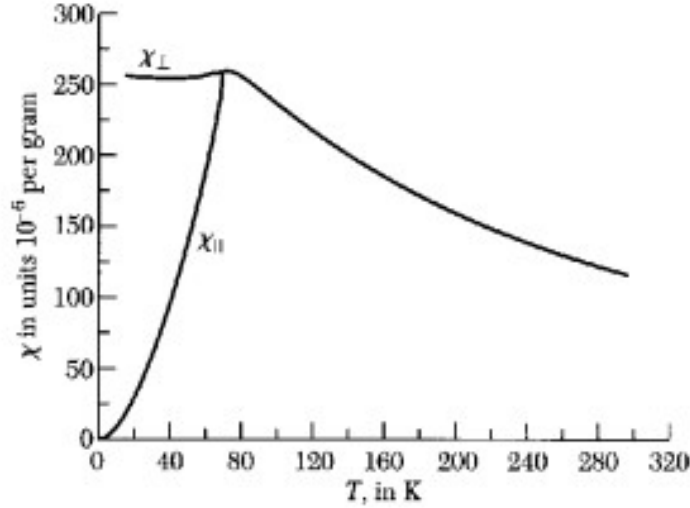


Figure 1.3: An example of the magnetic susceptibility of AFM MnF_2 as a function of temperature. The Néel temperature is denoted by maxima in the susceptibility at 68 K. Below the Néel temperature the susceptibility is resolved into the susceptibility parallel and perpendicular to the direction of the Néel vector. Above the Néel temperature the material is PM and follows the Curie-Weiss law, for $\theta < 0$, described above in Equation 8. Adapted from [43].

In Figure 1.3, the susceptibility below the Néel temperature is separated into the $\chi_{\perp}$ and $\chi_{\parallel}$ components. Susceptibility measurements are taken in the presence of an applied magnetic field, the $\chi_{\perp}$ and $\chi_{\parallel}$ components correspond to the measurements taken when the applied field is applied perpendicular and parallel to the AFM magnetisation direction respectively. In an applied field, the AFM moments become weakly magnetised and can become slightly canted or tilted in response to this. When the field is applied perpendicular to these weakly magnetised AFM moments it is easier to cant them than when the field is applied parallel to the moments. Thus $\chi_{\perp} > \chi_{\parallel}$ for all $T \leq T_N$ [36]. It follows then that, in the absence of any other competing effect, AFM moments prefer to align perpendicular to any applied field. In a polycrystalline material, where AFM magnetisation direction is unknown, the susceptibility will be some convolution of the two components, such that the maxima at the Néel temperature becomes far more distinct than in Figure 1.3.

Table 1.2 shows some of the AFM materials that have already been referred to in this thesis and some important AFM materials in the context of the field of AFM spintronics. The bulk Néel temperature of each material is also shown. It should be noted that in thin AFM films, of which this thesis will primarily focus on, the Néel temperature can be reduced when one of the dimensions is reduced such as the thickness [15, 44] or the grain size [45]. This effect can be quite large with measurements of the Néel temperature of a 2 nm thick layer of IrMn_3 via two different techniques estimating the Néel temperature to be in the range of 173 K-200 K, which is approximately 24-27% of the bulk value [44, 46]. This reduction in Néel temperature will be referred to as

the finite size Néel temperature (T_N^*).

Table 1.2: A table listing the Néel temperatures of some of the AFM materials described in this work and key AFM materials in AFM spintronics.

AFM Material	T_N Bulk	Reference
MnF ₂	68 K	[20]
MnO	118 K	[47]
Cr	310 K	[36]
FeRh	≈ 380 K ²	[20]
CuMnAs	480 K	[20]
γ -IrMn ₃	730 K	[46]
IrMn	1150 K	[20]
Mn ₂ Au	≈ 1400 K	[23]

Thus far, only the simplest type of AFM texture has been described, with two FM spin sublattices which align antiparallel to each other. The simplest form of this AFM moment arrangement is where each moment is aligned antiparallel to its nearest neighbour. An example of a material with this AFM moment arrangement is MnO, and its unit cell and AFM moment arrangement are shown above in Figure 1.4. The AFM moment orientation is usually dictated by a combination of the exchange energy and the magnetocrystalline anisotropy energy of the crystal lattice. A more complex spin structure is that of Mn₂Au [23], where neighbouring moments in one plane have FM coupling and the coupling between these adjacent FM planes is AFM. Finally, there are also what are called non-collinear AFMs, where there are more than two spin sublattices and the AFM moments can't align antiparallel to each other. In these non-collinear AFMs, which occur primarily in hexagonal or face centred cubic (fcc) lattices, moments are grouped triangularly in sets of three. If two of the three moments were aligned antiparallel to each other, the third would experience “frustration” where no direction it points would sum the net moment of the triangle to zero. Thus the 3 moments align non-collinearly to fulfil the zero net moment requirement. An example of a non-collinear AFM is IrMn₃ [48]. It is more complex to define the Néel vector orientation in non-collinear AFMs such as IrMn₃ than in collinear AFMs like Mn₂Au [49]. There are other more complex AFM spin structures, such as helimagnetism, etc. but they are not necessary for an understanding of the work presented in this thesis.

²Based on the point of AFM-FM transition which can range from 300 K-400 K.

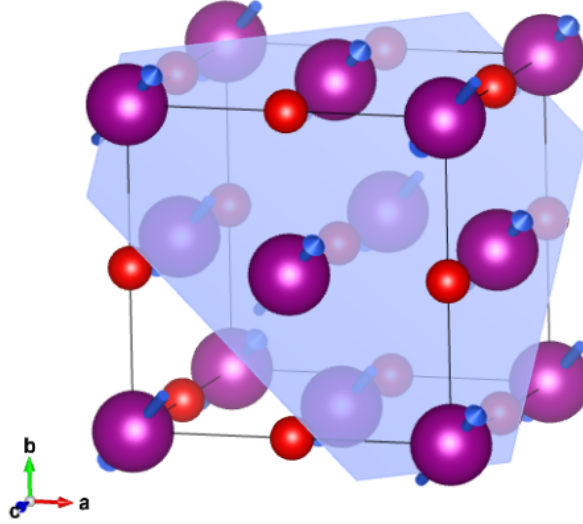


Figure 1.4: Unit cell of the AFM MnO displaying the AFM moment arrangement. The Mn atoms are shown in blue and the O atoms are in red. The AFM moments are shown by the blue arrows pointing along the $[111]$ direction where each moment is ordered antiferromagnetically with its nearest neighbour. The (111) plane bisects the unit cell in purple.³

1.2.2 Anisotropies and their related Energies

This section will deal with some of the anisotropies and their related energies that lead to stable magnetisation in both FMs and AFMs and others that are necessary to understand macroscopic effects. These energies and anisotropies are in addition to the exchange energy which was previously mentioned in Equation 9.

1.2.2.1 Demagnetisation Energy and Shape Anisotropy

As well as being affected by external magnetic fields, magnetic moments can be affected by the dipolar field generated by neighbouring magnetic moments. The dipolar field generated by the neighbouring magnetic moments also affects the magnetic moments. This resulting additional field is called the demagnetising field ($\mathbf{H}_d$) or also referred to as the stray field. The demagnetising field is related to the shape of the sample or object which produces it. The demagnetising field is related to total magnetisation through:

$$\mathbf{H}_d = -N_d \mathbf{M} \quad (13)$$

where N_d is the demagnetising factor, which is a tensor relating to the geometry of the

³Image adapted from <https://crystallography365.wordpress.com/2014/03/28/spins-and-arrows-the-magnetic-story-of-mno/>

object. The trace of this tensor satisfies the following relation:

$$\text{Tr}(N_d) = 1 \quad (14)$$

Below is an example of N_d for a spherical magnetic object:

$$N_d(\text{Sphere}) = \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \quad (15)$$

For a thin film with a finite thickness in the z -axis, this becomes:

$$N_d(\text{Thin Film}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (16)$$

Finally the energy related to the demagnetising field (E_d) is defined as:

$$E_d = -\frac{\mu_0}{2} \int_V \mathbf{M} \cdot \mathbf{H}_d dV \quad (17)$$

In materials with a net magnetisation, such as FMs and ferrimagnets, the demagnetising field results in shape anisotropy. For a thin film with a finite thickness along the z -axis, its magnetisation prefers to orient in the plane of the film along the x or y axes.

1.2.2.2 Induced Anisotropy

One of the ways in which anisotropy can be induced in FM materials is through annealing in a magnetic field. At high temperatures in a magnetic field, atomic diffusion allows the magnetic moments of atoms to align along the same direction as the magnetic field. This is an important part of inducing the exchange coupling effect between FM and AFM materials. Another form of induced anisotropy is when a magnetic unit cell is further strained from its standard lattice parameters, which causes magnetostrictive effects. An example of this is the perpendicular magnetic anisotropy of Co/Pt multilayers [50] caused by the straining of the Co lattice parameters. It should be noted that this exists in addition to the static equilibrium strain which gives rise to magnetic domains.

1.2.2.3 Magnetocrystalline Energy

The magnetocrystalline energy is essential in determining the easy axis or axes in a magnetic material. It is usually small with respect to the exchange energy. Magnetocrystalline anisotropy is defined as the energy necessary to rotate the magnetisation from along the easy axis to along the hard axis. It originates from the spin-orbit coupling, where the interaction of the spin magnetic moment with the crystal lattice gives rise to a more energetically favourable orientation of the magnetic moment along a single or a set of crystalline axes.

1.2.2.4 Stoner-Wohlfarth Model

The Stoner-Wohlfarth Model is the simplest model which describes total energy in a magnetically ordered system. It assumes a uniformly magnetised ellipsoid with uniaxial anisotropy (K_u), and that all magnetic moments rotate uniformly. In this model, the exchange energy is also constant and does not change with the rotation of the magnetisation. Figure 1.5 defines the angles for the rotation of the magnetic field, the FM magnetisation and the Néel vector in relation to the easy axis of this system which lies along the x -axis.

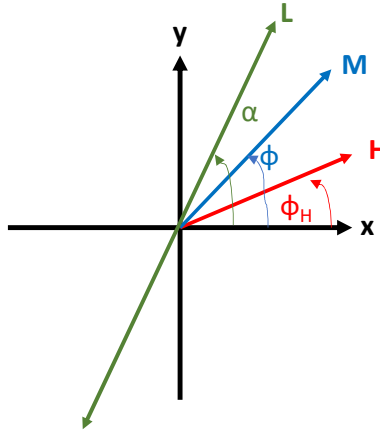


Figure 1.5: Definition of the angles of rotation with respect to the easy magnetisation axis, for the magnetic field, the FM magnetisation and the Néel vector. The Néel vector is denoted by $\mathbf{L}$ and its angle of rotation by the angle α .

The total energy of the system is given by:

$$E_{tot} = -\mu_0 \mathbf{M} \cdot \mathbf{H} \cos(\phi_H - \phi) + K_u \sin^2 \phi \quad (18)$$

where ϕ_H and ϕ are the angles of the applied magnetic field and the FM magnetisation direction with respect to the x easy axis. The first term is known as the Zeeman term and the second term accounts for the magnetocrystalline anisotropy. The shape anisotropy is ignored in this model. In the Stoner-Wohlfarth model, an expression for the coercive field (H_c) can be found from Equation 18 when $\phi_H = \phi = \frac{\pi}{2}$:

$$H_c = \frac{K_u}{\mu_0 M_s} \quad (19)$$

1.2.3 Exchange Coupling Effect

The exchange coupling effect (ECE) was first defined as so by *Reichlova et. al.* [12], is also referred to as exchange anisotropy [5] but is best known under the moniker of exchange bias (EB). The effect was first discovered in 1956 by Meiklejohn and Bean, where FM Co particles which were covered in their native AFM oxide, CoO, were cooled in a magnetic field through the Néel temperature of 77 K in an applied magnetic field. Hysteresis loops measured below the Néel temperature of CoO showed increased coercivity and the centre of the loops was shifted along the field axis. It is this shift of the hysteresis loop that gives rise to the name exchange bias. The effect is a result of the introduction of unidirectional anisotropy. The term ECE is more useful than EB as the bias only refers to the shift of the hysteresis loop. In the case that there is no bias but only increased coercivity of the loop, this will be referred to as EC or ECE and when the bias field is present it will be referred to as EB.

The coercivity of the descending and ascending branches of the magnetisation loop are defined as H_{c1} and H_{c2} respectively. The bias field can then be defined as:

$$H_{eb} = \frac{H_{c1} + H_{c2}}{2} \quad (20)$$

While the coercive field is defined by:

$$H_c = \frac{H_{c1} - H_{c2}}{2} \quad (21)$$

Figure 1.6 shows the intuitive view of how EB is induced. Typically the FM/AFM bilayer is annealed at a temperature above the Néel temperature of the AFM layer, but below the Curie temperature of the FM layer in an applied magnetic field. The bilayer is then cooled below the Néel temperature in the applied field, causing the AFM moments to go from a disordered state to an ordered one aligning themselves relative to the FM moments creating unidirectional anisotropy in the bilayer. In the intuitive model shown in Figure 1.6, this is along the same axis as the FM moments but in real systems, this is not strictly the case.

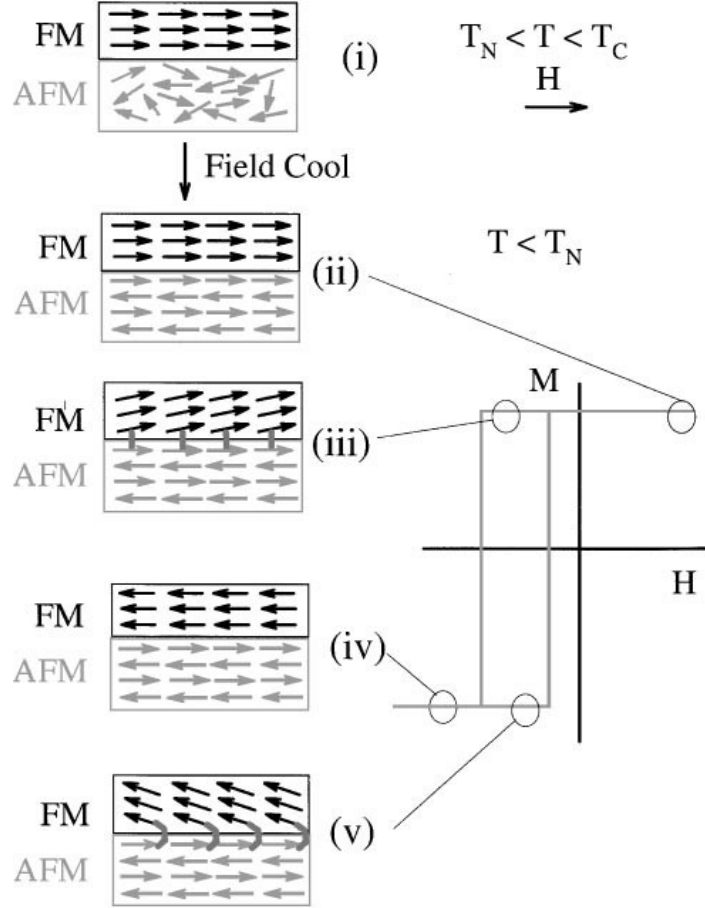


Figure 1.6: An intuitive picture of how EB typically arises. The sample is heated above the Néel temperature of the antiferromagnetic layer in the presence of an applied magnetic field. The applied field is maintained as the sample is cooled through the Néel temperature and the antiferromagnetic moments are reoriented to align with the ferromagnetic moments. This results in both a shift of the hysteresis loop known as the exchange bias field (H_{eb}) and a broadening of the hysteresis loop, known as the coercive fields (H_{c1} & H_{c2}). The figure also shows that the direction of the applied field during field cooling opposes that of the resultant H_{eb} shift. Figure adapted from [51].

Once the field cooling (FC) procedure is complete, EB should be present in any magnetisation loop which is measured. The bias shift arises from the microscopic torque applied by the AFM moments to the FM moments in an attempt to keep their original orientation when the applied field is reversed until some value of the field where its no longer possible. Phrased differently the sheet of AFM moments at the interface is considered to be completely rigid after the FC, and they remain “pinned” upon magnetisation reversal of the FM layer which leads to the appearance of the bias field in the hysteresis loop. The direction of the bias shift is typically opposite that of the applied field direction (i.e. $+H_{FC} = -H_{eb}$, $-H_{FC} = +H_{eb}$). Examples of this can be seen in Mn_2Au (001)/Fe (001) bilayers [32] and in $\text{Ni}_{80}\text{Fe}_{20}$ /FeMn bilayers [52]. In this intuitive model in Figure 1.6, the AFM moments are considered to be *uncompensated* which is to say the sheet of moments at the AFM interface aligns FM if considered on

its own. If the moments were to order AFM in a single sheet of the material at the interface the moments would be considered *compensated*.

The magnitude of both H_{eb} and H_c typically decrease with increasing temperature, until some critical temperature at which the H_{eb} disappears, which is known as the blocking temperature (T_b) of that particular FM/AFM system. The blocking temperature can be well below the bulk Néel temperature of the antiferromagnet and is dependent on factors such as the antiferromagnetic grain size and thickness of the antiferromagnetic layer [20, 53]. Typically H_c is still present above the blocking temperature and increases around the region of T_b , with a maximum at approximately T_b . The increase in coercivity can be ascribed to the decreasing anisotropy in the AFM layer, which causes the AFM moments to rotate in tandem with the FM moments [51]. H_c decreases with increasing temperature from T_b until it disappears. In ultra-thin AFM films, this typically coincides with T_N^* of the AFM thin film [12, 54]. In some cases, the AFM and FM can become EC due to the deposition temperatures but the FM/AFM will exhibit EC along two axes, due to the lack of an applied magnetic field to create uniaxial anisotropy [32]. In this case, the biaxial EC mirrors the biaxial nature of the FM easy axes.

The dependence of H_{eb} and H_c on the thickness of the FM layer for a fixed AFM thickness [51, 55] is typically given by:

$$H_{eb}, H_c \propto \frac{1}{t_{FM}} \quad (22)$$

This implies that for decreasing FM thickness, H_{eb} and H_c are both found to increase which highlights the interfacial nature of the EB effect. This relationship begins to degrade when the FM layer gets ultra-thin, which is largely due to discontinuity in the thin film which is affected by the growth method of the film among other factors. The AFM thickness dependence for a fixed FM thickness is more complex and an example of this can be seen in Figure 1.7 for a $\text{Ni}_{80}\text{Fe}_{20}/\text{FeMn}$ system [52]. In Figure 1.7, H_{eb} and H_c are mapped for thicknesses of the FeMn layer between 0 nm-14 nm, for a constant $\text{Ni}_{80}\text{Fe}_{20}$ thickness of 7 nm. H_{eb} and H_c are zero up to ≈ 2 nm, likely due to discontinuity of the AFM layer or the effective Néel temperature being exceeded at the temperature of measurement. In the thickness region from 2.5 nm-5.5 nm, H_{eb} increases rapidly until it reaches a saturation point, while H_c reaches a maximum before declining steadily. This region indicates that the anisotropy of the AFM layer is low and the AFM moments are not rigid. As the AFM layer gets thicker, its anisotropy increases and the AFM moments become more rigid, as evidenced by the declining H_c . When the H_c field becomes negligible, while the H_{eb} field is at maxima, this implies the AFM anisotropy is high and the AFM moments can be assumed to be unaffected by the rotation of the FM moments.

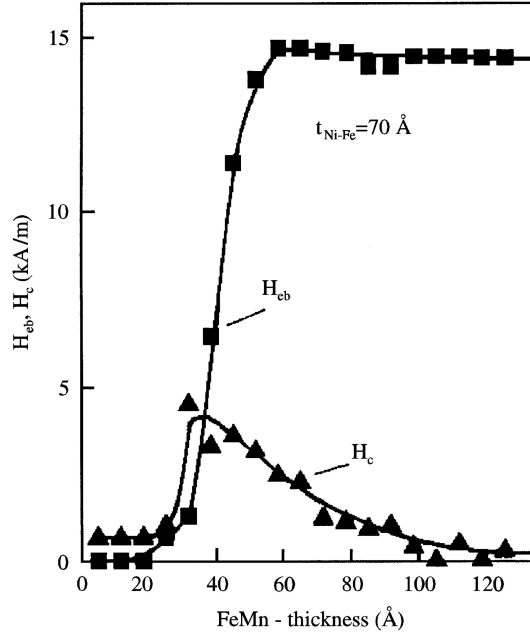


Figure 1.7: The dependence of H_{eb} and H_c on the thickness of the AFM layer for a fixed FM thickness in an exchange biased system. The thickness of the FM $\text{Ni}_{80}\text{Fe}_{20}$ layer is fixed at 7 nm, while the thickness of the AFM FeMn layer is varied between 0 nm-14 nm. Adapted from [52].

1.2.3.1 Models of EB

There are several models for explaining the EB effects in various systems and several review papers have been published on the topic [51, 53, 56, 57]. Given the complexity of modelling FM/AFM interfaces, no model is universally accepted and each describes different aspects of the effect in better detail. Several models relevant to this work will be discussed here.

Meiklejohn and Bean Model

In its simplest form, the Meiklejohn and Bean model (MB) expands on the Stoner-Wohlfarth model by adding a new anisotropy term describing the EB effect to Equation 18 [58]. This term is related to the anisotropy of the AFM layer (K_u^{AFM}) and the effective interface exchange coupling (J_{eb}) and then added the total energy of the system becomes:

$$E_{tot} = -\mu_0 \mathbf{M} \cdot \mathbf{H} t_{FM} \cos(\phi_H - \phi) + K_u^{FM} t_{FM} \sin^2(\phi) + K_u^{AFM} t_{AFM} \sin^2(\alpha) - J_{eb} \cos(\phi - \alpha) \quad (23)$$

where t_{FM} and t_{AFM} are the thickness of the FM and AFM layers respectively. The angle of rotation of the Néel vector $\mathbf{L}$ is given by α . Note that in this model the FM and AFM magnetisation directions are expected to be collinearly coupled, but that the AFM magnetisation tilts during magnetisation reversal i.e. ($\alpha \neq 0$). The exchange

coupling constant from the MB model is given by the following relation:

$$J_{eb} = H_{eb} M t_{FM} \quad (24)$$

The MB exchange coupling constant does not rely on the thickness of AFM layer and the model implies that EB occurs when the following relation is satisfied:

$$\frac{K_u^{AFM} t_{AFM}}{J_{eb}} \geq 1 \quad (25)$$

which occurs when the total energy in Equation 23 is minimised, i.e. ($\phi_H = \phi = 0$) and the measurement is performed along the direction of field cooling. The MB model relies on some large assumptions that result in it being a model of an idealised system that is hard to achieve in reality. The model assumes an atomically smooth interface between the FM and AFM layers. It also assumes that the Stoner-Wohlfarth model applies to both the FM and AFM layers: the AFM and FM both consist of a single magnetic domain, the FM layer rotates uniformly, and the AFM layer is perfectly rigid; The FM/AFM coupling is occurring equally at all points of the interface to an equal extent and finally, that the AFM moments are completely uncompensated at the interface [58]. When compared to experimentally observed parameters, the MB model overestimates a lot of the system parameters for EB. Another peculiarity when compared to real systems, is that it cannot account for the simultaneous appearance of H_{eb} and H_c seen in real systems. This arises from the total energy minimisation: For values of Equation 25 that are less than 1 the MB model predicts only H_c is apparent and for values greater than 1 it predicts the appearance of H_{eb} .

AFM Domain Wall

To improve the microscopic understanding of EB and improve upon the MB model several approaches were taken. Néel considered the formation of an AFM domain wall during the reversal of the FM magnetisation direction [6]. Néel also did calculations for very thin AFM layers and showed that H_{eb} disappears in this case while only H_c remains. This work was later expanded on by Mauri [59], who considers an exchange coupled FM/AFM bilayer. The FM and AFM layers are assumed to each consist of a single magnetic domain. If the anisotropy of the AFM layers is small, then under a uniformly rotating magnetic field the FM layer will rotate rigidly, while the AFM moments are partially rotated at the interface, as it is energetically favourable for the AFM layer to form a domain wall. If the AFM layer is sufficiently thin, the domain wall will not fully form and AFM moments at the opposite interface to the FM layer will partially rotate. This effect later became known as the exchange spring effect in AFMs. The Néel (1967) and Mauri (1987) models for AFM domain wall formation in exchange coupled FM/AFM bilayers were not experimentally confirmed until 2004,

when the domain wall formation was observed in a Co (2.5 nm)/NiO (single crystal) sample via X-ray magnetic linear dichroism (XMLD) spectroscopy [60].

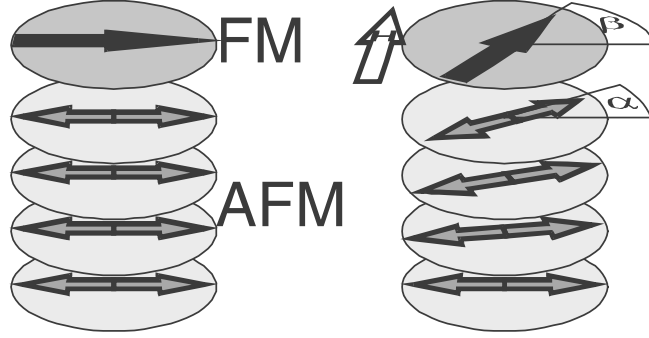


Figure 1.8: Diagram illustrating the creation of an AFM exchange spring. In the exchange coupled AFM/FM layer, as the FM magnetisation is rotated, the AFM magnetisation is partially rotated at the interface but not in the bulk illustrating the formation of a planar domain wall. $\beta = \phi$ in this work. Adapted from [60].

Uncompensated Moments and Interface Roughness

At the same time Mauri proposed his model for AFM domain wall formation in 1987, Malozemoff proposed a different model which considered the role of AFM/FM interface roughness as a parameter which would affect EB [61]. The model considered that atomic-scale roughness or magnetically frustrated domains caused by defects would drive the formation of AFM domains or domain walls perpendicular to the direction of anisotropy at the interface. These domain walls result in the reduction of the number of moments contributing to the EB effect. Thus a term accounting for the energy of domain walls had to be added to the total energy of the system, which then leads to a change in the EB. It was not until 2000 that this model was experimentally tested by diluting the AFM with non-magnetic defects [62]. At some dilution concentrations, the magnitude of H_{eb} was increased by 2-3 fold, which was attributed to the creation of uncompensated moments at the interface. Further works used X-ray magnetic circular dichroism (XMCD) spectroscopy, which is element sensitive, to separate the contributions of different elements to the interfacial moments [63, 64]. These works concluded that it was the small fraction, on the order of a few percent, of uncompensated moments at the interface which are pinned, that are responsible for the H_{eb} field. The rest of the uncompensated moments are able to rotate freely which contributes to the increased H_c . Domain wall formation described by the Malozemoff model were not ruled out as a contributing factor but the effect was deemed minimal in comparison to the pinned moments. It was speculated that the pinned moments, the fraction of which was consistent across multiple FM/AFM bilayer compositions, resulted from the AFM grain boundaries which covered a similar percentage of the interface.

Out-of-Plane AFM Moments

Some orientations of certain AFM materials have out-of-plane AFM moments in the case that bulk spin structure is preserved. FeF₂ is one such material; the AFM moments lying in-plane for the (110), out-of-plane for the (001) orientation and with the moments lying intermediary between the two for the (101) direction. The ECE in all of these orientations of FeF₂, which were coupled with an Fe layer, the dependence of the interfacial orientation of the AFM moments was studied [65]. When the AFM moments lay in-plane, the H_{eb} field observed was at a maximum. For the intermediary moment orientation this a H_{eb} was observed, but it was approximately half the value of the in-plane moments. Finally, for the out-of-plane moments, no H_{eb} was observed. An intuitive explanation of this is described by the spin-spin interaction strength between the AFM/FM which can be written as:

$$\mathbf{S}_{AFM} \cdot \mathbf{S}_{FM} = S_{AFM} S_{FM} \cos \alpha \quad (26)$$

where α is the angle between the AFM moments and the interface plane. Thus when $\alpha = 0^\circ$, H_{eb} is a maximum and when $\alpha = 90^\circ$, there is no H_{eb} observable, as seen experimentally in FeF₂. A similar argument can be made with the effective anisotropy of the AFM layer, which is also has a cosine dependence for the angle of the AFM moments with respect to the FM moments [51]. This is also observed in various orientations of the AFM FeMn [52, 55, 66].

1.2.4 Antiferromagnetic Spintronics

As previously mentioned, there have been a number of review papers on the field of AFM spintronics which cover the topic in far more detail than is possible here [17–22]. Each review has its merits but [20] gives a comprehensive overview of the field including some of the basics of antiferromagnetism, a materials survey and the primary effects which are being researched in the field. Many of these effects will only be covered in passing here for the sake of brevity and some are not mentioned at all as they are beyond the scope of this thesis. Such effects are the spin hall effect, inverse spin hall effect, spin galvanic effect; spin-orbit torque, which can be generated by the spin hall effect from a NM material and via inverse spin galvanic effects, as in Mn₂Au [27] and CuMnAs. These effects are described in far more detail in the reviews mentioned above but also in [67] and in [68]. A particular emphasis will be given to the magnetoresistive effects upon which the field of spintronics was founded, with a focus on how each effect relates to antiferromagnetism.

Antiferromagnetic materials are of interest in future spintronic applications due to their robustness against perturbation from applied magnetic fields and their ultrafast magnetisation dynamics which are typically in the THz regime; which can be used

to address the current THz gap not utilised in the electromagnetic spectrum to date. Additionally, antiferromagnets have the potential to generate large magnetotransport effects [20]. It is this that has led the community working on antiferromagnetic materials to both review existing materials and search for new, novel materials. Materials comprising of alloys between $3d$ and $5d$ metals display large spin-orbit coupling and large Néel temperatures, providing the ideal combination of properties for studying strong magnetic anisotropy phenomena, such as AMR and TAMR, have become of the highest priority. Mn_2Au is one such material.

1.2.5 Magnetoresistive Effects

Magnetoresistance (MR) is the relative change in resistance in a current carrying material under the application of an external magnetic field. This can be expressed by the following equation:

$$\frac{\Delta R}{R} = \frac{R(H) - R}{R} \quad (27)$$

where R denotes the resistance under no applied magnetic field, while $R(H)$ is the resistance measured under an applied magnetic field. Almost every conducting material exhibits some form of MR, regardless if it displays magnetism or not [69]. Amongst non-magnetic semiconductors, there are materials which exhibit MRs of several thousand percent [70, 71]. MR effects are widely researched and are continuously relevant in the detection of the microscale magnetic orientation of the magnetic media used in the storage industry. There are a plethora of differing MR effects, some of which will be briefly explained here in the context of their history and relevance to AFM spintronics.

1.2.5.1 Anisotropic Magnetoresistance

Anisotropic magnetoresistance (AMR) was first discovered in 1856 by William Thomson, the first Lord Kelvin [72]. Simply, AMR is a change in the resistance as there is a relative change in the magnetisation direction with respect to that of the current. Lord Kelvin observed that in a piece of Fe, the resistance increased when the magnetic field was applied longitudinally to the current direction and decreased when it was applied transversely to the current direction. The effect in Fe was noted to be on the order of 1% at room temperature. The effect was also noted to be larger in Ni in the same work. Over a century after its discovery, the effect was used in the first magnetoresistive read heads developed by IBM in 1990. The origin of the effect is in the spin-orbit coupling of the material and it is thus an intrinsic property, which is present in both bulk and thin films. There are two components to the AMR, the first is known as the non-crystalline AMR (ncAMR) which is only dependent on the orientation

of the magnetisation with respect to the current direction as previously described. This component of the AMR is typically on the order of 0.1% to a few % at room temperature. For example, $\text{Mn}_2\text{Au}/\text{Fe}$ bilayers were demonstrated to show an AMR of approximately 0.1% at room temperature [30], while a large AMR of approximately 6% was demonstrated in epitaxial Mn_2Au (001) thin films where the AMR change was driven by the manipulation of the AFM Néel vector via NSOT [27]. The second is the crystalline component of AMR (cAMR) which arises from the interplay between the crystal symmetry and magnetocrystalline anisotropies. This component is also typically small, for example in the same $\text{Mn}_2\text{Au}/\text{Fe}$ bilayers mentioned previously this crystalline component was found to be on the order of 1% at 10 K in a 14 T applied field [30]. However, this crystalline component can be significant for oxides comprising a 5d transition metal. For example the AFM semiconductor Sr_2IrO_4 ($T_N = 240$ K) was demonstrated to have a crystalline AMR of up to 14% in a 200 mT applied field at 77 K via point contact MR measurements [73]. A general expression for the longitudinal (ΔR_{xx}) AMR is:

$$\Delta R_{xx} = r_{nc} \cos(2\phi) + r_{c1} \cos(2\psi) + r_{c+2} \cos(4\psi) + r_{nc,c} \cos(4\psi - 2\phi) \quad (28)$$

And the transverse (ΔR_{xy}) AMR is:

$$\Delta R_{xy} = r_{nc} \cos(2\phi) + r_{nc,c} \cos(4\psi - 2\phi), \quad (29)$$

where ϕ describes the angle between the current and the magnetisation and ψ describes the angle between the magnetisation and a specific crystalline direction, which is system dependent. In the longitudinal AMR expression shown in Equation 28, the first term describes the ncAMR component, while the second and third terms describe the lowest-order cAMR components. The final term is the lowest order crossed ncAMR and cAMR term. The transverse AMR expression in Equation 29 is much simpler, with no purely cAMR terms which are excluded through symmetry arguments. The transverse AMR is sometimes referred to as the planar Hall effect.

AMR is present in both FM and AFM materials, and several studies have demonstrated AMR in materials of interest in the field of AFM spintronics, such as Mn_2Au [24, 27, 30], FeRh [16] and CuMnAs [74].

1.2.5.2 Giant Magnetoresistance

The GMR effect was independently discovered by both Albert Fert [75] and Peter Grünberg [76] in the late 1980s. Both Fert and Grünberg jointly received the Nobel laureate in physics for this work in 2007. The effect was dubbed the GMR due to its order of magnitude increase on any AMR effect that had been observed to that

point. Devices which are based on the GMR effect generally consist of a FM/NM/FM sandwich where the NM material is metallic. The two FM materials must possess a different magnetic hardness, either by using two different alloys or by fixing one of the FM electrodes via EB with an AFM layer. This allows the “free” FM electrode to be switched using a magnetic field between parallel ($\uparrow\uparrow$) and antiparallel ($\uparrow\downarrow$) configurations. Devices utilise both the current-in-plane and current-perpendicular-to-plane geometries. The effect works on the basis of the scattering of electrons at interfaces with the FM materials due to the misalignment of the electrons’ spins with that of the direction of magnetisation of the FM electrodes. This results in two resistance states where the resistance is high for the $\uparrow\downarrow$ state and low for the $\uparrow\uparrow$ state. The magnitude of the GMR effect is given by the resistance ratio between the two states which can be written as:

$$\frac{\Delta R}{R} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} \quad (30)$$

Devices based on the GMR effect are generally referred to as spin-valves and came to prominence as read heads which helped detect the magnetic bits used in the data storage industry. The increased magnitude of the GMR effect, in comparison to the AMR effect and the resulting increase in the sensitivity of devices based upon the GMR effect, helped increase the storage density of magnetic recording media throughout the late 1990s and early 2000s.

As mentioned in the introduction there have been several theoretical works on the AFM GMR effect (AGMR) [8–10]. In the earliest theoretical work, there was a suggestion that the AGMR effect should depend on the relative orientations of the Néel vector, but the effect should be small due to the spin-independent nature of scattering in AFMs in comparison to FMs [8]. The manipulation of the AFM vectors would require the utilisation of the ECE, however, given that the effect is expected to be small and the experimentally difficult nature of creating an AGMR spin valve, there have been no experimental works demonstrating it to date.

1.2.5.3 Tunneling Magnetoresistance

The structure of tunnel magnetoresistance devices are similar to that of GMR devices, with the key difference being that the NM layer is replaced with an insulating dielectric barrier layer. The insulating layer is sufficiently thin that electrons can tunnel across the barrier and the junctions are biased to increase the probability of electrons tunneling. For electrons tunneling from one FM electrode to another, there must be available states at the Fermi level for that electron to tunnel into, and this will be dependent on the orientation of the magnetisation in both FM electrodes relative to each other. For the parallel arrangement of the FM electrodes, there will be available states for the

electrons to tunnel into meaning the resistance of the junction will be lower, and for the antiparallel orientation, there will be fewer states available for electrons to tunnel into meaning the resistance of the junction will be higher.

The effect was first discovered in 1975, where a tunnel junction of the form Fe/GeO/Co exhibited a TMR of 14% at 4.2 K [77]. As junction quality increased and AlO_x barriers began to be incorporated into TMR devices the TMR ratio increased considerably [78]. TMR ratios of up to 600% have been observed at room temperature with junctions based on an epitaxial MgO tunnel barrier [79].

Figure 1.9 shows a typical example of the TMR measurement with relative orientations of the two FM layers indicated at varying positions of the applied magnetic field for the device.

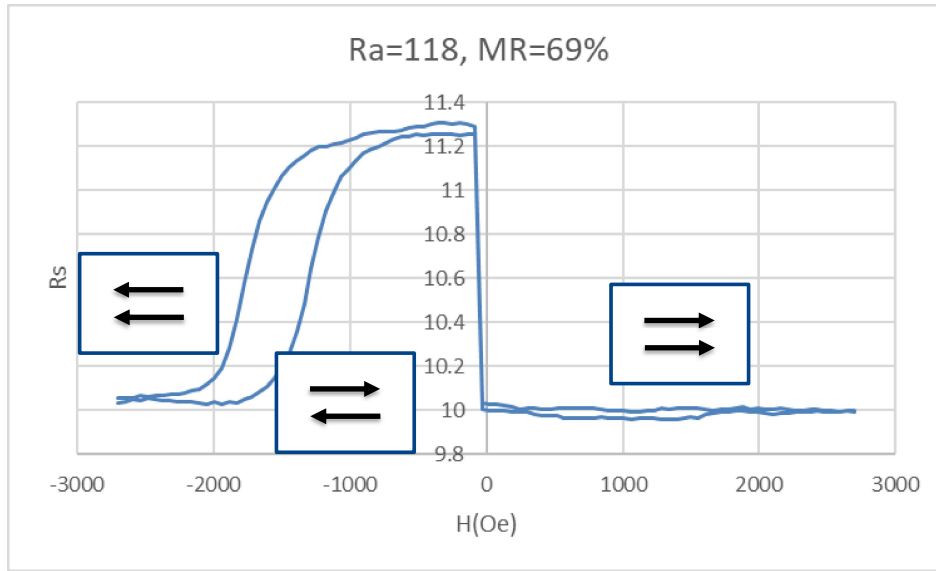


Figure 1.9: An example of a TMR measurement. The plot shows the sheet resistance of the tunnel junction stack versus the magnetic field with the relative orientation of the free and pinned layers indicated at each point of the applied field⁴. Note that R_a denotes the resistance per unit area of the stack in units of $\Omega/\mu\text{m}^2$.

Similar to GMR, the role of AFMs in TMR structures has primarily been to pin one of the FMs. Antiferromagnetic TMR (ATMR) has been experimentally demonstrated, through the asymmetric rotation of IrMn_3 moments on either side of the tunneling barrier via the exchange spring effect. In junctions where no domain wall was formed in the IrMn_3 layer there was a minute change in resistance between the two states ($\approx 0.1\%$) [80]. The effect is far lower in AFMs as the interfacial DOS tends not to exhibit spin polarisation. There has been magnetic coupling demonstrated in an all AFM junction of the form Cr/MgO/Cr, although no magnetotransport effects were measured [81].

⁴TMR stack with the form $\text{IrMn}_3/\text{Co}_{75}\text{Fe}_{25}/\text{CoFeB}/\text{MgO}/\text{CoFeB}$ grown and measured by our collaborators at Western Digital.

1.2.5.4 Tunneling Anisotropic Magneto-Resistance

The TAMR effect is essentially the change in resistance of an antiferromagnetic material as the direction of magnetisation is rotated, and a current is passing perpendicularly through the AFM material and a tunneling barrier. The electrode on the opposite side of the tunnel barrier need only be a NM material, which is in contrast to both TMR and ATMR. The effect is typically largest in materials with strong spin-orbit coupling which results in large anisotropy of the density of states with respect to magnetisation orientation. This has resulted in TAMR being included in a sub-field of spintronics dubbed spin-orbitronics. TAMR is very similar to AMR as they both possess crystalline and non-crystalline components, with the difference being that in TAMR these components are hard to separate from each other. This arises as TAMR usually occurs in multilayer stacks, where the crystal is asymmetric in the in-plane and out-of-plane directions (it is typical in AFM layers of a thickness less than 10 nm) [20]. The first instance of TAMR was in 2002, where a scanning tunneling spectroscopy study of the local density of states in Fe magnetic domains and domain walls revealed a difference in the local DOS between the two [82].

TAMR was subsequently studied in a variety of ferromagnetic tunnel junctions [83–85] with the spin-valve shown in (Ga,Mn)As tunnel junctions [83]. The effect was only apparent at low temperatures with no more than a 6 or 7 percent change in resistance. The reason for this is that ferromagnetic transition metals with the potential for room temperature TAMR have weak spin-orbit coupling. TAMR was found to be slightly larger, up to 10% at 4 K in [Co/Pt] multilayers, where the heavy metal Pt increased the strength of the spin-orbit interaction [85]. This realisation shifted the focus of TAMR research to finding alloys consisting of a 3d transition metal with large spontaneous moments and a 5d noble metal to maximize the spin-orbit coupling strength.

In 2010, both IrMn and Mn₂Au were predicted to have large TAMR signals with calculations of the densities of states showing that Mn₂Au has the larger anisotropy of the two materials [11]. Both of these materials order antiferromagnetically, as do many of the bimetallic alloys containing Mn. The large TAMR signal predicted for IrMn₃ was experimentally confirmed for a NiFe/IrMn₃/MgO/Pt in-plane anisotropy stack configuration where a signal of up to 160% at 4 K was observed [14, 86]. Figure 1.10 shows the 130% TAMR effect from that work observed in a 1.5 nm IrMn₃ layer. The IrMn₃ antiferromagnetic moments were manipulated through the exchange spring effect, where the IrMn₃ layer was exchange coupled to the adjacent NiFe layer. A further study of these stacks revealed the optimum ratio of thickness' of NiFe/IrMn₃ to be 10/4 nm each [12]. This was done by measuring the exchange bias field and the coercive field for a range of temperatures for stacks where the IrMn₃ thickness was varied. When both the coercive and exchange bias field were present it indicated that the antiferromagnetic moments were partially rotated through the exchange spring

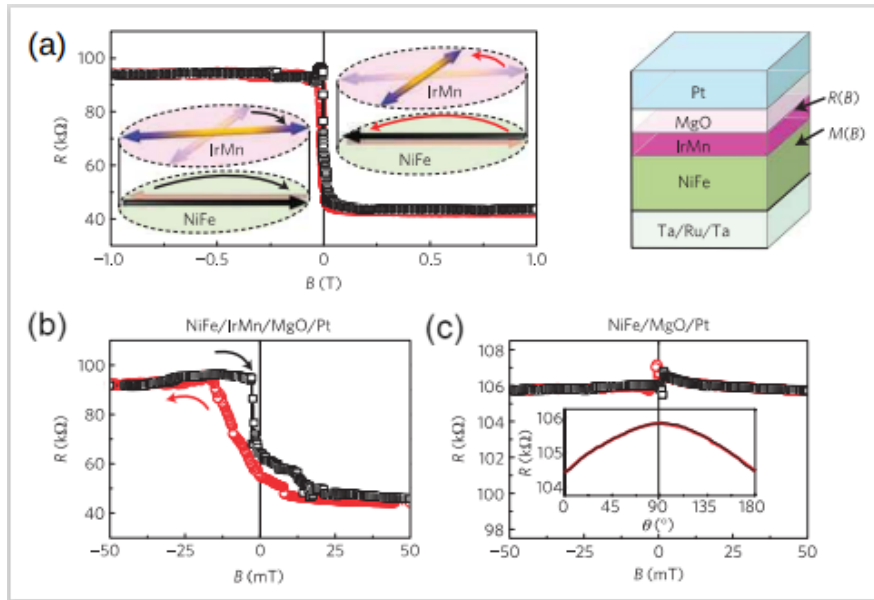


Figure 1.10: An example of a TAMR measurement taken from a NiFe/IrMn₃/MgO/Pt tunnel junction. The composition of the stack is indicated in the top right of the figure. (a) Shows the 130% TAMR signal measured for a 1.5 nm IrMn₃ layer, with a schematic illustration of the manipulation of the AFM moments through the exchange spring effect inset. (b) Hysteretic profile of the 130% TAMR signal in the magnetic field range of -50 mT- 50 mT. (c) Measurement of the MR of a stack with no IrMn₃ present, illustrating that the IrMn₃ layer is almost solely responsible for the TAMR signal observed in the other stacks. Adapted from [86].

effect. The 4 nm IrMn₃ layer showed a small stable signal up to 250 K, which became unstable thereafter. Further work showed the TAMR effect in FM-free tunnel junction, where 2 nm of IrMn₃ was used as the active layer. The orientation of the IrMn₃ moment was set by cooling the junction through the Néel temperature in an applied magnetic field; different orientations of the magnetic field during cooling resulted in different resistance states of the device [15]. TAMR was also demonstrated in a tunnel junction with perpendicular magnetic anisotropy, consisting of [Co/Pt] multilayers with IrMn₃ as the active layer. Magnetisation reversal of the FM layer resulted in the partial reorientation of the AFM moments via the exchange spring effect, which gave a stable room temperature signal of $\approx 0.2\%$. Similar work patented by this group claims that using [Co/Pd] multilayers as the ferromagnetic layer achieved an out-of-plane TAMR signal of up to 5% [87, 88]. Further work by this group investigated the magnetisation dynamics in the AFM FeMn layer of similar stacks to those above, via XMLD and X-ray absorption spectroscopy measurements. TAMR measurements were also performed in this work [89].

1.2.6 Mn₂Au

This section is divided up into three sections. Firstly Mn₂Au is discussed in the context of its history, given it was mischaracterised upon its first synthesis. The second section

will cover in detail the thin film synthesis of Mn_2Au , the methodologies, substrates and buffer layers necessary for high quality growth. The final section will cover in depth the broad range of research that has been performed on Mn_2Au in the last number of years.

1.2.6.1 History and Crystal Structure

Mn_2Au is one of a number of alloys consisting of Mn-Au. Many of the Mn-Au alloys display magnetic structure: these include the antiferromagnets MnAu ($T_N \approx 513\text{ K}$) [90], MnAu_3 ($T_N \approx 140\text{ K}$) and Mn_3Au_5 ($T_N \approx 345\text{ K}$), and the ferromagnetic alloy MnAu_4 ($T_C \approx 373\text{ K}$) [91]. Very little study has been done on Mn rich alloys due to the fact that Au has very limited solubility in Mn. If one looks at the Mn-Au phase diagram, seen in Figure 1.11, it is evident that the only stable, Mn rich compound that emerges is the Mn_2Au alloy [92, 93].

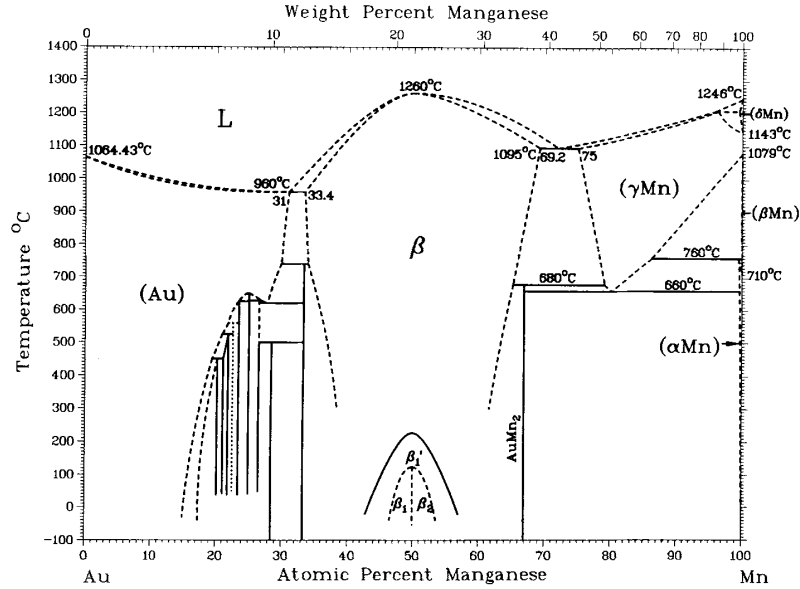


Figure 1.11: Phase diagram of Mn-Au alloys. Mn_2Au is the only stable Mn rich alloy that can be seen due to the limited solubility of Au in Mn. Adapted from [93].

Mn_2Au was first reported as being non-magnetic from studies of the 197 Au Mössbauer spectra [94] and from magnetisation measurements. The magnetic susceptibility was found to have a maximum at low temperatures ($\approx 5\text{ K}$) and display a low almost value for temperatures up to 650 K, without exhibiting any significant anomaly that would indicate a phase transition from magnetic order to disorder. The behaviour of the susceptibility at low temperatures is very similar to that of metamagnetic materials in an applied external magnetic field. Metamagnetism is characterised by a number of different effects, such as an anomaly in the susceptibility away from the magnetic order-disorder transition, or a large increase in magnetisation for a relatively small change in the applied field; the physical explanations of these anomalies are varied

and are dependent on the properties of the material system in question. From this, it was concluded that Mn_2Au was paramagnetic and it was suggested that the magnetic moments on Mn are delocalised [95]. Although the authors suggested that a neutron diffraction study of Mn_2Au was highly desirable this was never completed.

However, in 2008 a first principles local spin-density approximation study found that Mn_2Au should possess a high Néel temperature of approximately 1600 K [96], which would give it the highest Néel temperature of all known AFMs. The Néel Temperature is much higher than the peritectoid phase transition of approximately 950 K [93] which explains the absence of any magnetic order-disorder transition in the experimental data prior to 2008.

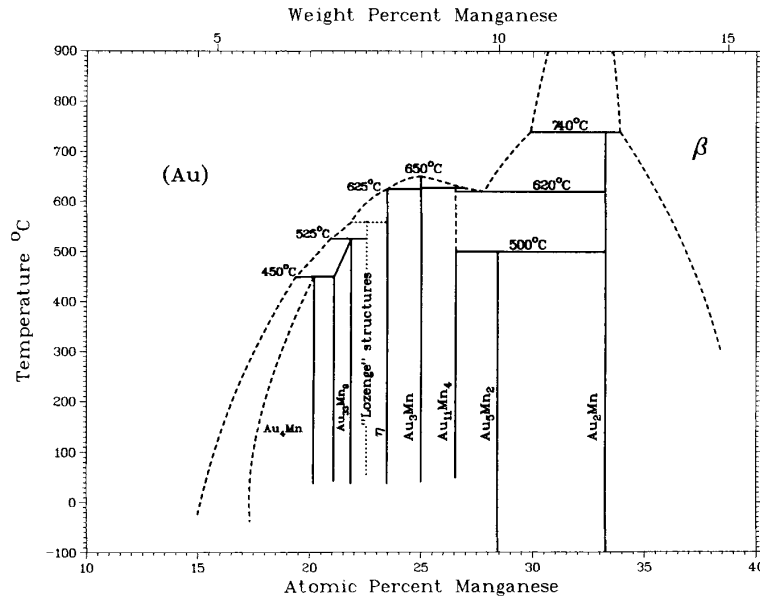


Figure 1.12: An enlargement of the Mn-Au phase diagram between the Mn atomic percentage of 10-40% showing the detail of the Au-rich Mn-Au alloys. Adapted from [93].

Mn_2Au has a body-centred tetragonal crystal structure, which can be seen in Figure 1.13, with lattice parameters of $a = 3.328 \text{ \AA}$ and $c = 8.539 \text{ \AA}$, and a space group of $I4/mmm$ [92]. It was originally thought the magnetic moments of Mn_2Au would align along the c -axis, as the moments did in other AFMs with a similar crystal structure, however in 2013 it was revealed through neutron diffraction experiments on powdered Mn_2Au , that the moments actually lay perpendicular to the c -axis. Additionally in this study, they found that the moments in the material have a magnitude of $4 \mu_B$ at 2 K, and that it lies solely on the Mn atoms with the moment direction alternating from one sheet of Mn atoms to the next, corresponding to a magnetic space group of $Im'mm$. In another neutron diffraction study, it was shown that the moments lie along the $[110]$ axis, with an equivalent easy moment direction along the $[1\bar{1}0]$ [25]. Interestingly it was also found that the Mn atoms held 85% of their ground state value at 900 K, suggesting that the Néel Temperature is in the region of 1300 K-1600 K [23].

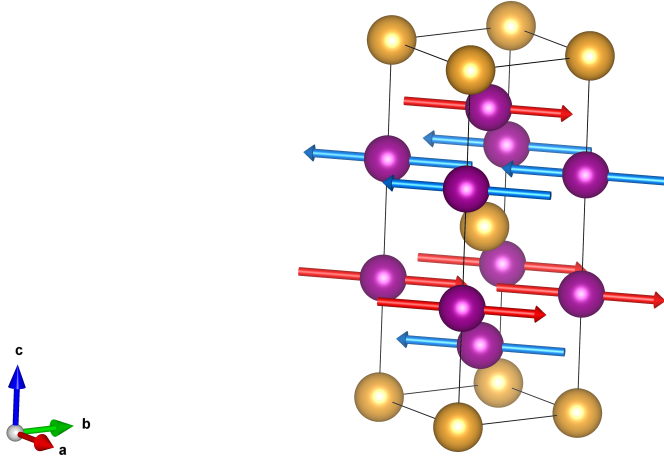


Figure 1.13: A single unit cell of Mn_2Au , with a body-centred tetragonal structure and a space group of $I4/mmm$ and a magnetic space group of $Im'mm$. The purple-coloured atoms are Mn, while the gold-coloured atoms are Au. The arrows represent the magnetic moments lying along the easy $[110]$ direction.⁵

The following paragraphs will summarise some of the more recent experimental papers which have been published on Mn_2Au in the area of AFM spintronics. There have been several experiments demonstrating the ECE in Mn_2Au [31, 32, 68, 97]. AMR has also been demonstrated in various works [24, 27, 30] and as previously mentioned NSOT has been demonstrated in Mn_2Au several times [27–29], and SOT several others [98, 99]. The effects of Néel vector rotation on the Mn_2Au valence states have been probed via bulk sensitive Hard X-ray Angular Resolved Photoemission Spectroscopy (HARPES) and the more surface sensitive Soft X-ray (SX-)ARPES [100]. The Néel vector in Mn_2Au has been optically read out using complex XMLD and PEEM techniques [101], while more recent work has shown Néel vector rotation in tensile strained Mn_2Au which was triggered optically using a laser [102]. In other work, the antiferromagnetic spin hall effect was observed in Mn_2Au [103].

Free-space electromagnetic emissions in the THz regime have been observed in $\text{Mn}_2\text{Au}/\text{Co}$ bilayers, which were excited using femtosecond optical pulse and measured using THz time-domain spectroscopy in a dry air environment [104]. Mn_2Au was also recently determined to have a “giant” spin torque efficiency, in samples with a single out-of-plane (001) crystalline orientation [105]. Both field-like torque and anti-damping torque have been experimentally observed in Mn_2Au [99]. A large damping-like SOT efficiency (ξ_{DL}) was also observed in magnetron sputtered Mn_2Au (001) thin films on a SrTiO_3 (001) substrate ($\xi_{DL} = 0.731$) [105], which was reportedly three times larger than that

⁵Image generated using <https://jp-minerals.org/vesta/en/>

previously reported in sputtered Mn_2Au (001) thin films ($\xi_{DL} = 0.22$) [27]. The effective AFM exchange constant (J_{eff}) in Mn_2Au has been determined to be 24(5) meV, using a combination of X-ray absorption spectroscopy and XMCD measurements on a 10 nm Mn_2Au (001) thin film [106]. Note that $J_{eff} = \frac{(4J_1+J_2)}{2}$, where J_1 and J_2 describe the antiferromagnetic interaction between the neighbouring Mn planes in Mn_2Au .

1.2.6.2 Growth Methods

Table 1.3: Table summarising the methodologies, substrates, buffer layers and resultant crystallographic orientations for thin film growth of Mn_2Au . Where there are multiple instances of similar substrates, buffer layer and methodologies used only the first instance is referenced. The crystallographic reflexes are ordered in terms of intensity, not angle. Where possible the specific growth method is also noted in the table.

Substrate	Buffer Layer	Growth Method	Out-of-Plane Orientation	Reference
MgO (001)	Fe (001)	MBE (e-beam)	(101), (110), (200)	[31]
Al_2O_3 (1 $\bar{1}$ 02)	Ta (100)	RF Magnetron	(101), (00n)	[33]
Al_2O_3 (1 $\bar{1}$ 02)	None	Magnetron	(00n), (200),	[107]
Si/SiO ₂	Pt (111)	Magnetron	(110), (112)	[107]
MgO (001)	ZrN (001)	DC Magnetron	(00n), (n0n)	[108]
MgO (111)	None	Magnetron	(103), (206)	[109]
SrTiO ₃ (100)	None	Magnetron	(101), (202)	[109]
MgO (220)	None	Magnetron	(204)	[109]
Al_2O_3 (1 $\bar{1}$ 02)	Ta (100)	MBE (Au e-beam & Mn effusion)	(00n)	[34]

The synthesis of crystalline Mn_2Au in thin film form has only been achieved in a handful of different ways in the 11 years since it was cast into renewed focus. Table 1.3 lists the methodologies by which Mn_2Au has been grown, the substrates and buffer layers used and the reflections observed via XRD are listed in order of intensity of diffraction peak. The first paper detailing thin film growth, achieved poly-crystalline Mn_2Au grown on top of a 5 nm epitaxial Fe seed layer on MgO (001). The Mn and Au were deposited separately via e-beam evaporation in 1.2 nm and 0.8 nm increments respectively, at a substrate temperature of 200 °C [31]. Later “epitaxial” (101) oriented Mn_2Au was grown by a similar method, however, this time the Mn and Au increments were 0.6 nm and 0.4 nm respectively, while the substrate was kept at 300 °C [30]. Both of these Mn_2Au films were grown via Molecular Beam Epitaxy (MBE).

By far the most prominent method of synthesizing Mn_2Au is via Magnetron Sputtering from a single stoichiometric target of Mn_2Au onto a Ta seed layer, which has been sputtered onto Al_2O_3 (1 $\bar{1}$ 02) substrate at 600 °C. The Ta grows in the (100) direction while the Mn_2Au grows in the (001) direction on top of this [27, 33, 106, 107]. The epitaxial relation between the layers was confirmed via XRD [33]. Mn_2Au films of higher quality were grown via MBE using the same Ta (001) buffer layer and Al_2O_3 (1 $\bar{1}$ 02) substrate and compared to the magnetron sputtered samples more recently

[34]. These methods have since been refined, such that the Ta buffer layer is no longer necessary and Mn_2Au can be sputtered directly from a stoichiometric target directly onto an Al_2O_3 ($1\bar{1}02$) substrate at 600°C [28].

Less ubiquitous methods include the utilisation of a ZrN (001) buffer layer. The layer was deposited via reactive argon/nitrogen sputtering onto a MgO (001) substrate. ZrN grows epitaxially on MgO with a 45° rotation of the basal plane. Mn_2Au was then deposited via DC magnetron co-sputtering of separate Mn and Au targets. Mn_2Au was found to grow epitaxially on the buffer layer in the (001) orientation, such that the epitaxial relation can be described as $\text{MgO} [100] \parallel \text{ZrN} [100] \parallel \text{Mn}_2\text{Au} [110]$ [29]. It must be noted that there is no confirmation shown of the epitaxial relation in the paper itself and that in XRD patterns of the various growth temperatures used, there are indications of other Mn_2Au phases. The authors suggest that the use of a ZrN buffer layer gives rise to films with a true fourfold rotational symmetry, which is in contrast to the pseudo-fourfold symmetry seen in samples grown on a Ta buffer layer and $r\text{-Al}_2\text{O}_3$ substrate, due to the average 3° tilt of the Mn_2Au c-axis due to the tilt of the $r\text{-Al}_2\text{O}_3$ surface.

Similarly, sputtering of a single Mn_2Au target onto different substrates has been reported. The results rendered “quasi-epitaxial” (103), (101) and (204) Mn_2Au films on single crystal MgO (111), SrTiO_3 (100) and MgO (110) substrates respectively [109]. Similarly (103) oriented Mn_2Au films were grown on a piezoelectric PMN-PT ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}\text{O}_3$) (011) substrate [110].

Possibly the most relevant, for this body of work at least, is the growth of Mn_2Au on a Pt seed layer. Both the Pt and Mn_2Au are DC sputtered from single targets onto a thermally oxidised SiO_2 on a Si wafer. The Pt grew in its (111) orientation and the Mn_2Au grew (110) textured on top of it [107].

Chapter 2

Experimental Methods

This chapter outlines and explains the techniques used throughout the course of this work. The majority of the samples were grown in Ultra High Vacuum (UHV) conditions via Molecular Beam Epitaxy in a system designed and supplied by DCA. The samples were deposited using a combination of electron beam (e-beam) evaporators and Knudsen effusion cells. The samples were characterised using a variety of *in-situ* (reflection high energy electron diffraction, low energy electron diffraction) and *ex-situ* (X-ray Diffraction, X-ray reflectometry, etc) techniques. The magnetic characterisation technique used was vibrating sample magnetometry.

2.1 Molecular Beam Epitaxy

Molecular Beam Epitaxy is a deposition technique renowned for its low growth rate, in the region of 1 - 10 mono-layers per second and extreme control of growth parameters such as thickness, stoichiometry and crystal phase. The technique is characterised by the pressure at which deposition occurs, ultra-high vacuum ($\sim 1 \times 10^{-9}$ torr), a regime where the distance from the growth source to the substrate in the vacuum chamber is larger than the mean free path of interactions between the atoms or molecules of an evaporated species at this pressure, i.e. the molecular flow regime. Each atom can thus be assumed to be non-interacting on its path from source to substrate. This is what partially gave rise to the “molecular beam” in 1970 when Alfred Cho, known as the father of MBE, coined the technique “Molecular Beam Epitaxy” [111]. The “epitaxy” portion is a portmanteau of the greek words “ $\epsilon\pi\iota$ ” and “ $\tau\alpha\chi\iota\sigma$ ”, which mean “above” and “in an ordered manner”, respectively [112].

There are two distinct forms of epitaxy; epitaxy where the film and substrate are the same material, which is classified as homoepitaxy, and epitaxy where the film and substrate are different materials, known as heteroepitaxy. An example of the former would be MgO thin films grown on MgO substrates, while the latter would be Pt thin

films on Al_2O_3 . Figure 2.1 shows an example of homoepitaxy and two examples of heteroepitaxy. True epitaxy can only occur when the in-plane lattice parameters of the film and substrate are equal or within a few percent of each other. The lattice mismatch between two lattice parameters is then defined as;

$$\frac{\Delta a}{a} = \frac{a_{\text{film}} - a_{\text{substrate}}}{a_{\text{film}}} \quad (1)$$

where a denotes the in-plane lattice parameter.

Generally, the two lattice parameters will not be the same, as the film is typically a different material from the substrate. The slight difference will cause the thin film to grow epitaxially strained until a certain point at which it then becomes more energetically favourable for defects to form, usually when the film reaches a critical thickness. These defects may be grain boundaries, and screw or edge dislocations.

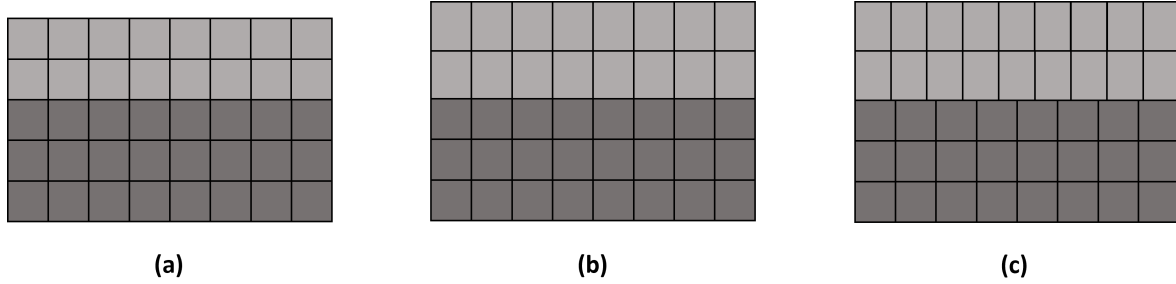


Figure 2.1: A diagram showing three different forms of epitaxy that can occur. The dark grey blocks represent the substrate unit cells while the light grey blocks represent the film unit cells. (a) An example of a homoepitaxial film. The film and the substrate unit cells have the same in-plane and out-of-plane lattice parameters. (b) An example of a strained heteroepitaxial film. The film unit cell has distorted its in-plane lattice parameter in order to match that of the substrates, while it retains its intrinsic out-of-plane lattice parameter. (c) An example of a relaxed heteroepitaxial film. The film has an in-plane lattice parameter 88% that of the substrates.

If one were to think about the ideal way for thin film growth to proceed, one would imagine that one layer of atoms would be complete before the next layer of atoms starts and that the growth would proceed in a layer-by-layer fashion. This ideal growth mode is known as Frank van der Merwe growth. It occurs when the force between atoms landing on the substrate, known as adatoms, and the atoms on the substrate, is greater than the force between the adatoms. This growth mode is typical in homoepitaxial depositions or in certain chemical vapour deposition (CVD) techniques, such as atomic layer deposition (ALD). The other extreme to this ideal growth mode occurs when the inter-adatom cohesive force is greater than the substrate adatom adhesion force [113]. This causes the adatoms to agglomerate into 3-dimensional islands on the surface, which is known as the Volmer-Weber growth mode. The intermediate of these two extremes is known as Stranski-Krastanov growth, where the film starts to grow in a

layer-by-layer fashion, and at some critical thickness proceeds to 3-dimensional island growth. This critical thickness is governed by parameters such as the lattice parameters and surface energies of the film and substrate materials [114]. Figure 2.2 shows these modes in cross-sectional format.

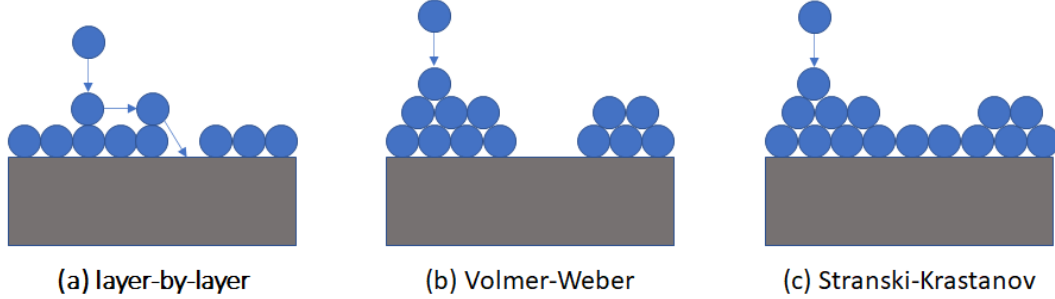


Figure 2.2: Diagrams of the three central modes of thin film growth. (a) Layer-by-layer, where one layer is completed before the next starts, (b) Volmer-Webber, where atoms form discontinuous islands, and (c) Stranski-Krastanov, which is a mixture of (a) and (b).

2.1.1 The DCA M600 MBE System

The MBE system used in this work is a DCA M600 MBE system with a base pressure of 2×10^{-10} torr. A schematic of the deposition chamber is shown below in Figure 2.3. The deposition chamber is connected to a load-lock chamber with a base pressure of $\sim 5 \times 10^{-7}$ torr. Substrates are placed in a Molybdenum substrate holder, which is then placed into a sample cup holder on a linear motion, magnetically coupled transfer arm. The transfer arm has two sample cup holders, which allows for the growth of two samples without the need for venting the load-lock chamber. The deposition chamber has a linear motion sample manipulator, with rotation enabled via magnetic coupling, which enables smooth transfer of the substrate holders from the load-lock to the deposition chamber. The sample manipulator also has an oxygen-resistant high temperature heater which can heat substrates up to 850°C , and a pneumatically controlled shutter covers the manipulator when not in use. A water-cooled panel bisects the top and bottom of the deposition chamber, with holes in the line of sight for sources enabling deposition and a large volume cryopanel envelopes the top half of the chamber to prevent thermal cross-talk between components.

Both the deposition chamber and the load-lock chamber have oil-free pumping systems. Each has a scroll pump for roughing and backing a turbomolecular pump. The deposition chamber has a 1000 L s^{-1} turbomolecular pump, while the load-lock has a 70 L s^{-1} turbomolecular pump. The deposition chamber also has a 500 L s^{-1} triode ion pump. Each chamber has a hot-cathode ionisation gauge for measurement of pressures $> 5 \times 10^{-4}$ torr, while the load-lock also has a Pirani gauge. The deposition chamber

also contains the *in-situ* monitoring tools; Reflection High Energy Electron Diffraction (RHEED) and a Residual Gas Analyser (RGA).

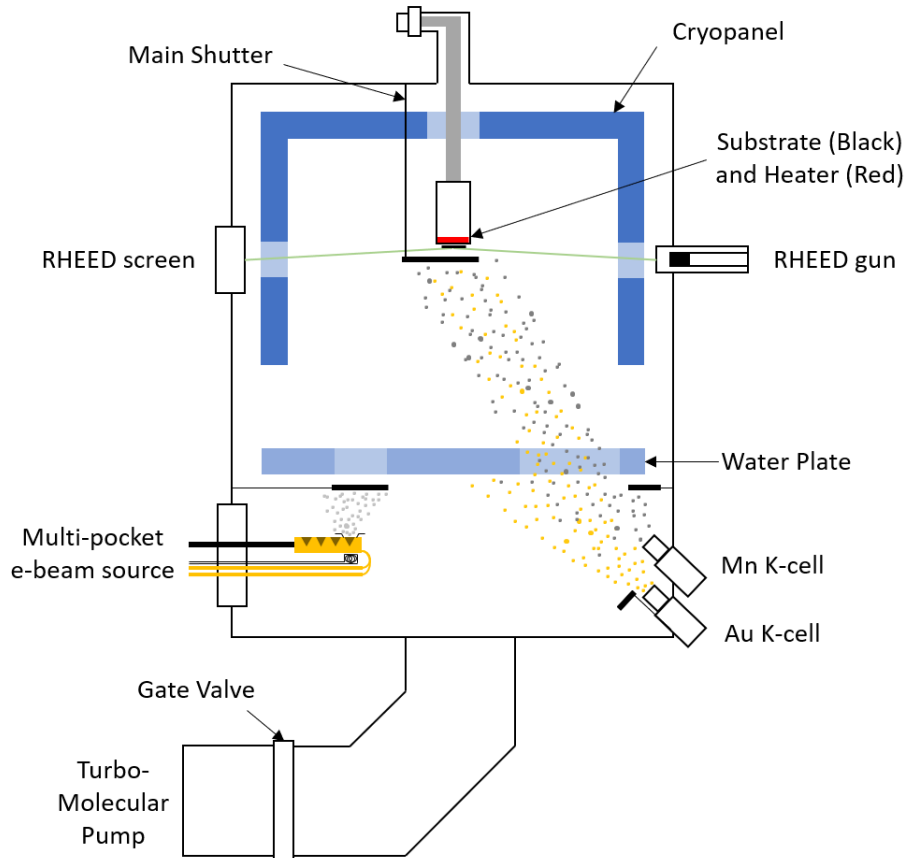


Figure 2.3: A schematic of the DCA M600 MBE system. The Mn and Au Knudsen cells are shown open, while the multi-pocket e-beam source is shown with its shutter closed. The main shutter covering the sample manipulator is closed preventing growth. For clarity, the single pocket e-beam source, the load-lock, the ion pump and RGA are not shown. The K-cells are located equidistant from the sample holder and are located radially around the chamber.

There are two main types of evaporators utilized on this MBE, electron beam (e-beam) evaporators and Knudsen effusion cells (K-cells). E-beam guns consist of an electron-emitting filament and a crucible containing the evaporation material. The filament is located directly beneath the crucible. The filament is rated to carry up to 50 A, which can typically provide an emission current of up to 1 A. As the electrons are emitted, a potential of 8 kV, applied between the filament and the crucible, accelerates the electrons while a permanent magnet deflects the electron beam onto the crucible. Two electromagnets beside the crucible allow for the precise control of the beam position within the crucible and also allows for the e-beam to be rastered to provide even heating over the area of the material. In addition, all e-beam sources have a pneumatically controlled shutter which allows precise control of layer growth as well as layer thickness. There are two e-beam evaporators in our MBE, a single pocket 25 cm³, crucible evaporator and a 4 pocket, 7 cm³ crucible evaporator, each of which

is equipped with a water-cooled, quartz crystal monitor. The crystal monitor is set at such an angle that the rate of deposition of material can be measured without opening the shutter preventing deposition on the substrate. Each quartz crystal monitor also has a small shutter to protect the lifetime of the crystal when not in use.

In this work, both the Mn and Au are deposited simultaneously using separate K-cells. The premise of operation for the K-cells is essentially a crucible (typically made from an inert ceramic such as alumina or boron nitride) filled with the material to be evaporated. This crucible is wrapped in a tungsten filament. As current is passed through the filament, it heats up and also heats the crucible and thus the evaporation species. K-cells are typically able to reach temperatures of $\sim 1400^\circ\text{C}$ with specialised versions stretching to $\sim 2000^\circ\text{C}$. This limits the materials that can be evaporated with K-cells as the material must have an appreciable vapour pressure below the maximum temperature of the K-cell, and many transition metals and oxide materials do not. E-beam evaporators are much more versatile in this respect as a multitude of different materials with much lower vapour pressures can be evaporated.

2.1.2 Stoichiometry Control

Initially, the MBE chamber was fitted with a third water-cooled quartz crystal monitor at sample height which was mounted onto a linear axial drive such that it could be positioned into the sample zone to get an accurate deposition rate from the K-cells. This was used for a small number of the samples shown in this thesis and they will be highlighted accordingly. This was replaced with what is known as a Beam Pressure Monitor (BPM), which is essentially a hot-cathode ion gauge covered with shielding in all directions except that facing the sublimated species. The BPM is similarly fitted on a linear axial drive allowing for it to be positioned into the sample zone. Unless otherwise stated, all other samples deposited using the K-cells were deposited using the BPM to guide the stoichiometry.

The BPM can be used to extract the flux of each of the cells at a range of temperatures. The flux is given by the relationship;

$$\text{flux} = BEP - BG \quad (2)$$

where BEP is the Beam Equivalent Pressure, and BG is the background pressure. To expand, the BEP , for a specific temperature, can be defined as the pressure recorded on the BPM , when the BPM is in the sample zone, and the K-cell shutter is open. The BG pressure is the pressure recorded on the BPM when the shutter on the K-cell is closed. If the flux is determined for a range of temperatures for a cell then an Arrhenius plot can be produced, an example of which is shown in Figure 2.4.

To do that, the Arrhenius equation for the temperature dependence of reaction rates must first be considered:

$$k = Ae^{\frac{-E_a}{k_B T}} \quad (3)$$

where k is the rate constant of the reaction, A is some pre-exponential factor independent of temperature, E_a is the activation energy for the reaction, k_b is Boltzmann's constant and T is the reaction temperature in K. In the case of the rate of reaction of a K-cell, k can be considered equal to the derived flux using the BPM to measure BEP and BG. Thus:

$$\ln(\text{flux}) = \ln(A) - \frac{E_a}{k_B} \frac{1}{T} \quad (4)$$

This can be re-expressed in the form of $y = c - mx$ as:

$$\ln(\text{flux}) = C - \frac{E_a}{1000k_B} \frac{1000}{T} \quad (5)$$

where $C = \ln(A)$. By plotting the measured flux and cell temperatures for the Mn and Au K-cells, in the form shown in Figure 2.4, the flux for either cell at any desired temperature can be accurately estimated. The flux measurements and a new Arrhenius plot were produced after every vent to atmosphere of the MBE.

This flux can also be defined as:

$$\text{flux} = \frac{N_s}{t_g} \quad (6)$$

where N_s is the number of atoms in the sample and t_g is the growth time in seconds for that sample. But N_s can also be expressed as:

$$N_s = \frac{m_s N_A}{M_s} \quad (7)$$

where m_s is the mass of the sample, N_A is Avagadro's Number and M_s is the Molar mass of the sample species in question. The mass of the sample can be redefined, in properties easily estimated by modelling an XRR scan, such as the thickness (t_s) and density (ρ_s), as:

$$m_s = \rho_s t_s A_s \quad (8)$$

For co-deposition of a material requiring fine control over the stoichiometry. The ratio

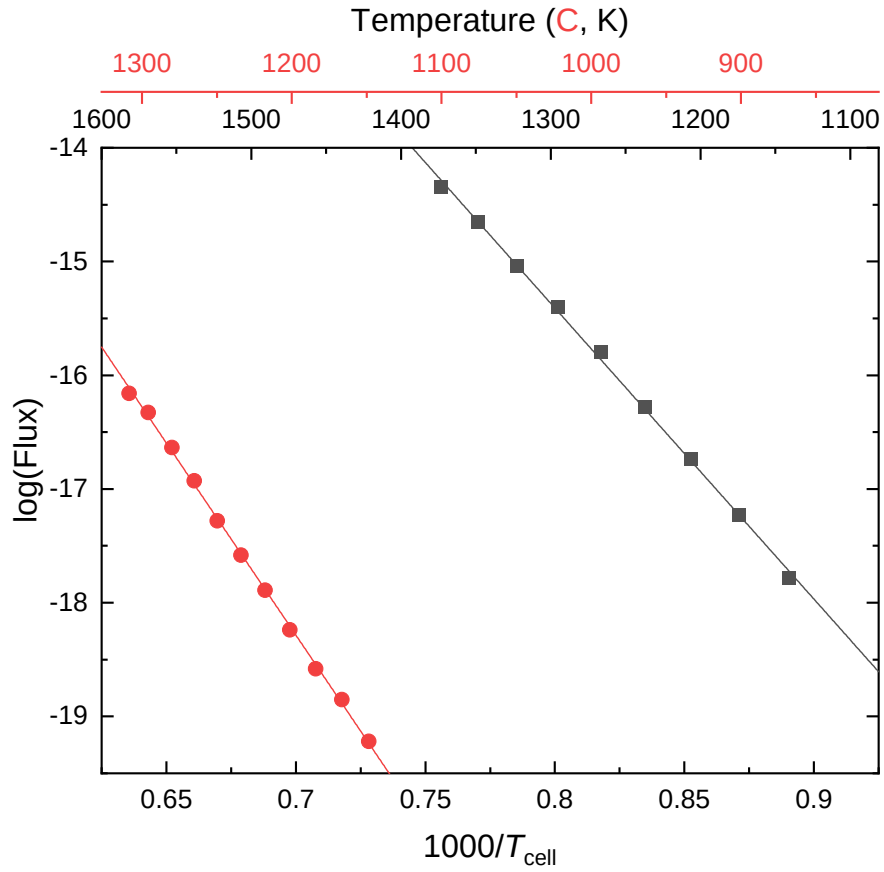


Figure 2.4: An example of an Arrhenius plot produced using the values of flux measured using the BEP, at a range of temperatures for the Mn (grey) and Au (red) cells. A straight line fit of the data was produced for each cell to determine the slope and the intercept of equation (5) of each flux series, which then allowed the cell temperature for a given flux to be calculated.

of the two fluxes can be calculated using the above equation.

where A_s is the surface area of the sample. Thus equation (6) can be expressed as:

$$\text{flux} = \frac{\rho_s t_s A_s N_A}{M_s t_g} \quad (9)$$

Once an Arrhenius plot was produced as in Figure 2.4, samples of Mn and Au were grown on room temperature substrates. The samples were grown at room temperature as the sticking factor for atoms can be assumed to approximate 1 at this substrate temperature, which allows the assumption that the entirety of the flux arriving at the sample surface is incorporated into each Mn and Au film. After measuring and modelling the XRR data for each Mn and Au sample produced, equation (9) was used to calculate the flux for each species and their resulting ratio of Mn:Au was assumed to be the stoichiometry for any Mn:Au films produced using those cell temperatures thereafter. The stoichiometry was assumed to be the same as the flux ratio of the

vapour pressures of both Mn¹ and Au² at the substrate growth temperatures used ($\leq 400^\circ\text{C}$), are so low as to be considered negligible, that the re-evaporation of Mn and Au atoms is likely minimal. If the measured flux was not 2:1 Mn to Au as desired, then the Mn cell temperature which would provide that ratio was derived from the Arrhenius plot for the Mn cell using the data derived from the fit. The Au cell temperature used for this remained constant throughout the project at 1282°C , this was to ensure an appreciable Au deposition rate of $\approx 0.11\text{ \AA s}^{-1}$.

2.2 Structural and Crystallographic Characterisation

In this section, an overview of the various techniques that were used to characterise the structural and crystallographic nature of the thin film samples are discussed. Firstly, X-ray diffraction is briefly described and the Bragg's Law is explained. Techniques such as symmetric XRD scans, in-plane XRD scans and reciprocal space maps are described. Following this X-ray reflectometry is described briefly. Sections 1.2.3 to 1.2.5 will deal with the electron characterisation techniques, namely; reflection high energy electron Diffraction, Low Energy Electron Diffraction and Scanning Electron Microscopy (SEM).

2.2.1 X-Ray Diffraction

The wavelengths of X-rays make them suitable probes for the inter-atomic spacing crystalline lattices of atoms, as both are of the same order of magnitude; $\approx 1\text{ \AA}$. The theory of X-ray diffraction can be described in two different, but comparable manners; the Bragg formulation and the von Laue formulation. Only the Bragg formalism is shown here but the von Laue formalism is described in detail in reference [115].

The Bragg theory was developed in 1913 around, by William H. Bragg and his son William L. Bragg [116]. They considered crystals as sheets of semi-transparent atomic layers, from which specular reflection of X-rays occurs. Figure 2.5 shows two atomic sheets (i.e crystal planes), separated by a distance d , with X-rays of wavelength λ incident on them. If the crystal planes are considered to act as a diffraction grating for incoming X-rays, and also that X-rays will undergo specular reflection from each crystal plane parallel to the surface. Then constructive interference can occur between X-rays reflected from different crystal planes when the difference in the path lengths between them is an integer number of wavelengths n . For the angles which satisfy this interference relationship, a diffraction peak will occur. This is explained simply by Bragg's Law shown in the equation below;

¹<https://www.mbe-komponenten.de/selection-guide/element/mn.php>

²<https://www.mbe-komponenten.de/selection-guide/element/au.php>

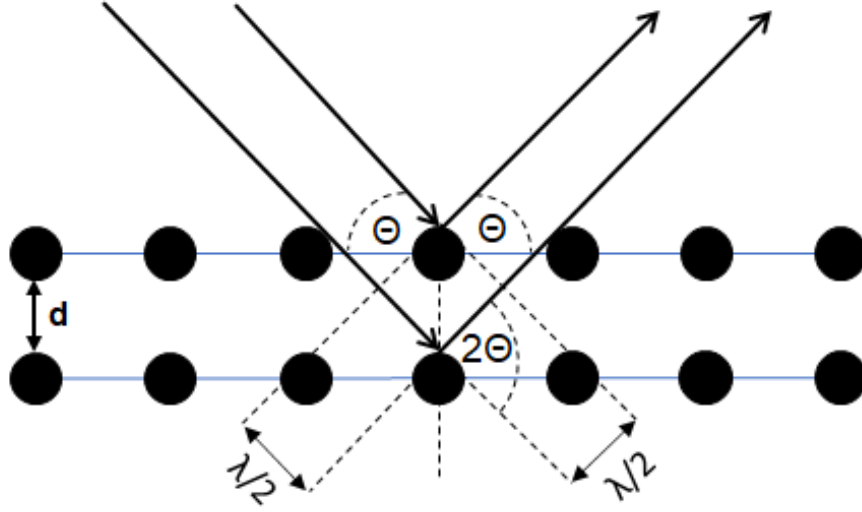
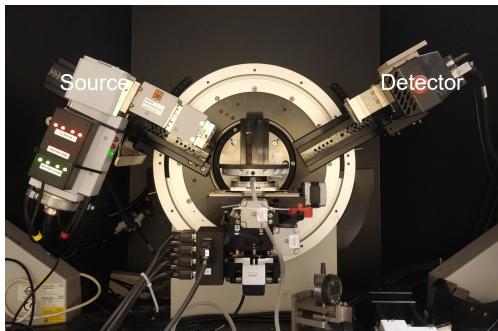


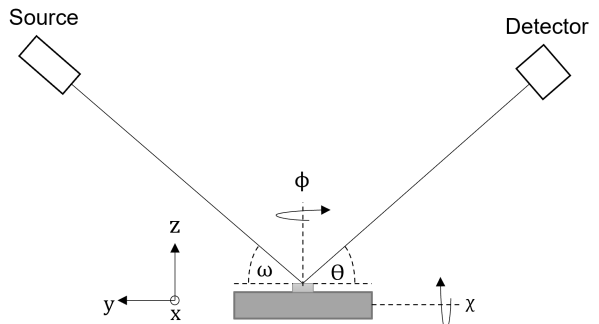
Figure 2.5: Geometrical model showing Bragg diffraction from sheets of atomic layers.

$$n\lambda = 2d \sin \theta \quad (10)$$

XRD can be performed in different modes to scan differing orientations of crystal planes. The parallel-to-surface crystal planes are probed by using the XRD in symmetric mode. Scans performed in this manner are known as $\theta - 2\theta$ scans. This involves the X-ray source and detector being set to an angle where $\omega = \theta$ ³, where the resulting scattering vector is normal to the plane probed i.e Parallel to the sample plane. The source and detector are then moved in unison probing all angles of 2θ that satisfy Bragg's Law. An example of an XRD operating in this mode can be seen in Figure 2.6(a).



(a)



(b)

Figure 2.6: (a) A photograph of the Bruker D8 Advance in HRXRD mode used for this project. The X-ray tube is highlighted on the left of the picture, while the Lynx-eye 1-D detector is highlighted on the right (b) A diagram of the sample plate illustrating the axes of translation and rotation available for alignment in the HRXRD shown in panel (a).

³Figure 2.6 (b) shows the rotation angles of each element of the XRD and denotes the symbols associated with each element.

Symmetric scans are used to show if a given film is single crystalline, polycrystalline or amorphous. A single crystal or epitaxial thin film will have only one crystal plane parallel to the surface, for example, the (001) crystal plane, then only diffraction peaks that will be seen in $\theta - 2\theta$ mode will be of the form (00 n) where $n \geq 1$. A measured diffraction pattern can be compared with a reference database diffraction pattern, to determine the crystal structure of the measured material ⁴. Some films with only one crystal plane parallel to the surface may have a number of different rotational crystalline domains, which contain varying orientations of crystal planes perpendicular to the surface. Depending on the symmetry relationships of the unit cell of the material in question, these rotational domains may be equivalent to each other. Given that polycrystalline films consist of an extremely large number of randomly oriented crystallites, a polycrystalline film will always have some small fraction of each crystal plane parallel to the surface, meaning the diffraction peaks related to all of these crystal planes will be visible in a symmetric scan. Amorphous films have no long-range crystalline order, meaning a symmetric scan of an amorphous film will show no diffraction peaks but only a diffuse, broad background.

The diffraction peaks of epitaxial films and single crystals are generally narrower in width with increased intensity, in comparison to those from polycrystalline films. The spacing d , between planes parallel to the surface, can be extracted by analysing the θ position of diffraction peaks using Bragg's Law. Depending on the crystal plane being analysed, one or all lattice parameters may be calculated and information on the strain of an epitaxial film may be gained.

XRD can also be used to probe crystal planes which are not parallel to the surface. These scans are generally referred to as asymmetric scans, so called because one manner of performing them involved a source-detector configuration where ω , which is the angle of the X-ray tube w.r.t the crystal plane being probed, and θ , which is the angle of the XRD detector w.r.t same crystal plane, are not equal. Figure 2.7 (a) shows a symmetric 2θ geometry to probe the (011) crystal plane in a (001) cubic crystal; here the X-ray source (ω) and the detector (θ) are kept symmetric while the sample (χ) is rotated to make the (011) crystal plane being probed parallel to the surface. Figure 2.7 (b) shows the X-ray source and detector at asymmetric 2θ angle, while the sample geometry is unchanged from the geometry used for a symmetric $\theta - 2\theta$ scan.

If a thin film sample is considered; by aligning to an asymmetric crystal plane and then by performing a rotational (ϕ) scan through 360° about surface normal. The number of diffraction peaks present in this full rotational scan can then be compared to the number expected to be seen from a particular material's crystal structure and space grouping. This can help elucidate if the thin film in question is epitaxial and depending on the

⁴Crystallography Open Database (www.crystallography.net) is an example of a freely accessible crystal structure database.

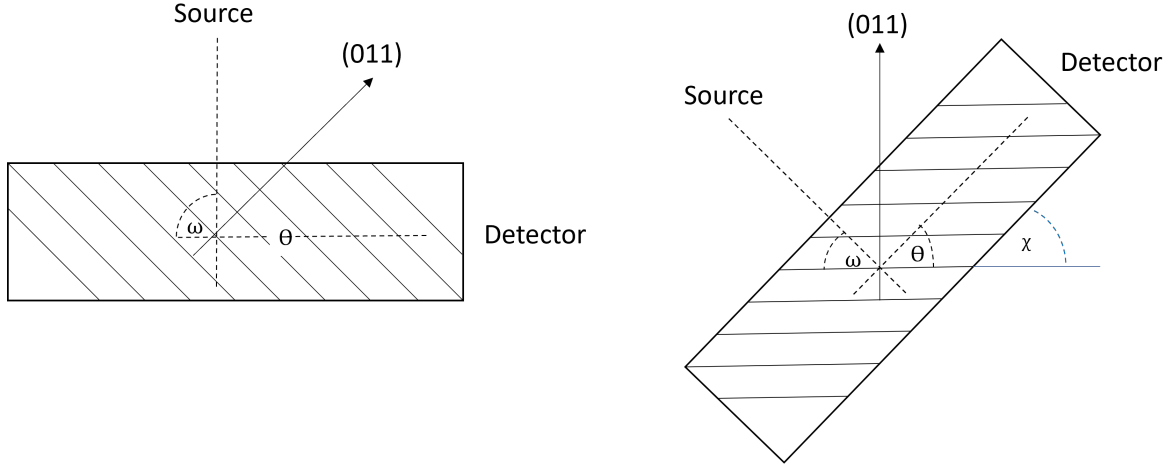


Figure 2.7: Geometrical model of the two XRD configurations to probe the (011) crystal plane of a cubic crystal, which is not parallel to the surface plane (001). (a) Shows the source and detector at an asymmetric 2θ angle to each other, while the sample χ angle is ~ 0 . (b) shows the source and detector at a symmetric 2θ angle, while the χ angle of the sample plate is rotated to make the (011) plane parallel to the source and detector. In practice the crystal is rotated along χ azimuthally, which is rotated 90° away from the detector; this is not shown here for simplicity.

symmetry of the plane if the film has a number of equivalent rotational domains.

Reciprocal Space Maps (RSMs) are another type of scan that can be taken of both symmetric and asymmetric peaks. This involves taking two scans in different dimensions to form the map. Typically detector scans (2θ) and rocking curves (ω) are used to form the reciprocal space map, but any convolution of scans can in principal be used. While $\theta - 2\theta$ scans on symmetric peaks can help elucidate the out-of-plane lattice parameter of a film, RSMs of an asymmetric peak can be used to determine the in-plane lattice parameter. Additionally, information on the degree of mosaicity of thin film, which is the degree of misorientation of the individual grains in a thin film, can be qualitatively measured via a rocking curve (ω) around a specific 2θ where an out-of-plane diffraction peak occurs.

The X-ray Diffractometer used for all the patterns presented in this work is a Bruker D8 Advance XRD. It has an X-ray tube with a Cu anode operated with an accelerating voltage of 40 kV and a 40 mA emission current. A Göbel mirror is used to convert the diverging output of the tube into a parallel beam, and a 2 bounce monochromator is used to separate the Cu $K\alpha_1$ emission, which has a wavelength of $1.54056 \text{ \AA}$, from the Cu $K\alpha_2$ emission. It is equipped with a solid-state 1D detector, consisting of 192 individual elements of 0.075 mm width. The detector is oriented such that each individual element width is parallel to the θ direction, allowing it to measure 2.6° along this direction simultaneously. This allows faster measurements than an XRD utilising a point detector. An Euler cradle sample stage allows a 360° rotation about the sample normal (ϕ), and a 90° rotation about an axis perpendicular to the sample normal.

The stage also allows translational movements in three dimensions (x, y, z) facilitating samples to be precisely aligned.

2.2.2 X-Ray Reflectivity

X-ray reflectometry to study material properties was first done by Lyman G. Parrat in 1954 when it was used to analyse copper films deposited on glass substrates [117]. The technique is based on the principle that different materials have varying electron densities. If we consider a thin film on a substrate, with a shallow angle X-ray incident upon it, X-rays will undergo reflection from the thin film surface and substrate/layer interface. If the angle of the incidence of the incoming electron is varied, the difference in the electron densities will cause oscillations in the intensity of the reflected X-rays as a result of interference between those X-rays reflected from the surface and those from the interface. These oscillations are named Kiessig fringes, who first observed them in 1931 [118]. This measurement of reflected X-ray intensity vs. incident X-ray angle is known as X-ray reflectivity.

Specular reflection of X-rays occurs for those incident at extremely shallow angles to a surface. This occurs as the refractive index of solid materials is typically less than 1 at X-ray energies. This emerges from the classical theory of dispersion [119], where we consider electrons in a material to be a negatively charged shell attached to a positively charged nucleus via a “spring”. If light, which is a time-varying electric field of amplitude E_0 , is then incident on a material it causes these “springs” to oscillate sinusoidally with the frequency (ω) of the incident light. The amplitude of the oscillation A is then:

$$A = \frac{eE_0}{m_e} \frac{1}{\omega_0^2 - \omega^2} \quad (11)$$

where e is the charge of the electron, m_e is the mass of the electron and ω_0 is the resonant frequency of the electron-nucleus spring. For simplicity, damping is neglected here. By relating the induced electric field to the incident field, the dielectric constant of the material containing these electron nucleus “springs” can be determined. The refractive index (n) for that material can be expressed as a function of frequency, which is shown in the following equation:

$$n^2 = 1 + \frac{Ne^2}{\epsilon_0 m_e} \frac{1}{\omega_0^2 - \omega^2} \quad (12)$$

where ϵ_0 is the permittivity of free space and is the electron density within the material. For X-rays with high energies, such as those used in XRR, $\epsilon \gg \epsilon_0$ means the refractive index of the material becomes less than one. This results in materials having a refractive index less than that of air for X-rays, meaning any incident X-ray will undergo total

external reflection at low angles of incidence.

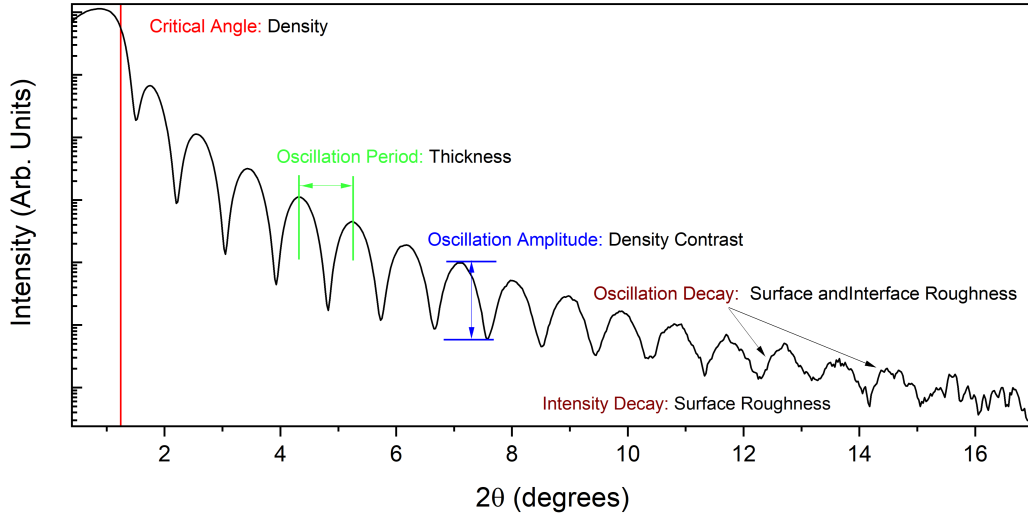


Figure 2.8: An example of XRR scan is shown with labels on the parts of the curve that can be used to extract the physical properties of the sample measured. The sample shown is a Pt thin film grown via MBE, on an Al_2O_3 substrate. The sample has a thickness of 9.44 nm, a density of 21.5 g/cm^3 , with surface roughness of 0.2 nm and with interface roughness of 0.07 nm. The scan has a critical angle of 1.24° .

Figure 2.8 is an example of data measured via XRR. It can be seen that the data decays rapidly as the angle of incidence θ increases, as the reflected intensity is inversely proportional to θ^4 [120]. The reflected intensity can be seen to be approximately constant until 1° . When the intensity falls to half of its maximum value, this is defined as the critical angle (θ_c). For values of $2\theta \geq \theta_c$, the X-rays incident on the sample no longer undergo total external reflection but begin to penetrate the film through refraction. θ_c can be used to extract information on the density of the measured layer. Additionally, the period of the oscillations can be used to extract the thickness of a layer of a sample. The amplitude of the oscillations can be used to extract information on the density contrast between two or more different layers. The effect of interface roughness on the oscillations can simply be described, as the rougher the interfaces the lower the 2θ angle at which the oscillations dissipate. Both surface and interface roughness will contribute to the rate of oscillation decay at higher 2θ angles, while only surface roughness will contribute to the decay of the intensity of the oscillations at higher 2θ angles. Using an effective model, information on the roughness of all the interfaces in a given sample can be gained. An example of such a model is described in [121].

The Bruker D8 Advance was also used to take XRR measurements. Figure 2.9 shows the setup in XRR mode. Typically an XRR measurement will cover five or more orders of magnitude in reflected X-ray intensity, meaning the X-ray optics need to be reconfigured to provide linear, high dynamic range X-ray detection. Physically, this

is done by rotating the 1-D detector 90°, which causes incident X-rays to strike all detecting elements rather than a single one. If a single detector element were to be used, absorber slits would be needed to prevent detector saturation. A 0.1 mm slit placed in front of the detector, is used to achieve high resolution in the measurements. The XRR setup is shown in Figure 2.9 and it can be used to measure thicknesses in the range of 5 nm-120 nm. The beam-knife collimator is used to keep the illuminated area of each sample identical.

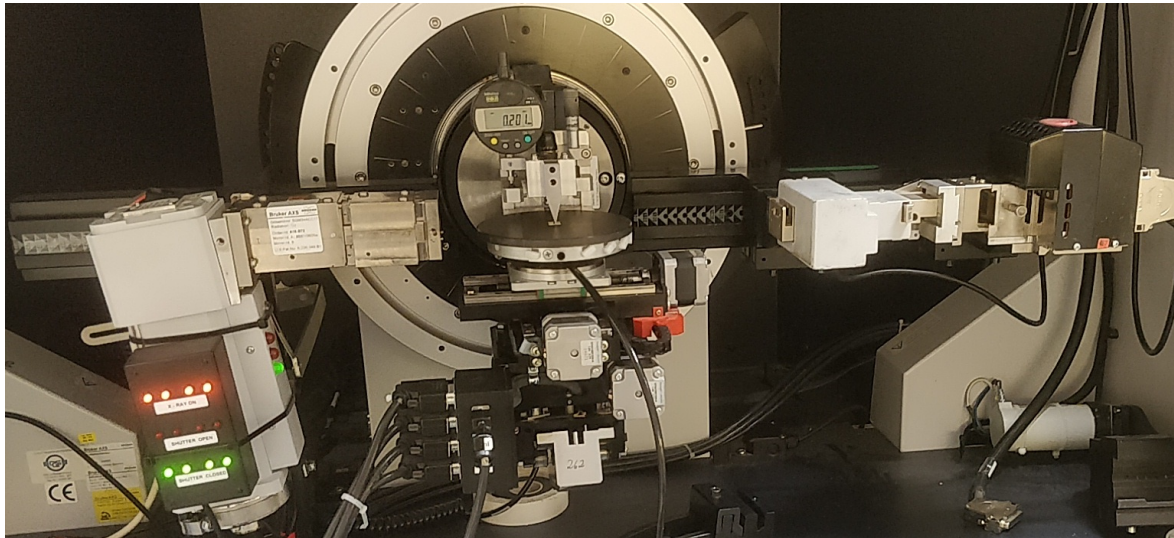


Figure 2.9: A photo of the Bruker D8 Discover XRD operating in XRR mode. The beam knife stops the X-rays from travelling directly from the Cu-source to the detector, while the detector is rotated 90° such that the incident X-rays strike all its elements.

LEPTOS fitting software, provided by Bruker, was one software used to model the thickness, density and roughness of each layer in a sample. The thickness of each measured sample was first estimated using a fast Fourier transform of the measured data in LEPTOS. A model was then generated using the expected nominal thickness of each layer as a starting point for the fit to the measured data. The model was then fit to the data using the “Genetic” algorithm in LEPTOS. Another fitting tool used was GenX, which operates in a similar fashion, and details on it can be found in [122]. The accuracy of the values of thickness, roughness and density generated by the model are only as good as the fit of the model. Typically the thickness of a film can be estimated to a precision of less than 1 nm.

2.2.3 Reflection High Energy Electron Diffraction

The first high energy electron diffraction experiments conducted with a low angle incidence of the electron beam, were conducted in 1928 by Nishikawa and Kikuchi, on single crystals of mica and calcite [123–125].

Typically, an experimental reflection high-energy electron diffraction setup consists of an electron gun and a photo-luminescent screen both offset at a shallow angle (θ) in

plane with the sample. The electron gun typically contains a tungsten filament, due to its low work function, which acts as a cathode emitting thermionic electrons. The electrons are accelerated using a bias voltage on the anode of the order of 20 kV towards a small aperture to collimate the beam of electrons. After the aperture, the electrons are focused using a magnetic lens to produce a finely collimated beam of electrons. The beam then passes through two quadrupole deflection coils, which provide x and y deflection of the beam, allowing for the beam to be steered onto a sample surface. Given the shallow angle of incidence ($\theta \approx 6^\circ$) the irradiated area along the sample beam will be on the order of 1 mm-3 mm meaning that the resulting diffraction pattern will be a representative average of surface conditions across the sample surface. The small angle of incidence also results in a low electron penetration depth meaning a typical electron will only interact with atoms in the top few mono-layers in the sample surface [126]. The diffracted electrons are collected on a fluorescent screen allowing the diffraction pattern to be visualised. Images of the patterns are taken using a charge-coupled device (CCD) camera.

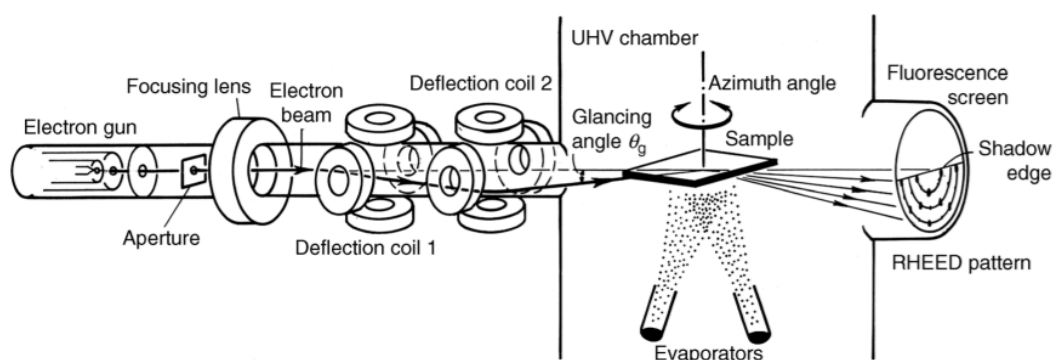


Figure 2.10: A schematic of a typical RHEED gun and apparatus. Adapted from [126].

The DCA M600 MBE is equipped with RHEED for *in-situ* monitoring of the growth modes of materials. It consists of an electron gun and a photo-luminescent screen, both of which are at a distance of approximately 30 cm from the sample. Electrons are focused in the gun, and accelerated towards the sample surface at a shallow angle; the resulting reflected/diffracted beams continue on their path until they then strike the photo-luminescent screen.

Figure 2.11 shows some of the possible RHEED patterns that may be observed from the surface of a thin film during deposition. Panel (a) shows a point-like diffraction pattern indicating that the surface is of very high crystalline quality, comprised of a single crystalline domain. Such a diffraction pattern is typically accompanied by fainter lines, known as Kikuchi lines, where often the diffraction spot occurs at the intersection of one or more Kikuchi lines. The Kikuchi lines only occur in samples with high crystallinity, which causes diffuse electron channelling in the bulk of the sample. Panel (b) shows a set of vertical diffraction streaks which occur when a surface is of high crystalline quality but is made up of a multitude of crystalline domains. The intensity and width

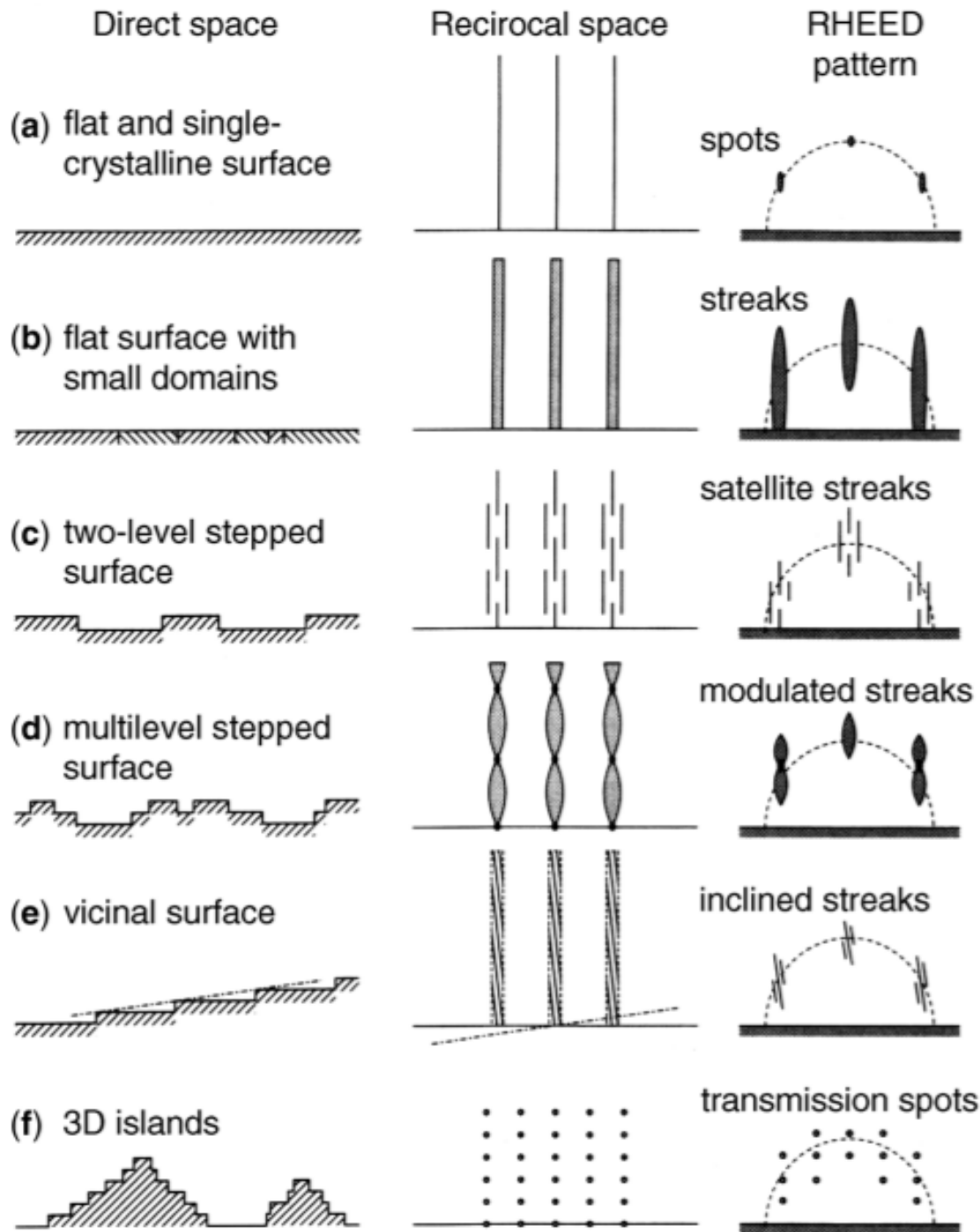


Figure 2.11: Examples of realistic thin film surfaces in direct space which can be probed with RHEED, their reciprocal space counterparts and the resulting RHEED patterns each for (a) a flat and single crystalline surface (b) a flat surface with small domains (c) a two-levelled stepped surface (d) a multilevel stepped surface (e) a vicinal surface (f) a surface with three-dimensional islands. Adapted from [126].

of these streaks can be used qualitatively to imply the size of the crystalline domains. For example, a surface consisting of many smaller crystalline domains will result in a pattern with broad diffuse streaks, while a surface with fewer larger crystalline domains will result in patterns with narrower, more intense peaks. Those with larger grains still may show faint Kikuchi lines. If there is no modulation in the streaks, this indicates

that the surface is flat and qualitatively has minimal roughness. The streaks can also be used to infer if the layer has been deposited epitaxially on the previous surface; in cases where the width of the streaks of the deposited layer are the same as the width of the spots/streaks of the previous layer, the two layers can be said to be in register with each other. Panel (c) shows a pattern that could be expected from a surface consisting of two distinct levels. (d) shows modulated diffraction streaks indicating that the surface in question consists of a rough multilevel surface, this is indicative of increased surface roughness but is still useful in determining the epitaxial nature of the surface. (e) shows the pattern that any vicinality, also known as the angle of cutting off of a crystalline plane, may produce. (f) shows what are known as transmission spots and are an indication of a surface consisting of disparate islands. The spots are caused by the electron beam diffracting after passing through the island structures, rather than reflecting from a surface. The structure of the islands can be calculated from the positions of the transmission spots. Given that the islands are isolated a sample with this pattern can be said to have a high relative level of roughness.

RHEED is often used to measure the growth rates of a film in units of mono-layers per second. This is done by measuring the intensity of the specular spot as a function of time. As material arrives at the sample surface and begins to form a layer, this increases the surface roughness of that layer, thus decreasing the intensity of the specular spot at the moment. The intensity will decrease as the surface layer coverage reaches 50 %, after which the intensity of the specular spot will increase as the surface layer coverage increases, decreasing its roughness. This will continue until which time the growth of the layer is complete, and the specular spot intensity reaches a maximum. Thus the time between two intensity maxima is the time needed for one complete layer of the material to be formed.

The variation in the oscillation intensity from what has been described previously can be used to determine alternative growth modes also, for example, in the case of some homoepitaxial semiconductor growths a doubling in the period of the oscillations is noted for increased substrate temperatures during deposition. This indicated a transition from mono- layer-by-mono-layer to a bilayer growth mode [127, 128]. For the case of GaAs homepitaxy in particular, an increase in the As:Ga flux ratio led to a RHEED oscillation pattern where there was a rapid decay of the RHEED oscillations which eventually devolved into just a stable intensity of the RHEED specular spot [128]. This pattern characterises what is known as step-flow growth where the diffusion length of an atom on the surface is considered to be longer than the step distance, and there is no formation of the 2-D nuclei which causes a minima in the RHEED oscillation intensity. Finally, if there were no RHEED oscillations and the intensity dropped off dramatically without recovering, this would be characteristic of a 3-D island growth mode. Other more complex growth modes exist but they are outside of the purview of the work presented here.

2.2.4 Low Energy Electron Diffraction

Low energy electron diffraction is similar in principle to RHEED, with two stark differences; geometry and electron energy. The electrons in LEED are incident normal to the sample surface and are accelerated to energies in the region of 10-500 eV. Similarly to RHEED, we get a diffraction pattern when electrons scatter elastically from the atoms and constructive interference occurs. Not all electrons scattered from the sample scatter elastically and so LEED utilizes a number of retardation grids placed before the photo-luminescent screen which ensures that only those electrons which are elastically scattered make it to the screen.

LEED and RHEED are both extremely surface-sensitive techniques, which are characterised by a parameter known as the Inelastic Mean Free Path (λ_{IMFP}), which essentially describes the average distance an electron travels in a solid before undergoing inelastic scattering. In general, approximately 99.3% of electrons contributing to a diffraction pattern come from within $5 \lambda_{IMFP}$ of the surface which, depending on the material, is usually 5 or so mono-layers. In the case of LEED, this distance is on the order 1 nm for electrons of energy 100 eV, meaning the majority of elastically back-scattered electrons which make up the resulting diffraction pattern from an ordered surface. For RHEED the Inelastic Mean Free Path for electrons arriving with 20 000 keV is on the order of 2 nm, still making it comparably surface sensitive. However, due to the large energy of incident electrons, the atomic elastic cross section of electron scattering becomes much larger in the direction of electron propagation. Thus necessitating the grazing incident geometry employed in RHEED, which has the added benefit of being functional during growth, which is typically not possible with LEED. Moreover, the relation between the wavelength of an electron probe (λ) and its energy is given by;

$$\lambda = \frac{h}{\sqrt{2m_e E}} \quad (13)$$

where the energy E is the charge on the electron e times it's accelerating voltage V , where h is Planck's constant and m_e is the rest mass of the electron. It is apparent that as the electron energy increases the wavelength decreases; for example, an electron with an energy of 20 eV has a wavelength of 2.7 Å which is already comparable to typical atomic spacings.

For RHEED, given the high acceleration energy of 20 keV, the equation must be modified to account for the relativistic effects on the electron. The relativistic wavelength of an electron λ_R can be expressed as:

$$\lambda_R = \frac{hc}{\sqrt{T^2 + 2m_e c^2}} \quad (14)$$

where T is the relativistic kinetic energy of the electron. and γ is the Lorentz factor. For the RHEED with its acceleration energy of 20 keV this results in a wavelength on the order of 8.6 pm which is again much less than the typical atomic spacings. It should be noted at this acceleration energy of 20 keV the differences in electron wavelength between the classical and relativistic models is low, on the order of 1%.

2.2.5 Scanning Electron Microscopy

Scanning electron microscopy is a technique used to visualise the features of a sample in the range of micrometres to nanometres. It involves accelerating electrons towards a surface, at energies of 0.5 keV-20 keV, in a high vacuum chamber. Using a set of magnetic lenses, the electron beam is rastered across the sample surface. The primary electron beam strikes the sample, which produces secondary electrons, X-rays, backscattered electrons and more, at each point of the raster. While the backscattered electrons and X-rays/other characteristic radiation can be used to garner much interesting information, the low-energy secondary electrons which are emitted provide useful information on the surface topography. These low-energy secondary electrons are emitted from within a few nanometres of the surface, the number of these electrons produced and detected will be thus sensitive to the topography of the surface. Features on the sample such as steps, pinholes, etc, cause changes in the local electron interaction volume of the primary beam. The signal produced is proportional to the number of secondary electrons detected. All this means that as the electron beam is rastered a two-dimensional image can be built up.

The criteria for a sample to be measured by SEM is that the surface material is conductive, as non-conductive materials quickly charge as the electron beam is applied to the sample, causing distortion on any images taken. All SEM images presented here were taken with a Carl Zeiss Ultra SEM, which has a resolution limit of 10 nm.

2.3 Magnetic Annealing and Characterisation

2.3.1 Magnetic Annealing Furnace

All samples subjected to a magnetic annealing cycle were done so in the system schematically shown in Figure 2.12. The system consists of a Halbach array with a circular bore in the middle, which applies a magnetic field of 800 mT uniformly across the bore. The annealing furnace can be placed in the bore to apply the field during the annealing cycle. The annealing furnace is connected to a turbo-molecular pump backed by a rotary vane pump. The vacuum components are sealed with KF flanges meaning a high vacuum of better than 5×10^{-6} mbar. The furnace is heated using a resistive heater wrapped around the sample mount, connected to a PID and power

supply which are controlled via LabVIEW software. The sample mount can be rotated so that the field is applied along the desired direction of the substrate.

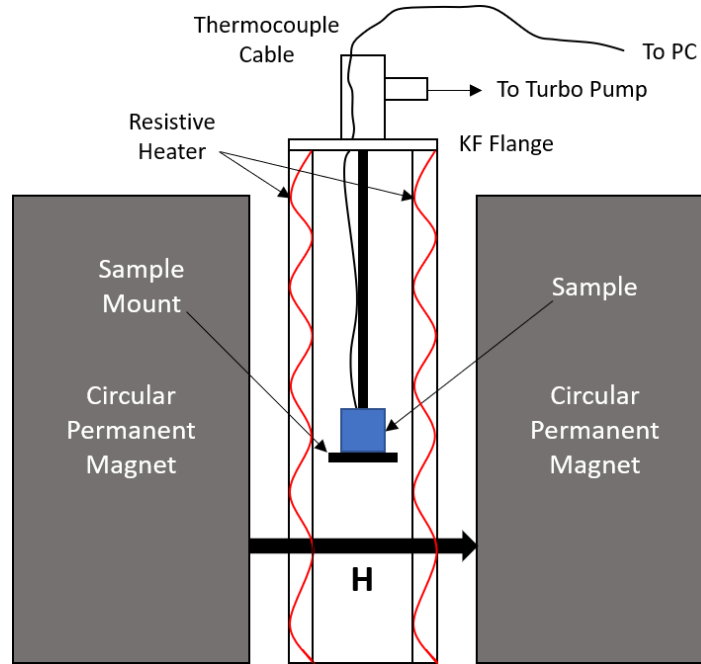


Figure 2.12: Cross-Sectional schematic of the Annealing Furnace and 800 mT Halbach magnet used for the magnetic annealing of samples throughout this project.

2.3.2 Vibrating Sample Magnetometry

Vibrating sample magnetometry is the most widespread, and inexpensive method of measuring the magnetisation of materials today. A similar concept called the vibrating coil magnetometer was first developed [129], after which S. Foner developed the VSM in 1956 [130]. A VSM consists generally of an electromagnet with stationary pickup coils located near the poles and a motor-driven sample rod which oscillates up and down at a specific frequency. The pickup coils are arranged in a quadrupole formation to create a saddle point, about which the sensitivity is independent of sample positioning. The top pair and bottom pair of coils are counter-wound with respect to each other such that induced voltage in each will add. It works on the basis of Faraday's law of electromagnetic induction. A magnetic sample which is oscillated sinusoidally will induce an AC voltage in the pickup coils, the magnitude of which is proportional to the magnetisation of the sample and thus the magnetic moment. However, it also depends on the magnitude of the oscillation and the frequency which can lead to errors in the measure of the moment, if it is just measured through the induced AC voltage in the pickup coils. A vibrating capacitor generates a reference signal which varies in a similar manner to that of the pickup coils and when processed correctly eliminates the errors relating to oscillation magnitude and frequency of the driving rod [131]. The advantage of using a VSM is that the measurements are generally fast to make, however, in comparison to other methods, the sensitivity is not optimal, limited to

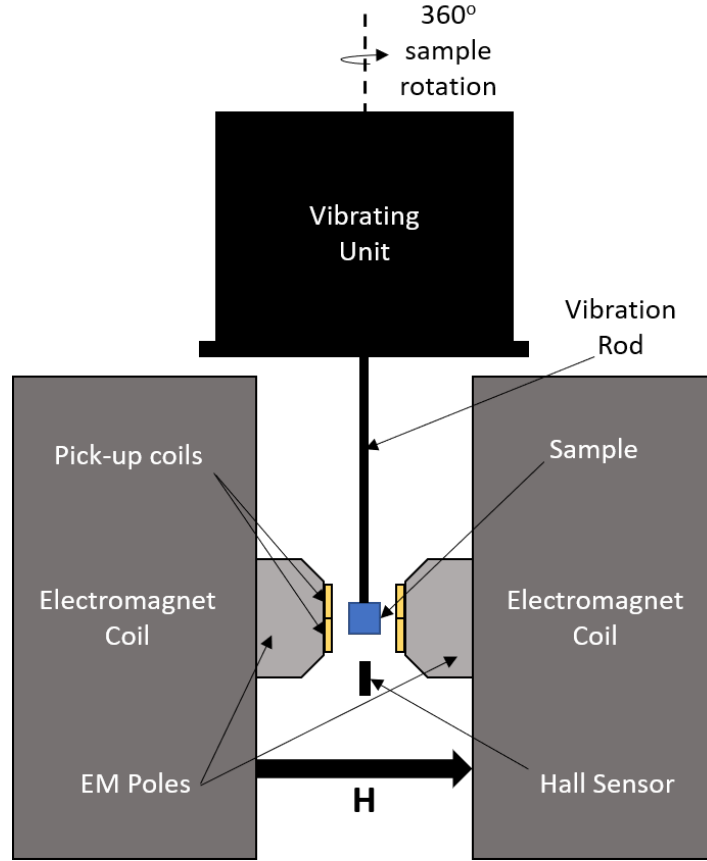


Figure 2.13: A schematic of PMC Micromag 3900 VSM used throughout the project.

10^{-9} Am^2 (or 10^{-6} emu), meaning that for ultra-thin layers of ferromagnetic materials with a low moment, it is not the ideal instrument to be using. The VSM primarily used in this work is a PMC Micromag 2900 VSM with a 1 T electromagnet at room temperature. This system had a quadrupole arrangement where each of the coils were made of deoxygenated copper which were 2 cm in diameter. Each of the adjacent coils on the pole pieces were counterwound with respect to each other, while each of the poles were separated by 1 cm. The driving rod of the VSM oscillated at a frequency of 83 Hz with an oscillation amplitude of 0.3 cm. The low temperature magnetometry was performed using the VSM option on a Quantum Design M6000 series physical property measurement system (PPMS) equipped with a 14 T superconducting magnet.

2.4 Electrical Measurements

All resistance measurements in this work were performed using a Keithley 2400 200 V source meter controlled via LabVIEW software. The samples were contacted in a linear four-point probe geometry, using four equally spaced, spring loaded, gold contacts which were 2 mm apart, and the spacing, perpendicular to the linear arrangement of the probes, between the probes and substrate edge was on the order of 4 mm. The measurements were taken by applying a current across the outer two probes and measuring the resulting voltage between the inner two probes. A typical bias current

between the probes was on the order of $10\text{ }\mu\text{A}$. Given that the distance between the probes is typically 5 orders of magnitude larger than the thickness of the films, this setup can be used to measure the sheet resistance of the films and thus calculate their resistivity. For the purposes of this work the setup was used to check if the probes could form an ohmic contact through the Mn_2Au films on insulating substrates, to help quickly elucidate the continuity of the films. This was complemented by the use of SEM to visualise the film surfaces.

Chapter 3

MBE growth of thin film Mn_2Au

3.1 Motivation

The goal of this work was to find a reliable method for deposition of high crystalline quality MBE grown Mn_2Au via co-deposition, which did not rely on complex layering techniques [31], or magnetron sputtering from a stoichiometric target [33, 107]. As detailed in Table 1.3 in Chapter 1, most studies of Mn_2Au films report one or more parasitic out-of-plane orientations. Co-deposition, in the manner outlined in Chapter 2, provides much finer control over stoichiometry compared to deposition from a stoichiometric target. The use of MgO (001) and Al_2O_3 ($1\bar{1}02$) substrates for our co-deposition methodology were examined initially, before moving on to a Pt seed layer as this has been employed to some success for magnetron sputtered samples [107]. Pt is a commonly used seed layer for the growth of magnetic materials and heterostructures due to its high crystalline quality when grown on Al_2O_3 (0001) [132]. Pt has also been shown to grow epitaxially on Al_2O_3 (0001) with an out-of-plane relationship of Pt (111)|| Al_2O_3 (0001) and in-plane with Pt (110)|| Al_2O_3 ($10\bar{1}0$), but with two equivalent in-plane orientation domains [133]. Pt has also been used for $[\text{Co} (111)/\text{Pt} (111)]_n$ multilayers to create stacks with PMA when the Co layers are a specific thickness [50], which were later optimised on a Pt seed layer [133]. These PMA multilayers provided a useful test bed to explore perpendicular exchange bias with a FM layer [134], the TMR effect in junction with AFM active layers [89] and in a junction demonstrating room temperature TAMR [13]. The Pt (111) surface has a surface unit cell which is hexagonal, with a lattice parameter of $2.774 \text{ \AA}$ [135]. This matches well with the inter-atomic spacings on the Mn_2Au (110) surface, which ranges between $2.747 \text{ \AA}$ - $2.852 \text{ \AA}$ [92]. For this reason, Pt was chosen as a seed layer for the growth of Mn_2Au on Al_2O_3 . The following work has been published in part and can be found in the Journal of Applied Physics [136].

3.2 Mn_2Au growth on MgO (001) and Al_2O_3 ($1\bar{1}02$) substrates

3.2.1 Co-deposition of Mn_2Au on MgO (001)

This section deals with the growth of Mn_2Au samples directly onto MgO (001) substrates. The MgO (001) substrate was previously used for the growth of Mn_2Au via layer-by-layer deposition on an Fe (001) seed layer [30, 31]. The goal was to optimise the growth of Mn_2Au thin films grown directly on MgO (001) substrates for a specific growth temperature. Before growth the substrates were chemically cleaned in an ultrasonic bath, using propan-2-one (Acetone) and propan-2-ol (Iso-Propyl Alcohol), before blowing dry with nitrogen gas. Each of the substrates were subsequently vacuum annealed *in-situ* at 600°C for 1hr in the MBE prior to growth. This was previously found to give a smooth MgO surface via RHEED [137]. The Mn and Au were co-evaporated from the K-cells which were kept at 990°C and 1282°C , respectively. The growth time of each of the samples was 1200 s. These temperatures corresponded to rates of $0.309\text{ \AA s}^{-1}$ and $0.108\text{ \AA s}^{-1}$, respectively, confirmed *in-situ* using a quartz crystal monitor. The rate was confirmed through the growth of several calibration samples of Mn and Au, which were measured with XRR to confirm that the crystal monitor was reading the correct deposition rate. Figure 3.1a shows XRD scans of 3 samples grown at substrate temperatures of 200°C , 400°C and 600°C . The gold dashed reference lines denote the reference positions of the Mn_2Au peaks, while the red dashed reference line denotes the reference position of $\alpha\text{-Mn}$ peak, the asterisks denote the $\{002\}$ peaks of the MgO (001) substrate. The $\wedge$ symbols denote the peaks which were also observed on a clean MgO substrate scan and originate from the sample stage on the XRD. These peaks from the sample plate are observed due to a portion of the X-rays striking the sample plate, which was likely caused by a slight misalignment of the substrate height, during the aligning procedure. The presence of excess Mn is evidenced by the $\alpha\text{-Mn}$ (004) peak present in the XRD scans of each sample. The excess Mn is likely driven by the flux ratio of Mn to Au of approximately 3:1 as determined from the crystal monitor readings. As expected the crystalline quality appears to improve at higher temperatures, however, the films remain polycrystalline as evidenced by the multiple Mn_2Au XRD reflections present. This is to be expected given that as the surface temperature increases the adatoms will have higher surface mobility. The increase in crystallinity can be qualitatively seen from the increasing intensity of the Mn_2Au (110) from the 400°C to 600°C sample. The FWHM of the Mn_2Au (200) peak from the 400°C and 600°C samples were fit using a Gaussian function. The estimated FWHM of the Mn_2Au (200) decreases from approximately $(0.38 \pm 0.03)^\circ$ for the 400°C sample to approximately $(0.20 \pm 0.55)^\circ$ for the 600°C sample, which quantitatively indicates this increase in crystallinity.

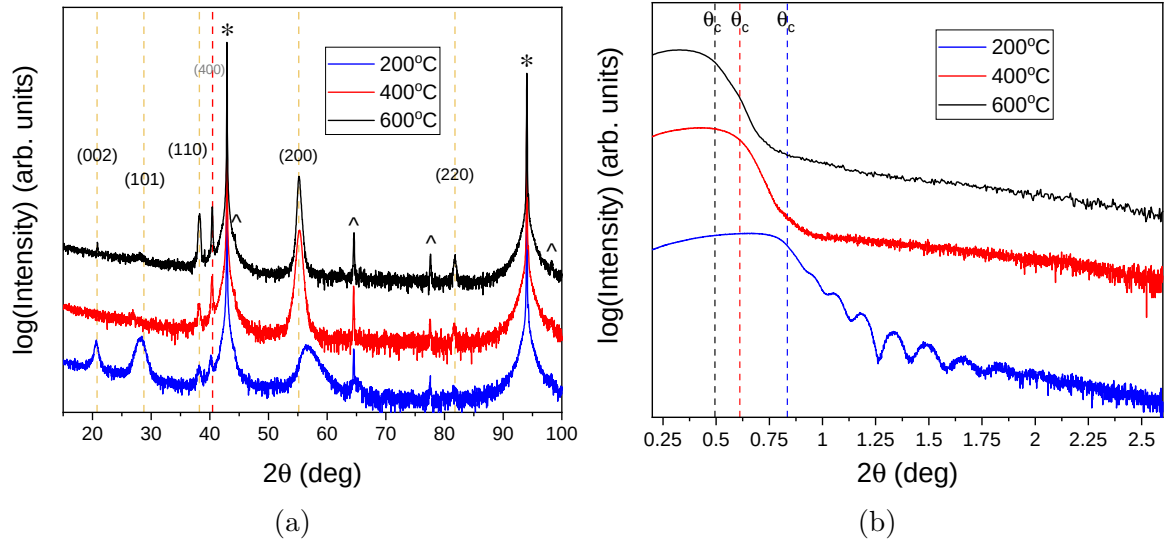


Figure 3.1: (a) XRD scans of Mn_2Au thin films grown on MgO (001) substrates at 200 °C, 400 °C and 600 °C and (b) XRR scans of the same films. In (a) the gold and red reference lines indicate the reference positions for the Mn_2Au and $\alpha\text{-Mn}$ diffraction peaks. The MgO {002} peak positions are marked by asterisks, while the peaks marked with ^ show the positions of peaks originating from the XRD sample stage. In (b) the dashed reference lines note the approximate position of the critical angle θ_c for each XRR scan.

Figure 3.1b shows raw XRR data from all of the samples with the critical angle of each marked by the dashed reference lines. It is apparent that the density of each of the films is different, given that the critical angle for each scan is different. The approximate critical angle for each sample is shown by the dashed reference lines in Figure 3.1b. As the substrate temperature increases the critical angle decreases, which indicates that the density of the samples also decreases with increasing substrate temperature. The roughness of the films is seen to be very large at temperatures in excess of 400 °C, such that their thickness can't be measured via XRR, as evidenced by the lack of visible oscillations. The films are expected to have the same nominal thickness given the growth time was kept constant. Though these films show excess Mn, driven by the 3:1 ratio of Mn:Au, there is some indication that the optimum substrate temperature for co-deposition of Mn_2Au films will require substrate temperatures ≥ 400 °C to balance the crystallinity and smoothness of the films via co-deposition.

The resistance of each film was measured using a four-point probe electrical system in order to determine each film's conductivity. The sample grown at 200 °C sample was conductive, while samples grown at higher temperatures were insulating. Given that Mn, Au and Mn_2Au are metallic [33], this suggests that the insulating films are discontinuous. Figure 3.2a and Figure 3.2b show Scanning Electron Microscopy (SEM) images of the 400 °C and 600 °C sample respectively. The grains in Figure 3.2a appear to form irregularly shaped regions which are isolated from one another, while in Figure 3.2b the grains are large, with a diameter of 100 nm-200 nm but very

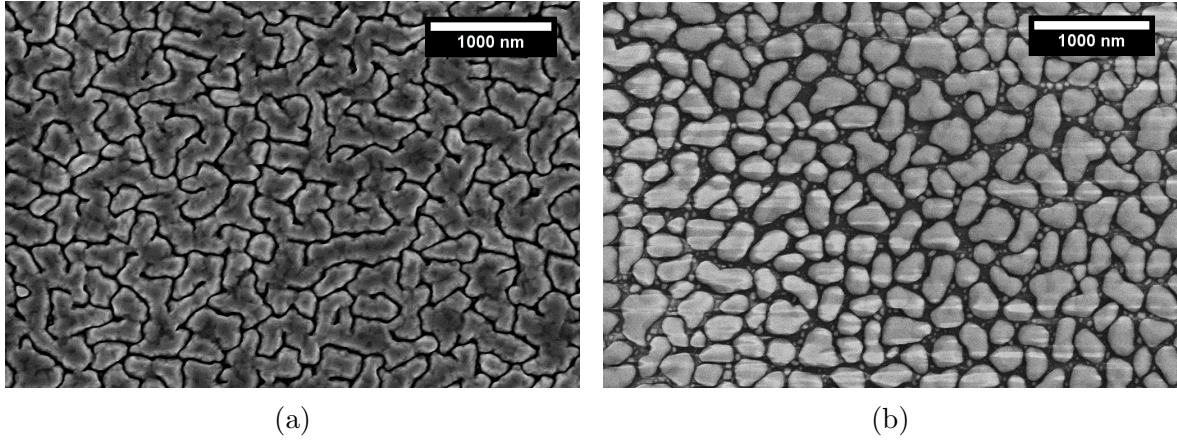


Figure 3.2: SEM images of Mn_2Au thin films grown on MgO (001) substrates at (a) 400°C and (b) 600°C . The scale bar on the top right of each image indicates a length of $1\mu\text{m}$.

sparsely separated. The SEM images agree well with the analysis of the critical angle from the XRR data, with the 600°C sample visibly less dense than the 400°C sample. Typically for the growth of metals on oxides, the growth mode of the metal is in 3-D granular islands, rather than in a layer-by-layer fashion as the oxide has a lower surface energy than that of metal and so it is more energetically favourable to maximise the amount of oxide surface. As the substrate temperature increases, the metallic atoms landing on the surface will have increased energy to either diffuse across the surface or to desorb from the surface, as the atoms agglomerate together this minimises their surface energy. For example, MgO (001) has a typical experimentally measured surface energy of 1.15 J m^{-2} [138]. Experiments on an fcc Au (111) surface measured its surface energy to be 1.50 J m^{-2} while experiments on an fcc Mn (111) surface measured its surface energy to be 1.60 J m^{-2} [139]. The final conclusion from this work is that MgO (001) is not an ideal substrate for the growth of Mn_2Au due to the lower surface energies of the oxide surface in comparison to that of the Mn_2Au crystallites. One other oxide surface was examined in an effort to repeat previously published work [28].

3.2.2 Mn_2Au on R-plane Al_2O_3 ($1\bar{1}02$)

This section deals with the growth of Mn_2Au films at various substrate temperatures on Al_2O_3 ($1\bar{1}02$). Epitaxial Mn_2Au (001) was previously grown directly on an Al_2O_3 ($1\bar{1}02$) substrate via magnetron sputtering from a stoichiometric Mn_2Au target at a substrate temperature of 600°C [28]. The goal was the co-deposition of Mn_2Au on the Al_2O_3 ($1\bar{1}02$) substrate by MBE and to examine if the epitaxial Mn_2Au (001) films could be achieved in this manner. All samples were grown with Mn and Au cell temperatures of 937°C and 1282°C respectively, which corresponds to a flux ratio of 2:1. Section 2.1.2:Stoichiometry Control deals with this in more detail. The 2:1 ratio was chosen as the ratio of 3:1 used in the previous section led to the presence of $\alpha\text{-Mn}$ in the Mn_2Au films.

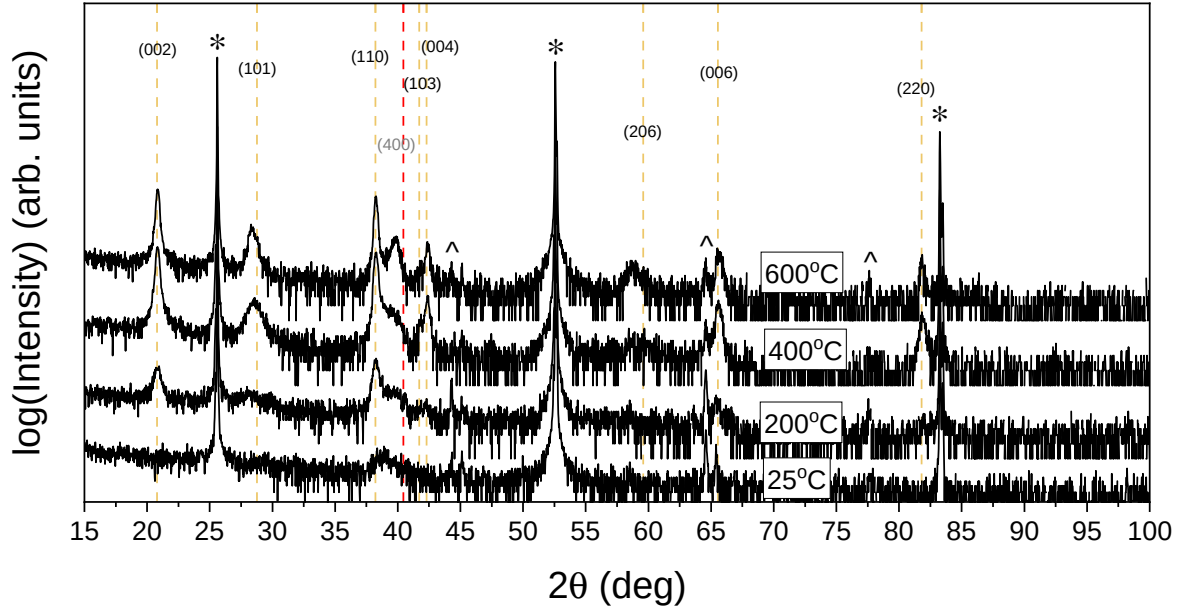


Figure 3.3: XRD scans of Mn_2Au films grown on Al_2O_3 ($1\bar{1}02$) at substrate temperatures of 25°C , 200°C , 400°C and 600°C . The Mn_2Au peaks are noted in black brackets with the reference positions for the peaks denoted by the dashed gold lines, while the $\alpha\text{-Mn}$ peak is noted in the grey brackets with the dashed red reference line denoting the reference position of the peak. The Al_2O_3 $\{1\bar{1}02\}$ substrate peaks are denoted by the asterisks, while the peaks marked by the $\wedge$ symbol are those which emanate from the XRD sample plate.

Samples were grown over 1200 s at substrate temperatures of 25°C , 200°C , 400°C and 600°C . XRD was performed on each sample and can be seen in Figure 3.3. The black labels refer to the Mn_2Au peaks, while the grey labels refer to the $\alpha\text{-Mn}$ peak visible. The reference positions for Mn_2Au are marked by the dashed gold reference lines, while the $\alpha\text{-Mn}$ peak is marked by the dashed red reference line. The clearest difference between this work and that presented in [28] is that the samples are polycrystalline at temperatures above 200°C , while showing little to no crystalline order at room temperature. It is difficult to compare magnetron sputtering to thermal evaporation techniques; even for similar substrate temperatures the evaporated Mn and Au will very likely have different adatom mobilities in comparison to the sputtered Mn_2Au . As with the samples grown on MgO , the resistance of each of the films was checked via four-point probe electrical measurements. All deposited films were conductive excluding the film grown at 600°C , indicating that this was the only film that was discontinuous. Interestingly, the film which showed the highest crystalline order was the sample grown at 400°C with an increase in the intensity of the (001) and (110) peaks and a decrease in the (101) peak, in comparison to the sample grown at 600°C . All of these comparisons were made after normalising the intensity of the patterns to that of the intensity of the 400°C Al_2O_3 ($1\bar{1}02$) peak. Given the difficulty of achieving single orientation Mn_2Au films via co-deposition on oxide surfaces, the use of seed layers, such as Pt, was then explored.

3.3 Epitaxial Mn_2Au (110) on a Pt (111) seed layer

3.3.1 Growth of Pt (111) on Al_2O_3 (1000)

Pt layers were grown via e-beam evaporation in the DCA MBE. Each of the Al_2O_3 (0001) substrates used were sonicated in acetone and isopropyl alcohol each for 15 minutes before being loaded into the MBE. The substrates were then annealed at 600°C for 1 hr prior to Pt deposition. Although Farrow *et al.* reported Pt samples that were optimally grown at a substrate temperature of 600°C , the decision to optimise the substrate temperature for the DCA M600 MBE system was taken.

3.3.1.1 Pt Substrate Temperature Optimisation

Pt samples were grown at substrate temperatures of 450°C , 500°C and 550°C at a nominal thickness of 10 nm for each, as measured on the calibrated quartz crystal monitor. The rate of deposition was measured to be $0.05 \text{ \AA s}^{-1}$.

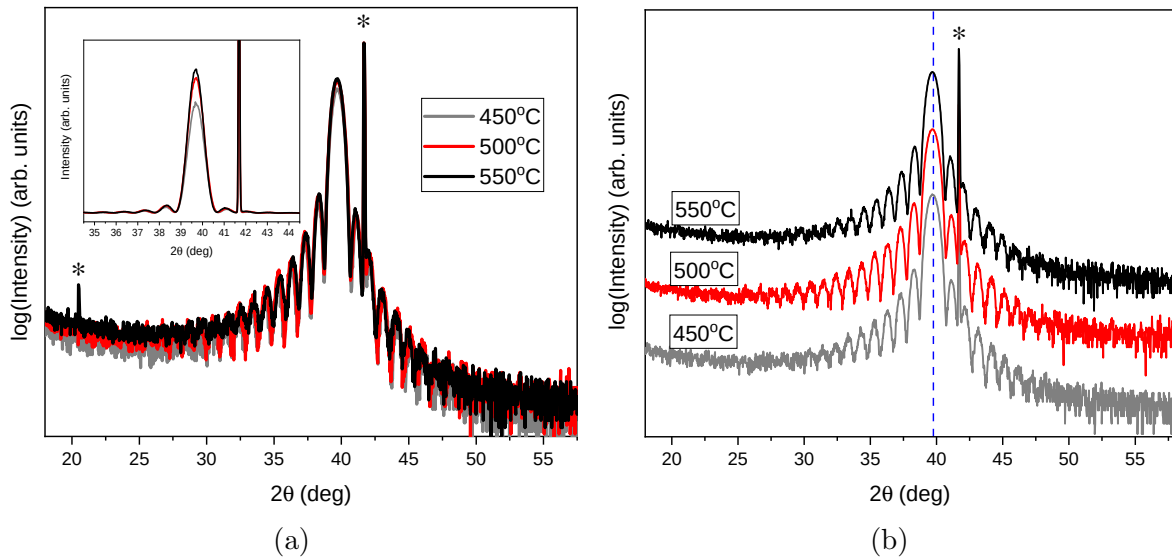


Figure 3.4: XRD scans of the Pt films grown at 450°C , 500°C and 550°C . (a) Shows the scans overlayed to determine the intensity of the Pt (111) peak, after they were normalised to the intensity of the Al_2O_3 (0006) from the 550°C Pt sample. Inset shows the Intensities on a linear scale for clarity. While (b) shows the scans separated to show the Pendellösung fringes

Figure 3.4 shows the measured XRD scans of each film. The asterisk on the XRD scans indicates the $\{0001\}$ diffraction peaks from the Al_2O_3 substrate, while the dashed blue line at $\theta = 39.764^\circ$ indicates the reference value of the Pt (111) diffraction peak [140]. All three films grow (111) oriented out-of-plane, with no other detectable crystalline phases. In Figure 3.4a the magnitude of the intensity of each of the Al_2O_3 (0006) peaks is normalised to that of the 550°C sample. Each of the samples are coloured

differently for clarity. The purpose of this is to determine the most intense Pt (111) peak. The inset of Figure 3.4a shows the intensities of the Pt (111) peak on a linear scale; the 450°C sample (grey) has the least intense Pt (111) peak, with only 76.5% the intensity of the most intense Pt (111) peak. While the 550°C sample (black) has the most intense Pt(111) with the 500°C sample (red) having a magnitude of 93.3% of the intensity of the 550°C sample.

Figure 3.4b shows the same XRD scans, un-normalised and translated such that the oscillations around the Pt (111) peak are visible. These oscillations are known as Pendellösung fringes and are indicative of the high crystalline quality of the Pt films. The Pendellösung fringes occur when there is the presence of coherent crystalline domains in the out-of-plane direction of a thin film. Similar to XRR, these oscillations can be used to determine the approximate thickness of the out-of-plane crystallites. The decay of the intensity of the oscillations around the central diffraction peak from which they are associated is related to the roughness of the thin film [141]. Using a simple Pendellösung fitting function, from equation (1) in [141], the coherent thickness of the out-of-plane crystallites could be estimated. The equation is described using the following equations below.

$$I_N(\phi) = N^2 u^2 \frac{\sin(\phi)}{\phi} \quad (1)$$

where

$$\phi = N b a(\theta) \Delta\theta \quad (2)$$

and

$$a(\theta) = \frac{2\pi}{\lambda} \cos(\theta) \quad (3)$$

In these equations, N is the number of parallel lattice planes in an ideal film, which leads to an interference pattern whose intensity is given by $I_N(\phi)$. b is the distance between lattice planes, u represents their scattering amplitude, λ the X-ray wavelength and $\Delta\theta$ the deviation from the Bragg diffraction angle θ .

The out-of-plane coherent thicknesses were estimated to be 9.7 nm, 9.7 nm and 9.9 nm for each of the samples, in increasing order of sample temperature, respectively. These values compare well with the nominal thickness values and the estimated XRR thickness values, which will be discussed below, indicating that the crystallites are continuous throughout the thickness of the film, in all three samples. From Figure 3.4b it is evident that the sample grown at 500°C has the largest number of visible oscillations in the 25° - 35° range of 2θ , while the 550°C sample has the lowest number of visible

oscillations. This indicates qualitatively that the 500°C sample is the smoothest film and the 550°C sample is the roughest film.

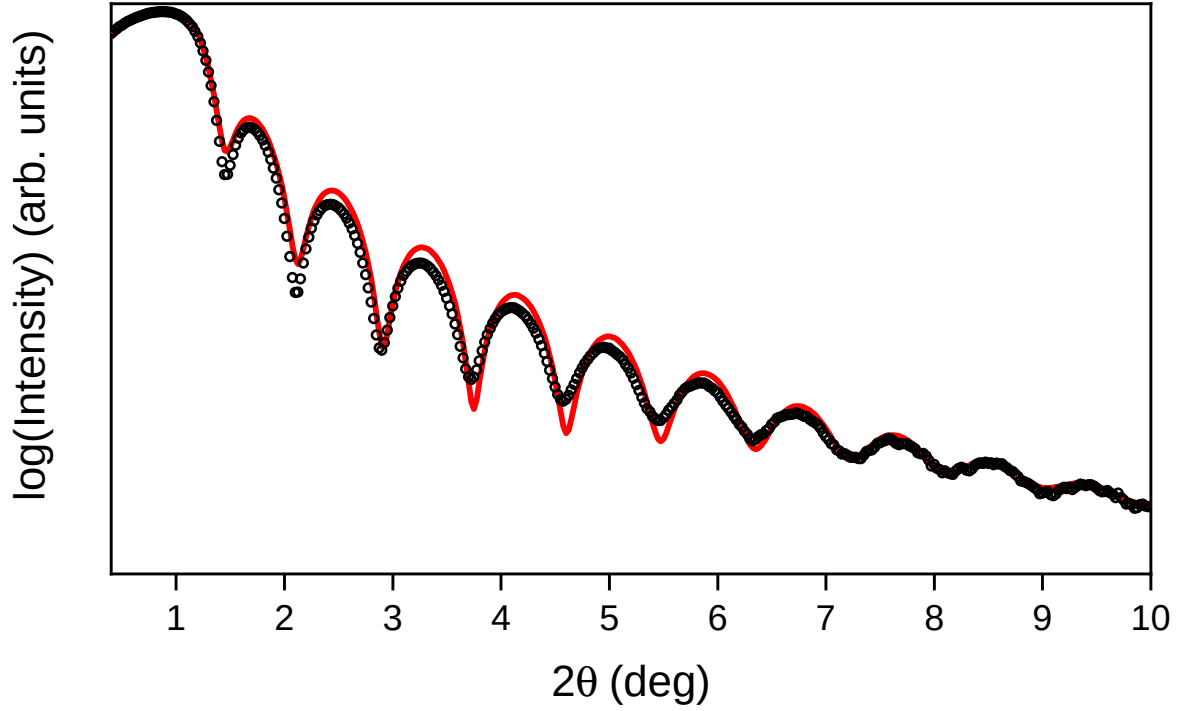


Figure 3.5: XRR scan of the Pt film grown at 500°C . The black circles are the data, while to red line shows the best fit to the data.

Figure 3.5 shows the XRR scans of the sample grown at 550°C , where the data (black dots) and the line of best fit (red) are shown together. The smoothness of the films is highlighted by the persistence of oscillations out to a 2θ value of at least 10° in the case of all films. The fitting data from all three films are shown in Table 3.1. The thickness estimates for each of the films correspond well to the fit of the Pendellösung fringes, within the margin of error of the fit. It is also worth noting that the surface roughness is less than $5\text{ \AA}$ for each of the films, and the numeric estimate of roughness matches well with the qualitative analysis of the roughness from the Pendellösung fringes, with the sample grown at 550°C as the roughest and the sample grown at 500°C as the smoothest.

Table 3.1: Table of the parameters of best fit from XRR scans for the Pt samples. T_g represents the substrate growth temperature, t_{Pt} represents the thickness of each layer, ρ_{Pt} the density of each layer, σ_{int} and σ_{sur} the roughness of the interface between the Al_2O_3 and Pt and the surface roughness respectively.

T_g ($^\circ\text{C}$)	t_{Pt} (nm)	ρ_{Pt} (g/cm^3)	σ_{int} ($\text{\AA}$)	σ_{sur} ($\text{\AA}$)
450	9.43	20.2	0.8	2.4
500	9.61	20.5	1.0	2.1
550	9.90	19.8	1.1	3.8

Given that there was a marginal difference in intensity between 500°C and 550°C films, and roughness of less than $5\text{ \AA}$ for both films, 550°C was chosen as the substrate temperature for Pt film deposition, throughout the rest of this work.

3.3.1.2 Pt Layer Thickness Optimisation

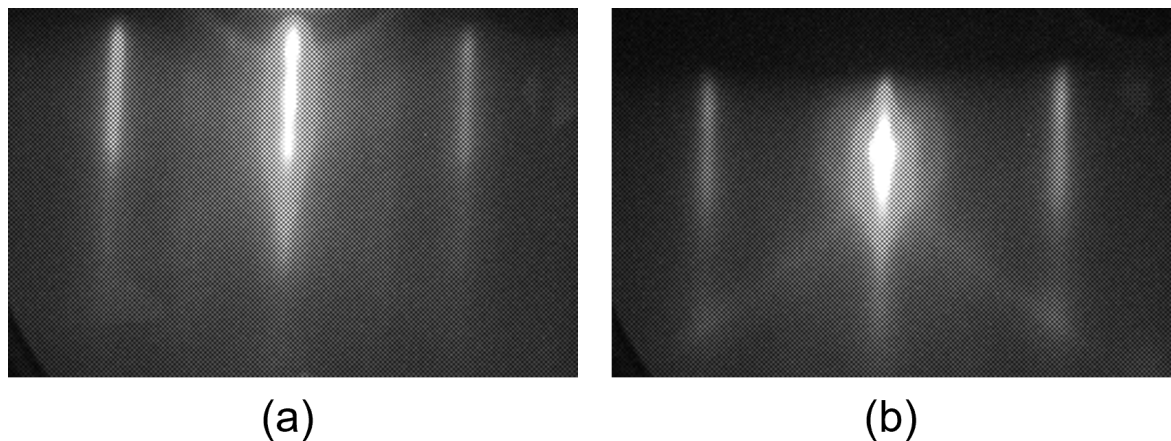


Figure 3.6: RHEED images taken along the Al_2O_3 $[10\bar{1}0]$ high symmetry direction during the growth of a Pt layer. (a) Shows the RHEED image of the Pt layer after 1.5 nm of deposition while (b) shows the RHEED image of the Pt layer after 4.5 nm of deposition.

Due to the high crystalline quality of the MBE-grown Pt films, as evidenced by the Pendellösung fringes, consideration had to be given to the thickness of the Pt seed layer used for Mn_2Au thin films. This is because the Pendellösung fringes gives rise to broadening of the Pt (111) peak around its expected 2θ value of 39.764° , which causes it to overlap the expected 2θ value of 38.213° for the Mn_2Au (110) peak. Furthermore, the Pt (111) reflection is the most intense of all the Pt reflections, while the Mn_2Au (110) reflection has a relative intensity of 65.8% of the most intense (103) reflection. Thus, the Pt layer thickness would have to be minimised to prevent obscuring of the Mn_2Au diffraction peaks.

Figure 3.6 shows the evolution of the Pt RHEED pattern during growth. Second order streaks are faintly visible in 3.6 (a), halfway between the first order streaks. These features are from the Al_2O_3 substrate and disappeared completely at a Pt thickness of $\approx 3.5\text{ nm}$ as evidenced in 3.6 (b). Although not visible in either image above, splitting of the first order Pt fringes were observed in some samples, which disappeared completely, in all instances, at a Pt thickness of $\geq 3.8\text{ nm}$. For these reasons, the thickness of the Pt seed layer was kept between 3.8 nm-5.5 nm, for the Mn_2Au samples grown in the following work.

Figure 3.7 shows an out-of-plane XRD scan of a 27.4 nm Pt sample, grown at 550°C . This sample was grown to confirm the in-plane epitaxial relationship of the Pt (111) layer to the Al_2O_3 (0001) substrate. This in-plane scan will be discussed in detail in a

following section.

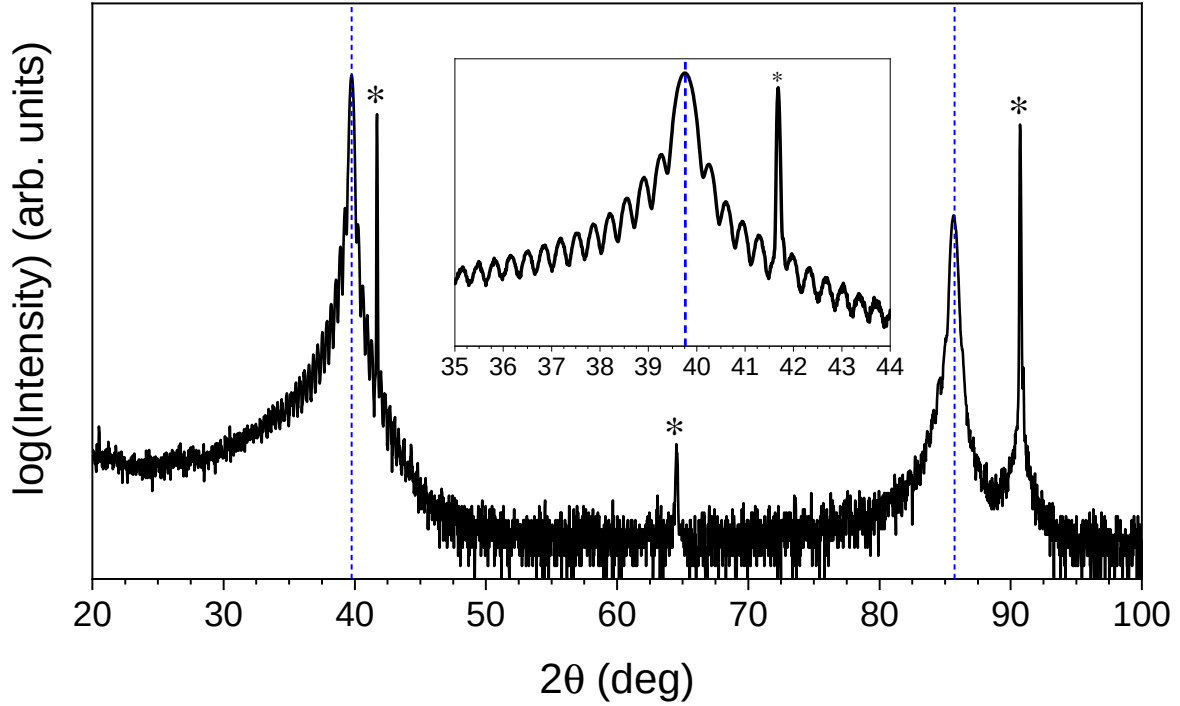


Figure 3.7: XRD scan of a 27.4 nm thick Pt layer grown on Al_2O_3 (0001). The dashed blue line denoted the expected 2θ position of the $\{111\}$ position and the asterisks indicate $\{0001\}$ peaks. Inset shows the Pendellösung fringes around the Pt (111) peak. Fitting of the oscillations around the (111) peak estimates the crystallites in the out of plane direction as (27.2 ± 0.2) nm.

3.3.2 Growth of Mn_2Au layer

The Mn_2Au thin films were also grown in the DCA M600 MBE growth chamber. The Mn and Au were evaporated simultaneously from separate K-cells. The Au K-cell was held continuously at 1282°C while the Mn cell was adjusted to a temperature which would provide a flux ratio of Mn:Au of 2:1, which in this case was 937°C . A more detailed outline of the stoichiometry control can be found under the "Stoichiometry Control" heading in Section 2.1.2. These cell temperatures resulted in an overall growth rate for Mn_2Au of approximately $0.25 \text{ \AA s}^{-1}$. In all cases, the substrate temperature was reduced from the Pt growth temperature of 550°C to the desired growth temperature upon completion of the Pt layer. The temperature of the Mn and Au K-cells were simultaneously raised to their respective growth temperatures.

3.3.2.1 Mn_2Au substrate temperature optimisation

In order to find the optimal growth temperature for Mn_2Au , samples were grown, for 1200s, at substrate temperatures of 100°C , 200°C , 250°C , 300°C and 400°C . Figure 3.8 shows the out-of-plane XRD scans of each of the samples, with all showing only the Mn_2Au $\{110\}$ and the Pt $\{111\}$ peaks, which correspond well to the expected values as denoted by the dashed gold and dashed blue lines on the graph.

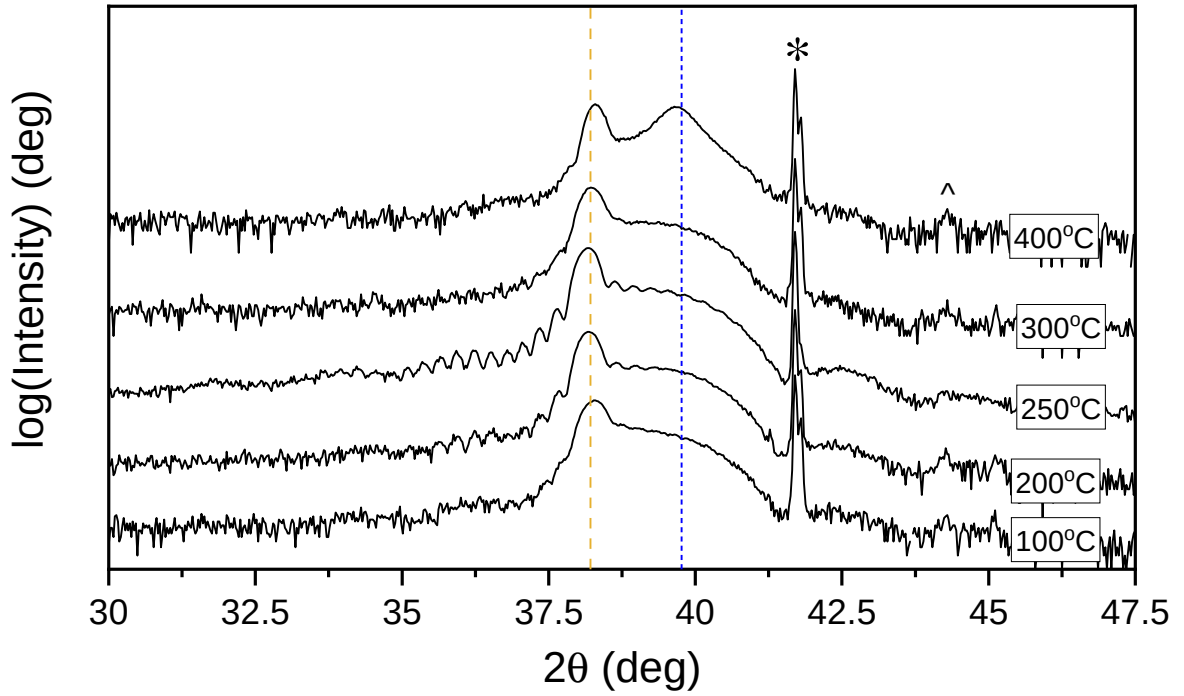


Figure 3.8: XRD scans of the Mn_2Au films grown on a Pt seed layer at substrate temperatures between 100°C - 400°C . The expected 2θ positions for the Mn_2Au (110) peaks are shown by the dashed gold lines, the Pt (111) peaks are shown by the dashed blue lines, while the Al_2O_3 (0006) peak is denoted by the asterisks. Note that there appear to be two Al_2O_3 (0006) peaks, each separated by approximately 0.1° . This is characteristic of twinning in the substrate likely due to a defect such as an edge dislocation which occurred during the growth of the Al_2O_3 crystal. The carat symbol shows the position of a peak emanating from the XRD stage, rather than the sample.

Pendellösung fringes are apparent on all of the samples, with low frequency fringes visible from the Pt (111) diffraction peak, which are most prominent in the 40° - 45° for the samples grown at less than 250°C . High frequency fringes are visible around the Mn_2Au (110) diffraction peak. The frequency of the oscillations is related to the thickness of each layer. From Figure 3.8, it becomes immediately clear that the substrate temperature of 400°C is not optimal as there is clear degradation of the Pendellösung fringes (low frequency) around the Pt (111) peak as evidenced by the narrower Pt (111) peak in comparison to the other samples. Pendellösung fringes (high frequency) are also seen around the Mn_2Au (110) peak on the samples grown at less than 250°C , with the largest amount of low and high frequency oscillations prevalent of the 250°C sample, qualitatively indicating that that has the lowest surface and inter-layer roughness.

XRR scans were measured and the data from the line of best fit is contained in Table 3.2. The values of Mn_2Au thickness decrease with increasing substrate temperature indicating that there is increased Au and Mn adatom desorption given that estimate of density from the fit is broadly similar for all substrate temperatures. The values for surface roughness estimated from the fit broadly agree with the qualitative analysis of the Pendellösung fringes, with the 250°C sample being the smoothest.

Table 3.2: Table of the parameters of best fit from XRR scans of the Mn_2Au samples grown on a Pt Seed layer. T_g represents the substrate growth temperature, t_{Pt} and $t_{\text{Mn}_2\text{Au}}$ represent the thickness of each layer, ρ_{Pt} and $\rho_{\text{Mn}_2\text{Au}}$ the density of each layer, σ_{int} and σ_{sur} the roughness or the interface between Pt and Mn_2Au and the surface roughness respectively.

T_g ($^{\circ}\text{C}$)	T_{Pt} (nm)	σ_{int} (nm)	$T_{\text{Mn}_2\text{Au}}$ (nm)	$\rho_{\text{Mn}_2\text{Au}}$ (g/cm^3)	σ_{sur} (nm)
100	4.3	0.41	28.4	10.4	0.9
200	4.4	0.38	28.0	10.75	1.02
250	4.2	0.33	28.4	11.0	0.44
300	4.8	0.54	26.7	10.77	0.71
400	4.5	0.38	24.3	11.2	1.8

The Mn_2Au (110) rocking curves were measured for each of the samples and the FWHM of each was determined by fitting each of the rocking curves using a pseudo-Voigt curve. The FWHM as determined by the fit is plotted in Figure 3.9a in black. For the samples grown in the range of 100°C - 250°C the FWHM of the Mn_2Au (110) rocking is $\leq 0.013^{\circ}$ which is the resolution limit for the diffractometer used for this measurement. Rocking curves with widths this narrow are indicative of minimal mosaicity in the Mn_2Au films grown below 250°C . The surface roughness (red) of the Mn_2Au layer is plotted alongside the FWHM fit data in Figure 3.9a which shows a minimum at 250°C substrate temperature.

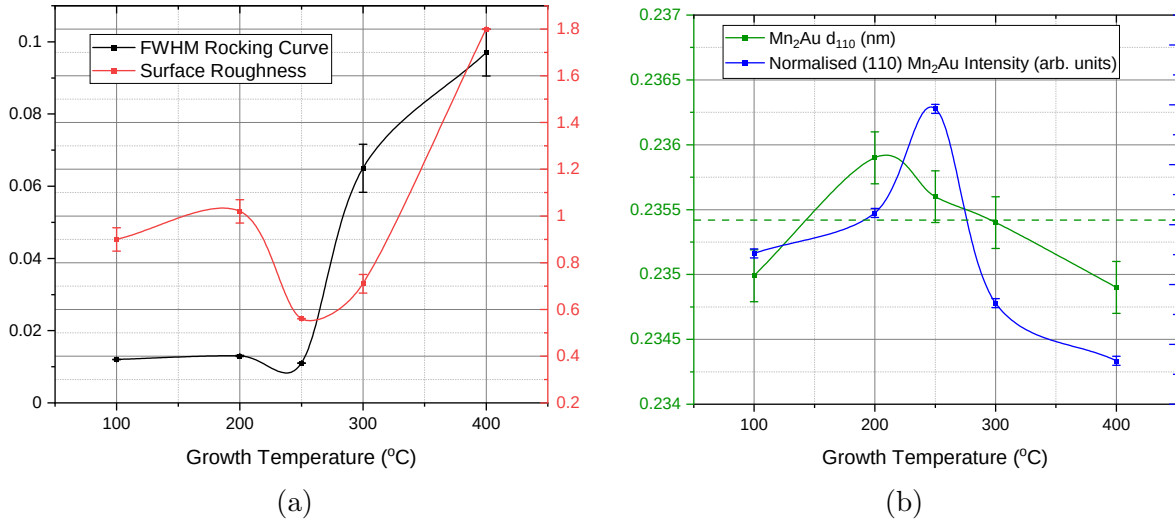


Figure 3.9: (a) shows the FWHM (black) of the Mn_2Au (110) rocking curve as determined via fit, for each of the samples grown. The surface roughness (red), as estimated from the line of best fit from XRR scans of each sample. (b) The normalised intensity of the Mn_2Au (110) diffraction peak (blue), normalised with respect to the magnitude of the Al_2O_3 (0006) diffraction peak. The out-of-plane inter-planar spacing d_{110} (green) as determined from the central 2θ value of the Mn_2Au (110) diffraction peak as estimated via fitting, with the indexed bulk d_{110} value of $2.354 \text{ \AA}$ marked by the dashed green line. The data points are connected via a modified b ezier to guide the eye.

Figure 3.9b shows the normalised intensity of the Mn_2Au (110) diffraction peaks in blue. The samples were normalised with respect to the intensity of the Al_2O_3 (0006) diffraction peak from the sample grown at 250°C . It should be noted that the XRD scans for every sample were taken after the same alignment procedures. The sample grown at 250°C shows the largest intensity indicating that it is more crystalline than the other samples. Figure 3.9b also shows the out-of-plane inter-planar spacing d_{110} the central 2θ position of the Mn_2Au (110) diffraction peak for each sample in green, as determined through a Gaussian fit of the (110) peak, with the bulk d_{110} value of $2.354\text{ \AA}$ shown by the dashed green reference line [92]. A Gaussian was chosen as it fits the profile of the Mn_2Au (110) peak better than a pseudo-Voigt in this case. The samples with peak positions above the reference line show contraction of the d_{110} spacing with respect to bulk Mn_2Au , while the samples below it show expansion of the d_{110} spacing with respect to bulk Mn_2Au . For example, the 250°C sample has a 2θ value of 38.172° which corresponds to a $d_{110}=2.356\text{ \AA}$ which corresponds to an expansion along the [110] direction by 0.085% . The combination of XRD, XRR and FWHM of the (110) Mn_2Au rocking curve all indicate that 250°C is the optimum temperature for deposition of Mn_2Au (110) on a Pt (111) seed layer.

3.3.2.2 Surface Morphology

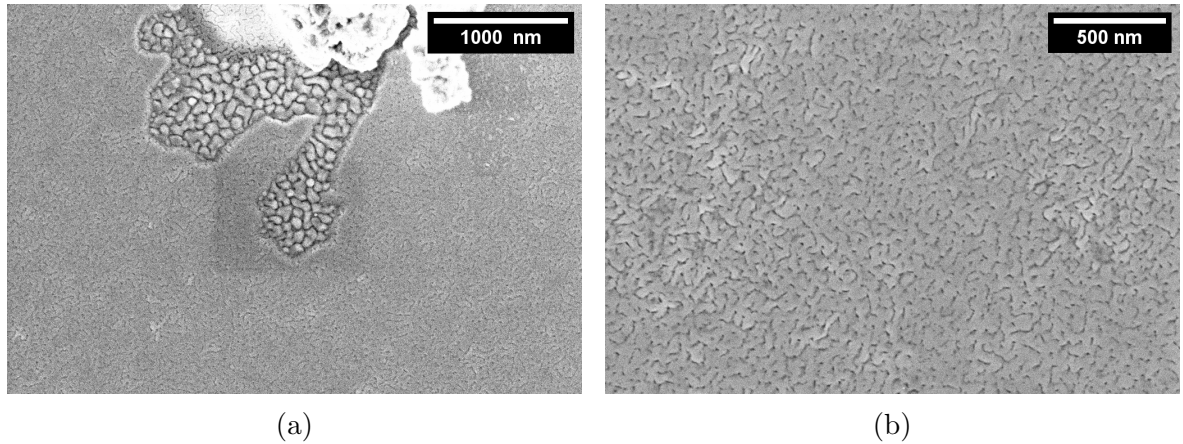


Figure 3.10: SEM images of a typical Mn_2Au (110) thin film grown on an Al_2O_3 (0001) substrate with a 3.8 nm Pt (111) seed layer. (a) shows a part of the sample that has been damaged with the Pt seed layer and substrate exposed by the damage, while (b) shows a different part of the same Mn_2Au surface.

The morphology of the films was probed using two methods. Firstly typical films grown at 250°C were analysed using SEM and one film, grown at 200°C was analysed using STM. Figure 3.10 shows two SEM images of a 28.2 nm thick Mn_2Au (110) thin film grown on a 3.8 nm thick Pt (111) seed layer on an Al_2O_3 (0001) substrate. Figure 3.10a shows a damaged region of the thin film. The Pt seed layer can be seen to be exposed next to the high contrast unknown material at the top of the image. This damage was likely caused by a tweezer when affixing the sample to the SEM sample

holder. The Pt seed layer consists of a mixture of smaller grains of the order of 100 nm and larger irregular-shaped regions which appear isolated, as evidenced by the black contrast between them. The irregular-shaped region appears to be made up of multiple smaller grains which have coalesced together. The Mn_2Au layer is more easily seen in Figure 3.10b and is largely continuous, with the dark regions appearing to be the edges of grains exposed due to the topological roughness.

For the STM analysis, a sample was grown at 200°C with a Pt buffer layer on Al_2O_3 , in the MBE and transferred *in-situ* to the STM via a "Vacuum Suitcase", which consists of a transfer arm, gate valve, an ion pump and a Non-Evaporable Getter (NEG) pump, and has a base pressure below 1×10^{-10} torr. The growth took place immediately following the growth of the 200°C sample discussed earlier under the same growth conditions, with the only exception being that an STM-compatible sample holder was used. The STM used for these measurements is a commercial system built by Createc which has a base pressure better than 5×10^{-11} torr, which was operated at liquid nitrogen temperatures of 77 K. All of the data was collected using a single crystalline W (001) tip, which was operated in constant current mode.

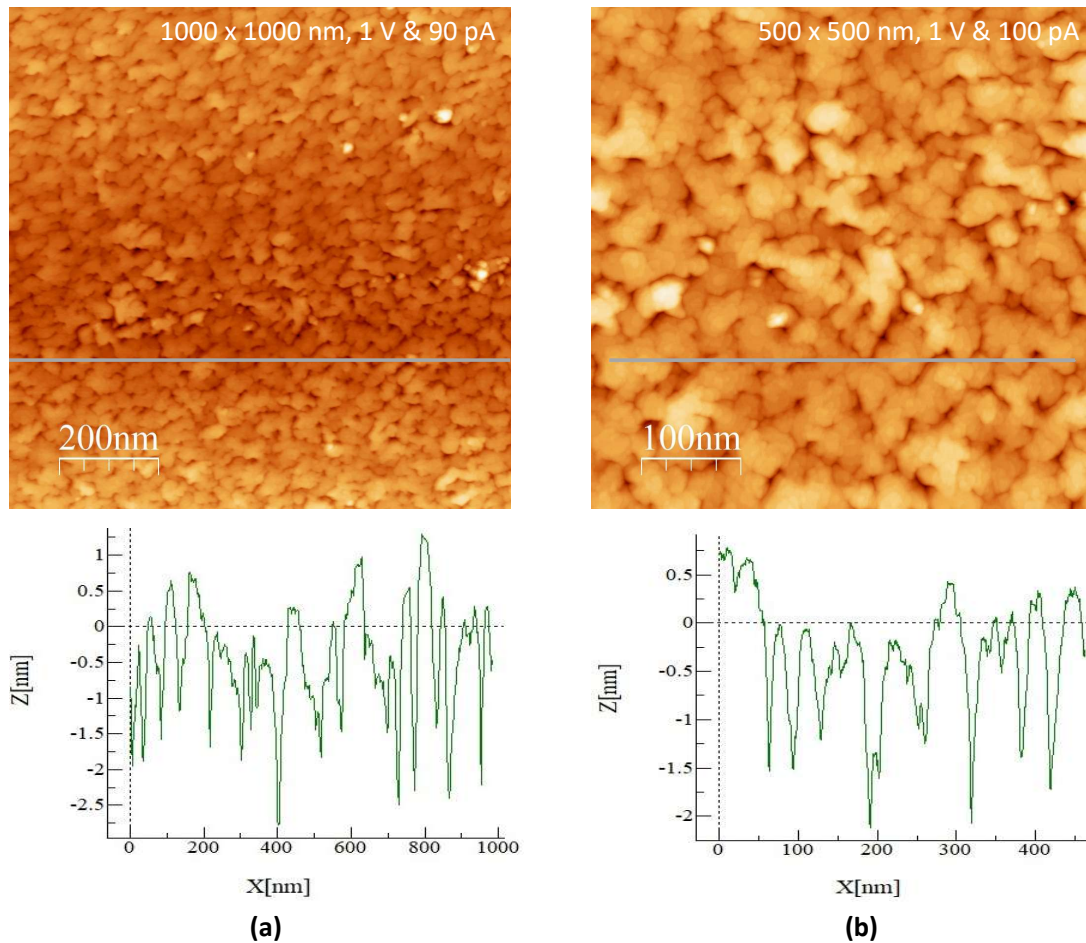


Figure 3.11: Large area STM images of the (110) Mn_2Au sample grown at 200°C and line profiles displaying the peak to valley roughness along the line beneath. The size of each image is (a) 1000 nm by 1000 nm area and (b) 500 nm by 500 nm area.

Figure 3.11 shows in (a) a 1000 nm by 1000 nm area image and in (b) a 500 nm by 500 nm area STM images taken in constant current mode where the current and voltage used during scanning can be seen in the top right-hand corner of the images. The morphology of the images in Figure 3.11 is similar to what is seen in Figure 3.10 with the film appearing largely continuous with the dark regions appearing to be the edges of grains which have coalesced together. Qualitatively, the STM images in Figure 3.11 appear rougher than those shown in the SEM images in Figure 3.10. This analysis is consistent with that observed in the surface roughness as estimated via XRR which can be seen above in Figure 3.9a, with the sample grown at 200°C having a higher degree of roughness than that grown at 250°C . The images in Figure 3.11 show horizontal grey lines, the topological line profile of which can be seen beneath each of the images. This gives a quantitative measure of the peak-to-valley roughness which is on the order of 2 nm-3 nm in both instances. This is much larger than the approximately 1 nm value observed for a similar 200°C sample via XRR. This is not unusual as XRR typically results in a lower value for the roughness of thin films than scanning microscopy methods, due to it representing a macroscopic average value of the roughness over the whole film [142].

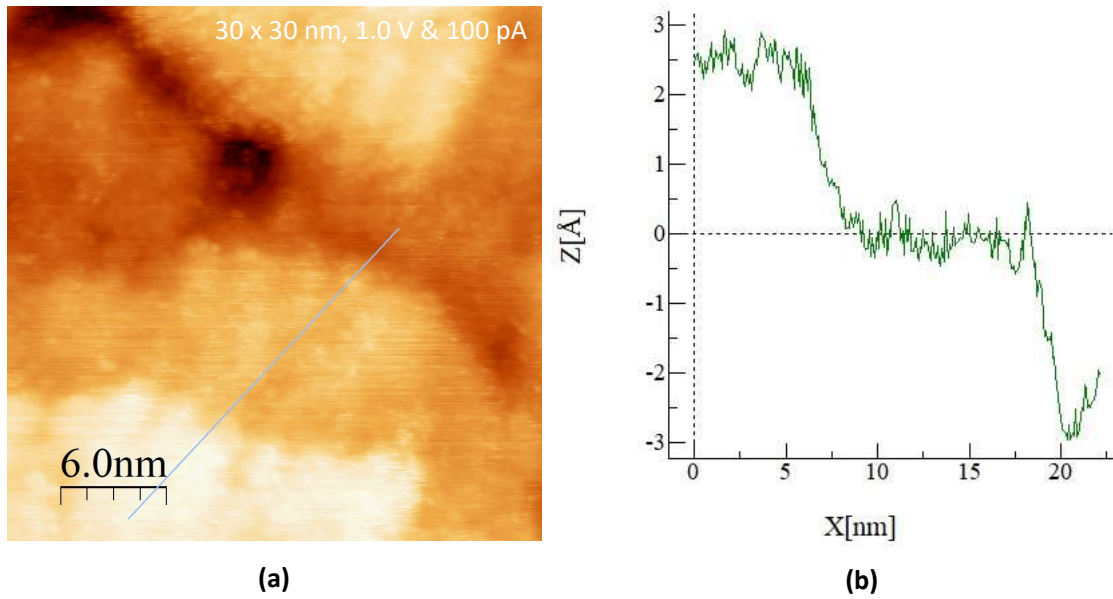


Figure 3.12: (a) 30 nm by 30 nm STM image of the (110) Mn_2Au sample grown at 200°C which was transferred *in-situ* from the MBE to the STM. and (b) a representative line profile taken of a (110) Mn_2Au monatomic step along the grey line in (a).

Figure 3.12a shows a small area scan of one of the grains taken in a 30 nm by 30 nm area taken in constant current mode. Clear terraces are observed in the image, however, no atomic resolution could be obtained. The image also shows a grey line along a drop in the terraces, the line profile of which can be seen in Figure 3.12b. The image shows a

vertical drop between the adjacent terraces along the line profile on the order of $2.5 \text{ \AA}$ which suggests the terraces are actually monatomic steps. The reference value for the $\text{Mn}_2\text{Au}d_{110}$ spacing is $2.354 \text{ \AA}$ [92] and the measured value for the d_{110} spacing from a similar 200°C of $2.236 \text{ \AA}$ via HRXRD. In both cases, the value produced by STM is much larger. This is typical for STM as the step height that is measured is both a function of the real space distance and also the DOS of the surface atoms.

3.3.2.3 RHEED and LEED

Figure 3.13 shows typical RHEED images taken of the Pt and Mn_2Au layers along the two high symmetry directions of the Al_2O_3 substrate which are separated by 30° . Each of the RHEED images shown were produced at an electron beam energy of 20 keV . The RHEED images were taken at temperatures of 600°C , 550°C and room temperature for each of the Al_2O_3 substrate, the Pt and the Mn_2Au layers respectively. The Al_2O_3 RHEED is characterised by sharp diffraction spots and Kikuchi lines along both high symmetry directions, which is indicative of a high quality single crystal surface. The RHEED images of the Pt and Mn_2Au layers both consist of elongated streaks, indicating that each layer has a flat surface consisting of grains/crystalline domains smaller than the coherence length of the electron beam [126].

The Mn_2Au RHEED pattern was typically present after $\sim 5 \text{ nm}$ of Mn_2Au was deposited and persisted throughout the growth, even for the thickest sample grown, which was $\approx 120 \text{ nm}$. In Figure 3.13, along the Al_2O_3 $[10\bar{1}0]$ direction, the Mn_2Au layer possesses the same streak spacing as the underlying Pt seed layer and the Al_2O_3 substrate. This corresponds to the a lattice parameter of Al_2O_3 ; $4.758 \text{ \AA}$ [143]. The oxygen sublattice in Al_2O_3 appears to be in a Hexagonal Close Packed (HCP) arrangement, but in reality, it is only approximately so [144]. The deviations from the ideal HCP arrangement in Al_2O_3 result in the periodicity of the RHEED viewed along the $[11\bar{2}0]$ direction, which is equivalent to three times the atomic spacing resulting in the smaller streak spacing observed. The Mn_2Au image along this high symmetry direction has higher intensity first order streaks that line up with the Pt streaks, but also less intense second order streaks which line up with the 3 times periodicity shown in the Al_2O_3 RHEED. This is not due to surface lattice distortions on the Mn_2Au surface, but rather, due to the presence of both Mn and Au atoms in the Mn_2Au (110) surface. When viewed along the Al_2O_3 $[11\bar{2}0]$ direction, the Mn and Au atoms are both present in the rows of atoms perpendicular to this direction, which results in the periodicity shown which is three times the inter-atomic spacing of the Mn_2Au surface, and thus giving the same periodicity as shown in the Al_2O_3 RHEED image. Figure 3.14 shows a schematic of the growth relations of the three surfaces overlaid, and highlights the presence of both Mn and Au perpendicular to the Al_2O_3 $[11\bar{2}0]$ direction. Along the Al_2O_3 $[10\bar{1}0]$ direction, the rows of atoms perpendicular to this in the Mn_2Au consist of only one element and so the RHEED image has the same streak spacing as the Al_2O_3 and the Pt layer. A

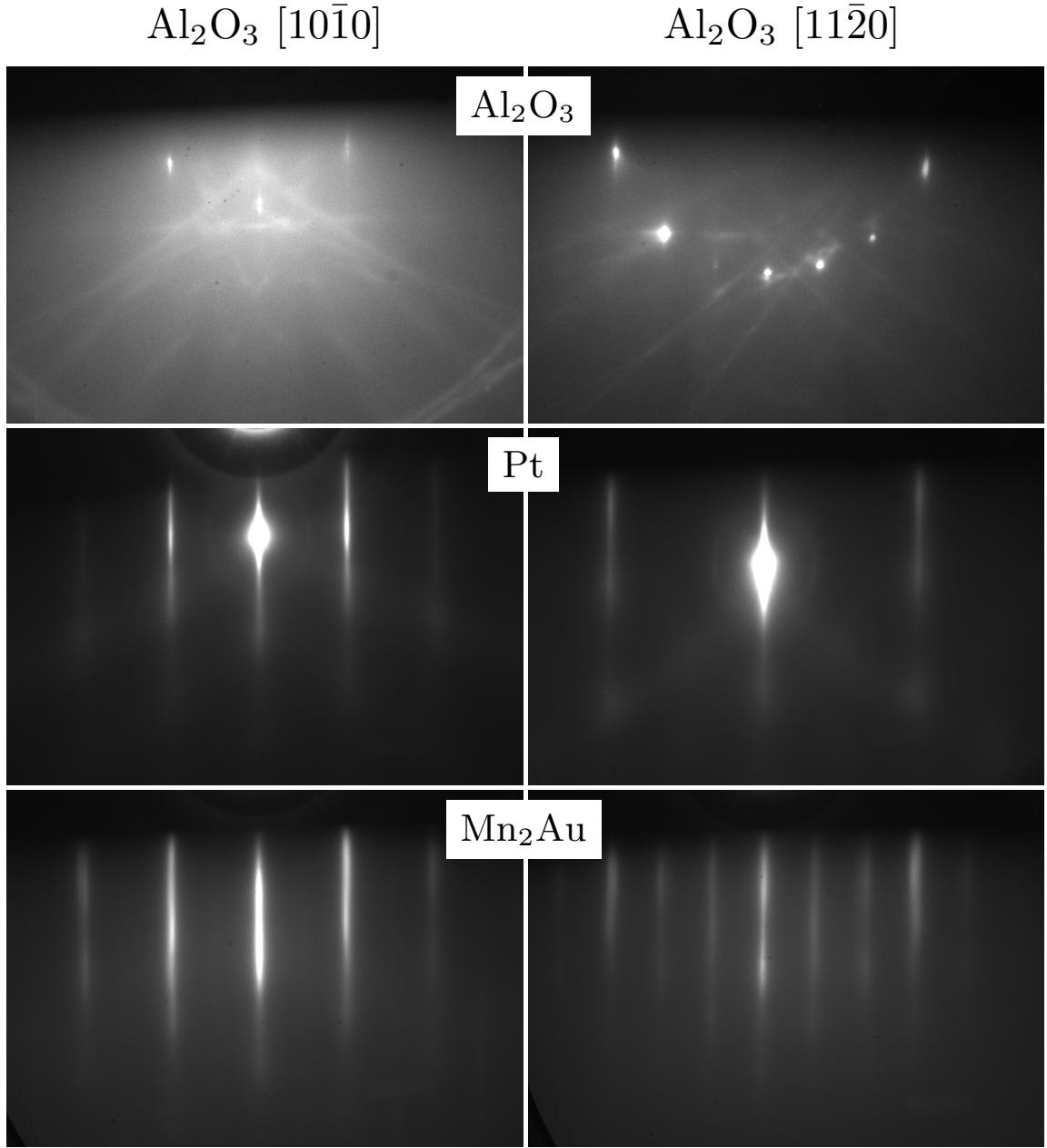


Figure 3.13: RHEED images of a typical $\text{Mn}_2\text{Au}/\text{Pt}/\text{Al}_2\text{O}_3$ sample, taken along the Al_2O_3 $[10\bar{1}0]$ and $[11\bar{2}0]$ high symmetry directions, which are separated by 30° .

word on the Pt RHEED; given the lack of second order peaks in the RHEED images along both high symmetry Al_2O_3 directions, it can be concluded that the Pt layer forms the expected HCP surface lattice rather than continuing the lateral symmetry of the underlying Al_2O_3 oxygen lattice. Given the high quality of the RHEED post Mn_2Au deposition, all samples were cooled from their deposition temperature to room temperature upon completion of the Mn_2Au layer.

Post *in-situ* transfer from the MBE to the STM main chamber for surface scanning, the 200°C Mn_2Au film was characterised using LEED in the STM prep chamber. LEED images were obtained for various different energies and are shown in Figure 3.15. The LEED pattern is exactly what one would expect for a hexagonal close packed surface,

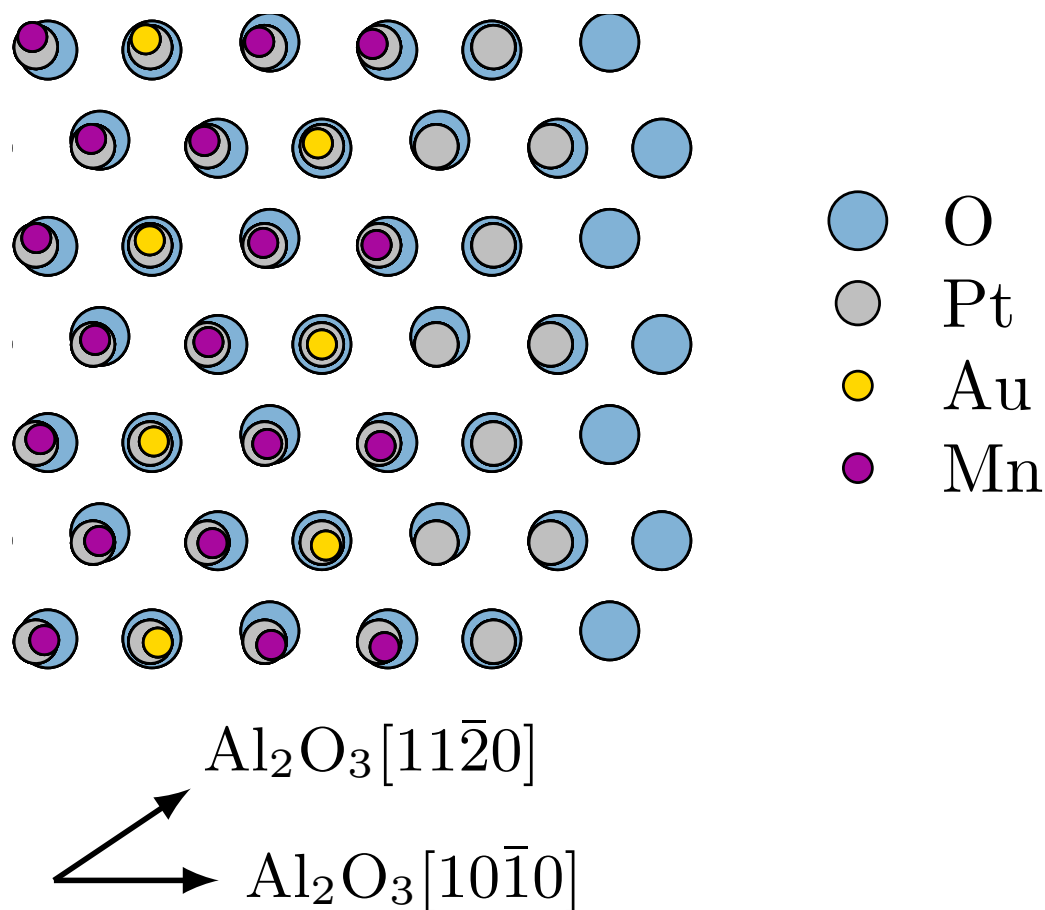


Figure 3.14: A plan view of the Mn_2Au (110) surface overlaid on the Pt (111) and Oxygen terminated Al_2O_3 (0001) surfaces with the growth relationship between the layers shown.

which the (110) surface of Mn_2Au is. The presence of the diffraction spots indicates the high quality of the Mn_2Au thin film, however, the broad nature of these diffraction spots makes it impossible to discern the number of domains present in the sample.

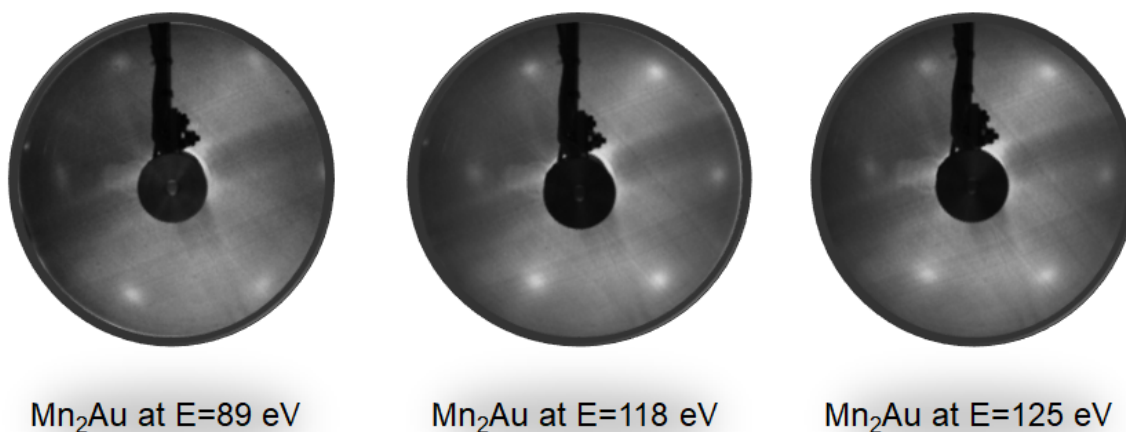


Figure 3.15: LEED Images of a sample grown at 200 °C and transferred in vacuum to the STM. The hexagonal pattern seen is as expected from the Mn_2Au (110) surface.

3.3.2.4 In-Plane XRD

Although the RHEED indicates that each of the Mn_2Au and Pt layers are in register with each other and with the Al_2O_3 substrate and that the fit of the Pendellösung fringes for each layer indicates that the crystals are a continuous crystal of single orientation out-of-plane, neither can discern if the film is made up of a single in-plane rotational domain or of multiple rotational domains. Given the six-fold symmetry of the Pt (111) HCP surface lattice, it is possible that there are up to six individual Mn_2Au rotational domains. To elucidate the number of rotational domains a 120 nm Mn_2Au sample was grown to perform in-plane XRD or azimuthal (ϕ)-scans on. This large thickness was chosen as the peaks being probed are weakly diffracting asymmetric peaks. The XRD scans of this are shown in Figure 3.16.

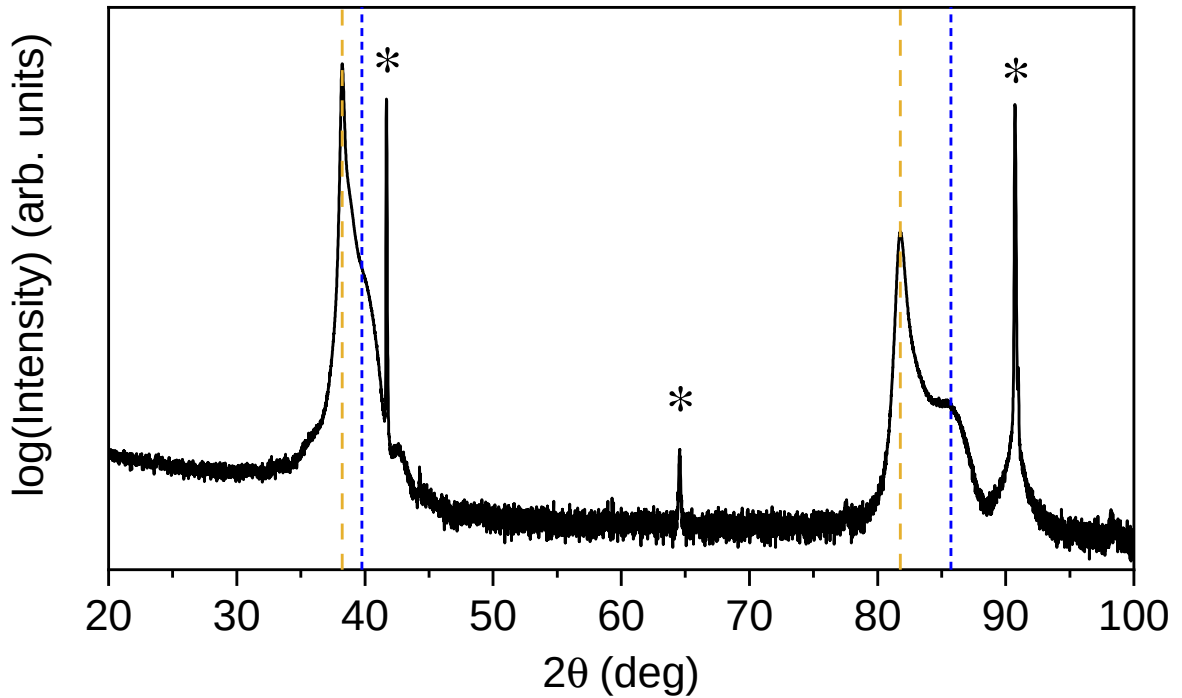


Figure 3.16: XRD of an ≈ 120 nm Mn_2Au (110) film, grown for in-plane XRD scans. The expected 2θ positions of the Mn_2Au {110} peaks are represented by the gold dashed lines, while the Pt {111} peaks are represented by the dashed blue lines. The Al_2O_3 {0001} substrate peaks are denoted by the asterisks.

Figure 3.17 shows these azimuthal ϕ -scans. The Al_2O_3 ϕ -scan of the {1 0 10} peaks shows the expected three-fold symmetry. The ϕ -scan of the Pt {100} peaks is expected to show three peaks separated by 120° each if the sample consisted of a single rotational domain, instead six peaks are observed. This implies that there are two equivalent rotational domains, each rotated 60° with respect to the other. The approximately equal intensity of all the Pt {100} peaks indicates that both domains are present in equal quantities across the sample. This agrees with the published work of Farrow *et al.* [133]. Similarly, the Mn_2Au {310} ϕ -scan is expected to show two peaks separated by 180° , however, six primary peaks can be seen, as well as six secondary peaks rotated

from the primary peaks by 30° . The intensity of the secondary peaks are on the order of a few percent of the primary peaks. This indicates that there are three equivalent primary crystalline in-plane domains, each rotated by 60° with respect to each other, and three parasitic crystalline in-plane domains, each rotated by 60° with respect to each other. The Mn_2Au $\{222\}$ peaks are expected to have the same twofold symmetry as the $\{310\}$ peaks, but with their positions rotated by 90° with respect to those of the $\{310\}$ peaks. The $\{222\}$ ϕ -scan shows the same three equivalent rotational domains, with the expected 90° separation.

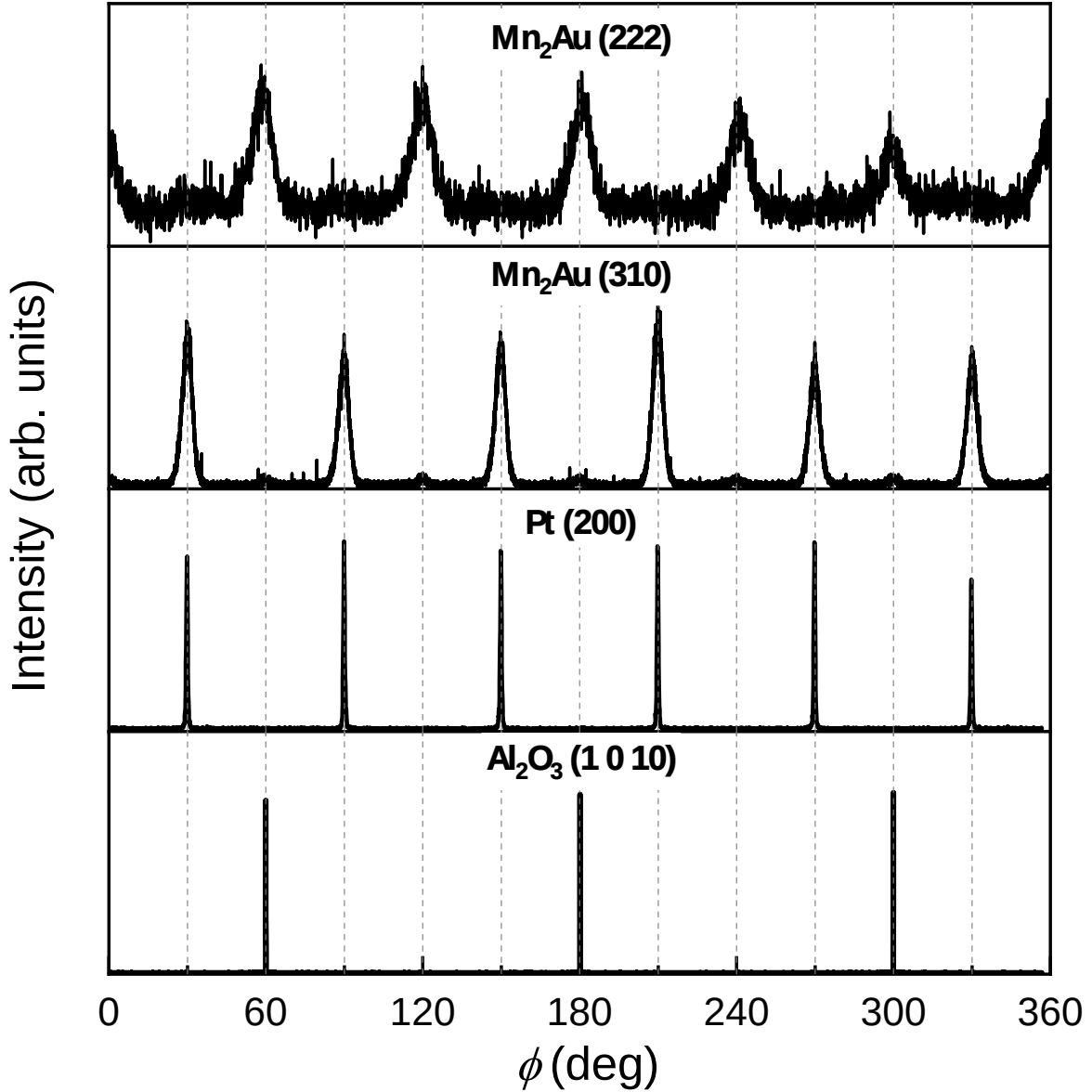


Figure 3.17: Azimuthal (ϕ)-scans of the Al_2O_3 substrate (1 0 10), the Pt seed layer (100), and the Mn_2Au film (310) and (222) diffraction peaks, demonstrating the in-plane relation between the layers. The substrate and Pt scans are from the 27.4 nm Pt sample in Figure 3.7, while the Mn_2Au scans are from the 120 nm sample in Figure 3.16

The full out-of-plane epitaxial relation can be expressed as Al_2O_3 [0001]||Pt [111]|| Mn_2Au [110]. The in-plane relationship, determined via the ϕ -scans can be expressed

as Al_2O_3 $[10\bar{1}0] \parallel \text{Pt}$ $[1\bar{1}0] \parallel \text{Mn}_2\text{Au}$ $[001]$.

Combined, the XRD and RHEED measurements show that Mn_2Au can be grown smoothly, with a high degree of crystallinity when grown on a Pt seed layer on a c-plane Al_2O_3 substrate. An estimate for the strain of the Pt and the Mn_2Au layers can be made from these measurements. By first correcting for the thermal expansion of Al_2O_3 and Pt [145, 146], it was found that the Pt RHEED spacing along both Al_2O_3 high symmetry directions results in room temperature in-plane lattice parameter of $4.758 \text{ \AA}$, which is 1.5% smaller than the expected in-plane lattice parameter of $4.8305 \text{ \AA}$. This indicates that the Pt layer grows in a pseudomorphic fashion to a thickness of at least 5 nm . The d-spacing of the out-of-plane Pt (111) as determined from the XRD of a film of the same thickness, indicates that there is an increase of d_{111} of Pt from the bulk of 1.8% , partially compensating the in-plane strain. Interestingly, this relaxes to 0.68% for the 10 nm film grown at 550°C in Figure 3.4. This value is bulk-like for the 27.4 nm film shown in Figure 3.7, indicating that the strain present in the Pt films relaxes in the thickness range of 10 nm - 27.4 nm .

The Mn_2Au (110) d -spacing was determined to be within 1% of the expected value for both the 28.4 nm and the $\approx 120 \text{ nm}$ films. Similar to the Pt in-plane lattice parameter, in principle, the Mn_2Au c lattice parameter can also be determined from the streak spacing along the Al_2O_3 $[11\bar{2}0]$ high symmetry direction, however, the presence of multiple rotational domains precludes an accurate value being obtained. The Mn_2Au streaks along this Al_2O_3 high symmetry direction arise either from the periodicity perpendicular to the $[1\bar{1}0]$ (c) or that perpendicular to the $[1\bar{1}1]$ direction, corresponding to bulk values of $8.539 \text{ \AA}$ and $8.250 \text{ \AA}$ respectively. The width of these streaks in Figure 3.13 is too large to distinguish between these two spacings, as the streaks appear as a single streak with no splitting or fine structure present. The spacing of these streaks is found to correspond to $8.319 \text{ \AA}$, which is a value intermediate between the two possible values stated above. Given that the ϕ -scans in Figure 3.17 indicates that all of the rotational domains are present in approximately equal quantities, the expected average streak spacing is $8.3466 \text{ \AA}$. The measured value is 0.33% less than this expected value. This indicates that there is minimal in-plane strain present in this 28.4 nm sample.

The a and c lattice parameters of Mn_2Au can also be determined from a RSM of an asymmetric XRD peak, one which has an in-plane and out-of-plane component. Using the $\approx 120 \text{ nm}$ Mn_2Au (110) film a RSM of the Mn_2Au (213) peak was measured and it can be seen in Figure 3.18. Given the broad nature of the peak, each axis was fit with a Gaussian to determine the centre point of the peak along each axis; the centre point values for each axis are denoted by the dashed grey lines. The (213) reciprocal space point can be decomposed into a combination of the out-of-plane $[\frac{3}{2}\frac{3}{2}0]$ and the in-plane $[\frac{1}{2}\frac{1}{2}3]$ vectors. The (213) RSM shown in Figure 3.18 was fit using a 2-D Gaussian surface to estimate the centre points along each axis; the estimates for each are shown

by the dashed grey lines. Using the out-of-plane value of q , as determined from the best fit as $6.380\,35\,\text{nm}^{-1}$, the Mn_2Au a lattice parameter was determined to be $3.325\,\text{\AA}$, which is within 0.09% of the indexed value of $3.328\,\text{\AA}$.

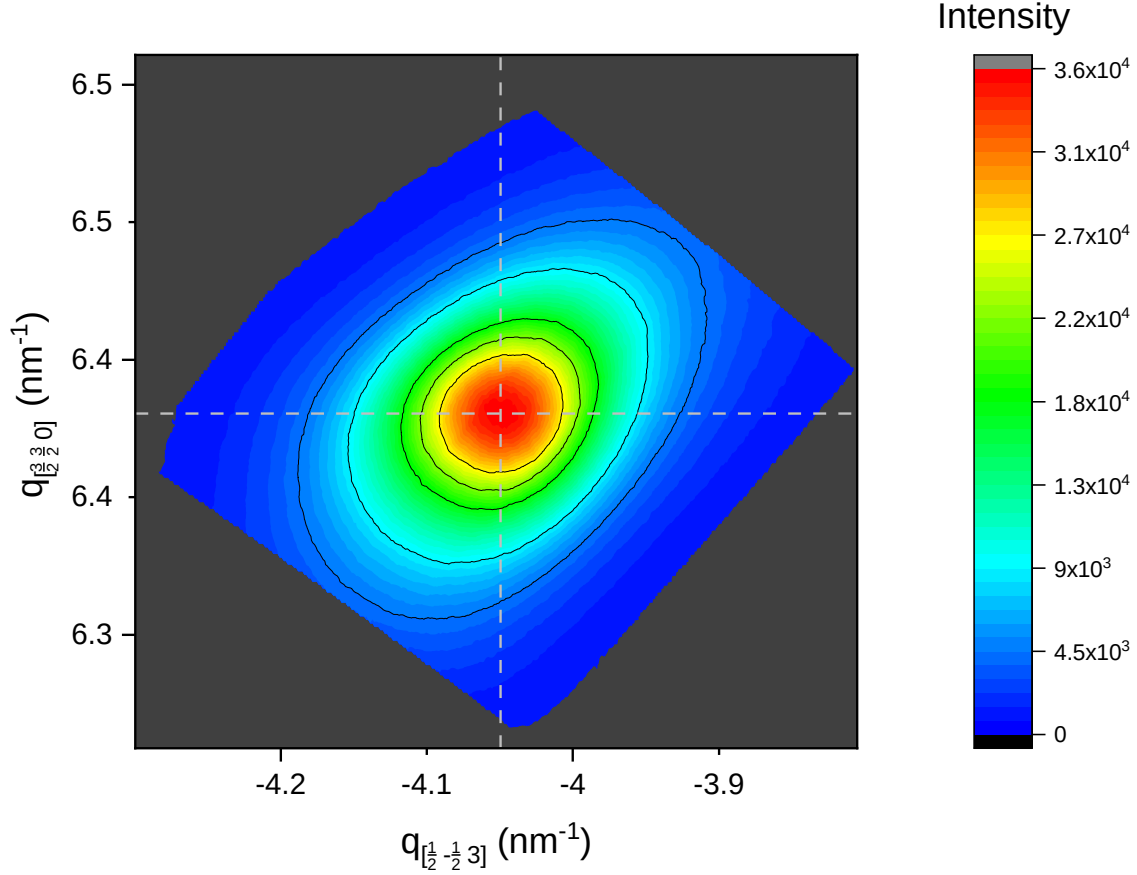


Figure 3.18: A reciprocal space map of the Mn_2Au (213) peak. The grey lines denote the centre point along each axis as determined by best fit.

Similarly, using the in-plane value of q , which was estimated to be $4.049\,63\,\text{nm}^{-1}$ from the best fit, the Mn_2Au c lattice parameter was determined to be $8.705\,\text{\AA}$. This represents an expansion of the Mn_2Au c lattice parameter of 1.94% from the indexed value of $8.539\,\text{\AA}$. It is also in contrast to the strain analysis performed on the $28.4\,\text{nm}$ Mn_2Au (110) sample, which indicated minimal c parameter strain. There are a few possible reasons for the discrepancy, the most obvious of which is that the stoichiometry of this $\approx 120\,\text{nm}$ sample is likely not perfectly 2:1 Mn:Au and also likely different to that of the $28.2\,\text{nm}$ sample, as the stoichiometric mix drifts over time and needs to be re-calibrated. If there was a slight excess of gold in the sample it could cause an overall change in cell volume as indicated by the derived a and c lattice parameters from this RSM. Another possibility is a minor misalignment of the sample during the alignment to the (213) peak before measurement. This was likely caused by the broad nature of the peak and its low intensity caused by the geometry of the measurement, which required a tilt of the sample stage perpendicular to the detection axis by 45° , which reduces the number of detected counts dramatically. If this was the case then

the resulting fit of the centre points of the RSM would be unreliable. It is difficult to disentangle which is the case without measuring the RSM or performing a stoichiometry analysis of the film using a technique such as XPS.

3.3.2.5 Stoichiometry of Mn_2Au

The stoichiometries of the Mn_2Au films were qualitatively assessed using XRD scans. Similar to the films shown in Figure 3.1a, when the Mn flux was too high α -Mn phases could be seen in the XRD scans. When the Mn flux was too low MnAu phases could be seen in the XRD scans. This off-stoichiometric growth was accompanied by a concomitant change in the observed RHEED pattern post-growth. The RHEED pattern would range from modulation in the streaks of the pattern to a transmission-like pattern depending on the qualitative closeness to Mn_2Au stoichiometry. The quantitative approach taken to determine the stoichiometry of the films via X-ray photoelectron spectroscopy (XPS) can be found in the supplementary information of [136].

3.4 Conclusion

To summarise, the growth Mn_2Au on MgO via co-deposition of Mn and Au was studied. This yielded predominantly rough, polycrystalline films, with an excess of Mn, which were discontinuous for substrate deposition temperatures above 400°C . This was largely driven by the flux ratio of Mn:Au of 3:1. Similarly, the co-deposition of Mn and Au on r- Al_2O_3 was examined. This attempted to emulate the epitaxial Mn_2Au (001) films previously obtained by magnetron sputtering directly onto r- Al_2O_3 substrates [28]. Although a Mn:Au flux ratio of 2:1 was used, the samples produced were polycrystalline at a number of deposition temperatures and the Mn_2Au (001) single out-of-plane orientation was not replicated. Similar to the Mn_2Au on MgO (001) samples, the samples grown on r- Al_2O_3 were discontinuous above 400°C .

The latter half of this chapter presented co-deposited Mn_2Au (110) on a Pt (111) seed layer grown on Al_2O_3 (0001) substrates. Again, a flux ratio of 2:1 for Mn:Au was used. High quality Mn_2Au (110) was obtained as evidenced by the XRD which showed only the Mn_2Au {110} and the Pt {111} peaks present in our samples, as well as the presence of both Pendellösung fringes around the Mn_2Au (110) and the Pt (111) peaks in the best samples, indicating the presence of continuous crystalline domains throughout the thickness of each of those film layers. A combination of XRD, XRR and the FWHM of the Mn_2Au (110) rocking curve were used to determine the optimum substrate deposition temperature for co-deposition of Mn_2Au films; this was found to be 250°C . XRR indicated that the best films had a low roughness, less than 1 nm. XRD ϕ -scans showed that the Mn_2Au films had 3 in-plane crystalline domains, all present in roughly equal proportions. Analysis of the RHEED spacings indicated that

there was minimal strain present in the Mn_2Au thin films grown, by comparing the thin film lattice parameters with those of the reported bulk values [92].

The Mn_2Au (110) films shown in this work are one of three works which were able to obtain a single crystalline orientation and the first demonstration of single phase, (110) oriented films. The smooth morphology and lack of parasitic crystalline phases in our films present the opportunity for devices with reduced domain wall pinning, the large AFM domains as observed by SEM and smooth interfaces for heterostructures with smooth interfaces on the functional AFM layer.

Chapter 4

The Growth and Characterisation of FM/Mn₂Au heterostructures

4.1 Motivation

After the theoretical prediction of AFM order and a high Néel temperature, Mn₂Au was cast into a renewed focus [96]. Subsequently, density functional theory (DFT) calculations of the magnetic anisotropy phenomena in Mn₂Au and MnIr predicted that in bimetallic AFMs there would be a large magnetic anisotropy and thus a large tunneling anisotropic magneto resistance effect, with Mn₂Au possessing the larger anisotropy of the two materials. The 5d noble metal provides a large spin-orbit coupling while the 3d shell of Mn adds a complementary large spontaneous moment. The combination of large magnetic anisotropy and large SOC results in a highly anisotropic density of states which is necessary to maximise the tunneling anisotropic magneto resistance effect [11]. The large predicted TAMR effect was confirmed experimentally in a NiFe(10 nm)/Ir₂₀Mn₈₀(3 nm)/MgO/Pt magnetic tunnel junction (MTJ) structure with a magnitude of 160 % at 4 K [14, 86]. These stacks were later optimised for the thickness of the AFM layer; an Ir₂₀Mn₈₀ thickness of 4 nm resulted in a small TAMR effect close to room temperature [12]. Some of the limiting factors in achieving the TAMR effect at room temperature in Ir₂₀Mn₈₀ were the reduced Néel temperature of the AFM layer due to finite-size effects [44], the exchange stiffness of the AFM and the persistence of the exchange coupling effect [20]. The TAMR effect requires that the AFM moments are coupled to the FM moments but that anisotropy is not so high as the moments can't be rotated by the reversal of the FM moments, but also not so low as to completely rotate with the FM moments [12]. Mn₂Au has been suggested as a material that may provide a high room temperature TAMR signal given its large SOC and its higher Néel temperature of approximately 1400 K [23], than that of Ir₂₀Mn₈₀ (700 K) [147]. Combined, this may give Mn₂Au closer to ground state properties at the thin AFM thicknesses required to achieve the TAMR effect.

The goal of this work was to take a step towards TAMR in Mn₂Au by demonstrating the growth of Mn₂Au thin films on two FM materials (Fe and Co) building on the previous work in Chapter 3. The aim was to grow the Mn₂Au layers at the thicknesses necessary to realise the TAMR effect. The TAMR effect also relies on the ability to induce the ECE in FM/Mn₂Au bilayers. This requires field cooling of the FM/Mn₂Au bilayers in an applied magnetic field from above the effective Néel temperature of the Mn₂Au layer. This work aimed to understand the robustness of the Mn₂Au layer to the high annealing temperatures that may be necessary to induce the ECE in Mn₂Au. Further to this, the aim was to magnetically characterise the heterostructures before and after the annealing procedures to understand if EC could be induced in the FM/Mn₂Au bilayers.

4.2 The growth of Co/Mn₂Au bilayers on a Pt (111) seed layer

The heterostructures of the form c-Al₂O₃/Pt/Co/Mn₂Au(*x*)/Pt, were grown using a combination of e-beam evaporation and deposition using two K-cells in the DCA M600 MBE. The Al₂O₃ (0001) substrates were sonicated in acetone and IPA each for 15 minutes, prior to being loaded into the MBE. The substrates were annealed for 1 hr at 600 °C prior to the deposition of the Pt layer. For each sample, a Pt layer of 3.8 nm, as measured on a calibrated quartz crystal monitor, was deposited at a rate of 0.05 Å s⁻¹ at a substrate temperature of 550 °C using e-beam evaporation. After completion of the Pt layer the substrate temperature was allowed to cool to room temperature. Subsequently, 15 nm of Co was deposited, at a rate of 0.1 Å s⁻¹ via e-beam evaporation, with the thickness and rate determined via a calibrated quartz crystal monitor. The Co substrate temperature was chosen to be room temperature as this was previously shown to produce high quality Co layers [13, 50, 148]. Mn₂Au layers were deposited at nominal thicknesses of *x* nm where *x* was 2.5 nm, 5 nm, 7.5 nm and 10 nm, all using a substrate deposition temperature of 200 °C. This substrate deposition temperature for the Mn₂Au layer was chosen for two reasons; firstly there were minimal differences in crystalline quality between the Mn₂Au samples grown at 200 °C and 250 °C, as shown in the previous chapter, and secondly, 200 °C was chosen in an attempt to minimise diffusion between the Co and Pt layers [149, 150]. Similar to the previous chapter the flux ratio of Mn:Au was set to 2:1, which corresponded to cell temperatures in this case of 935 °C and 1282 °C. The Mn₂Au growth rate was determined via XRR to be 0.25 Å s⁻¹ for this sample set. Following deposition of the Mn₂Au layer, the samples were cooled to room temperature before being capped with 2 nm of Pt.

4.2.1 RHEED Characterisation

Figure 4.1 shows RHEED images, of the $x = 5$ nm heterostructure, for each of the Pt, Co, Mn₂Au and Pt layers. Only the RHEED from the $x = 5$ nm heterostructure are shown, but the qualitative features discussed are representative of all the heterostructures grown. The images shown were taken along the two high symmetry directions of the Al₂O₃ substrate, $[10\bar{1}0]$ and $[11\bar{2}0]$, which are separated by 30° and each image was produced at an electron beam energy of 20 keV. The RHEED images were taken at 600°C , 550°C , 200°C , 200°C and 25°C for each of the Al₂O₃ substrate, the Pt seed layer, the Co layer, the Mn₂Au layer and the capping Pt layer respectively. These temperatures correspond to the annealing temperature or the deposition temperature of the layer in all cases, excluding that of the Co layer, which was taken immediately prior to the deposition of the Mn₂Au layer. This was due to the slight change in the Co RHEED as a result of the increase in substrate temperature to 200°C .

The Al₂O₃ RHEED is characterised by sharp diffraction spots and Kikuchi lines along both high symmetry directions, indicating that the substrate is a high quality single crystal surface. The RHEED images of the Pt seed layer consist of elongated streaks and Kikuchi lines, indicating that the Pt layer has a flat surface of crystalline domains smaller than the coherence length of the electron beam, which is typically on the order of 100 nm-200 nm [126]. The Co RHEED shows modulated elongated streaks with faint Kikuchi lines, indicating that the surface consists of multiple stepped levels, again with domains smaller than the coherence length of the electron beam. It should be noted that a RHEED image of the Co layer was taken at room temperature for the purposes of analysis of the streak spacing. Figure 4.2 shows a line profile taken across the RHEED streaks, along the Al₂O₃ $[10\bar{1}0]$ direction, of the 15 nm at room temperature (black) and 200°C (red). The 200°C first order streaks (red) are narrower than the room temperature first order streaks (black). The Mn₂Au RHEED and the Pt capping layer RHEED also consist of elongated streaks which are modulated, with the degree of modulation of both patterns greater than that of the Co RHEED. This qualitatively indicates that the surfaces of these layers are rougher than that of Co and that the degree of roughness increases throughout the heterostructure. Again the elongated streaks indicate that the crystalline domain size in each of the layers is smaller than the coherence length of the electron beam, which is typically on the order 100 nm-200 nm [126].

From Figure 4.1, looking along the Al₂O₃ $[10\bar{1}0]$ direction, it can be seen that the Pt seed layer possesses the same streak spacing as the underlying Al₂O₃ substrate. This spacing corresponds to the a lattice parameter of Al₂O₃; $4.758 \text{ \AA}$ [143]. Similar to the Pt seed layers investigated in Chapter 3, when corrected for the thermal expansion of the Al₂O₃ [145] and Pt [146], the Pt layer is found to have an in-plane lattice parameter of $4.758 \text{ \AA}$ at room temperature. This is 1.5 % smaller than the expected in-plane

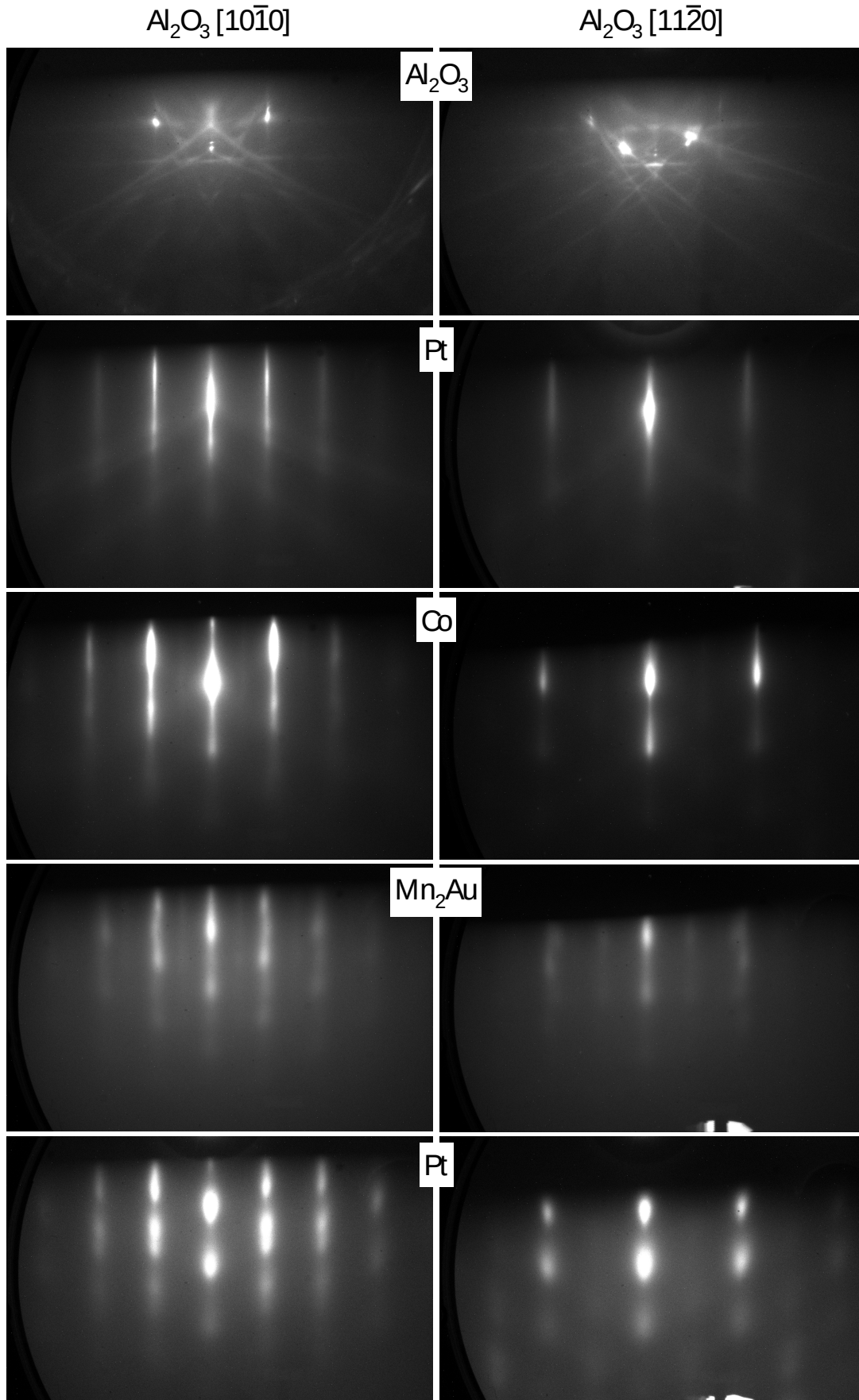


Figure 4.1: RHEED images of each of the layers post deposition in the $x = 5$ nm, c- $\text{Al}_2\text{O}_3|\text{Pt}|\text{Co}|\text{Mn}_2\text{Au}|\text{Pt}$ heterostructure along the two high symmetry directions of the Al_2O_3 substrate of $[10\bar{1}0]$ & $[11\bar{2}0]$, which are separated by 30° . See text for description.

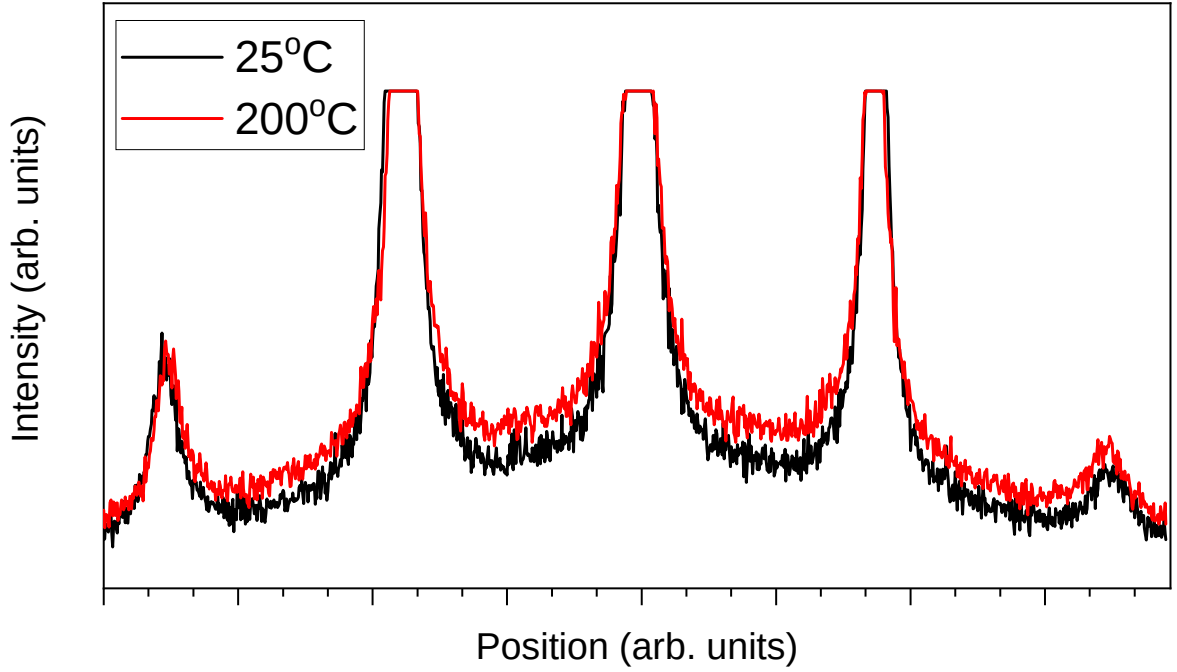


Figure 4.2: A line profile taken Al₂O₃ [10 $\bar{1}$ 0] direction of the 15 nm Co layer, from the $x = 5$ nm heterostructure, at room temperature (black) and at 200 °C.

lattice parameter of 4.8305 Å [140], again indicating that the Pt seed layer is growing in a pseudomorphic fashion. The Co layer possesses a larger streak spacing than the underlying Pt seed layer, qualitatively indicating that the Co interatomic spacing along the Al₂O₃ [10 $\bar{1}$ 0] direction is < 4.758 Å. At a thickness of 15 nm the in-plane lattice parameter of the Co layer, along the Al₂O₃ [10 $\bar{1}$ 0] direction, was found to be 4.296 Å at room temperature. This represents a contraction with respect to the bulk value of 4.345 Å of 1.1 % [151]. The Mn₂Au RHEED along the Al₂O₃ [10 $\bar{1}$ 0] high symmetry direction shows first order streaks with some modulation, but also with modulation of the streak spacing along the extent of the streaks. This indicates that there are multiple rotational crystalline domains present in the sample, and there are two possible interatomic spacings for the Mn₂Au atoms along this direction; 4.707 Å or 4.875 Å [92]. The streak spacing measured at the widest spacing yielded an interatomic value of 4.795 Å and when measured at the narrowest spacing give a value of 4.942 Å. It should be highlighted that the Mn₂Au RHEED images were taken at 200 °C, however, there is no literature on the thermal expansion coefficients of Mn₂Au. A crude stoichiometry weighted value can be calculated from the reference values of Mn and Au of $21.7 \times 10^{-6} \text{ °C}^{-1}$ and $14.2 \times 10^{-6} \text{ °C}^{-1}$ [152]. Given the stoichiometric ratio of Mn:Au of 2:1, using the formula $(2(Mn) + Au)/3$ the value for Mn₂Au was estimated to be $19.2 \times 10^{-6} \text{ °C}^{-1}$. Using this value suggests that a typical contraction from 200 °C to 25 °C would be on the order of 0.4 %. Both values represent an expansion of the interatomic spacings expected for bulk Mn₂Au of 1.9 % and 1.4 % respectively, larger than the expected thermal contraction. It should also be noted that there are faint second order streaks apparent in the Mn₂Au RHEED along the Al₂O₃ [10 $\bar{1}$ 0] direction

occurring at twice the periodicity of the first order streaks.

Table 4.1: Table showing the measured linear in-plane strain of the Mn₂Au layers from each of the Co/Mn₂Au heterostructures grown, taken from the RHEED images along the Al₂O₃ [10 $\bar{1}$ 0] and [11 $\bar{2}$ 0] high symmetry directions at 200 °C. The minimum and maximum strain along each direction is displayed as the Mn₂Au streaks RHEED display differing widths along their length. Each value is compared to that of bulk Mn₂Au [92]. The percentage change with respect to bulk values is shown beside the estimated values with respect to the Al₂O₃ spacings. An expansion is denoted by a positive value while a negative value indicates a contraction.

Mn ₂ Au x (Å)	[10 $\bar{1}$ 0] min (Å)	[10 $\bar{1}$ 0] max (Å)	[11 $\bar{2}$ 0] min (Å)	[11 $\bar{2}$ 0] max (Å)
Bulk [92]	4.707	4.875	2.747	2.852
25	4.920 (4.5 %)	4.985 (2.3 %)	2.767 (0.73 %)	2.943 (3.2 %)
50	4.795 (1.9 %)	4.942 (1.4 %)	2.812 (2.4 %)	2.905 (1.9 %)
75	4.877 (3.6 %)	5.052 (3.6 %)	2.763 (0.58 %)	2.955 (3.6 %)
100	4.911 (4.3 %)	5.075 (4.1 %)	2.727 (−0.73 %)	3.034 (6.4 %)

In Figure 4.1, looking at the Al₂O₃ [11 $\bar{2}$ 0] RHEED pattern, only the periodicity of the atomic spacing is observed, and not the atomic spacing. This is likely due to a slight tilt of the substrate caused by the sample manipulator. This periodicity is three times the atomic spacing and is a result of the Al₂O₃ oxygen sublattice having a pseudo-HCP arrangement [144]. This prevents a direct comparison between the Al₂O₃ [11 $\bar{2}$ 0] atomic spacing and the Pt seed layer atomic spacing along the same direction. However, the reference spacing from the Al₂O₃ [10 $\bar{1}$ 0] can be used to calculate the Pt interatomic spacing along the Al₂O₃ [11 $\bar{2}$ 0] direction. This provides a value of 2.745 Å after being corrected for thermal expansion, which represents a contraction of 1.1 % from the bulk value of 2.774 Å [135]. This corresponds well to the value of the contraction measured along the Al₂O₃ [10 $\bar{1}$ 0] direction. Measurement of the streak spacing from the room temperature Co RHEED provides a value for the Co interatomic spacing of 2.499 Å. This represents a contraction with respect to bulk value of 0.4 % 2.509 Å [151]. The Mn₂Au RHEED along the Al₂O₃ [11 $\bar{2}$ 0] direction, displays the same fine structure as that along the Al₂O₃ [10 $\bar{1}$ 0] direction; elongated streaks that are modulated in intensity and displaying differing widths along the extent of the streaks. This again suggests the film consists of multiple rotational crystalline domains. Considering the Mn₂Au (110) surface unit cell, with no favourable in-plane orientation the possible interatomic spacings that this RHEED represents include 2.747 Å, 2.752 Å, 2.843 Å and 2.852 Å. Measurement of the Mn₂Au streak spacings at their maximum and minimum extent gives values of the interatomic spacing along the Al₂O₃ [11 $\bar{2}$ 0] direction of 2.812 Å and 2.943 Å. When compared with the largest and smallest possible bulk values, they differ by 2.4 % and 3.2 %. This quantitative analysis is crude given the four possible values, but the qualitative trend agrees with the analysis in the previous paragraph;

the Mn₂Au layer undergoes an in-plane expansion of its lattice parameters with respect to bulk [92]. Table 4.1 shows Mn₂Au in-plane spacings, which were calculated from a similar analysis of the Mn₂Au RHEED from the other heterostructures. This shows that, generally, as the Mn₂Au layer thickness increases the magnitude of the in-plane strain increases indicating that the Mn₂Au layer grows in a pseudomorphic fashion on the Co underlayer. It should be clarified that the atomic spacings calculated from the RHEED streak spacings are not absolute, and are only calculated relative to the "known" values of the Al₂O₃ substrate [143].

4.2.2 X-ray Characterisation

Figure 4.3 shows the wide angle θ - 2θ XRD scans performed on the heterostructures. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140] and fcc Co (111) [153] peaks are shown by the dashed gold, blue and red reference lines respectively. The positions of the higher order planes are also noted. The XRD peaks from the Al₂O₃ (0001) substrate are marked with asterisks, while the carat symbol denoted peaks emanating from the XRD sample stage.

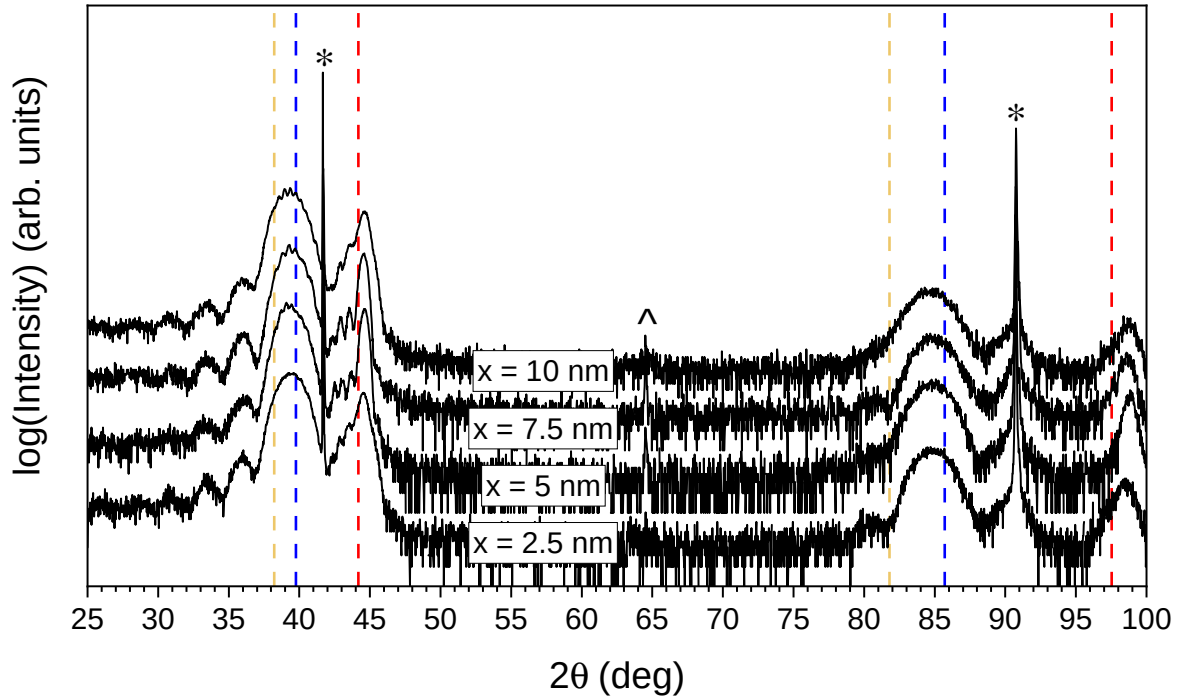


Figure 4.3: XRD scans of the Al₂O₃ (0001)|Pt (111)|Co (111)|Mn₂Au (110)|Pt as deposited heterostructures. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, while the Pt (111) reference lines are in blue and the Co (111) reference lines are in red. The Al₂O₃ substrate peaks are denoted by the asterisks.

Similar to the work in Figure 3.8 there are Pendellösung fringes (low frequency) emanating from the Pt (111) peak in all the samples, causing a broadening of this peak around its central position. Qualitatively, the oscillations for $\theta > 40^\circ$ all have similar frequencies and each film has approximately 3 fringes visible in this region. This

suggests the thickness of the out-of-plane Pt crystallites is similar in each of the films while having similar roughness at each interface. Using a simple Pendellösung fitting function from [141], as described in the previous chapter, the coherent thicknesses of the out-of-plane Pt crystallites were estimated to be 38.0 Å, 38.5 Å, 38.0 Å and 39.0 Å for each of the 2.5 nm, 5.0 nm, 7.5 nm and 10 nm samples. These fits are shown in Figure 4.4 below. Those values agree well with the nominal Pt thickness of 38 Å, as measured by the calibrated quartz crystal monitor. This indicates that the crystallites are coherent throughout the entirety of the film's thickness. There are a second set of Pendellösung fringes (high frequency) originating from the Co (111) peak, which are most easily seen between the approximate angles of 42°-45°. Qualitatively this indicates that the Co layers are of good crystalline quality with coherent out-of-plane crystallites throughout a large fraction of the Co layers in each of the samples. The Pendellösung fringes around the Co (111) peak in the $x = 2.5$ nm, 10 nm samples are less apparent than those from the $x = 5$ nm, 7.5 nm samples, indicating that interfaces are rougher in the $x = 2.5$ nm, 10 nm samples. This could be due to increased diffusion of the Co layer in those samples during the deposition of the Mn₂Au layer.

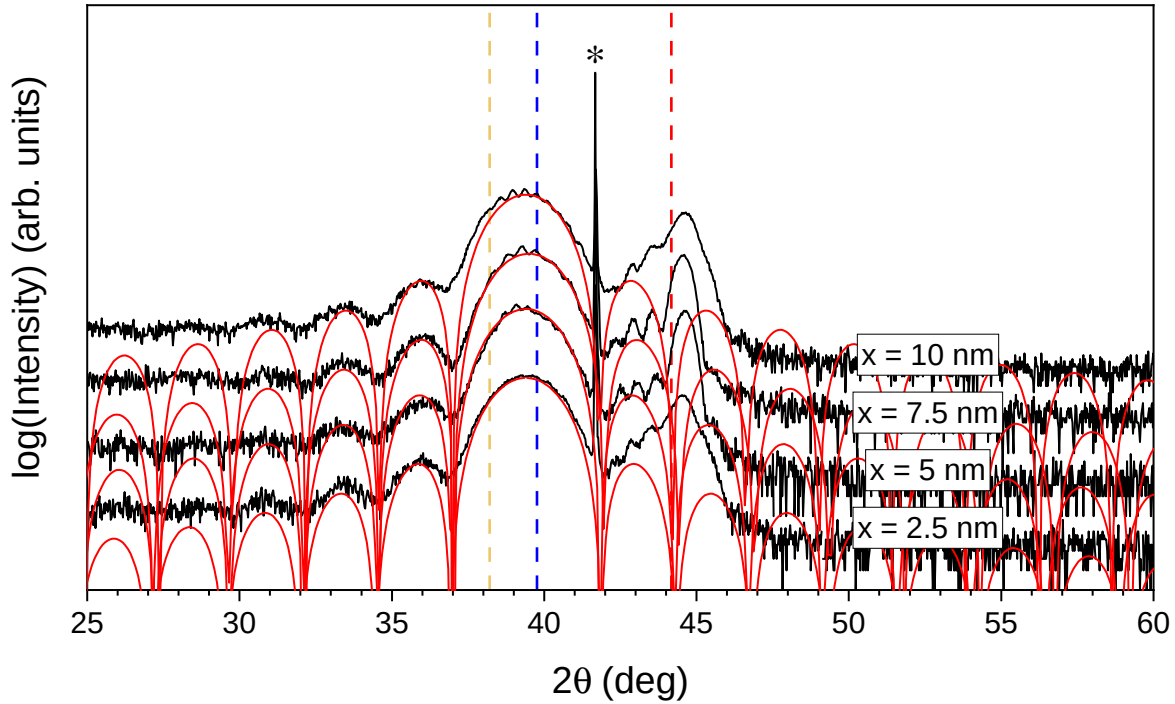


Figure 4.4: XRD scans of the Al₂O₃ (0001)|Pt (111)|Co (111)|Mn₂Au (110)|Pt as deposited heterostructures with the fits of the Pt Pendellösung fringes shown. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, while the Pt (111) reference lines are in blue and the Co (111) reference lines are in red. The Al₂O₃ substrate peaks are denoted by the asterisks.

The Mn₂Au (110) diffraction peak is obscured in all samples by the width of the Pt diffraction peak which is caused by the presence Pendellösung fringes and the thin nature of the Pt seed layer. In order to discern the influence of the Mn₂Au layer on the diffraction peaks the Pt (111) peaks were fit with a Gaussian function to determine their

FWHM. For each of the 2.5 nm, 5.0 nm and 7.5 nm samples the FWHM was estimated to be 1.75° , while for the 10 nm sample the FWHM was estimated to be 1.9° . Given that the Pendellösung fringes from the Pt (111) peak have the same frequency and the same 2θ value of approximately 39.4° , which suggests that the broadening of the Pt (111) FWHM of the 10 nm sample is due to the presence of the Mn₂Au (110) peak. The Pt (222) peak is also broadened in this sample in comparison to the others suggesting the presence of the Mn₂Au (220) diffraction peak. To further confirm this analysis, a sample consisting of c-Al₂O₃/Pt(3.8 nm)/Co(21 nm)/Mn₂Au(30 nm) was grown using the same growth conditions as the heterostructures. The thicker Mn₂Au layer was used to ensure a more intense (110) diffraction peak. Figure 4.5 shows the XRD scan taken from this stack where the positions of the Mn₂Au (110), Pt (111), and Co (111) reference lines are shown in gold, blue and red respectively. It is evident from this graph that the Mn₂Au (110) peaks are present, although they are convoluted with the Pt (111) peaks.

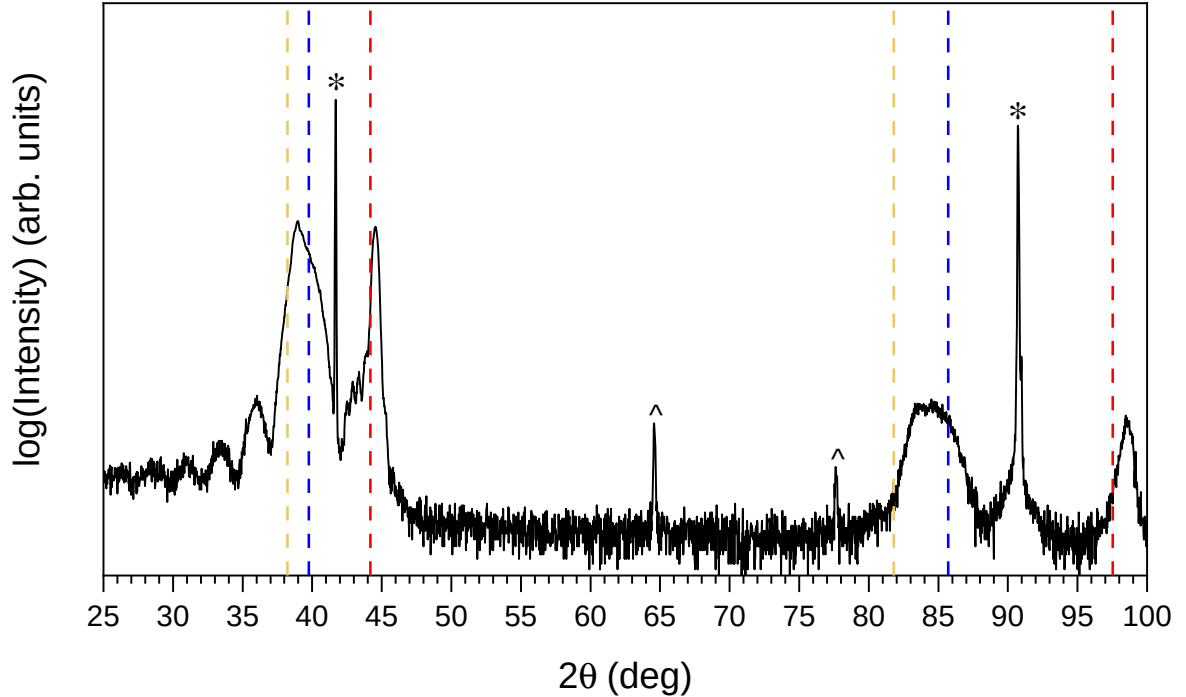


Figure 4.5: XRD scan of an Al₂O₃ (0001)/Pt (3.8 nm)/Co (21 nm)/Mn₂Au (30 nm) heterostructures. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, while the Pt (111) reference lines are in blue and the Co (111) reference lines are in red. The Al₂O₃ substrate peaks are denoted by the asterisks. The caret denotes peaks that occur from the XRD sample stage.

It is also clear in Figure 4.3 that the centre of the Co (111) XRD peaks are all shifted to higher angles compared to the bulk value [151]. This indicates that the d_{111} interlayer spacing of Co is contracted with respect to bulk values. For example, the value for d_{111} of the Co layer, from the $x = 5$ nm heterostructure, is $2.032 \text{ \AA}$. This represents a 0.8% contraction along the $[111]$ axis in this case. Combined with the contractions observed in the in-plane interatomic spacings taken from the RHEED images, this implies that

there is an overall change in the Co unit cell volume with respect to the reference [153]. Similarly, the Pt (111) peaks from each of the heterostructures are found at lower angles compared to the bulk value. This qualitatively indicates that the Pt d_{111} interlayer spacing is expanded with respect to bulk values. This correlates well with the interatomic strain analysis of the Pt RHEED, where a contraction in the in-plane interatomic distances was observed, indicating that there is an expansion along the [111] to compensate for the in-plane strain. From the $x = 5$ nm heterostructure, this represents an expansion along the [111] axis of 0.8 %. A similar analysis on the Mn₂Au layers in the heterostructures is difficult, due to the convolution of the Pt and Mn₂Au peaks. However, the XRD scan of the thick Mn₂Au layer in Figure 4.5 can be used. In this scan the Mn₂Au (110) peak is found at a higher angle than the gold reference line, qualitatively indicating a contraction of d_{110} . Calculation of d_{110} from a Mn₂Au 2θ value of 38.95° , provides a value of d_{110} of 2.316 Å. This represents a 2 % contraction compared to bulk values. It also agrees well with the RHEED analysis, suggesting that the contraction in the interlayer spacing compensates for the expansion of the in-plane atomic spacings that were observed in the heterostructures.

The combination of XRD and RHEED measurements indicates that Mn₂Au grows on a combination of Co and Pt seed layers with an out-of-plane epitaxial relationship of Al₂O₃ (0001)||Pt (111)||Co (111)||Mn₂Au (110). The RHEED indicates that there is no preferential in-plane epitaxy relationship and that the Mn₂Au film is comprised of multiple rotational domains. The RHEED and XRD also indicate that the Mn₂Au layer grows in a pseudomorphic manner with an in-plane expansion of the interatomic spacings compensated by a contraction along [110].

4.2.3 Structural Analysis after Annealing

After the *ex-situ* characterisation of the heterostructures, each 1 cm² substrate was cleaved into four approximately 5 mm×5 mm pieces using a diamond tipped pen. Subsequently, one of the 5 mm×5 mm pieces from each heterostructure, was subjected to a 1 h vacuum anneal at 350 °C and another different piece to a vacuum anneal at 500 °C. The annealing chamber was evacuated to a pressure better than 5×10^{-6} mbar prior to starting the anneal. An 800 mT field provided by a permanent magnet was applied in-plane arbitrarily along an in-plane axis of each of the samples during the annealing procedure. After the anneal the samples were allowed to cool to room temperature before being removed from the permanent magnet and then the vacuum furnace.

The two anneal temperatures were chosen for the following reasons. Generally, given the high Néel temperature of around 1400 K [23], to induce EC between Mn₂Au/FM layers they would need to be annealed at high temperatures, and the structural and magnetic properties investigated. The 350 °C anneal temperature was chosen as it was larger than the $\approx 225^\circ\text{C}$ FC temperature which failed to induce EB in single

orientation Mn₂Au (001)/Fe (001) bilayers [32]. Similarly, the 500 °C anneal temperature was chosen as it is closer to the peritectoid transition temperature of Mn₂Au of approximately 677 °C [154]. Although, there is a large gap between the anneal temperature and the peritectoid transition temperature of Mn₂Au, a reduction in the phase transition temperature had previously been observed during vacuum annealing of 30 nm Mn₂Au thin films, during which de-wetting of the films was observed at approximately 600 °C.

After the anneal each of the annealed heterostructures were characterised again by XRD to evaluate any changes to the structure that occurred as a result of the annealing process. Figure 4.6 shows the wide angle θ -2 θ XRD scans obtained from the heterostructures that were annealed at 350 °C. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140] and fcc Co (111) [153] peaks are shown by the dashed gold, blue and red reference lines respectively. The XRD peaks from the Al₂O₃ (0001) substrate are marked with asterisks, while the caret denotes the positions of peaks emanating from the XRD sample stage. In the $x = 5$ nm structure, there are no structure reflexes apparent above $2\theta = 50^\circ$. This is possibly due to a small misalignment of the sample prior to the scan, or the reduced substrate size of approximately 5 mm $\times$ 5 mm.

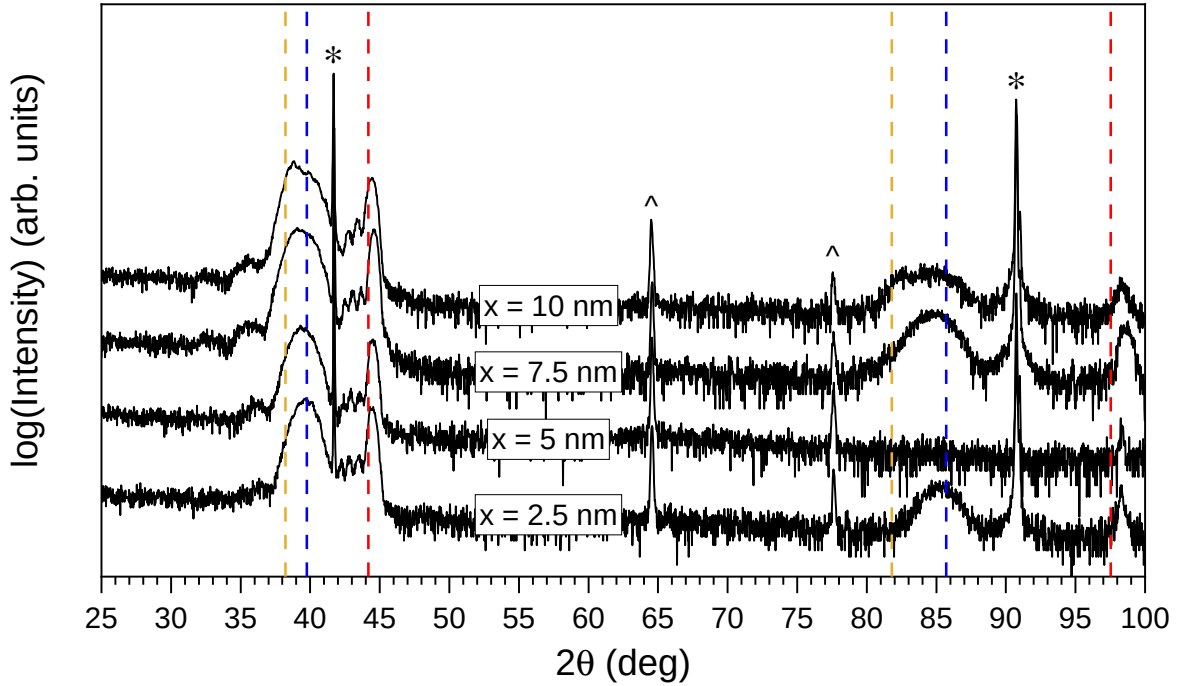


Figure 4.6: XRD scans of the Al₂O₃ (0001)|Pt (111)|Co (111)|Mn₂Au (110)|Pt heterostructures after a 350 °C vacuum anneal. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, while the Pt (111) reference lines are in blue and the Co (111) reference lines are in red. The Al₂O₃ substrate peaks are denoted by the asterisks. The caret denotes peaks that occur from the XRD sample stage.

The first thing to note in Figure 4.6 is the diminished prevalence of the Pendellösung

fringes around the Pt (111) peak when compared with the scans in Figure 4.3, evident in all the heterostructures. Qualitatively this indicates that there is increased roughness at the Pt/Co interface as a result of the annealing process. This is likely due to diffusion between the Pt layer and the adjacent Co layer. The Pendellösung fringes around the Co (111) peak are still apparent post anneal in each of the heterostructures, which qualitatively indicates that the level of roughness at the Co/Mn₂Au interface has increased by a minimal extent. The presence of the Mn₂Au (111) peak is also clear to see in the $x = 10$ nm sample, although it is obscured by the Pt (111) peak. This is further supported by the clear splitting of the Mn₂Au (220) and Pt (222) peaks in this scan also. Similarly, there appear to be two maxima to the Pt (111) peak in the $x = 7.5$ nm scan, indicating the presence of the Mn₂Au (110) peak. This is supported by the elongated tail on the left portion of the Pt (222) peak. Qualitatively this increase in the intensity of the Mn₂Au peaks is a sign of the increased crystalline quality of the Mn₂Au layer post annealing. In summary, the heterostructures underwent minimal changes to their structure after the 350 °C anneal while increasing the crystalline quality of the Mn₂Au layer in comparison to those in the un-annealed heterostructures.

From the $x = 2.5$ nm heterostructure, the maxima of the Pt (111) peak has shifted from a 2θ value of $\approx 39.42^\circ$ before the anneal, to a value of $\approx 39.65^\circ$ after it. This is closer to the reference peak position of 39.76° , indicating that the Pt layer has relaxed as a result of the anneal. Such a relaxation is not uncommon in annealed Pt (111) thin films and has previously been ascribed to the generation of vacancies at the free surface of the film and the coalescing of grains [155, 156]. In this case, though it is more likely that the relaxation is due to diffusion of Pt/Co at the interface due to annealing, which has been previously noted [157]. A similar analysis of the Pt layer in the other heterostructures is difficult due to the convolution of the Mn₂Au (110) and the Pt (111) reflexes. Calculation of the Mn₂Au d_{110} for the $x = 7.5$ nm and 10 nm, from the maxima 2θ values of 39.05° and 38.82° gives values of 2.311 Å and 2.323 Å. These represent contractions with respect to bulk of 1.8 % and 1.3 % respectively. Both values represent a relaxation of the d_{110} strain observed in the 30 nm Mn₂Au sample in Figure 4.5.

Figure 4.7 shows the wide angle θ - 2θ XRD scans obtained from the heterostructures that were annealed at 500 °C. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140], $Fm\bar{3}m$ L1₂ fcc Co₃Pt (111) [158], $Pm\bar{3}m$ A₁ fcc Co₃Pt (111) [159] and fcc Co (111) [153] peaks are shown by the dashed gold, blue, pink, purple and red reference lines respectively. The XRD peaks from the Al₂O₃ (0001) substrate are marked with asterisks, while the carat denotes the positions of peaks emanating from the XRD sample stage.

The Mn₂Au (110) peaks in Figure 4.7 are clearly visible in the $x = 7.5$ nm and 10 nm heterostructures, post the 500 °C annealing cycle. Similarly, the Mn₂Au (110) peak is

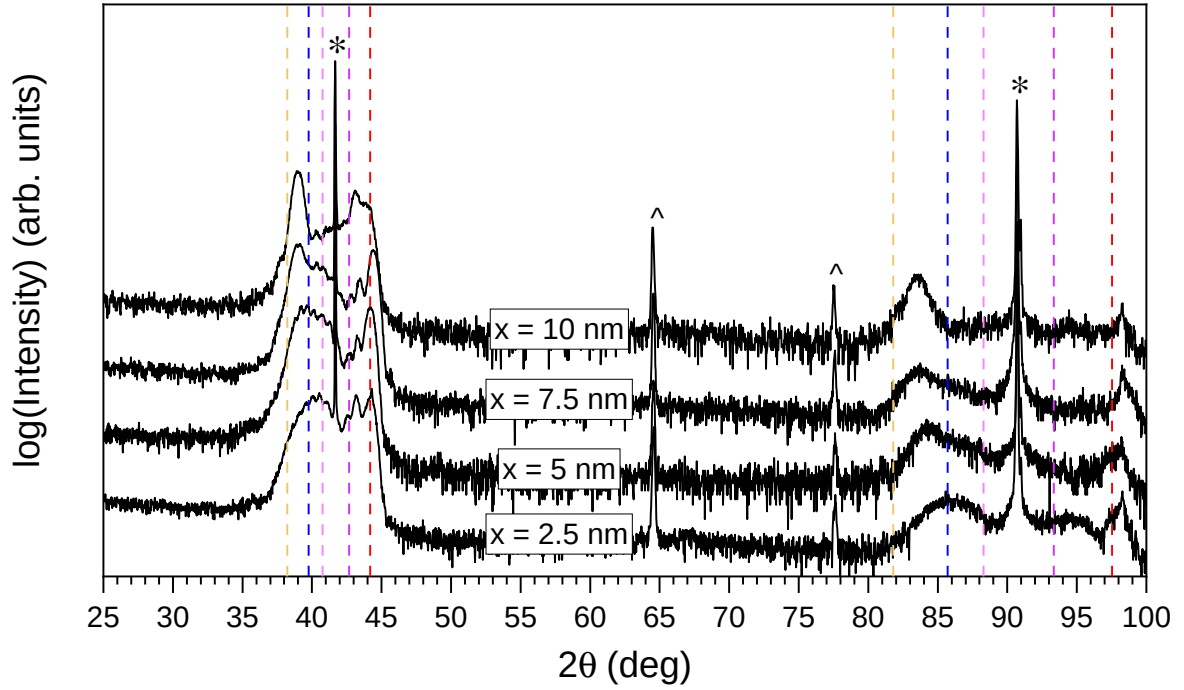


Figure 4.7: XRD scans of the Al₂O₃ (0001)|Pt (111)|Co (111)|Mn₂Au (110)|Pt heterostructures after a 500 °C vacuum anneal. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, the Pt (111) reference lines are in blue, the L₁₂ fcc Co₃Pt (111) reference lines in pink, the A₁ fcc Co₃Pt (111) reference lines in purple and the Co (111) reference lines are in red. The Al₂O₃ substrate peaks are denoted by the asterisks. The caret denotes peaks that occur from the XRD sample stage.

apparent in the 5 nm heterostructure also, but it is convoluted with the Pt (111) peak with both peaks of similar intensity. Qualitatively this indicates that the Mn₂Au layer is structurally robust under annealing cycles up to 500 °C, evidenced by the increased intensity in the Mn₂Au peaks relative to those in Figures 4.3 and 4.6. The Pendellösung fringes around the Pt (111) peak are no longer present after the 500 °C anneal. This is indicative of increasing roughness at the Pt/Co interface, which is likely caused by diffusion between the Pt and Co layers. Relative to the Co (111) peaks in Figures 4.3 and 4.6, the Co (111) peaks in Figure 4.7 are shifted to a lower 2θ value, indicative of relaxation towards bulk values of the d_{111} spacing. The evidence of diffusion is further supported by the appearance of a new reflection at $2\theta \approx 43^\circ$, which is most evident in the 10 nm scan. Considering the Co-Pt phase diagram [158, 160] and given that the ratio of thicknesses between the Pt and Co layers is approximately 1:4, there are two possible Co-Pt alloys which may form. Firstly the L₁₂ fcc Co₃Pt forms for bulk ratios of Co to Pt of around 3:1 at a narrow temperature around 550 °C [158, 160]. Above and below this temperature region it appears that the A₁ fcc Co₃Pt compound is more energetically favourable. Given that the heterostructures were only annealed to 500 °C in this case, it is more likely that the A₁ fcc Co₃Pt has formed which is evidenced by XRD peak near the purple reference line and no clear diffraction peak around the L₁₂ fcc Co₃Pt (111) pink reference line.

4.2.4 Magnetic Characterisation

After cleaving the samples into approximately 5 mm × 5 mm pieces, an in-plane moment vs. field loop was performed on one portion of each of the four heterostructures to characterise the in-plane magnetic properties of the stacks. The direction of in-plane measurement was picked arbitrarily for each heterostructure. After this initial magnetic characterisation, the direction of measurement was marked on the back of the substrates using a black permanent marker before the substrates were annealed at 350 °C, with the 800 mT field applied along the same axis as the initial measurement. Another portion of the heterostructures was annealed at 500 °C with the in-plane field direction noted on the back of the substrates, also using a black permanent marker. Subsequent to the annealing procedures moment vs. field loops were performed on the heterostructures with the measurement taken along the applied field direction.

Figure 4.8 shows the magnetisation vs. field loops after correction for the diamagnetic contribution of the substrate. The as deposited loops from the heterostructures are shown in black, the 350 °C loops are shown in red and the 500 °C loops are shown in blue, while panels (a)-(d) represent the 2.5 nm-10 nm heterostructures in order of thickness. Post-processing of each loop was performed using HystLab MATLAB software [161]. The software automatically corrects the diamagnetic contribution of the substrate, by either fitting the approach to saturation or the high field limits as appropriate. Further details can be found at [161].

In each of the graphs displayed in Figure 4.8 the magnetisations are all less than the bulk reference value of 1400 kA m⁻¹, this may be partially due to the fact that the exact substrate dimensions after the cleaving procedure are unknown, only that they are 5 mm × 5 mm ± 0.5 mm × 0.5 mm. This also accounts for the variation in the magnetisation from sample to sample. Generally, the magnetisation of the loops is less than the bulk value of around the saturation magnetisation after the 350 °C anneal (red) has a higher relative magnitude than that of the as deposited heterostructures (black). The red and black loops were performed on the same piece of each of the heterostructures, eliminating any error arising from their dimensions. An increase in magnetisation is unusual, given that the bulk saturation magnetisation (M_s) for bulk fcc Co is in the region of 1400 kA m⁻¹ and that for decreasing Co stoichiometry in Co_{100-x}Pt_x there is an accompanying decrease in saturation magnetisation [162, 163], the alloying at the Co/Pt interfaces of the heterostructure is unlikely to be the cause of this effect. The increase in magnetisation likely originates in the black marker used to mark the direction of annealing. The pigments used in these inks are usually paramagnetic ferrous oxides, which when subjected to a vacuum environment (such as that used during the annealing procedure) can be reduced into their constituent magnetic elements. This would cause an additive effect to the magnetisation between the as deposited sample and the 350 °C annealed sample.

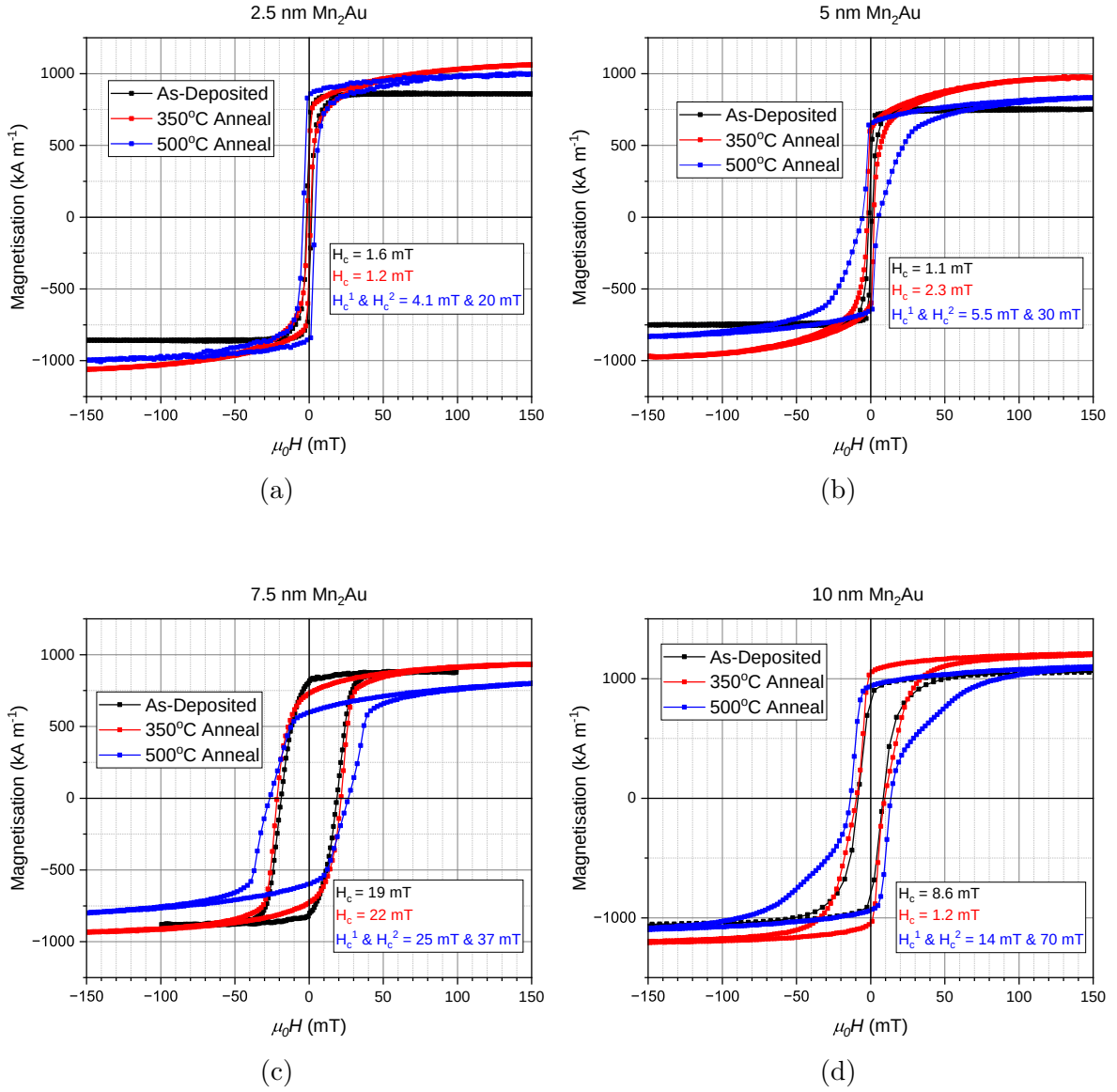


Figure 4.8: Post-processed in-plane magnetisation vs field hysteresis loops taken from the Co/Mn₂Au heterostructures prior to and post vacuum annealing at 350 °C and 500 °C in an 800 mT field, along the direction of the applied field. Panels (a)-(d) show the loops obtained from the 2.5 nm-10 nm heterostructures. For distinction, the as deposited loops are shown in black, while the 350 °C and 500 °C loops are shown in red and blue. The coercivities of each loop are also displayed beside each loop in the same colour as the loop it relates to.

In both Pt/Co multilayers and Pt/Co thin films, the intermixing of Co and Pt atoms at the interface during annealing reduces the saturation magnetisation of the Co layer [164–167]. Overall the saturation magnetisations of the 500 °C anneals are less than that of the 350 °C anneals, this is likely due to the reduced dimensions of the sample in comparison to the samples used for the 350 °C loops, but also the differing levels of diffusion between the Co and Pt layers as well as the reduction of the ferrous pigments in the dye of the black marker. It is likely that the reduction of magnetisation as a result of Co and Pt diffusion and the increase associated with the reduction of ferrous pigments are balancing each other in the case of both the 350 °C and 500 °C anneals.

There is a trend of increasing anisotropy of the M-H loops for increasing anneal temperature observed across all the heterostructures. This is evidenced by the higher fields at which it takes for both the ascending and descending branches of the loops to reconverge before saturation, with increasing annealing temperatures. This increasing anisotropy is characteristic of diffusion between the Co and Pt layers and the formation of Co/Pt alloys which are typically magnetically harder than exchange-coupled bilayers and Co/Pt alloys typically have PMA. This analysis is in good agreement with what was observed in the XRD analysis of the annealed heterostructures after annealing. The formation of the Co/Pt alloys at the interface is also what gives rise to the appearance of a higher coercivity component (marked H_c^2) which is clearly evident in the 500 °C loops, although the magnitude is different for each indicating the Co/Pt alloys forming at the interfaces in each heterostructure are not homogenous or consistent for each sample.

Table 4.2: Table displaying the measured values of the hysteresis loop coercivities (H_c) for each of the heterostructures; in the as deposited state, after a 350 °C anneal and after a 500 °C anneal. The error associated with each value is ± 1 mT.

Mn ₂ Au x (Å)	As Dep H_c (mT)	350 °C H_c (mT)	500 °C H_c (mT)
25	1.6	1.2	4.1
50	1.1	2.3	5.5
75	19	22	25
100	8.6	9.5	14

Table 4.2 shows the measured values of H_c or H_c^1 , as appropriate, taken from the hysteresis loops shown in Figure 4.8. For the as deposited loops of the 25 Å and 50 Å samples, H_c is comparable to that of Co thin films and is representative of soft magnetic moments. In contrast, the as deposited loops of the 75 Å and 100 Å samples display larger values for H_c . In the case of FM alloys, this would indicate that the alloy in question is a hard FM, but in the context of these heterostructures, in which the functional magnetic layers are a bi-layer of FM Co and AFM Mn₂Au this increased coercivity can be interpreted as Exchange Coupling (EC) between the FM/AFM layers and is indirect evidence of the AFM nature of the Mn₂Au layer. This implies that the growth temperature of 200 °C was sufficiently high to induce EC between the Co and Mn₂Au layers in the 75 Å and 100 Å samples. This provides evidence that the finite-size Néel temperature of these layers is between room temperature and the deposition temperature of 200 °C, as if the finite-size Néel temperature of these layers was higher than the deposition temperature there would be no increase in coercivity in the hysteresis loops characteristic of EC. Thus, in the 25 Å and 50 Å samples the effective Néel temperature is likely below room temperature. The presence

of EC between these layers was not confirmed during these experiments, as no low temperature magnetometry measurements were performed on them. Low temperature magnetometry for these heterostructures is planned for the future.

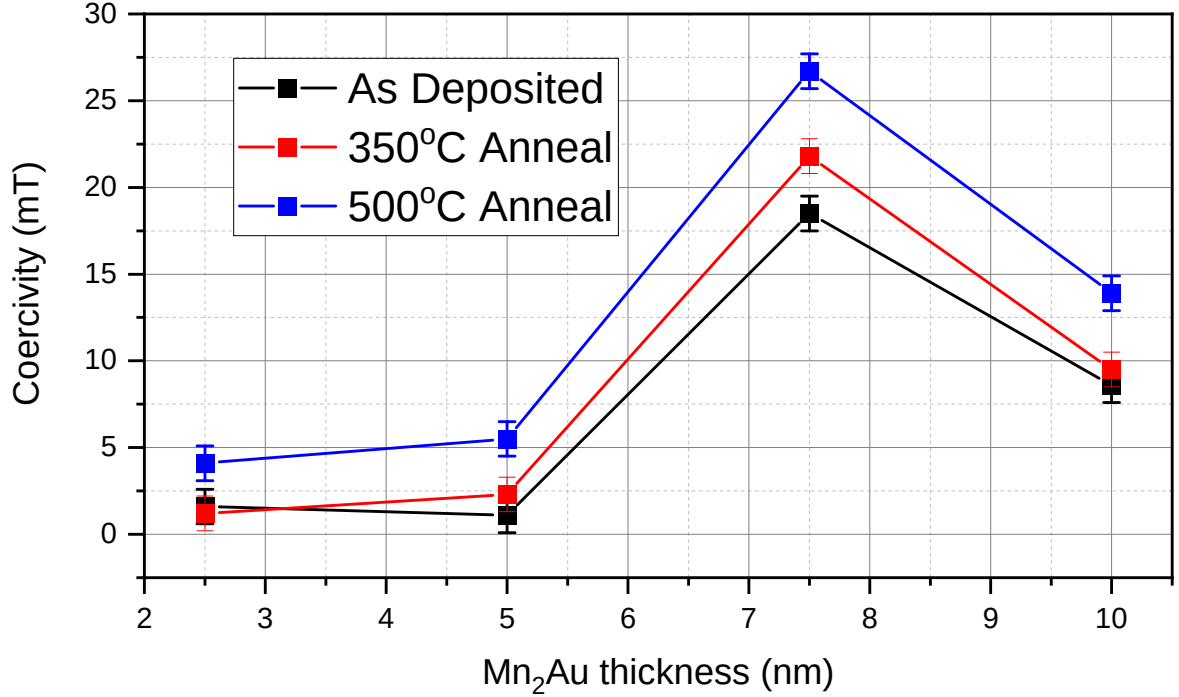


Figure 4.9: A plot showing the hysteresis loop coercivity of the heterostructures with increasing thickness of the AFM Mn₂Au layer, prior to and after annealing cycles at 350 °C and 500 °C. The as deposited, 350 °C anneal and 500 °C data are displayed in black, red and blue respectively.

After the 350 °C annealing cycle the coercivity of the hysteresis loops was either unchanged within experimental error or slightly increased, as evidenced by the data in Table 4.2. Similarly, the 500 °C annealing cycle caused increases in the coercivity of all the loops. The increasing coercivity is likely a result of the increasing crystalline order of the Mn₂Au as observed in the post-anneal XRD scans, which would in turn increase the AFM ordering temperature of the Mn₂Au layer [45, 168]. Figure 4.9 is a plot of the coercivities trend with increasing thickness of the Mn₂Au layers before and after annealing. The trend is the same before and after annealing and correlates well with what is seen in other EC FM/AFM systems with a varying AFM thickness and fixed FM thickness [12, 52]. As the AFM thickness increases from 25 Å to 50 Å there is a low to no increase in the coercivity of the loop followed, by a large increase in coercivity for the 75 Å loops before declining for the 100 Å loops.

The increased coercivity is just one aspect of the ECE, the other is the EB loop shift (H_{eb}) which is defined as the absolute sum of the coercivities of the descending (H_{c1}) and ascending (H_{c2}) branches of the loop, divided by two. In reality, this appears as a shift of the loop by some positive or negative field value. One of the requirements for EB is unidirectional anisotropy of the FM/AFM EC. In the case of the loops shown in Figure

4.8, there is no observable bias field for any of the heterostructures. There are a number of possible explanations for the lack of EB, each of which will be discussed below. Given that there was no loop shift introduced after the magnetic annealing procedures in any of the heterostructures, the most simple explanation is that the measurements at room temperature are above the blocking temperature (T_b), i.e the temperature at which the EB loop shift disappears. Similar work on Mn₂Au (001)/Fe (001) disordered bilayers found that the blocking temperature of their 4 nm Mn₂Au films was 200 K, which is well below the room temperature these hysteresis loops were performed at [32]. However, this explanation disregards that a single Mn₂Au (110) monolayer will have Mn atoms from each FM sublattice such that the total net moment of the sheet sums to zero and is compensated. Phenomenologically, it is believed that a requirement for EB to occur is that there are uncompensated AFM moments at the interface [58]. In practice this is not necessarily the case as microscopic roughness at the interface may create a layer of uncompensated moments [52, 65, 169–171]. However, more recent work in epitaxial thin films with compensated interfaces has shown no EB [172].

Moreover, bulk Mn₂Au has two equivalent easy axes along the [110] and [1-10] [25]. This means that (110) Mn₂Au thin films, not grown in the presence of a FM field, will likely have a roughly equal proportion of magnetic domains out-of-plane along [110] and in-plane along [1-10] [106]. For the Mn₂Au (110) films in these heterostructures, this may not be the case. The deposition of the Mn₂Au layer on the FM Co layer could favourably drive the formation of magnetic domains with one easy axis over the other. Incidental evidence that this is the case is provided in the minimal increase in coercivity after annealing of each of the hysteresis loops in Figures 4.8 and 4.9. If domains with both easy axes were present prior to annealing, there would be an increase in the coercivity due to the reorientation of the AFM domains. It should also be noted that if the [110] AFM domains are present this presents a situation where the AFM moments are lying orthogonal out-of-plane to the in-plane FM easy axis of the Co layer post annealing, in which case H_{EB} would be zero [51, 65].

In summary, it is impossible to determine if Co/Mn₂Au or any FM/Mn₂Au (110) oriented bilayers will display EB from the limited room temperature hysteresis loops presented here. A number of possible explanations for the lack of EB are discussed and the work in Chapter 5 will aim to investigate the ECE in Mn₂Au (110) bilayers in more detail.

4.3 The growth of Fe/Mn₂Au bilayers on a Pt (111) seed layer

The heterostructures, of the form c-Al₂O₃/Pt/Fe/Mn₂Au(*x*)/Pt, were grown using a combination of e-beam evaporation and deposition using two K-cells in the DCA M600 MBE. The Al₂O₃ (0001) substrates used were sonicated in acetone and IPA each for 15 minutes, prior to being loaded into the MBE. The substrates were annealed for 1 hr at 600 °C prior to the deposition of the Pt layer. The substrate temperature was lowered to 550 °C before depositing 5 nm of Pt at a rate of 0.5 Å s⁻¹ using e-beam evaporation. Subsequently, the substrate temperature was lowered to 200 °C, before depositing 6 nm of Fe via e-beam evaporation, at a rate of 0.1 Å s⁻¹. The Fe layer was reduced in thickness in comparison to the 15 nm used in the previous section, in an effort to increase the magnitude of the coercive field and any potential bias field generated by the EC between the Fe/Mn₂Au layers [59]. The Mn₂Au layers were grown at 200 °C, with thicknesses of *x* = 10 nm, 8 nm, 6 nm, 4 nm and 2 nm, in descending order. The ratio of Mn:Au was set to 2:1, which corresponds to cell temperatures of 959 °C and 1282 °C, and the growth rate was determined to be 0.3 Å s⁻¹ via XRR. Following this, the samples were cooled to room temperature before being capped with 3 nm of Pt.

4.3.1 RHEED Characterisation

Figure 4.10 shows the RHEED images, taken from the *x* = 6 nm heterostructure, of each of the Al₂O₃ substrate and the Pt, Fe, Mn₂Au and Pt layers. The RHEED images were taken along the two high symmetry directions of Al₂O₃, [10 $\bar{1}$ 0] and [11 $\bar{2}$ 0], which are separated by 30°. Each image was produced at an electron beam energy of 20 keV. The RHEED images shown were taken at substrate temperatures of 600 °C, 550 °C, 200 °C, 200 °C and 25 °C for each of the layers shown in Figure 4.10 in descending order. These temperatures correspond to either the anneal temperature or deposition temperature used for each respective layer. The *x* = 6 nm heterostructure was chosen as the RHEED images display characteristics that are intermediary for the Mn₂Au and Fe layers, between the first and last heterostructures, while also being representative of each of the other heterostructures.

The Al₂O₃ RHEED images, along both directions, consist of sharp diffraction spots and Kikuchi lines which indicate that the substrate has a high quality single crystal surface. The surface of the Pt seed layer displays RHEED images with elongated streaks, and in this case, they also display faint Kikuchi lines, which is in contrast to the other Pt seed layers shown in this thesis. Overall this indicates that the Pt layer has a flat surface. The RHEED images from the Fe surface show elongated, modulated streaks, indicative of a surface with some roughness. The first order streaks in each of the Fe

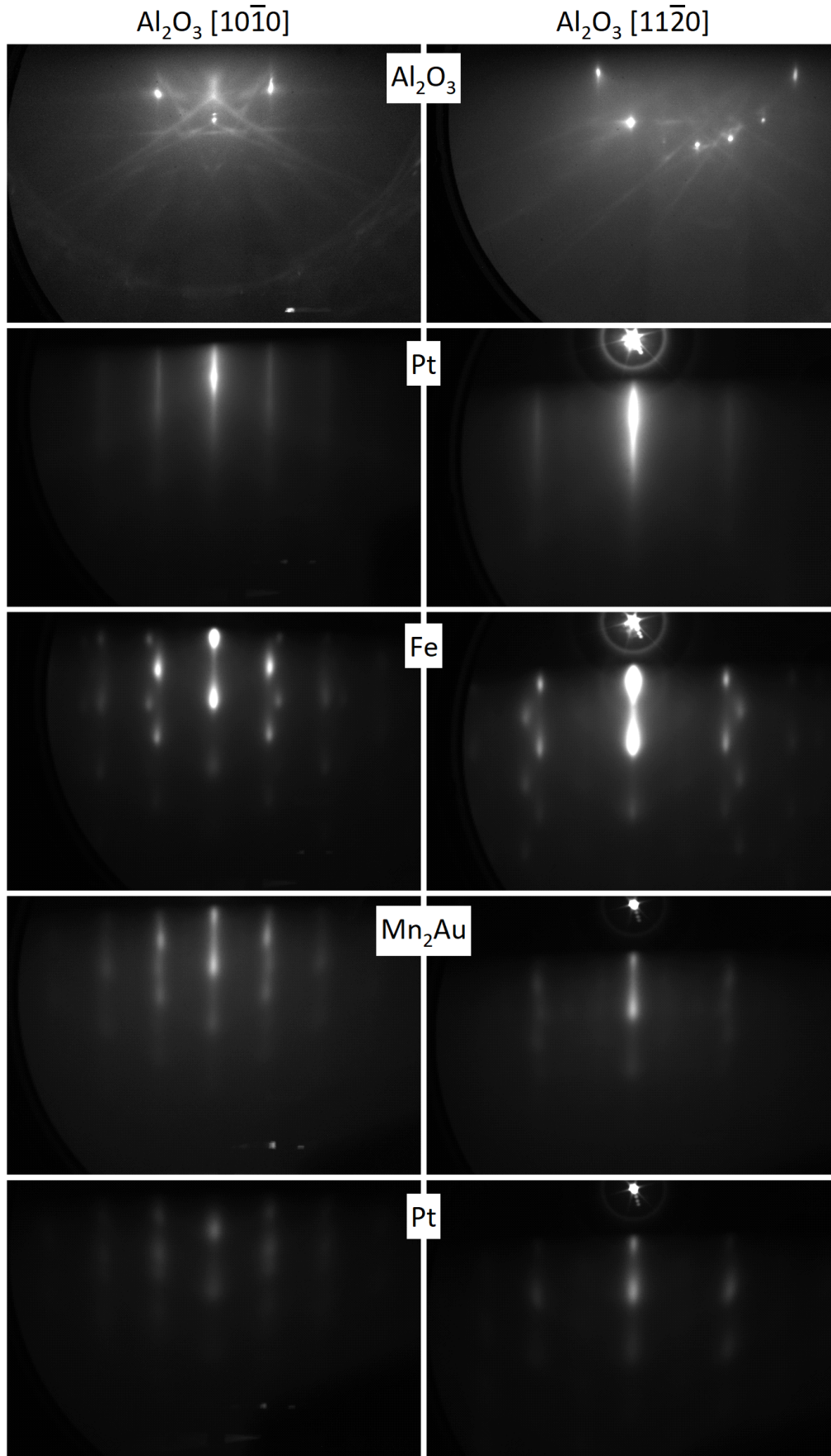


Figure 4.10: RHEED images of each of the layers post deposition in the $x=6$ nm, c-Al₂O₃|Pt|Fe|Mn₂Au|Pt heterostructure along the two high symmetry directions of the Al₂O₃ substrate of [10 $\bar{1}$ 0] & [11 $\bar{2}$ 0], which are separated by 30°. See text for description.

images show a clear fine structure, with two distinct modulated streaks indicating that there are at least two atomic spacings present in the film. This is likely due to the presence of multiple rotational Fe domains, of which there is an in-equivalence between the two. This arises as the Fe (110) surface is not an idealised hcp surface, like that of the Pt seed layer. A note on the evolution of the Fe RHEED from the 10 nm to the 2 nm heterostructures; the degree of modulation of the Fe streaks decreases from the 10 nm sample to the 2 nm sample i.e the 2 nm sample has less streak modulation than the 10 nm. This indicates that each successive Fe layer grown was smoother than the previous one. The Mn₂Au RHEED images consist of elongated streaks with a small degree of modulation along their extent. Similarly to the Mn₂Au RHEED images in Figure 4.1, the streaks have different widths at differing points along their extent. This is indicative of multiple atomic spacings along this direction of Mn₂Au, which also indicates that the Mn₂Au layer is likely made up of multiple rotational domains. Similar to the Fe RHEED, the Mn₂Au RHEED also underwent an evolution from the 10 nm to 2 nm heterostructures. The width of the Mn₂Au RHEED streaks decreased as each progressive sample was grown, in a similar fashion to the Fe layers, upon which the Mn₂Au layers were grown. The degree of modulation was similar in all the Mn₂Au RHEED images.

Looking along Al₂O₃ [10 $\bar{1}$ 0], the spot spacing corresponds to the a lattice parameter of 4.758 Å [143] after correction for thermal expansion [145]. From this, the in-plane lattice parameter of Pt can be calculated. Once corrected for thermal expansion [146], this was found to be 4.790 Å, which represents a contraction of 0.84 % with respect to bulk, indicating that the Pt layer continues to grow in a pseudomorphic manner up to 5 nm in thickness. Looking at the Fe layer there are two clear first order streaks which are split, this is indicative of two crystalline domains which are rotated by 30° with respect to each other. This occurs as a result of the pseudo-hcp nature of the Fe (110) surface, where the surface unit cell is effectively rectangular in comparison to square for hcp surface unit cells. The streaks represent two possible interatomic spacings of 4.0531 and 4.9641 Å [173]. When corrected for linear thermal expansion [174], the spacings were calculated to be 4.136 Å and 4.795 Å, which represent an expansion and contraction of 2.1 % and 3.4 % of each, respectively. This indicates there is an expansion along one axis of the Fe surface unit cell and a contraction along another in order to form a pseudo-hcp surface, implying that the Fe layer is growing in a pseudomorphic fashion on the hcp Pt (111) surface. As mentioned previously, there are multiple rotational domains present in the Mn₂Au layer as indicated by the modulation in the width of the streaks along their length. Along the [10 $\bar{1}$ 0] high symmetry direction, the Mn₂Au layer has two possible interatomic spacings; 4.707 Å and 4.875 Å. The Mn₂Au RHEED images were taken at 200 °C and again as there is no experimental thermal expansion coefficient for Mn₂Au the estimated value of linear thermal expansion (α_L) of $19.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ will be used. Using this value, suggests that a typical contraction

from 200 °C to 25 °C would be on the order of 0.4 %. At 200 °C, the two spacings were calculated to be 4.888 Å and 5.041 Å. These represent expansions with respect to bulk of 3.8 % and 3.4 % respectively, which is much larger than can be expected due to thermal expansion. This indicates that the Mn₂Au layer grows strained on the Fe (110) underlayer.

Table 4.3: Table showing the measured in-plane strain of the Mn₂Au layers from each of the FeMn₂Au heterostructures grown, taken from the RHEED images along the Al₂O₃ [10 $\bar{1}$ 0] and [11 $\bar{2}$ 0] high symmetry directions at 200 °C. The minimum and maximum strain along each direction are displayed as the Mn₂Au streaks RHEED display differing widths along their length. Each value is compared to that of bulk Mn₂Au [92]. The percentage change with respect to bulk values is shown beside the estimated values with respect to the Al₂O₃ spacings. An expansion is denoted by a positive value.

Mn ₂ Au x (Å)	[10 $\bar{1}$ 0] min (Å)	[10 $\bar{1}$ 0] max (Å)	[11 $\bar{2}$ 0] min (Å)	[11 $\bar{2}$ 0] max (Å)
Bulk [92]	4.707	4.875	2.747	2.852
20	4.927 (4.7 %)	4.992 (2.4 %)	2.849 (3.7 %)	2.889 (1.3 %)
40	4.921 (4.5 %)	5.036 (3.3 %)	2.836 (3.2 %)	2.878 (0.9 %)
60	4.916 (4.4 %)	5.047 (3.5 %)	2.820 (2.7 %)	2.918 (2.3 %)
80	4.895 (4.0 %)	5.052 (3.6 %)	2.817 (2.5 %)	2.933 (2.8 %)
100	4.843 (2.9 %)	5.058 (3.8 %)	2.810 (2.3 %)	2.918 (2.3 %)

From the Al₂O₃ [11 $\bar{2}$ 0] RHEED images in Figure 4.10, the threefold periodicity of the atomic spacing resulting in the pseudo-hcp of the surface Al₂O₃ oxygen lattice is apparent once again. The Pt inter atomic spacing can be calculated along the Al₂O₃ [11 $\bar{2}$ 0] high symmetry direction. Once corrected for thermal expansion this was found to be 2.778 Å, which represents a slight expansion of 0.2 % on the bulk value of 2.774 Å. Again along the Al₂O₃ [11 $\bar{2}$ 0] RHEED direction, the Fe RHEED displays clear splitting of the first order streaks, thus indicating the presence of two distinct interatomic spacings along this direction. The two possible values from bulk are 2.482 Å or 2.866 Å [173]. Using the reference streak spacings, and once corrected for thermal expansion, the Fe streak spacings were calculated to be 2.518 Å and 2.883 Å, respectively. These values represent expansions of 1.4 % and 0.6 % with respect to the bulk values, providing further evidence that the Fe layer is growing in a pseudomorphic fashion. Again the Mn₂Au streaks show modulation in streak spacing along their length with no fine structure. This implies that there are a mixture of atomic spacings contributing to the streak spacings that RHEED image. There are four possible interatomic spacings in the Mn₂Au (110) surface unit cell, which include 2.747 Å, 2.752 Å, 2.843 Å and 2.852 Å. Given the lack of fine structure, only the maximum and minimum values of the streak spacing can be used to calculate the interatomic spacings. The measured values from the maximum and minimum streak spacings were found to be 2.817 Å and 2.892 Å, which represents expansions on the minimum and maximum bulk atomic spacings of

2.5 % and 1.4 %. Although these values are taken at 200 °C, the measured expansions are still larger than the expected linear thermal contraction that the material would undergo if cooled to room temperature. Table 4.3 displays the values calculated from the Mn₂Au layer at 200 °C in each of the other heterostructures grown in this study. The general trend along the Al₂O₃ [10 $\bar{1}$ 0] direction is that as the Mn₂Au thickness increases, the maximum in-plane atomic spacing also increases, while the minimum in-plane atomic spacing decreases. This suggests that there is a distortion of the Mn₂Au interatomic spacing to more closely match that of the Fe underlayer causing the Mn₂Au to grow in a pseudomorphic fashion. It is more difficult to determine a trend in the interatomic spacings calculated along the Al₂O₃ [11 $\bar{2}$ 0] direction as each streak is likely an average of the 4 possible spacings, and given that there does not appear to be a preferential in-plane growth direction for the Mn₂Au film, the amount of each spacing may be different in each individual Mn₂Au sample grown.

4.3.2 X-ray Characterisation

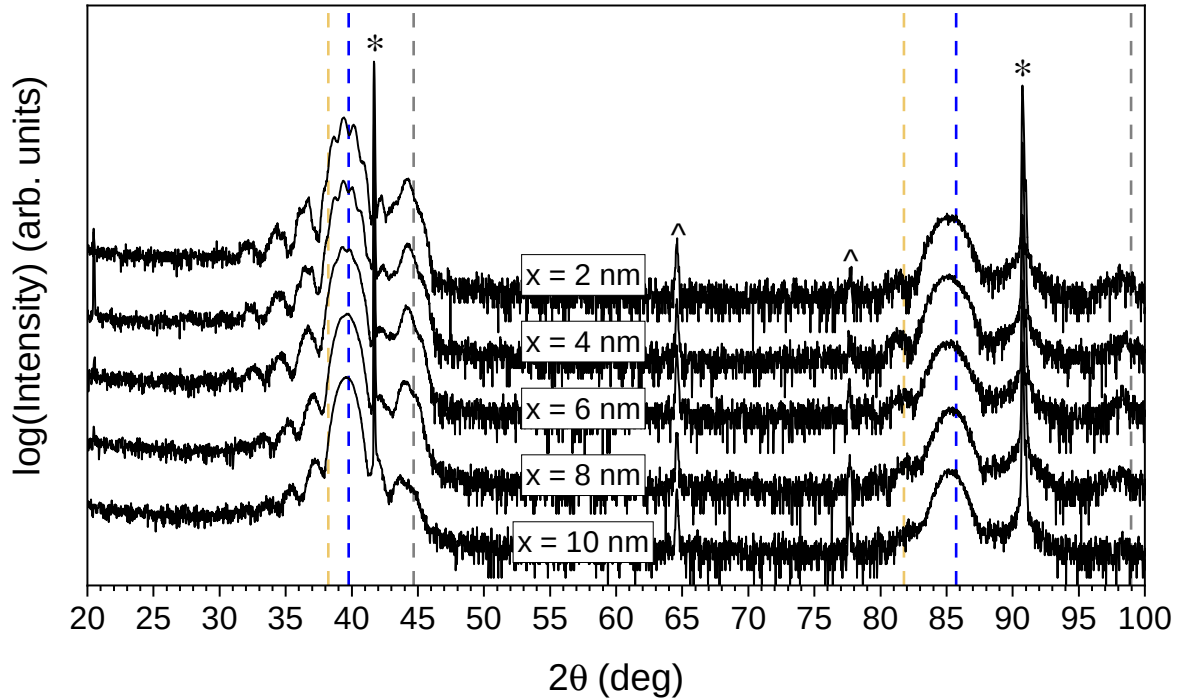


Figure 4.11: XRD scans of the Al₂O₃ (0001)|Pt (111)|Fe (110)|Mn₂Au (110)|Pt heterostructures as deposited. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, while the Pt (111) reference lines are in blue and the Fe (110) reference lines are in grey. The Al₂O₃ substrate peaks are denoted by the asterisks while peaks emanating from the XRD sample holder are denoted by the caret symbol.

Figure 4.11 shows the wide-angle $\theta - 2\theta$ XRD scans obtained from the heterostructures post-growth. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140] and Fe (110) [173] peaks are denoted by the gold, blue and grey reference lines. The

XRD peaks from the Al₂O₃ (0006) peaks are denoted by the asterisks, while the caret symbol is used to denote peaks occurring from the XRD sample plate.

There are Pendellösung fringes (lower frequency) emanating from the Pt (111) peak in each of the scans shown in Figure 4.11. There are the same number of oscillations around each of the Pt (111) peaks, with the same frequency, which qualitatively indicates that each of the Pt layers is of the same thickness and each has a similar surface roughness. A quantitative fit of the Pendellösung fringes gave similar values for the coherent thickness of the crystallites of 48 Å for each Pt layer. Pendellösung fringes (higher frequency) are also visible from the Fe (110) peaks in the 6 nm, 4 nm and 2 nm heterostructures. The higher frequency oscillations in the Fe layer are indicative of coherent crystals of a larger thickness than the Pt layer, which can be explained by the relative differences in the nominal thickness of the layers. More oscillations are apparent for the 2 nm sample than the 4 nm and the 6 nm sample. Qualitatively this indicates that the interface of the Fe layer is smoother in those samples with more oscillations present. Given that the heterostructures were deposited in order of 10 nm to 2 nm this is indicative of the increasing quality of the Fe layer throughout successive growths. This analysis correlates well with the observed evolution of the RHEED images for each successive Fe layer deposited. The Mn₂Au (110) peaks are not visible, likely due to the Pt (111) having a higher relative intensity and the broadening of the Pt peak due to the presence of the Pendellösung fringes. In addition, the small peak around the Mn₂Au (220) reference line, is more likely to be a Pendellösung oscillation, rather than the Mn₂Au (220) reflection. Furthermore, the RHEED analysis indicated that the Mn₂Au films are growing with an expansion of the in-plane lattice parameter, which was also seen in the Co/Mn₂Au heterostructures that were accompanied by a contraction of the d_{110} spacing in for the Co/Mn₂Au heterostructures. Given that the Fe/Mn₂Au films display similar characteristics via the RHEED analysis, it is likely that the Mn₂Au d_{110} for these heterostructures also undergo a contraction, which would result in a shift in their 2θ values closer to that of the Pt (111) bulk reference position. This would also contribute to the inability to discern the presence of the Mn₂Au (110) peak from the high relative intensity Pt (111) peak.

The peak position of each of the Pt (111) peaks for the heterostructures is shifted to a slightly lower 2θ value than that of bulk Pt. Qualitatively this indicates that there is an expansion of the d_{111} spacing for each of the Pt seed layers, offsetting the contraction in the in-plane lattice parameter measured in the RHEED spacing. Quantitatively, for the 6 nm heterostructure, the maximum 2θ value was found to be 39.56° which gives a d_{111} value of 2.286 Å representing an expansion along the [111] axis of 0.4 % for this 5 nm Pt seed layer. Similarly, the Fe (110) peaks all have a lower maximum 2θ value than the reference peak position indicated by the grey line, indicating that each of the Fe (110) films are expanded along the [110] axis with respect to the bulk. Again for the 6 nm heterostructure, this represents an expansion of 0.86 % along the [110] axis

and gives a value of 2.044 Å for d_{110} . This combined with the RHEED analysis implies that the distortion of the interatomic spacings to form a pseudo-hcp interface with the Pt seed layer causes an overall change in the volume of the Fe unit cell with respect to the reference values [173].

4.3.3 Structural Analysis after Annealing

After the *ex-situ* characterisation of the heterostructures, each 1 cm² substrate was cleaved into four approximately 5 mm×5 mm pieces using a diamond tipped pen. Subsequently, one of the 5 mm×5 mm pieces from each heterostructure, was subjected to a 1 h vacuum anneal at 350 °C and another piece subjected to a vacuum anneal at 500 °C, using the same procedures as the Co/Mn₂Au heterostructures.

After the annealing procedure, each of the heterostructures were characterised again to evaluate any changes that occurred to the structure as a result of the annealing process. Figure 4.12 shows the wide angle $\theta - 2\theta$ XRD scans obtained from the heterostructures after the 350 °C annealing cycle. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140], tetragonal FePt (111) [175], and Fe (110) [173] reflexes are shown by the dashed gold, blue, dark green and grey reference lines respectively. The XRD reflections from the Al₂O₃ substrate are marked with asterisks, while the carat symbols denote the positions of reflexes which occur from the XRD sample stage. The FePt reference positions were included for two reasons; Given that the thickness ratio of Fe to Pt in the heterostructures is 1.2:1, the only likely alloy to form at the interface would be FePt as this is the only alloy in the FePt phase diagram for that ratio of Fe:Pt [176]. Secondly, tetragonal FePt (111) forms a pseudo-hcp surface, similar to the hcp surface of the Pt (111) and that of the pseudo-hcp Fe (110) surface, thus the FePt (111) surface was the most likely to form in the case of diffusion during the annealing procedures. It should be noted that L1₀ ordered FePt is typically formed at annealing temperatures higher than 550 °C [176, 177], although instances have been noted at annealing temperatures of 400 °C [178].

Considering the XRD scan of the 10 nm heterostructure in Figure 4.12, the Pendellösung fringes are still apparent around the Pt (111) peak although diminished in comparison to the same sample before annealing. Similarly, the Fe (110) peak is still apparent, although it is broadened post annealing. Combined this indicates that there is some degree of diffusion between the Pt and Fe layers but that there is limited formation of FePt, which is in contrast to all the other heterostructures which show a small peak at 41° which corresponds to FePt (111). The formation of FePt was likely limited by the quality of the Fe layer in the case of the 10 nm heterostructure. Additional evidence for this is provided by the clear formation of Pendellösung fringes in the 6 nm and 4 nm samples accompanied by the disappearance of the Fe (110) peak in these samples post annealing. Looking at the 2θ region from 35°-45°, in the 8 nm to

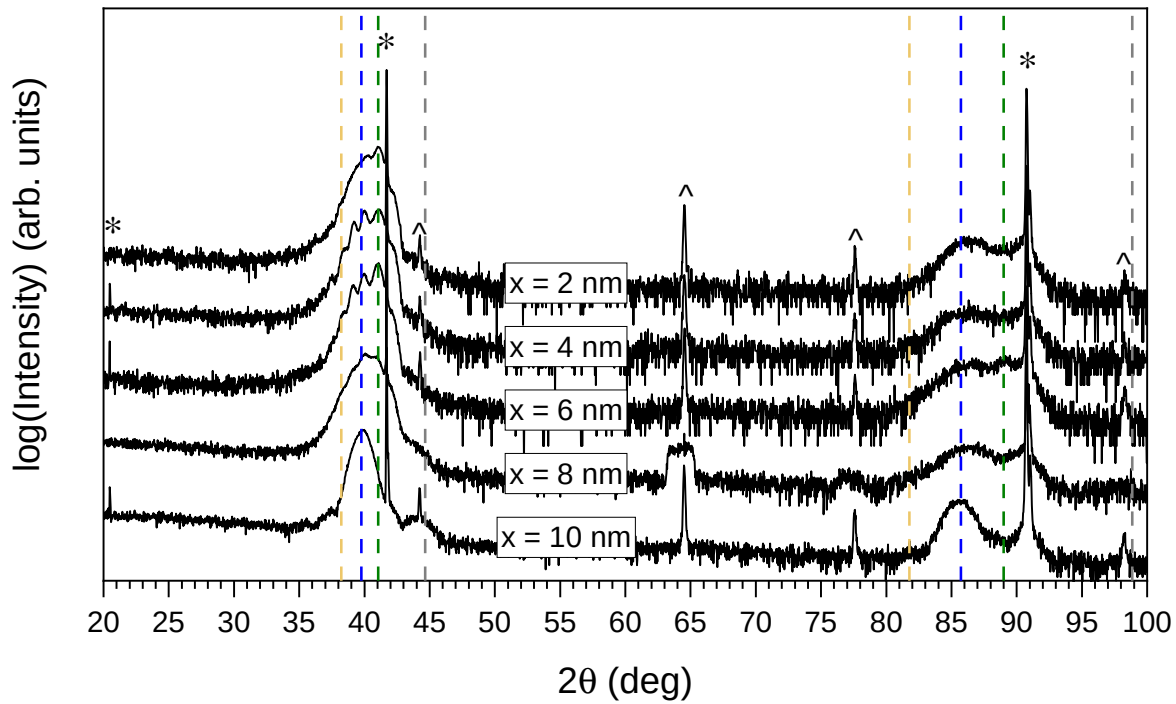


Figure 4.12: XRD scans of the Al₂O₃ (0001)|Pt (111)|Co (111)|Mn₂Au (110)|Pt heterostructures after a 350 °C vacuum anneal. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, the Pt (111) reference lines are in blue, the FePt (111) reference lines in green and the Fe (110) reference lines are in grey. The Al₂O₃ substrate peaks are denoted by the asterisks. The caret denotes peaks that occur from the XRD sample stage.

2 nm XRD scans, there is an elongated asymmetric tail to the left side of the convoluted peaks in that region. This is likely the presence of the Mn₂Au (110) reflection. A similar elongation of the Pt (222) peak is clearly evident for the 8 nm and 6 nm sample scans, indicating the presence of the Mn₂Au (220) peak.

Figure 4.13 shows the wide angle $\theta - 2\theta$ XRD scans obtained from the heterostructures after the 500 °C annealing cycle. The reference angles for each of the Mn₂Au (110) [92], Pt (111) [140], FePt (111) [175], and Fe (110) [173] reflexes are shown by the dashed gold, blue, dark green and grey reference lines respectively. The XRD reflections from the Al₂O₃ substrate are marked with asterisks, while the carat symbols denote the positions of reflexes which occur from the XRD sample stage.

The alloying of the Fe and Pt layers is complete after the 500 °C anneal, as evidenced by the clear FePt (111) and (222) reflections in the 6 nm to 2 nm scans. The (111) reflection in these heterostructures are accompanied by the continued formation of Pendellösung fringes, relative to the 350 °C anneal. These peaks correspond well to the green reference lines for the FePt peak positions, indicating that the FePt layer formed has a similar interplanar spacing as bulk FePt. The degree and quality of the Fe and Pt alloying are clearly different for the 8 nm and 10 nm heterostructures. This is clear from the lower relative intensity of the FePt (111) peak in the 8 nm sample and the shifted FePt (111) and (222) peaks in both samples. This is likely due to the

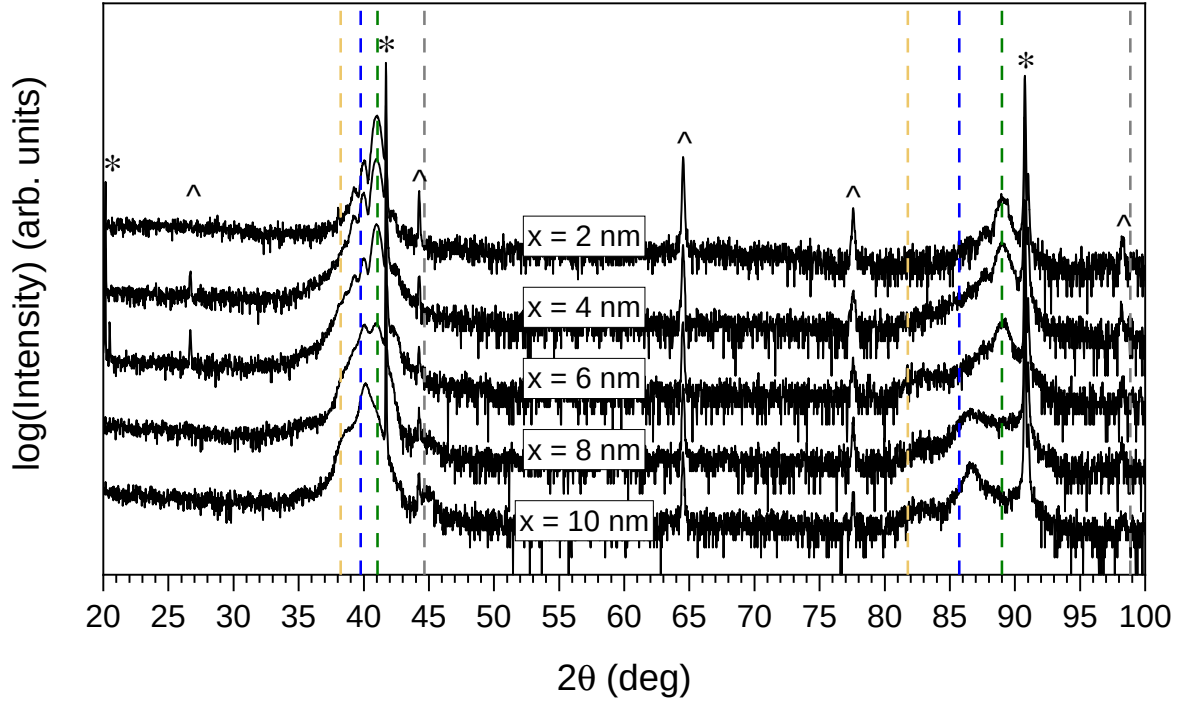


Figure 4.13: XRD scans of the Al₂O₃ (0001)|Pt (111)|Fe (110)|Mn₂Au (110)|Pt heterostructures after a 500 °C vacuum anneal. The reference positions for the Mn₂Au (110) peaks are shown by the dashed gold reference lines, the Pt (111) reference lines are in blue, the FePt (111) reference lines in green and the Fe (110) reference lines are in grey. The Al₂O₃ substrate peaks are denoted by the asterisks. The caret denotes peaks that occur from the XRD sample stage.

original quality of the Fe layer prior to the annealing procedure, as there is a clear trend from the quality of the FePt layer in the 10 nm to the 2 nm samples. Again the appearance of the Mn₂Au (110) peaks is characterised by an elongated left tail to the peaks in the 40° region of each of the heterostructures. Additionally, there is a clear Mn₂Au (220) peak evident around the 83° region of each scan except the 2 nm sample.

Combining the RHEED images taken of the Fe/Mn₂Au heterostructures along with the XRD scans taken pre and post annealing, the out-of-plane epitaxial relationship of the heterostructures can be described as Al₂O₃ (0001)||Pt (111)||Fe (110)||Mn₂Au (110). The RHEED indicates that as deposited the Mn₂Au layer has no preferential in-plane growth direction and the Mn₂Au thin film is comprised of multiple rotational domains.

4.3.4 Magnetic Characterisation

After cleaving the samples into approximately 5 mm×5 mm pieces, but prior to the vacuum anneal, the hysteresis loops of the heterostructures were measured in-plane via VSM to understand the magnetic properties of the stack in their as deposited state. The direction of the in-plane measurement was arbitrarily picked for each heterostructure,

with the direction of the measurement marked afterwards using a black-inked marker on the back of the substrate. These heterostructures were then annealed in a vacuum better than 1×10^{-6} mbar at 350°C for 1 hr, with an 800 mT field applied along the same axis as the initial measurement. A separate portion of each heterostructure was annealed at 500°C for 1 hr, again marking the applied field direction on the back of the substrates using a black-inked marker. Following the annealing procedures the in-plane hysteresis loops were again measured along the applied field direction. Post-processing of each loop was performed using HystLab MATLAB software [161]. Figure 4.14a shows the corrected magnetisation vs. applied field loops obtained from each of the heterostructures as deposited, while Figure 4.14b shows the loops obtained from each of the heterostructures after the 350°C annealing cycle. The crossing of the descending and ascending branches of each hysteresis loop is likely due to the thermal drift of the reference signal at the top of the VSM head and is likely due to a flaw in the design of this reference signal mechanism. This drift was usually present in the initial loops performed after the VSM was turned on and eventually disappeared after repeated loops.

In Figure 4.14a, the hysteresis loops are plotted for comparison of the magnitude of the saturation magnetisation of each heterostructure. The saturation magnetisation of each of the 2 nm-8 nm heterostructures are all similar values, while the 10 nm heterostructure has a much lower saturation magnetisation. The latter is likely due to the Fe layer in this case being deposited when the material was not properly degassed, which would suggest that there are oxygen impurities present in the film, reducing the saturation magnetisation. This analysis is consistent with the as deposited XRD scan of the 10 nm heterostructure in Figure 4.11, which shows the Fe layer in this heterostructure is of reduced crystalline quality than those in the other heterostructures. The coercivities of each of the 2 nm-10 nm heterostructures were measured to be 3.0 mT, 3.5 mT, 3.2 mT, 8.7 mT and 9.6 mT with associated errors of ± 10 mT, given the field increment of 10 mT. The absolute values of the coercivity for the 2 nm, 4 nm and 6 nm heterostructures are consistent with what is expected for Fe thin films, suggesting that in the as deposited state, there is no EC between the Fe/Mn₂Au layers. The coercivity of the 8 nm and 10 nm heterostructures is within the margin of error of what is expected for thin film Fe also.

In Figure 4.14b, the hysteresis loops of the 2 nm-8 nm heterostructures are characteristic of a mixture of high coercivity and low coercivity components of the hysteresis loop. This is typical of the formation of L1₀ ordered FePt (111) and thus any information regarding the interaction between the Fe and Mn₂Au or the FePt and Mn₂Au is obscured [179]. The coercivity of the hysteresis loops, on the order of 200 mT-270 mT, is less than FePt with a complete volume fraction of L1₀ ordered material [177]. The hysteresis loop taken of the 10 nm heterostructure is less characteristic of the formation of ordered L1₀ FePt, but it is still difficult to disentangle whether the increase in

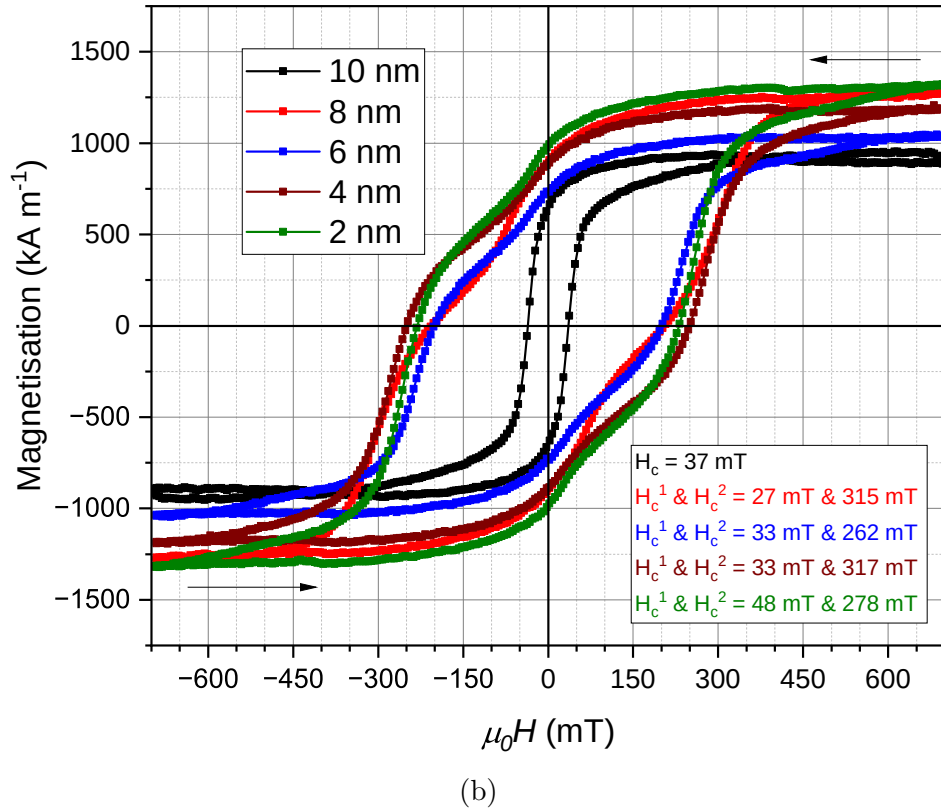
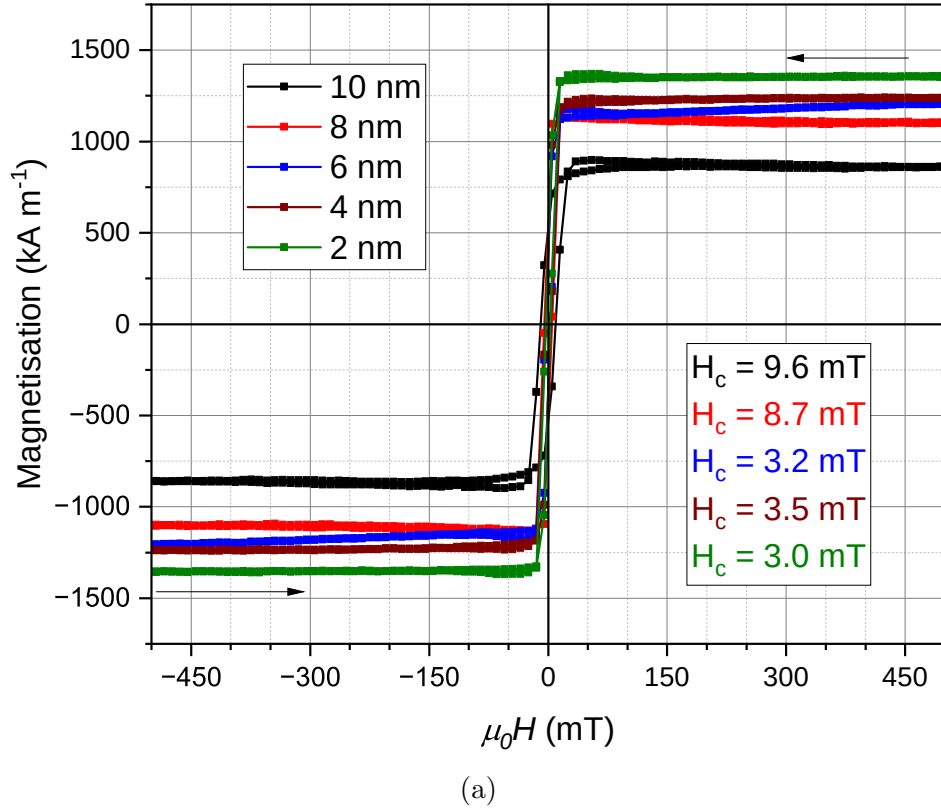


Figure 4.14: Post-processed in-plane hysteresis loops measured of the Fe/Mn₂Au bilayers (a) before annealing and (b) after magnetic annealing at 350 °C for 1 hr in vacuum. The loops from the 10 nm, 8 nm, 6 nm, 4 nm and 2 nm Mn₂Au heterostructures are in black, red, blue, wine and green respectively.

coercivity, from 9.6 mT to 36.9 mT, is due to the formation of some small portion of L1₀ ordered FePt or from EC between the Fe/Mn₂Au layers. However, given that there is no clear FePt XRD peak for this 10 nm heterostructures, combined with the single coercivity nature of this loop in comparison to the other heterostructures, the increased coercivity is more likely to be due to EC between the Fe and Mn₂Au layers. The hysteresis loops obtained from the 500 °C annealed heterostructures are not shown here as the ± 1 T range of the electromagnet on the PMC Micromag VSM was not sufficient to saturate any of the loops, and in some cases, the loops remained open at high fields. The data that could be seen from them was indicative of an increase in the volume fraction of L1₀ ordered FePt in the heterostructures [177, 180]. In summary, the use of both Fe and Pt seed layers in these Fe/Mn₂Au heterostructures were not suitable for studying the ECE in Mn₂Au.

4.4 Conclusion

The growth of pseudomorphic (110) Mn₂Au based heterostructures on fcc Co (111) and bcc Fe (110) seed layers were demonstrated. The Co/Mn₂Au heterostructures were determined to have an out-of-plane epitaxial relation of Al₂O₃ (0001)||Pt (111)||Co (111)||Mn₂Au (110) while the Fe/Mn₂Au heterostructures were determined to have an out-of-plane epitaxial relation of Al₂O₃ (0001)||Pt (111)||Fe (110)||Mn₂Au (110). The heterostructures were analysed using RHEED and out-of-plane XRD scans. The RHEED images of the Mn₂Au layers in both types of heterostructures were found to display streak spacings which varied along the length of the streaks, indicative of the presence of multiple rotational crystalline domains. The second order streak spacings from the Mn₂Au RHEED images, in contrast to those shown in the previous chapter, did not correspond to the unit cell spacing. Given that Co (111), Fe (110) and Mn₂Au (110) surfaces are all either hcp or pseudo-hcp in structure, and combined with the modulated width of the Mn₂Au streak spacings and second order streak spacings, it is likely that there are up to six possible rotational crystalline domains in the heterostructure, indicating that Mn₂Au has no preferential in-plane growth direction on Co or Fe. From the analysis of the Mn₂Au layer streak spacings, the possible in-plane atomic spacings were found to be expanded with respect to bulk, beyond what could be reasonably attributed to thermal expansion. The expansion of the in-plane atomic spacings was found to increase with increasing thickness of the Mn₂Au layer. In the case of the Co (111)/Mn₂Au (110) heterostructures the in-plane expansion was compensated by a concomitant contraction of the out-of-plane inter-layer spacing along the [110] direction.

Both types of heterostructures were subjected to annealing under vacuum conditions at 350 °C and 500 °C and characterised post-anneal via XRD. The Mn₂Au layers did not degrade during the annealing process with the XRD scans showing an increased

intensity of the Mn₂Au (110) peak after annealing at both temperatures, with the 500 °C scans showing a higher relative intensity. The robustness of the ~10 nm films to annealing at temperatures close to their peritectoid phase transition temperature ($\approx 676^\circ\text{C}$) will be key to inducing room temperature EB effects in Mn₂Au based bilayers and heterostructures.

The Pt/Co and Pt/Fe seed layers in both heterostructure types displayed alloying after the annealing cycles at both temperatures. The thickness ratio used for the Pt/Co heterostructures of approximately 1:4 resulted in less alloying of the Co layer and the formation of Co₃Pt at the Co/Pt [158, 160] interfaces which had minimal effects on the structural and coercive properties of the heterostructures. In contrast, the thickness ratio of Pt/Fe was 1:1.2 which resulted in the formation of L1₀ ordered FePt (111) after both annealing procedures [176, 180]. Given the large hysteresis coercivities associated with the formation of L1₀ ordered FePt, this dominated the magnetic properties of this type of heterostructure. In retrospect, it was unfortunate that the Pt seed layer, which is necessary for the growth of high quality metals on c-Al₂O₃ substrates, interfered with the intended magnetic effects of the heterostructure.

The magnetic properties of the Co/Mn₂Au were investigated in their as deposited state, after a 350 °C and a 500 °C vacuum anneal in an 800 mT permanent magnet. An initial magnetic characterisation was performed prior to the annealing cycles. The 7.5 nm and 10 nm heterostructures showed an increased coercivity, in excess of that for Co thin films, indicating that there was EC between the Co and Mn₂Au layers which was induced by the 200 °C growth temperature used for the Mn₂Au layer. The 2.5 nm and 5 nm heterostructures showed a coercivity representative of an uncoupled Co layer when combined with the coercivities of the thicker heterostructures, indicates that the room temperature measurements were above the effective Néel temperatures of the 2.5 nm and 5 nm Mn₂Au layers. There was a slight increase in the coercivities of each of the heterostructures after the 350 °C annealing cycle and again after the 500 °C cycle, which was attributed to the increasing crystalline quality of the Mn₂Au layer observed in the XRD scans. The trend in the coercivity with increasing thickness of the AFM Mn₂Au layer, for a fixed thickness FM layer, was similar to that observed in other FM/AFM exchange coupled systems [12, 52]. No exchange bias loop shift was observed in any of the hysteresis loops for any of the heterostructures, before or after magnetic annealing. There are a multitude of possible reasons for this, not limited to the expected compensated AFM moments at the interface in (110) oriented Mn₂Au films. To elucidate the scope and limitations of the ECE in (110) Mn₂Au bilayers will require further low temperature hysteresis loop measurements beyond what was possible for this work.

Chapter 5

Investigation of the Exchange Coupling Properties of Mn_2Au (001)/Fe (001) and Mn_2Au (110)/Fe (110) bilayers

5.1 Motivation

To date, little work has been undertaken in exploring the scope and limitations of the ECE in Mn_2Au based bilayers. Previously, the ECE was demonstrated in MBE grown, polycrystalline $\text{Mn}_2\text{Au}/\text{Fe}$ bilayers [31] and in disordered (001)/Fe (001) bilayers [32]. In the first work the Mn_2Au thickness was kept at 10 nm while the Fe layer thickness varied from 3 nm, 5 nm, 8 nm and 10 nm. The 3 nm and 5 nm Fe samples in this work displayed EB on the order of 3 mT at 300 K, with this increasing to between 20 mT and 30 mT at 5 K. The work suggests that the blocking temperature for their 10 nm Mn_2Au films is approximately 350 K, after FC from 380 K in a 5 T field. The work by *Sapozhnik et al.* also explored the ECE in Mn_2Au (001)/Fe (001) bilayers, grown on a Ta (001) seed layer via magnetron sputtering [32]. This work produced a number of Mn_2Au (4 nm)/Fe (3 nm) films with differing Mn_2Au substrate temperatures to vary the crystalline quality of the Mn_2Au layer. In the highest quality bilayers, due to limitations in the maximum field cooling temperatures (500 K), uniaxial EC was not induced, suggesting that the Néel temperature of the films was not exceeded during the FC process. It was also suggested that in these high quality bilayers, where the Néel temperature could be overcome during field cooling, the anisotropy of the AFM layer was too small for exchange bias to be induced. The reduction in Mn_2Au crystalline quality with reduced substrate deposition temperature was sufficient to drop the blocking temperature enough such that the maximum FC temperature could exceed it. This resulted in uniaxial EC, with unidirectional anisotropy, which

produced an EB shift of 20 mT at 20 K with the blocking temperature of these bilayers determined to be 200 K. The reduction in blocking temperature was attributed to the reduced crystallite size of the dominant Mn_2Au (001) oriented crystallites in the lower deposition temperature films, accompanied by an increase in the parasitic Mn_2Au (101) crystallite size.

The usefulness of AFM Mn_2Au in TAMR-based devices relies on a significant EC effect in thin Mn_2Au films at room temperature. The previous works on this are limited either by the crystalline quality of their films or limited by their FC setup. Room temperature EB in Mn_2Au will require Mn_2Au thin films of high crystalline quality, with large crystalline domains. This converges with the deposition of Mn_2Au bilayers via MBE. Recently, advances have been made in the deposition of Mn_2Au (001) films via MBE. Using a Ta (001) seed layer, Mn_2Au which is co-deposited using a substrate temperature of 270°C and a post annealing cycle for 1 hr at 450°C was found to produce superior Mn_2Au (001) thin films to magnetron sputtering [34]. This work correlates well with the work on Mn_2Au (110) thin films in Chapter 3, where 250°C was found to be the optimum temperature, but without the need for any annealing cycle [136].

One goal of this work was to build on the work on the ECE in top-pinned FM/ Mn_2Au bilayers conducted in the previous chapter. One of the key issues in studying the effect identified from that work was the alloying of the Pt seed layer with the FM layer in each of the heterostructures to form Co_3Pt and FePt alloys at the Pt/FM interface. To eliminate this effect, the choice was made to grow the samples in the traditional form of bottom-pinned Mn_2Au /FM bilayers. The (110) bilayers would be field cooled using similar annealing temperatures to those used in the previous chapter, and measurements performed to attempt to understand if EB is possible in Mn_2Au (110) bilayers. Another goal of this work was to replicate and build on the work on Mn_2Au (001) thin films grown via MBE and to try to investigate the ECE in Mn_2Au (001) films and understand the EB effects in these bilayers.

5.2 Growth and Characterisation of Mn_2Au (001)/Fe (001) bilayers

The heterostructure, of the form, r-cut $\text{Al}_2\text{O}_3/\text{Ta}/\text{Mn}_2\text{Au}/\text{Fe}/\text{TaO}_x$ was grown in the DCA M600 MBE using the K-cells for the Mn_2Au deposition and the e-beam evaporators for the deposition of the Ta and Fe layers. The Al_2O_3 ($1\bar{1}02$) substrate was sonicated in acetone and IPA each for a period of 15 minutes, before being loaded into the MBE. The Al_2O_3 ($1\bar{1}02$) substrate was then annealed for 1 hr at 650°C . An 8 nm Ta (001) seed layer was then grown on the Al_2O_3 ($1\bar{1}02$) substrate at a rate of $0.055 \text{ \AA s}^{-1}$ using a substrate temperature of 625°C . Following this the substrate temperature was

dropped to 270 °C before co-deposition of 5 nm of Mn₂Au at a known growth rate of 0.25 Å s⁻¹. Once the Mn₂Au layer was deposited, the substrate temperature was raised to 450 °C and annealed for 1 hr to improve crystallinity and surface morphology, as in [34]. Following this the substrate temperature was dropped to 250 °C and 4 nm of Fe was deposited at a rate of 0.1 Å s⁻¹. Finally, the substrate was cooled to room temperature before 3 nm of Ta was deposited at 0.1 Å s⁻¹ to cap the structure. A similar structure, with the form r-Al₂O₃/Ta(23 nm)/Mn₂Au(31 nm)/Fe(23 nm) was grown using the same deposition conditions.

5.2.1 RHEED

Figure 5.1 shows the RHEED images of the r-plane Al₂O₃ substrate, the Ta buffer, the Mn₂Au layer after deposition and again after the 1 hr anneal at 450 °C, and the Fe layer which were all taken along a high symmetry direction of the r-Al₂O₃ substrate. Each image was produced using an electron beam of 20 keV and at the same temperature used for the deposition or annealing of each layer as described previously.

The r-plane Al₂O₃ substrate RHEED image consists of a central intense streak caused by the intersection of multiple Kikuchi lines. The point-like spots at the intersection of the Kikuchi lines indicate that the surface consists of single crystalline domains which are larger than the coherence length of the electron beam (≈ 100 nm-200 nm). The Ta RHEED image consists of broad modulated streaks, qualitatively indicating that the layer consists of domains smaller than the coherence length of the electron beam and that the surface of the layer consists of multiple steps [126]. The RHEED image of the Mn₂Au layer taken post-deposition, displays modulated streaks, narrower than those of the Ta seed layer, qualitatively indicating that the Mn₂Au domains are slightly larger than those in the Ta layer but still smaller than the coherence length of the electron beam. The modulation again indicates that the Mn₂Au surface consists of multiple steps. The degree of modulation of the Mn₂Au layer is higher than that of the Ta layer, qualitatively indicating that the surface is rougher. This is also a qualitative indication that the Mn:Au ratio is not exactly 2:1 for these films, as was discussed previously in Chapter 3. The effects of the 1 hr anneal on the Mn₂Au layer are not readily apparent from the post anneal RHEED image. The image consists of modulated streaks which are of similar width and degree of modulation to that taken before the annealing procedure. This is in contrast to what was reported in [34], and is likely a result of this particular film not having the precise 2:1 stoichiometry. The Fe RHEED image consists of primarily modulated streaks indicating that the layer is stepped and that the films consist of domains smaller than the coherence length of the electron beam. There are also secondary streaks halfway between the first order streaks, which represent double the atomic spacing of the first order streaks indicating the Fe layer is of good crystalline quality.

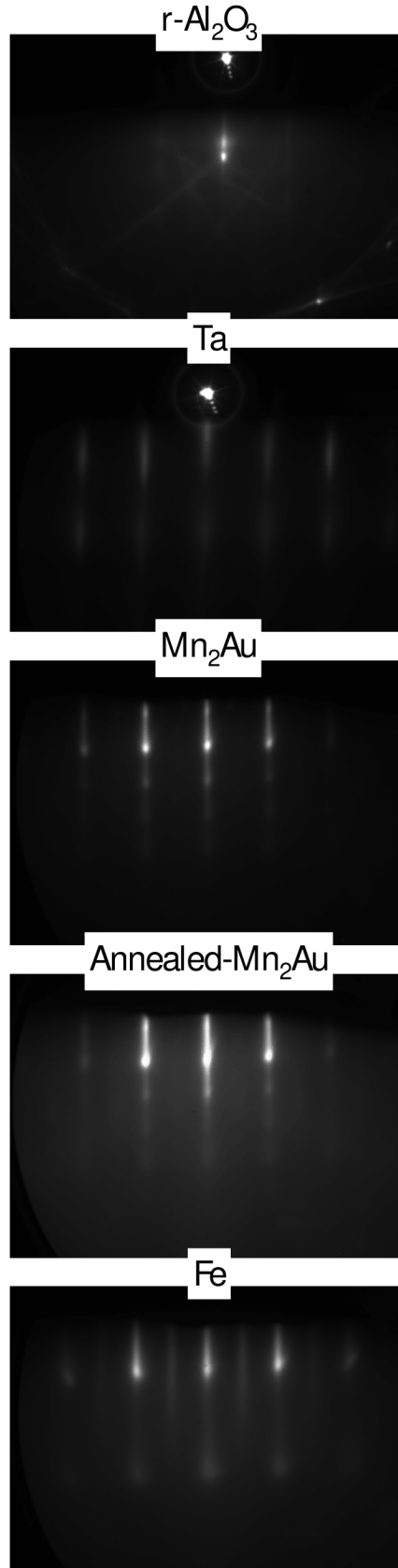


Figure 5.1: RHEED images of each of the layers in the Mn_2Au (001)/Fe (001) heterostructure post deposition, taken along the wafer flat of the r-plane Al_2O_3 substrate, which is rotated 45° counter-clockwise from the c-axis projection onto the r-plane surface of the wafer. See text for description.

The Ta capping layer is not shown as the RHEED image consisted of concentric circular streaks that indicated that the capping layer was polycrystalline. Finally, the RHEED images obtained from the “thick” Mn_2Au (001) stack contain all the same features discussed for the “thin” Mn_2Au (001) sample.

5.2.2 XRD characterisation

Figure 5.2 shows the wide-angle $\theta - 2\theta$ XRD scan obtained of the “thin” 5 nm Mn_2Au heterostructure. The reference angles for each of the Mn_2Au (00n) [92], Ta (002) [181] and the Fe (002) [173] reflexes are represented by the gold, wine and grey reference lines respectively. The $\text{TaO}_{0.9}$ (220) [182] and the TaO (220) [183] reference peak positions are shown in cyan and green respectively. The hash signs denote the Al_2O_3 (012) and (024) substrate peaks, while the carat symbol denotes the positions of peaks occurring from the XRD sample stage.

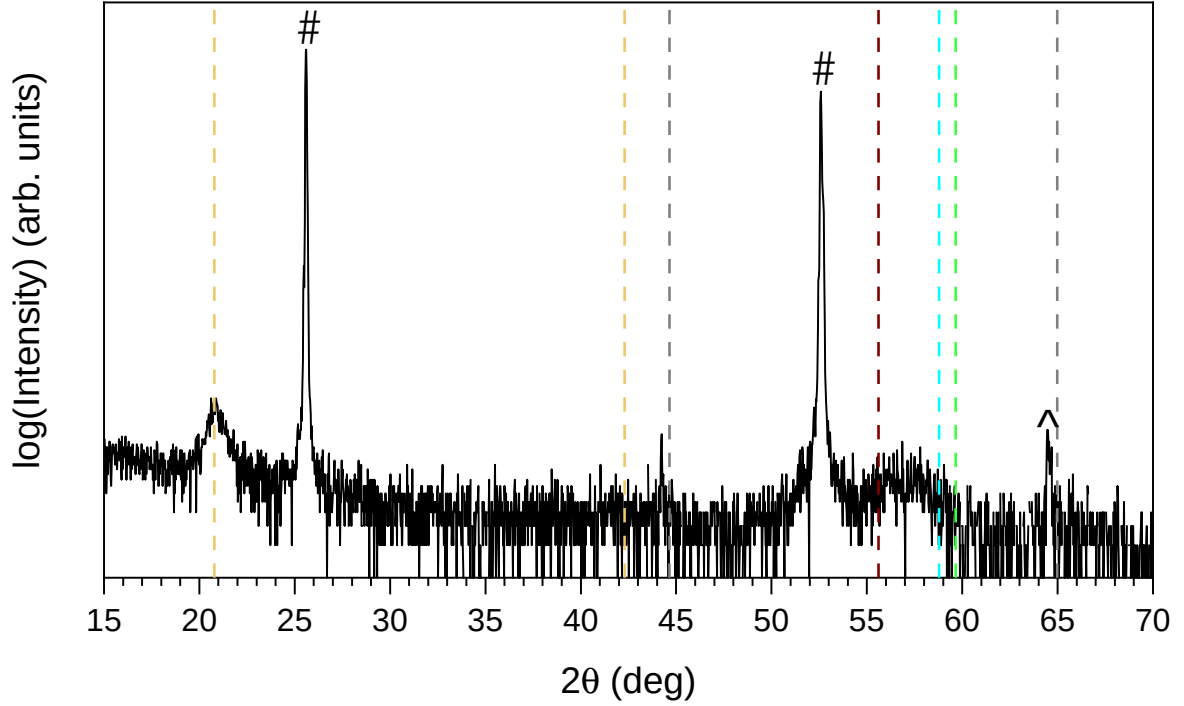


Figure 5.2: Wide angle $\theta - 2\theta$ XRD scan of the Al_2O_3 (1 $\bar{1}$ 02)|Ta (001)| Mn_2Au (001)|Fe (001) oriented heterostructure. The nominal thicknesses of the layers were 8 nm of Ta, 5 nm of Mn_2Au and 4 nm of Fe. The Mn_2Au (00n) [92], Fe (00n) [173] and Ta (00n) [181] reference peak positions are denoted by the gold, grey and wine dashed lines. The $\text{TaO}_{0.9}$ (nn0) [182] and the TaO (nn0) [183] reference peak positions are shown in cyan and green respectively. The hashtags denote the Al_2O_3 (012) and (024) substrate peaks, while the carat symbol denotes the positions of peaks occurring from the XRD sample stage.

Given the thin nature of the Mn_2Au layer, only the Mn_2Au (002) peak can be seen in the scan. No parasitic Mn_2Au phases are readily apparent in the XRD scans which correlates with the RHEED analysis in the previous section. The Ta (002) is also present in the scan, however, the peak is spread over a large angular range. The

$\text{TaO}_{0.9}$ (220) [182] and the TaO (220) [183] are unlikely to present in the film, but suggest that oxygen in the Ta film might be the issue, however with a lower oxygen content than those quoted above. These peaks also highlight that with decreasing oxygen stoichiometry on Ta-O compounds, the reflexes are shifted to lower angular positions. The Ta material had been in use for around eight months before these films were deposited and some level of oxygen contamination of the material over time. This coupled with an e-beam evaporator issue, which made it difficult to focus the electron beam are likely the cause of the oxygen content in the films. The Fe (002) is not present, which is likely because the Fe layer is extremely thin at 4 nm but also because of the low relative intensity of the Fe (002) reflex with an intensity on the order of 13% of the most intense Fe (110) reflex [173].

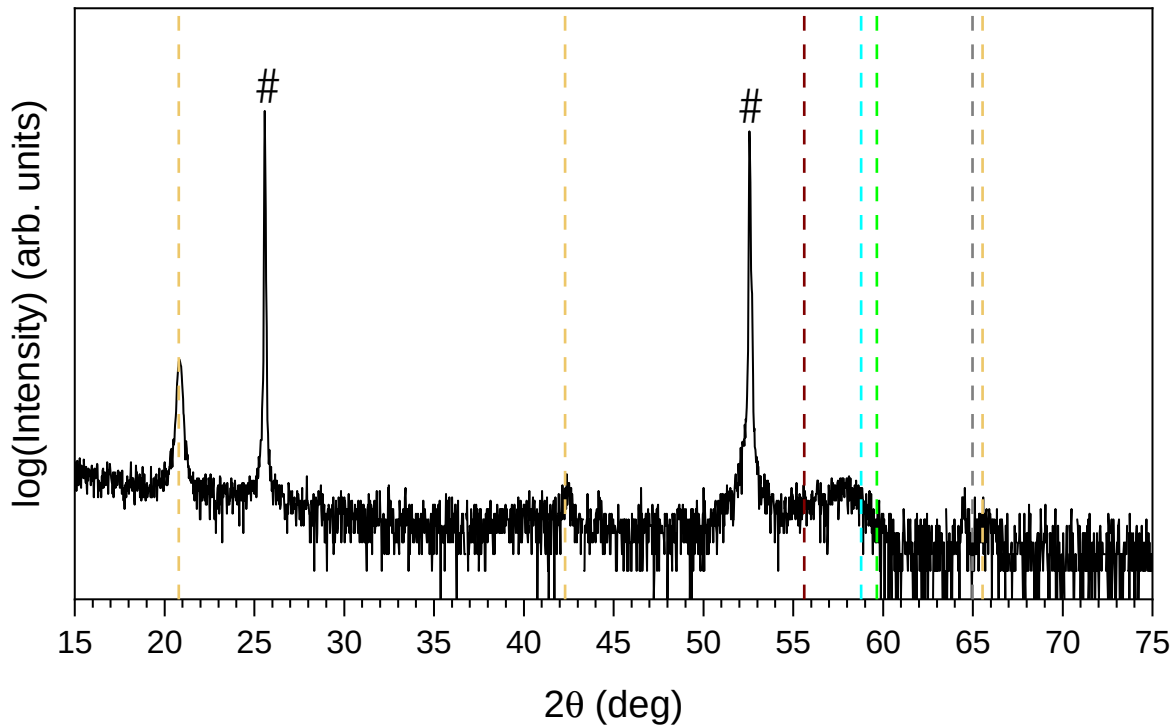


Figure 5.3: Wide angle $\theta - 2\theta$ XRD scan of the Al_2O_3 ($1\bar{1}02$)|Ta (001)| Mn_2Au (001)|Fe (001) oriented heterostructure. The nominal thicknesses of the layers were 23 nm of Ta, 31 nm of Mn_2Au and 23 nm of Fe. The Mn_2Au (00n) [92], Fe (00n) [173] and Ta (00n) [181] reference peak positions are denoted by the gold, grey and wine dashed lines. The $\text{TaO}_{0.9}$ (nn0) [182] and the TaO (nn0) [183] reference peak positions are shown in cyan and green respectively. The hashtags denote the Al_2O_3 (012) and (024) substrate peaks, while the carat symbol denotes the positions of peaks occurring from the XRD sample stage.

Figure 5.3 shows the wide-angle $\theta - 2\theta$ XRD scan obtained of the “thick” 31 nm Mn_2Au heterostructure. The reference positions for each material are denoted in the same manner as in Figure 5.2. The Mn_2Au (002) and (004) reflexes are present in the scan as well as the Ta (001) reflex. Again the Ta film is spread over a large angular likely due to oxygen contamination. The Fe (002) and Mn_2Au (006) peak positions are in close proximity to one another, and there is a small peak in this region which is more

likely to be the Fe (002) peak given it has a higher relative intensity than the Mn_2Au (006) peak.

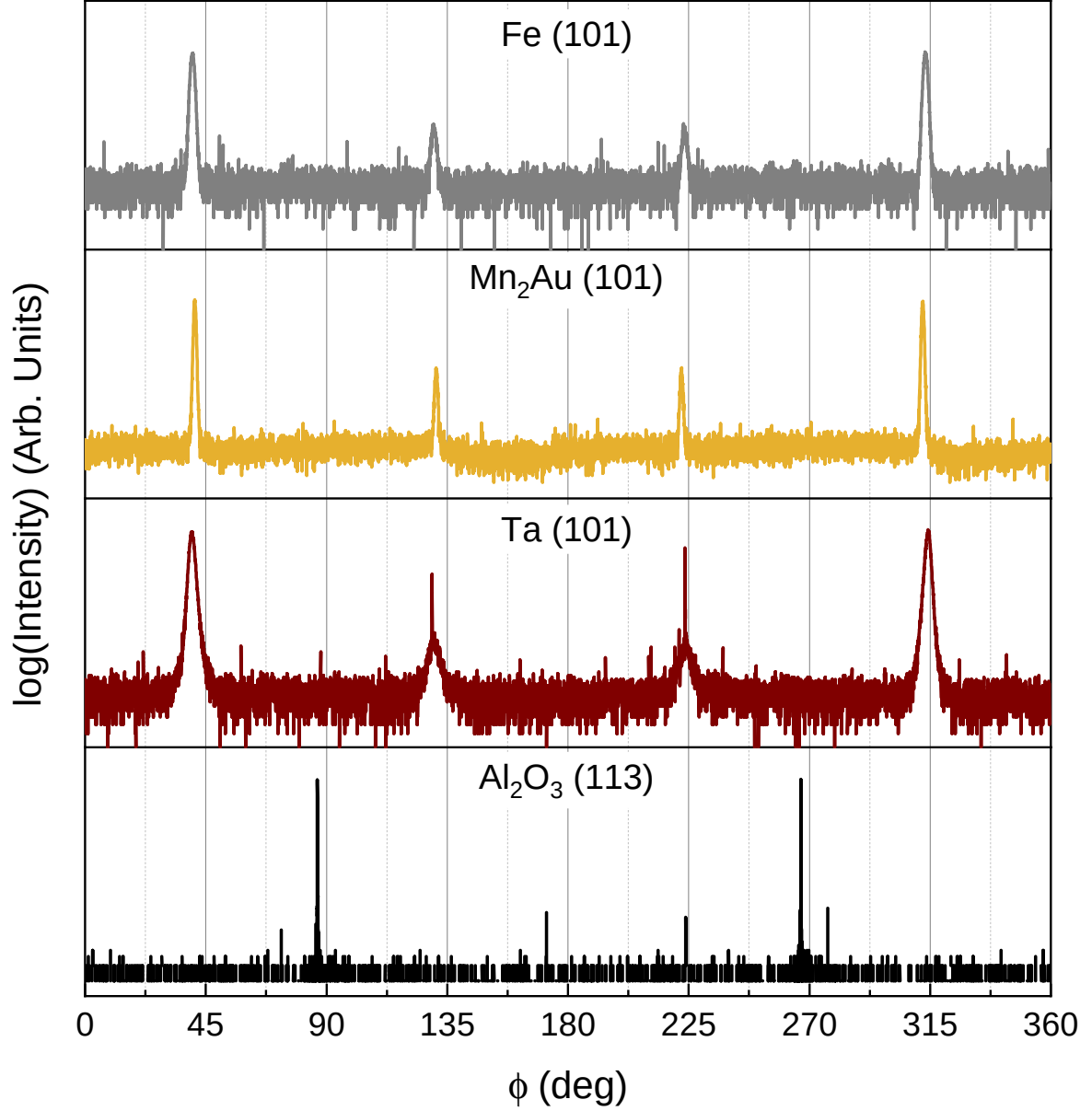


Figure 5.4: Azimuthal (ϕ) XRD scans of the Al_2O_3 {113}, Ta {101}, Mn_2Au {101} and Fe {101} peaks in an Al_2O_3 ($1\bar{1}02$)|Ta (001)| Mn_2Au (001)|Fe (001) oriented heterostructure. The thicknesses of the layers were estimated by best fit of XRR to be 23 nm of Ta, 32 nm of Mn_2Au and 30 nm of Fe.

The purpose of this “thick” sample was to confirm the in-plane relationship of the stack. Azimuthal ϕ -scans were performed on each layer of the stack and these can be seen in Figure 5.4. The Al_2O_3 {113} or {11 $\bar{2}$ 3} peaks can be seen in the bottom panel and the scan shows the expected two-fold symmetry. From the next panel up to the top panel are the Ta {101} scan, the Mn_2Au {101} scan and the Fe {101} scan respectively. Each is coloured according to the scheme used for the reference lines in the $\theta - 2\theta$ XRD scans. All of the peaks display the expected four-fold symmetry and are in line with each other confirming the in-plane epitaxy arrangement of the stack,

of Ta [100]|| Mn_2Au [100]||Fe [100], as was observed in a combination of [32–34]. The in-plane epitaxy relationship between the Al_2O_3 substrate and Ta seed layer has not been previously published, and as noted in [28] for the Mn_2Au (001) growth on r-plane Al_2O_3 substrate, which has the same in-plane order as the Ta (001) layer, the epitaxial relationship is not immediately obvious when looking at the r-plane Al_2O_3 surface. The Al sublattice of the r-plane Al_2O_3 surface appears to have a pseudo-four-fold symmetry, which appears to be rotated by approximately 45° with respect to the c-axis projection onto the r-plane surface. Similarly, the projection of the Al_2O_3 (113) peak onto the r-plane surface appears to lie at approximately 90° to the c-axis projection, which is consistent with the approximately 45° rotational difference observed between the Ta (101) peak and the Al_2O_3 (113) peak in the Figure 5.4. A more comprehensive analysis is necessary to conclusively confirm this, however.

The peaks are not equal in intensity for each of the scans and this is likely due to slight misalignment of the crystal during the alignment of the sample for the ϕ -scans as each of the Ta, Mn_2Au and Fe scans show the same trend in intensities for each of the four peaks.

5.3 Growth and Characterisation of Mn_2Au (110)/Fe (110) bilayers

A heterostructure of the form, $c\text{-Al}_2\text{O}_3/\text{Pt}/\text{Mn}_2\text{Au}/\text{Fe}/\text{TaO}_x$ was grown using the DCA M600 MBE. The Pt, Fe and Ta layers were deposited using the e-beam evaporators, while the Mn_2Au layer was co-deposited using the K-cells. The Al_2O_3 (0001) substrate was sonicated in acetone and IPA, each for a period of 15 minutes, prior to being loaded into the MBE. The Al_2O_3 substrate was annealed at 600°C for a period of 1 hr before the temperature was dropped to 550°C . An 8 nm Pt layer was then deposited at a rate of $0.055 \text{ \AA s}^{-1}$. After this the substrate temperature was dropped to 270°C before the deposition of an 5 nm Mn_2Au layer at a known rate of $0.25 \text{ \AA s}^{-1}$, which was subsequently annealed for 1 hr at 450°C . This method is in contrast to that used in Chapter 3 for the growth of the $c\text{-Al}_2\text{O}_3/\text{Pt}/\text{Mn}_2\text{Au}$ thin films but was chosen in order to be consistent with the Mn_2Au (001)/Fe (001) bilayer in the previous section. Following the anneal, the substrate temperature was cooled to 250°C and 4 nm of Fe was deposited at a rate of $0.1 \text{ \AA s}^{-1}$. The sample was cooled to room temperature before the structure was capped with a 3 nm Ta layer.

5.3.1 RHEED

Figure 5.5 shows the RHEED images obtained of the c -plane Al_2O_3 substrate, the Pt seed layer, the Mn_2Au layer after deposition and again after the 1 hr anneal at 450°C and the Fe layer, which were all taken along the Al_2O_3 $[10\bar{1}0]$ high symmetry direction of the c -plane Al_2O_3 substrate. Each image was produced using an electron beam energy of 20 keV and was taken at the same substrate temperature used for the annealing or deposition of that surface or layer, as described in the previous paragraph.

The RHEED image of the Al_2O_3 surface taken along the $[10\bar{1}0]$ direction, once again consists of spot-like points caused by the intersection of Kikuchi lines indicating that the substrate is single crystalline in nature. The Pt layer consists of narrow streaks and there is evidence of Kikuchi bands diagonally bisecting the streaks, indicating that it is a smooth high quality layer. This is consistent with the RHEED images of similar Pt seed layers used in Chapters 3 & 4, where the Pt grains were on the order of 100 nm, which accounts for the narrow streaks and Kikuchi bands seen in the image. The RHEED image of the Mn_2Au layer post deposition consists partially of very modulated broad streaks and concentric circular streaks. The broad modulated streaks indicate that the surface is rough and qualitatively made up of smaller grains than the Pt seed layer. The concentric circular streaks suggest that the surface is made up of crystalline domains which are not of a singular out-of-plane orientation, although when combined with the modulated streaks, this suggests that only a small portion of the surface consists of these parasitic crystalline domains.

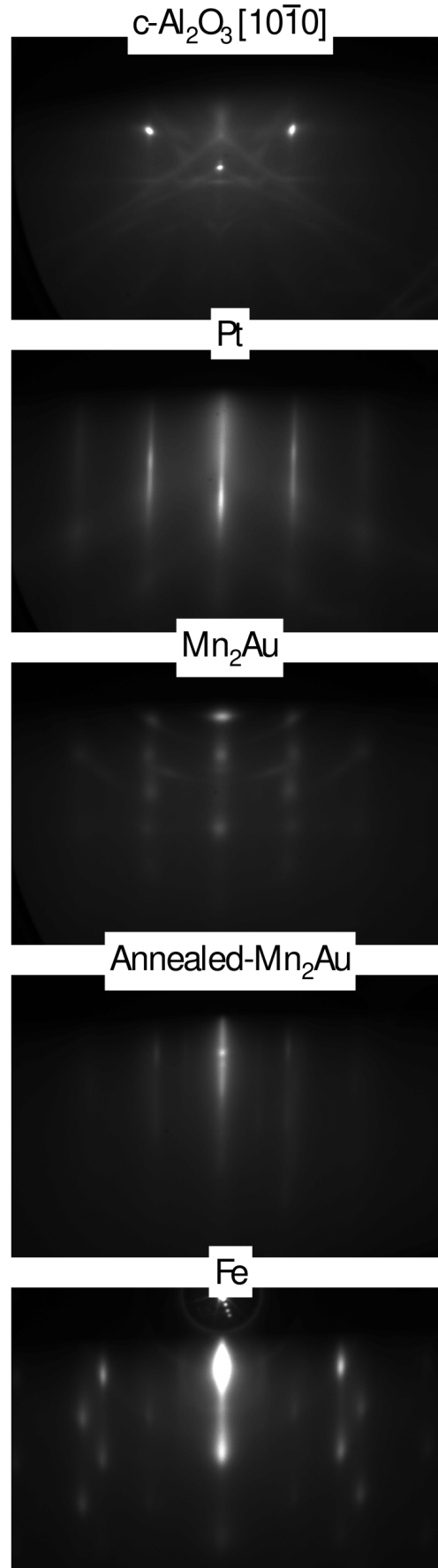


Figure 5.5: RHEED images of each of the layers in the Mn_2Au (110)/Fe (110) heterostructure post deposition, taken along the Al_2O_3 [10 $\bar{1}$ 0] high symmetry direction of the c-plane Al_2O_3 substrate. See text for description.

The presence of the parasitic crystalline domains is indicative of the Mn_2Au layer, as was observed in many samples not included in this thesis. After the 450°C anneal, the Mn_2Au RHEED displays streaks of consistent intensity and the concentric circular streaks have disappeared from the image. This suggests that the anneal allowed for diffusion of the Mn and Au atoms so that the surface of the film had a single out-of-plane crystalline orientation and that it reduced the surface roughness of the sample. As RHEED is only sensitive to the first few monolayers of the films, the removal of the parasitic crystalline domains from the bulk of the film cannot be inferred and will have to be investigated via XRD. The increased intensity and narrowing of the central streak in comparison to the pre-anneal RHEED image, suggests that the anneal increased the grain size. Unlike what was observed in the RHEED of the Mn_2Au (001) sample, this analysis aligns well with the necessity of the annealing procedure for smooth, single orientation Mn_2Au reported in [34]. The Fe RHEED consists of modulated streaks, with a splitting of the outer streaks which implies there are at least two distinct rotational crystalline in-plane Fe domains which are rotated 30° apart from each other. This was also observed for the Fe (110) films grown on a Pt (111) seed layer in Chapter 4 and is attributed to the pseudo-hcp nature of the Fe (110) surface. Similar to the Mn_2Au (001) structure, the Ta capping layer displayed concentric circular streaks indicating that the surface was polycrystalline.

5.3.2 XRD characterisation

Figure 5.6 shows a wide angle $\theta - 2\theta$ XRD scan of the Mn_2Au (110) heterostructure. The gold, blue and grey dashed reference lines denote the reference angles for the Mn_2Au (nn0) [92], the Pt (nnn) [140] and the Fe (nn0) [173] peaks. The asterisks denote the positions of the Al_2O_3 (000n) peaks while the carat symbols denote the peaks emanating from the XRD sample stage.

The Pt (111) and (222) diffraction peaks are clearly visible in the figure and match well with the blue reference lines. The usual Pendellösung fringes that are present around the Pt (111) peaks in Chapters 3 & 4 are almost non-apparent in this scan. This is likely a result of the annealing process on the stack, post-deposition of the Mn_2Au layer, which would have increased diffusion at the Pt/ Mn_2Au interface. The Fe (110) peak is also clearly visible in the scan and closely matches the grey reference line. The Mn_2Au (110) and (220) peaks are not clearly visible in the scan due to their close angular position to the Pt (111) and (222) peaks, which have a higher relative intensity than the Mn_2Au peaks. Moreover, the post-anneal Mn_2Au RHEED had broader streaks than the Pt seed layer indicating that the Mn_2Au surface grains are qualitatively much smaller (in the direction perpendicular to the incident electron beam [126]) than the Pt grains, which would result in a lower intensity Mn_2Au reflection. Although the Mn_2Au RHEED indicated that there was some portion of the film that was polycrystalline before the anneal, there are no other clear Mn_2Au reflections present in the scan above

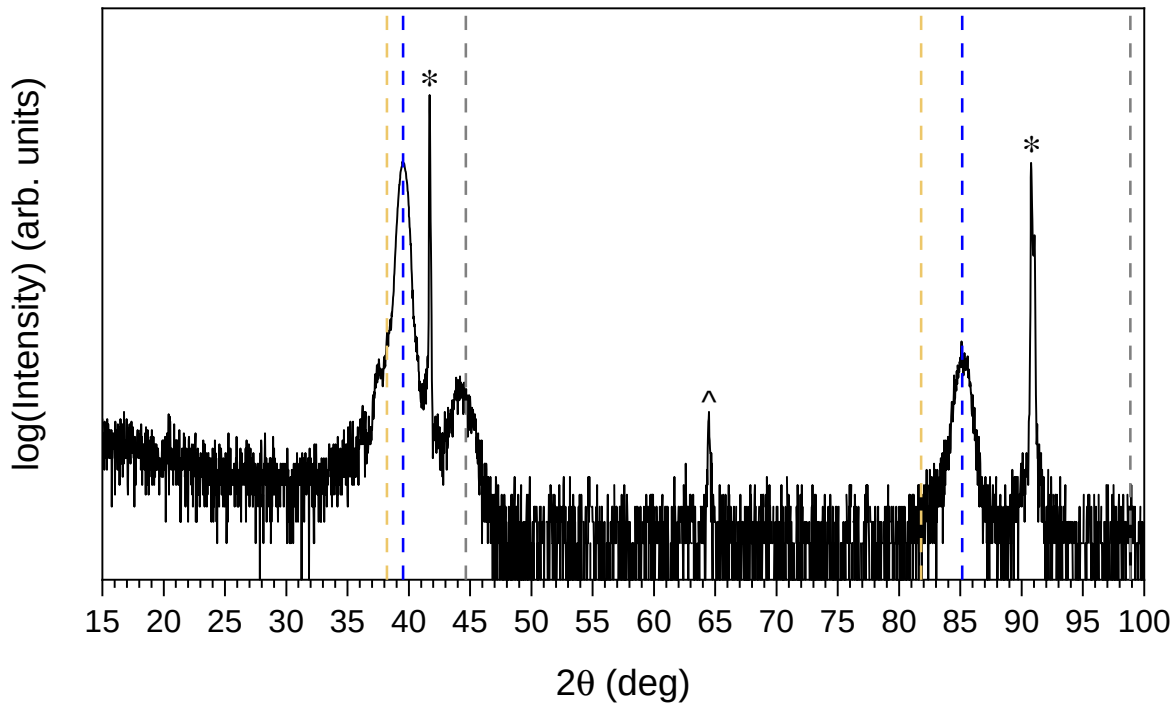


Figure 5.6: Wide angle $\theta - 2\theta$ XRD scan of the Al_2O_3 (0001)|Pt (111)| Mn_2Au (110)|Fe (110) oriented heterostructure. The nominal thicknesses of the layers were 8 nm of Pt, 5 nm of Mn_2Au and 4 nm of Fe. The Pt (nnn) [140], Mn_2Au (nn0) [92] and Fe (nn0) [173] reference peak positions are denoted by the blue, gold and grey dashed lines. The asterisks denote the Al_2O_3 (000n) substrate peaks, while the carat symbol denotes the positions of peaks occurring from the XRD sample stage.

the background noise. This indicates that if there are parasitic crystalline domains they are likely small and constitute a minimal fraction of the film.

Given that the Mn_2Au layer is expected to be (110) oriented, but that the Mn_2Au (110) reflection is not discernible in the $\theta - 2\theta$ XRD scan due to the higher intensity Pt (111) peak, the presence of the Mn_2Au layer had to be confirmed in an alternative manner. An azimuthal ϕ -scan of the Mn_2Au {101} peaks was performed to confirm that the film was oriented (110) as expected. Figure 5.7 shows the resulting ϕ -scan of the Mn_2Au {101} peaks. The peak shows the expected symmetry for a Mn_2Au (110) oriented film, which is two sets of two peaks, where the peaks within each set are separated by 57.7° and the sets are separated by 122.3° . It must be noted that ϕ -scans are typically difficult to perform on thin films with thicknesses less than 10 nm-20 nm, and as this film was 5 nm the scan displays a poor signal to noise ratio. These peaks were scanned by aligning to the theoretical positions of the Mn_2Au {101} peaks, which accounts for the slight asymmetry in the intensity of the sets of peaks. The peaks are also extremely broad with FWHM on the order of 30° which is a result of the ultra-thin nature of the films and the qualitatively small grain size.

The symmetry displayed in Figure 5.7 is also indicative that the Mn_2Au domains may have a single in-plane orientation, which is in contrast to the Mn_2Au (110) films grown in Chapter 3, that were not post-annealed, which consisted of three in-plane domains.

Given the poor signal to noise ratio and the broad FWHM of the peaks, this is difficult to confirm definitively. However, the film would display 6 sets of two peaks each set separated by $\approx 60^\circ$, with the peaks within each set separated by $\approx 4^\circ$ - 5° if the three in-plane domains were present¹. This does not appear to be the case for this film. A much thicker sample would be necessary to investigate whether the post-annealing cycle at 450°C is necessary to induce epitaxial Mn_2Au (110) on Pt (111) and to determine any in-plane relationship. Unfortunately, this was not possible in this particular work.

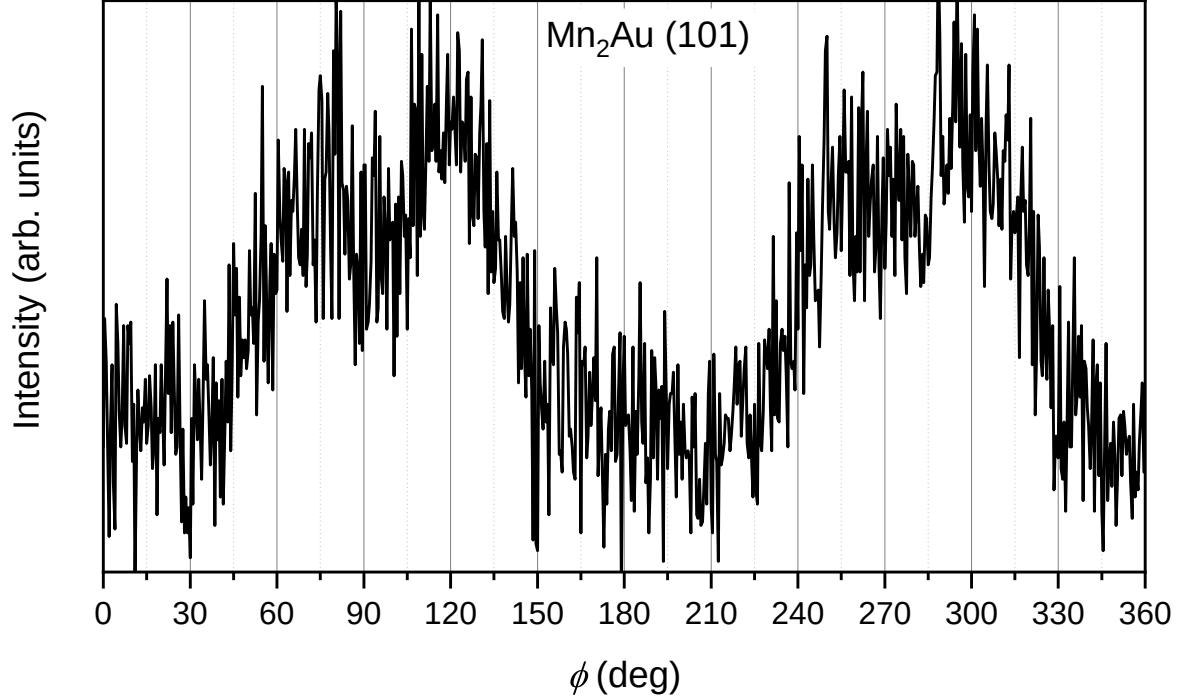


Figure 5.7: Azimuthal (ϕ) XRD scans of the Mn_2Au (101) peak from the Al_2O_3 (0001)|Pt (110)| Mn_2Au (110)|Fe (110) oriented heterostructure. The nominal thicknesses of the layers were 8 nm of Pt, 5 nm of Mn_2Au and 4 nm of Fe. The figure shows the expected symmetry for the Mn_2Au (101) peak, which is two sets of two peaks where the peaks within each set are separated by $\approx 58^\circ$ and the sets are separated by $\approx 122^\circ$ from each other.

5.4 RT Magnetic Characterisation

After the *ex-situ* characterisation of the stacks, each 1 cm^2 substrate was cleaved into four approximately $5\text{ mm} \times 5\text{ mm}$ pieces using a diamond tipped pen. One of the $5\text{ mm} \times 5\text{ mm}$ pieces from each of the Mn_2Au (001) and Mn_2Au (110) stacks was then chosen and an in-plane axis of each stack type was arbitrarily chosen, with the back of the substrate marked with an arrow along this axis. The arrow was drawn using a black permanent marker. Magnetisation vs. applied field loops of the stacks were measured along the arrow, in the as-deposited state using the PMC Micromag VSM. Magnetisation vs. applied field loops were also measured, in 5° increments for the 360°

¹All reciprocal space symmetry relationships were visualised using WinWulff stereographic projection software. <http://www.jcrystal.com/products/winwulff/>

of possible in-plane orientations of the arrow mark, using the rotational head on the PMC Micromag VSM. The angular in-plane rotation of the stacks will be defined using φ , where the tip of the arrow-mark points along $\varphi = 0^\circ$ of in-plane rotation.

Subsequently, a 5 mm x 5 mm piece from each heterostructure type, was subjected to a 1 h vacuum anneal at 350°C . The annealing chamber was evacuated to a pressure better than 5×10^{-6} mbar prior to starting the anneal. An 800 mT field provided by a permanent magnet was applied in-plane arbitrarily along the arrow-marked axis of each of the samples during the annealing procedure. After the anneal the samples were allowed to cool to room temperature before being removed from the permanent magnet and then the vacuum furnace. The stacks were characterised in the same manner after the annealing procedure as described for the as-deposited stacks in the previous paragraph. It should be noted that the diamagnetic contribution from the substrate, in all of the hysteresis loops obtained from the Micromag VSM in this section, were automatically corrected for using HystLab [161].

5.4.1 Mn_2Au (001)/Fe (001)

5.4.1.1 Magnetisation vs. Field Loops

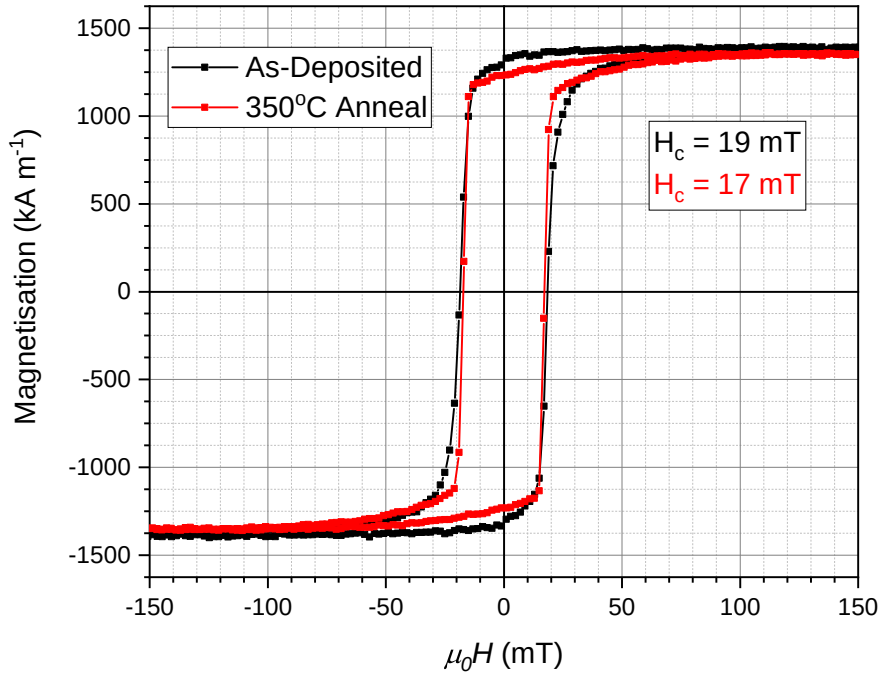


Figure 5.8: Magnetisation vs. field loops, measured along $\varphi = 0^\circ$ for the Mn_2Au (001)/Fe (001) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350°C in an 800 mT applied field. The associated error on $\mu_0 H$ for each point is ± 1 mT.

Figure 5.8 shows the as-deposited hysteresis loop of the Mn_2Au (001)/Fe (001) bilayer in black, which was measured along $\varphi = 0^\circ$. The coercivity of the loop is on the order of $19\text{ mT} \pm 2\text{ mT}$, which drastically exceeds the coercivity of a typical uncoupled Fe

thin film [184]. Thus indicating that there is strong EC between the Mn_2Au and Fe layers, likely induced by the elevated growth temperature of the Fe layer of 250°C . The red loop in Figure 5.8 is that measured along $\varphi = 0^\circ$ after the 1 hr vacuum anneal at 350°C in an 800 mT applied field. The coercivity of the loop was measured to be $17\text{ mT} \pm 2\text{ mT}$ which is the same as the as-deposited loop within experimental error. There is no loop shift evident in the FC loop as the measurement temperature of RT is likely above the blocking temperature [32]. Equally, though, the FC temperature may not have been large enough to exceed the effective Néel temperature of this 5 nm Mn_2Au layer. To try and discern which of these possibilities applied to the ECE, some of the properties of the azimuthal in-plane loops were investigated. The saturation magnetisation of both loops are on the order of 1350 k A m^{-1} , which is lower than the bulk value for Fe of 1710 k A m^{-1} but this is consistent with what has been observed in other thin films [185]. A slight reduction, on the order of 40 k A m^{-1} , in magnetisation is observed from the as deposited film to the FC film, which is likely due to diffusion of Fe atoms at the $\text{Mn}_2\text{Au}/\text{Fe}$ interface and at the Fe/Ta interface. There is also decreasing squareness of the loop after the anneal procedure indicative of a change in anisotropy of the film as a result of the FC process.

5.4.1.2 In-plane Anisotropy Profile

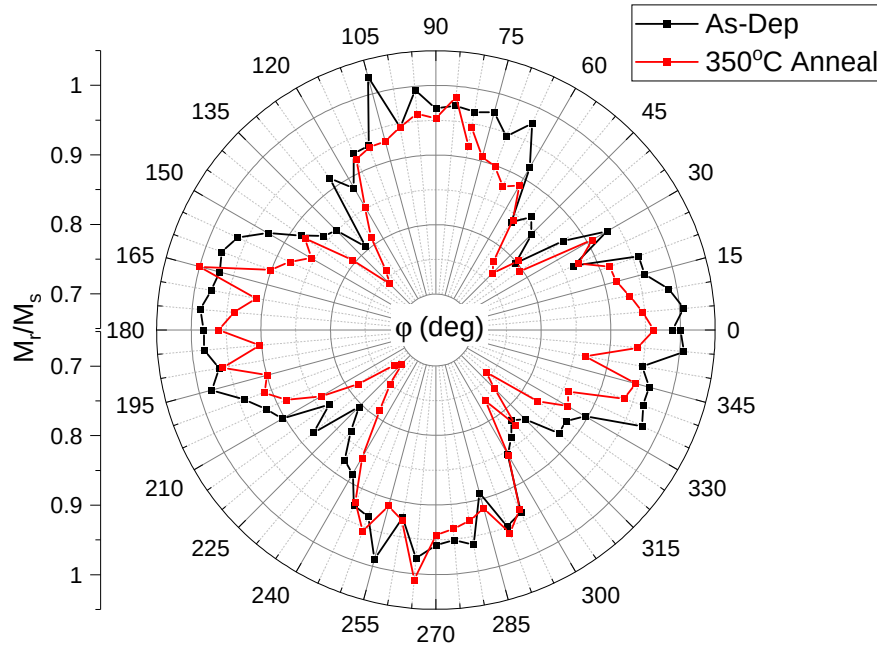


Figure 5.9: A polar plot showing the in-plane angular dependence, of the sample w.r.t to the VSM pickup coils, by plotting M_r/M_s to illustrate the in-plane anisotropy of the Mn_2Au (001)/Fe (001) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350°C in an 800 mT applied field. Each point represents an individual magnetisation vs. field loop from which the values for M_r and M_s have been taken.

Figure 5.9 is a polar plot of the remanent magnetisation as a fraction of the saturation magnetisation of each loop measured at an in-plane azimuthal angle φ , where each point

represents a measured loop every 5° . The resulting plot illustrates the magnetocrystalline anisotropy of the Fe layer. The as-deposited sample (black) and the sample after the FC procedure (red) both show fourfold symmetry of the magnetocrystalline anisotropy. The maxima in the angular profile correspond to the easy axes of the Fe thin films, while the minima correspond to the hard axes. As expected in the epitaxial Fe (001) thin films, the easy axes lie parallel to the square edges of the pseudo-cubic $\text{r-Al}_2\text{O}_3$ substrate, which is consistent with what was previously observed [32]. The fourfold symmetry of the magnetocrystalline anisotropy after FC (red) does not exclude either of the possibilities mentioned previously. To further investigate if the effective Néel temperature of the Mn_2Au layer was exceeded during FC, the coercivity of the in-plane loops are plotted.

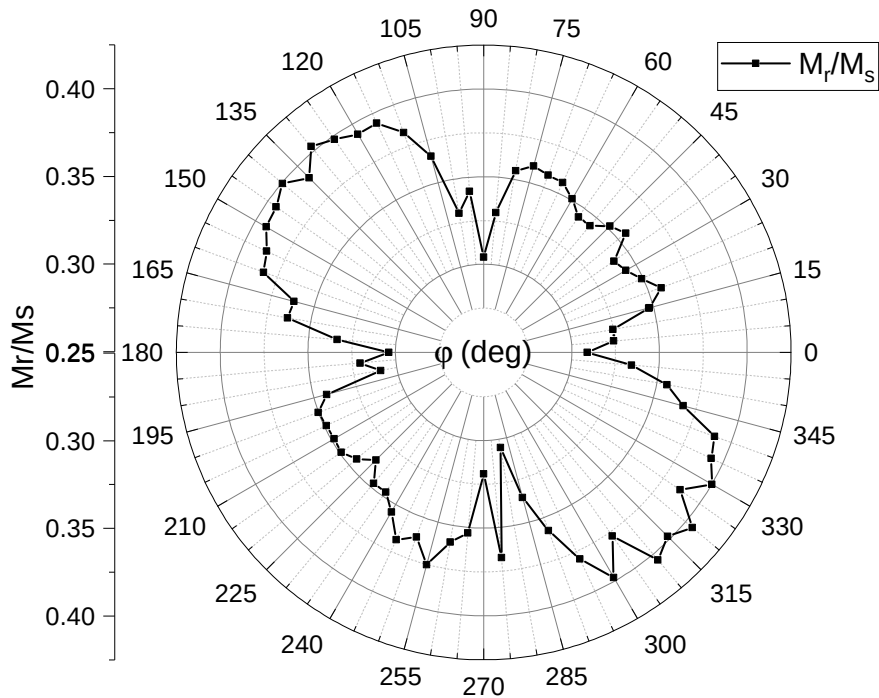


Figure 5.10: A polar plot showing the in-plane angular dependence, of the sample w.r.t to the VSM pickup coils, of M_r/M_s from in plane loops to illustrate the in-plane anisotropy of a Fe (001) thin film. Each point represents an individual magnetisation vs. field loop from which the values for M_r and M_s have been taken. The angle $\varphi = 0^\circ$ corresponds to the MgO [100] axis.

Figure 5.10 shows the in-plane anisotropy profile taken from in plane hysteresis loops of a 20 nm Fe (001) thin film on an MgO (001) substrate. The in-plane epitaxy relationship between the film and substrate is Fe [110] $\parallel$ MgO [100] meaning the [100] plane is rotated at a 45° to the MgO [100] axis [186]. Given that the easy axes of Fe lie along the $\langle 100 \rangle$ axes, these easy axes will lie along a 45° angle to the MgO [100] axis. The angle $\varphi = 0^\circ$ corresponds to the MgO [100] axis. It can be seen that there fourfold symmetry of the magnetocrystalline anisotropy axes in the Fe (001) thin film as was observed for the Mn_2Au (001)/Fe (001) bilayer above in Figure 5.9, however, the Fe

easy axes are rotated by 45° to the MgO [100] axis, due to the epitaxial relationship of Fe (001) and MgO (001) described above.

5.4.1.3 In-plane Coercivity Profile

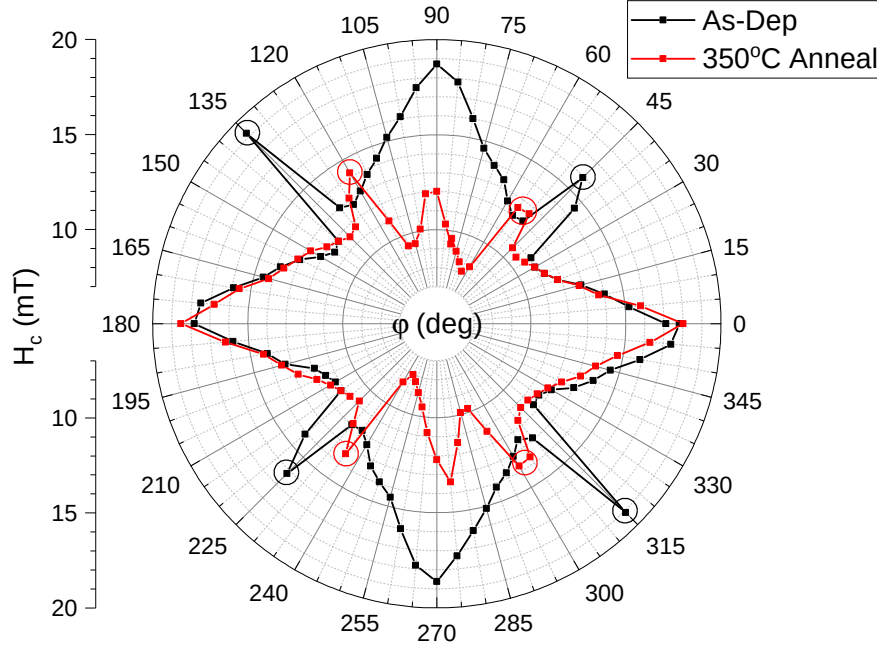


Figure 5.11: A polar plot showing the in-plane angular dependence of H_c of the Mn_2Au (001)/Fe (001) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350°C in an 800 mT applied field. Each point represents an individual magnetisation vs. field loop, taken at an in-plane angle φ from which the value for H_c have been taken.

Figure 5.11 shows a polar plot of the coercivity of each in-plane loop measured along φ for the as-deposited stack (black) and the FC stack (red). Dealing first with the as-deposited polar plot of H_c in Figure 5.11, there are maxima in the coercivity along $\varphi = 0^\circ, 90^\circ, 180^\circ$ and 270° , which correspond with the easy axes of the Fe layer illustrated in Figure 5.9. However, there are also maxima in the coercivity along $\varphi = 45^\circ, 135^\circ, 225^\circ$ and 315° which are unexpected. Under the Stoner-Wohlfarth model, the coercivity of a FM material is maximum along the easy axes and minimum along the hard axis [36, 187]. Given that the maxima at $45^\circ, 135^\circ, 225^\circ$ and 315° (circled in black on the as deposited plot) are along the hard axes of the FM Fe layer, there must be another cause of the maxima in coercivity at these positions. The AFM moments of Mn_2Au lie along the equivalent easy axes of $[110]$ and $[1\bar{1}0]$ [25]. For epitaxial Mn_2Au (001) thin films ($\approx 240\text{ nm}$) on a Ta (001) seed layer [33], the easy axes were also found to lie along $[110]$ and $[1\bar{1}0]$ in roughly equal proportions [188]. In this Mn_2Au (001)/Fe (001) bilayer, the maxima at $45^\circ, 135^\circ, 225^\circ$ and 315° in coercivity match the expected positions of the $[110]$ and $[1\bar{1}0]$ easy axes of the Mn_2Au layer. This suggests that the maxima in the coercivity at these positions may be due to the presence of a significant percentage of re-switchable moments in the AFM layer.

The polar plot of the coercivity, consisting of loops taken after the 350 °C FC procedure (red) in Figure 5.11 shows some differences to that of the as-deposited plot (black). The 800 mT magnetic field was applied along $\varphi = 0^\circ$, and along this axis, there are two primary maxima in the coercivity, which represent the preferential axes of the EC. There are six secondary maxima present in the coercivity profile, two of which lie along the $\varphi = 90^\circ$ axis. Combining the reduced coercivity of this axis with the anisotropy profile in Figure 5.9, it suggests that this axis still represents an easy axis of the FM layer but that it is no longer a preferential axis for the EC, as evidenced by the reduction in coercivity from the as-deposited profile. Figure 5.12a shows the loops along the direction of FC (red), which is representative of the loops from the two primary maxima, and at $\varphi = 90^\circ$ to the direction of FC (blue), which is representative of the loops from the six secondary maxima.

The maxima in coercivity which previously were at 45° , 135° , 225° and 315° (black circles) are now secondary maxima at approximately 53° , 120° , 235° and 303° (red circles) which represents a 10° - 15° rotation away from the axis along $\varphi = 0^\circ$. Assuming that these maxima represent the easy axes of the AFM moments, this would suggest that the FC process was sufficient to partially reorient the AFM easy axes. The direction of rotation, around 7° - 15° , away from the direction of the applied field would correlate well with the preference for AFM moments to align perpendicular to the direction of an applied magnetic field, as $\chi_\perp \neq \chi_\parallel$. This lends credence to the hypothesis that those secondary maxima mentioned do represent the Mn₂Au easy axes, but also that the FC temperature of 350 °C is above T_N^* for this 5 nm Mn₂Au layer.

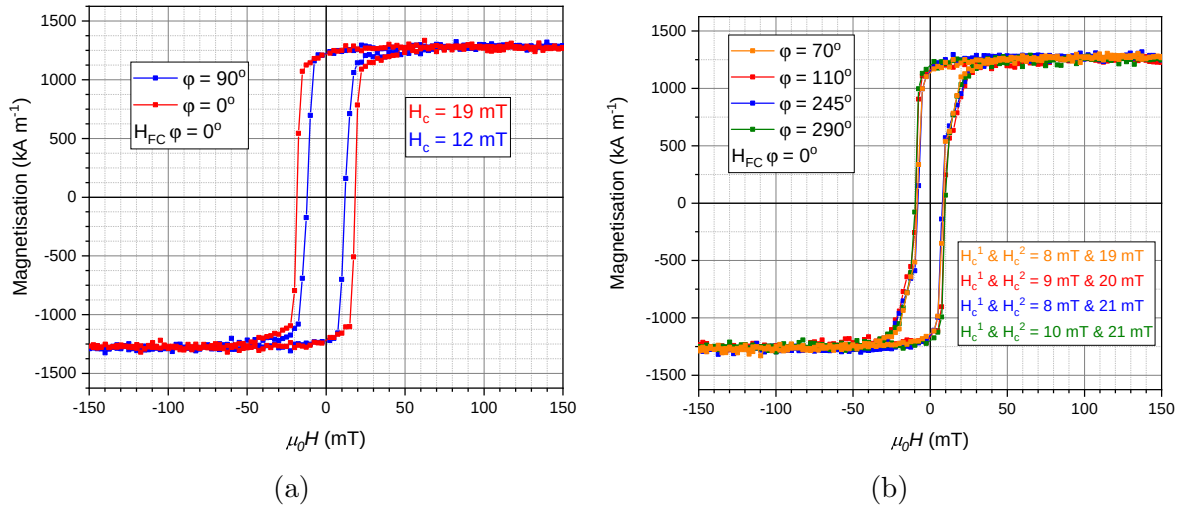


Figure 5.12: Magnetisation vs. field loops of the Mn₂Au (001)/Fe (001) bilayer measured after the FC from 350 °C where φ represents the in-plane angle at which the loop was measured. (a) The loops measured along $\varphi = 0^\circ$ and 90° illustrating the primary maxima in coercivity along the direction of the FC (red) and the secondary maxima in coercivity perpendicular to the anneal direction (blue). (b) The loops measured at the minima in the coercivity profile shown in Figure 5.11 which were at $\varphi = 70^\circ$, 110° , 245° and 290° . The associated error on $\mu_0 H$ for each point is ± 1 mT.

The loops from the minima in the coercivity profile from Figure 5.11 are plotted in Figure 5.12b are shown for completeness. The loops are symmetric in the ascending and descending branches, but the magnetisation profile upon applied field reversal appears to take place in two distinct phases before re-saturation for both branches. First, an initial steep change in magnetisation around ± 10 mT likely caused by magnetisation reversal of the FM moments in the EC Fe layer, giving rise to the relatively low values for H_c . The second, is a more gradual change in magnetisation from ± 10 mT-40 mT, likely correlating with the rotation of the AFM Mn_2Au moments. This is in contrast to the coherent rotation of the FM and AFM moments upon magnetisation reversal in the Fe layer which is indicated in the more “square” (M_r/M_s closer to 1) loops in Figure 5.12b.

Overall, this analysis suggests that through the EC of the FM and AFM layers, the FM layer may act as an indicator layer for its own easy axes and the easy axes of the AFM domains, as well as the preferential axes of the EC by measuring the coercivity profile. A necessary qualification though; much of the explanations here are speculation based on the available information and need to be experimentally corroborated via other methods. A direct imaging method such as XMLD-PEEM or XMCD-PEEM may be one option but has been shown to be tricky in samples of this form (i.e. $\text{Mn}_2\text{Au}/\text{Fe}$) [68]. If the growth of the Fe and Mn_2Au layers could be reversed (from $\text{Mn}_2\text{Au}/\text{Fe}$ to $\text{Fe}/\text{Mn}_2\text{Au}$)² and the epitaxial relationship maintained, these methods may have more success.

To summarise, the FC temperature of 350°C was sufficiently large to overcome T_N^* of the 5 nm Mn_2Au layer, but the measurement of the loops at RT was not sufficiently low to pin the AFM moments (i.e., not cooled through the blocking temperature). This is primarily evidenced by the reduction in the coercivity of the FC sample, along angles different from the direction of the applied field during the FC. Low temperature VSM measurements should elucidate if this system has a blocking temperature.

5.4.2 Mn_2Au (110)/Fe (110)

5.4.2.1 Magnetisation vs. Field Loops

Figure 5.13 shows the hysteresis loops of the Mn_2Au (110)/Fe (110) stack measured before (black) and after the annealing cycle (red), along $\varphi = 0^\circ$. The as-deposited loop has a coercivity of $11\text{ mT} \pm 2\text{ mT}$ which is larger than expected for an uncoupled Fe layer [184], indicating that there is EC between the AFM and FM layers induced by the 250°C deposition temperature of the Fe layer. The annealed (red) loop has a much larger coercivity of $26\text{ mT} \pm 2\text{ mT}$, again indicative of EC between the FM/AFM layers. This large increase in coercivity is in contrast to what was previously observed

²Fe (001)/ Mn_2Au (polycrystalline) bilayers have been grown in Chapter 5.4 of [68].

in Co (111)/ Mn_2Au (110) bilayers (see Figure 4.8) which were also FC from 350°C in Chapter 4. In those Co (111)/ Mn_2Au (110) bilayers, the deposition of the Mn_2Au layer onto the FM Co layer was suggested to cause the AFM moments to lie preferentially along one of the easy axes as the Mn_2Au layer was deposited. Given that Mn_2Au (110) was grown directly onto the Pt (111) seed layer here, both easy axes of Mn_2Au should be present in roughly equal proportions, similar to the Mn_2Au (001)/Fe (001) samples in [188]. This is to say that the Mn_2Au films should have one easy axis out-of-plane along $[110]$ and one in-plane axis along $[1\bar{1}0]$. The most likely explanation for the large increase in coercivity is the reorientation of the AFM moments during FC such that both sets of moments contribute to the EC. Note that no demagnetisation corrections were performed on the loops given the loops were all measured in the plane of the sample. Due to the large lateral dimensions ($5 \times 10^{-3}\text{ m}$ w.r.t the thickness of the heterostructure ($9 \times 10^{-9}\text{ m}$), the correction would be very small and so can be considered negligible for this analysis.

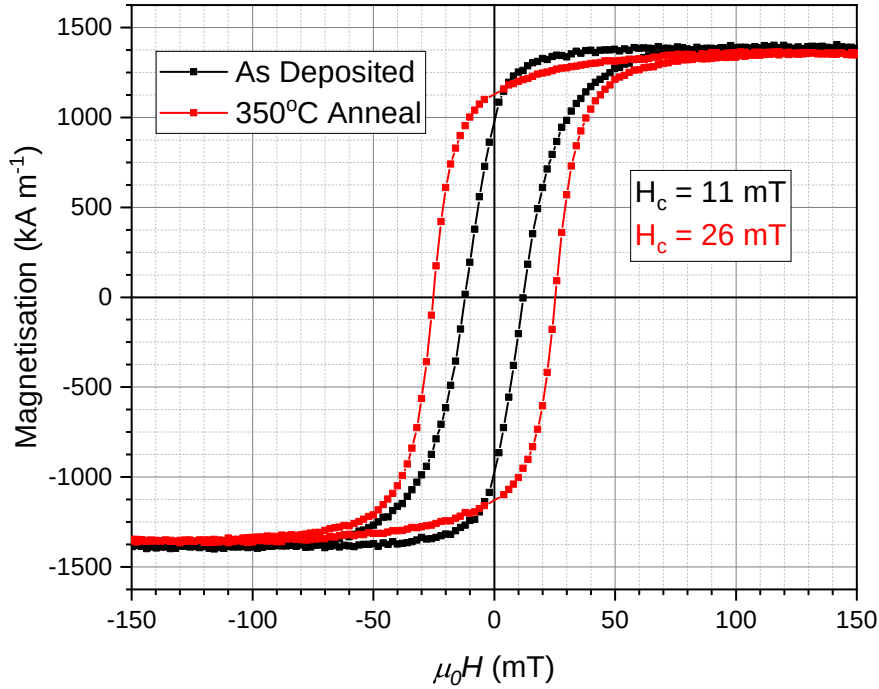


Figure 5.13: Magnetisation vs. field loops, measured along $\varphi = 0^\circ$ for the Mn_2Au (110)/Fe (110) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350°C in an 800 mT applied field. The associated error on $\mu_0 H$ for each point is $\pm 1\text{ mT}$.

The magnetisation of both the as deposited and FC loops are on the order of 1350 kA m^{-1} , which is a typical value for thin film Fe films [186]. However, there is a clear reduction in the FC loops magnetisation visible in Figure 5.13 by approximately 30 kA m^{-1} . This is similar to what was observed in the Mn_2Au (001)/Fe (001) heterostructure in Figure 5.8, and is indicative of diffusion between the Fe and Mn_2Au interfaces and the potential formation of interfacial phases. One possible interfacial phase which would account for the reduction in magnetisation is FeMn which orders antiferromagnetically

[20] and has a wide stoichiometry range of formation at temperatures close to the 350°C annealing temperature used here [154].

The “squareness” of the as-deposited loop appears less than that of the FC loop in Figure 5.13 indicating that the loop may not be measured along an easy axis of the FM layer. This is best illustrated by the smaller slope in the magnetisation upon magnetisation reversal for the black loop, in comparison to the red loop. Given that the shape anisotropy of thin films means that thin film FMs generally only have twofold or fourfold magnetocrystalline anisotropy, this suggests the Fe layer has uniaxial anisotropy, which has been reoriented during the FC process. To try and understand this better the magnetisation vs field loops for the Mn_2Au (110)/Fe (110) bilayer, measured along $\varphi = 0^\circ$ and 90° both (a) before (black, blue) and (b) after (red, blue) the FC cycle are plotted in Figure 5.14. Comparing the shape of the $\varphi = 90^\circ$ loop in (a) (blue) and the $\varphi = 0^\circ$ loop in (b) (red), the overall shape is nearly identical, with the loops appearing much “squarer” to the eye than the other loops in both (a) and (b). This provides evidence that the FM has uniaxial anisotropy which is reoriented by the FC process. Thus the coercivity maxima along the easy anisotropy direction is $16\text{ mT} \pm 2\text{ mT}$ before the FC procedure and $26\text{ mT} \pm 2\text{ mT}$ after, which is still a substantial increase and aligns with the hypotheses of AFM moment reorientation post FC. The $\varphi = 0^\circ$ loop in (a) (black) and the $\varphi = 90^\circ$ loop in (b) (blue) have a similar loop profile, consistent with the measurement along the hard axis of the FM layer. The coercivity increases from $11\text{ mT} \pm 2\text{ mT}$ before the FC to $17\text{ mT} \pm 2\text{ mT}$ after. To provide further evidence for the uniaxial anisotropy of the FM layer post deposition and reorientation of the anisotropy axis after the FC, the “squareness” profiles of the azimuthal in-plane loops are plotted.

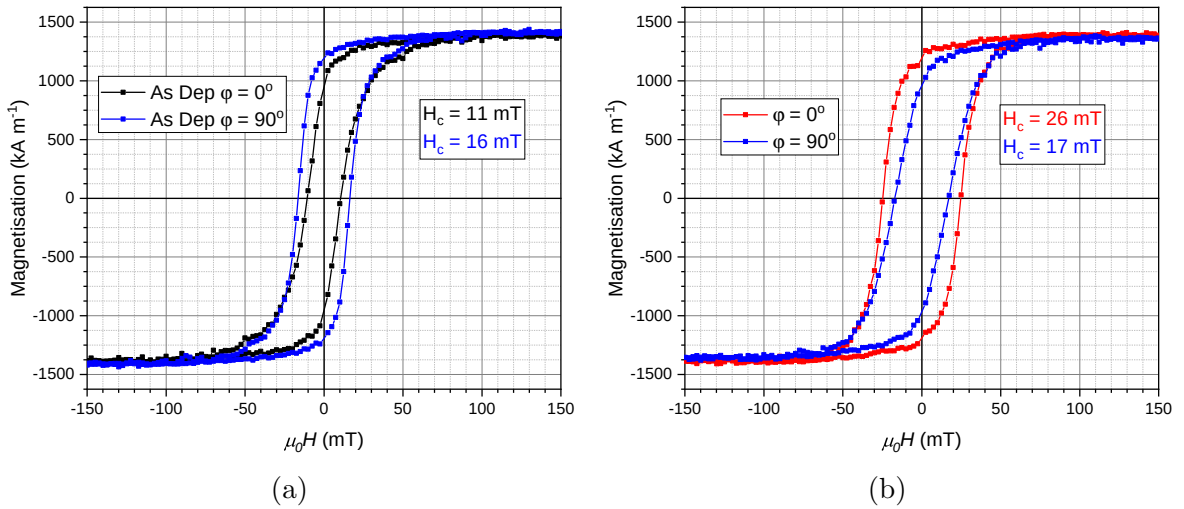


Figure 5.14: Magnetisation vs field loops for the Mn_2Au (110)/Fe (110) bilayer, measured along $\varphi = 0^\circ$ and 90° both (a) before and (b) after the FC cycle. The loops measured along $\varphi = 0^\circ$ are shown in the same colours as in Figure 5.13 which are black for (a) and red for (b). The loops measured along $\varphi = 90^\circ$ are shown in blue for both (a) and (b). The associated error on $\mu_0 H$ for each point is $\pm 1\text{ mT}$.

5.4.2.2 In-plane Anisotropy Profile

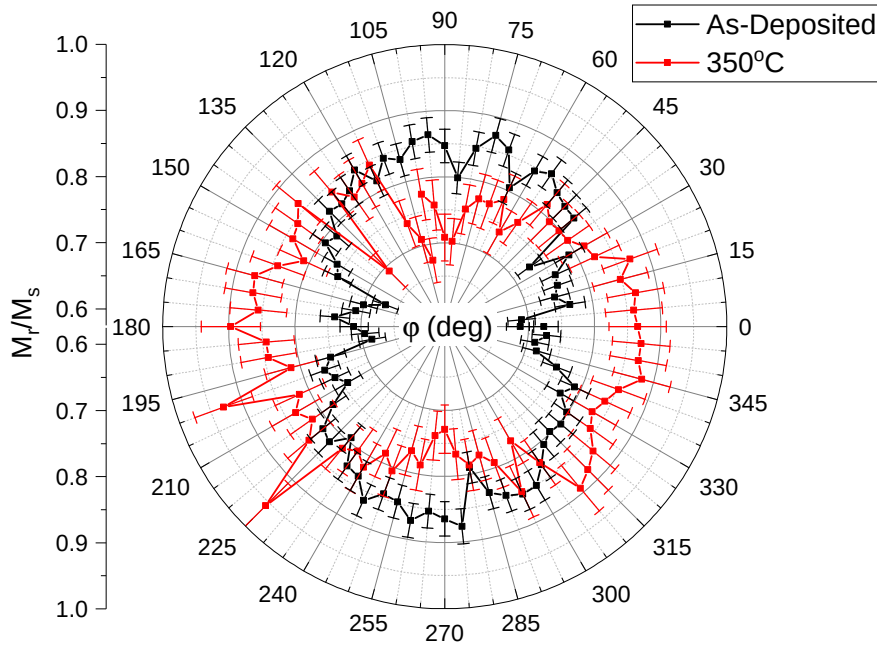


Figure 5.15: A polar plot showing the in-plane angular dependence of M_r/M_s to illustrate the anisotropy of the Mn₂Au (110)/Fe (110) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350 °C in an 800 mT applied field. Each point represents an individual magnetisation vs. field loop from which the values for M_r and M_s have been taken.

Figure 5.15 is a polar plot of the remanent magnetisation as a fraction of the saturation magnetisation (“squareness”) of each loop measured at an in-plane azimuthal angle ϕ , where each point represents a measured loop every 5°. The profile indicates the magnetocrystalline anisotropy of the Fe layer, before the FC process (black) and after (red), where the maxima in the angular profile illustrate the easy axes (along 90° and 270°) of the Fe layer. Dealing first with the as-deposited profile; the profile indicates that the Fe layer has uniaxial anisotropy in the as-deposited state, which is in good agreement with the assessment of the loops in Figure 5.14a. Considering this, along with the azimuthal ϕ XRD scans in Figure 5.7 confirms the analysis that the Mn₂Au (110) film is indeed epitaxial. This appears to cause the preferential formation of Fe domains with uniaxial anisotropy rather than the expected biaxial anisotropy for typical FM thin films. As the in-plane crystallographic directions (colloquially referred to as “flat”) of the substrate are not known, the direction of the Mn₂Au epitaxy, and thus the easy axes of the AFM moments, in relation to the FM anisotropy of the Fe layer is impossible to determine from this work.³ Although, one possibility is that the FM easy-axes may align perpendicular to the in-plane $[1\bar{1}0]$ AFM easy axis (which would maximise the AFM susceptibility). The FC anisotropy profile (red) in Figure 5.15 contains larger variations in the values of $\frac{M_r}{M_s}$ than the as-deposited profile (black),

³This will be addressed in future work.

but the sustained maxima in the “squareness” is clearly along the $\varphi = 0^\circ$ axis indicating reorientation of the FM easy axes along the same direction by the FC procedure. This is also in agreement with the analysis of the loops in Figure 5.14b. This is a clear indication that the FC procedure was conducted at a sufficiently large temperature to overcome T_N^* of the Mn_2Au layer.

5.4.2.3 In-plane Coercivity Profile

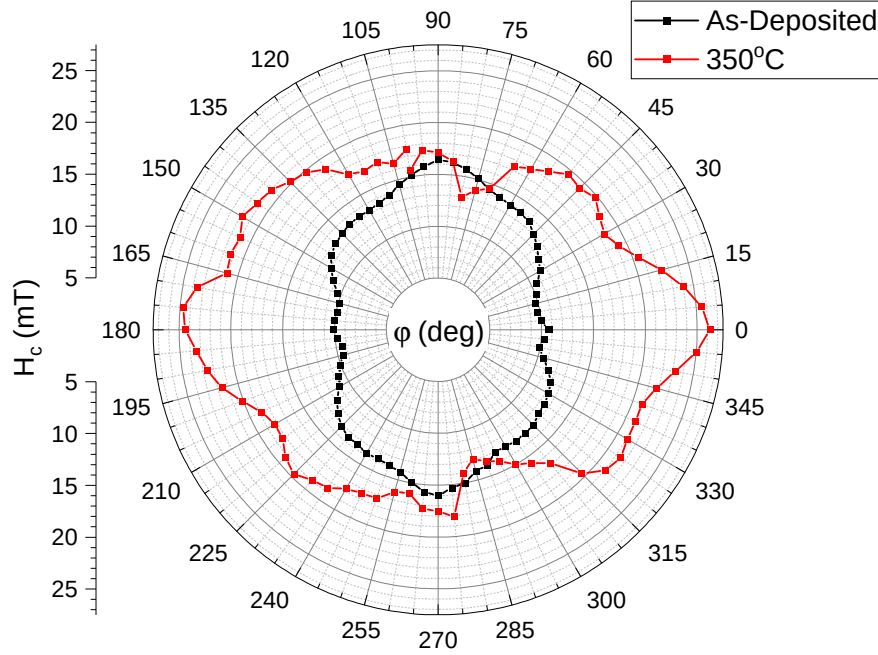


Figure 5.16: A polar plot showing the in-plane angular dependence of H_c of the Mn_2Au (110)/Fe (110) bilayer before (black) and after (red) a 1 hr vacuum anneal at 350°C in an 800 mT applied field. Each point represents an individual magnetisation vs. field loop from which the value for H_c have been taken.

Figure 5.16 shows a polar plot of the coercivity of each azimuthal in-plane magnetisation vs. field loops measured along φ , of the Mn_2Au (110)/Fe (110) stack as-deposited stack (black) and after FC (red). The primary maxima in both the as-deposited plot and the FC plot mirror the anisotropy profiles in Figure 5.15, with maxima in coercivity corresponding to the direction of the FM easy axes. The red plot indicates reorientation of the FM easy axes along $\varphi = 0^\circ$ as a result of the FC process, which is in good agreement with the other magnetometry data.

To summarise, there is strong EC between the Mn_2Au (110)/Fe (110) layers as deposited, evidenced by an increased coercivity with respect to Fe, which also increases significantly after FC from 350°C . The loops, anisotropy profiles and coercivity profiles indicate that there is uniaxial anisotropy of the FM layer before and after FC, which is reoriented as a result of the FC process. The uniaxial anisotropy of the FM layer correlated well with the azimuthal XRD of the Mn_2Au layer, which is epitaxial, thus driving the formation of the uniaxial FM domains in the Fe layer. The increase in the

coercivity can be explained by the presence of the Mn_2Au AFM moments with both possible easy axes present as a result of the deposition conditions, which are reoriented after the FC process. There is no bias present in this stack at room temperature. Low temperature magnetometry is necessary to elucidate if a bias is present at lower temperatures.

5.5 Low Temperature Magnetic Characterisation

The low temperature magnetic characterisation was performed using a Quantum Design PPMS equipped with a 14 T superconducting magnet and the VSM option. The portion of each stack, which had been used for the RT measurements in the previous section, were also used for the low temperature characterisation. Prior to loading the samples in the PPMS, they were FC from 350 °C in the 800 mT permanent magnet at a vacuum better than 1×10^{-5} mbar for 15 minutes before cooling to room temperature. Again the field was applied along $\varphi = 0^\circ$. The samples were sonicated in acetone and IPA to remove the black marker used to mark the FC direction. The FC direction was preserved by scratching an arrow into the back of the substrate. The stacks were subsequently loaded into the VSM using straws to position the sample with $\varphi = 0^\circ$ along the direction of the applied field of the superconducting magnet. A 1 T field was applied along $\varphi = 0^\circ$ at 300 K, before the stacks were cooled 5 K. Eight magnetisation vs. field loops were measured of each stack between 5 K-270 K. The loops were taken in the field range of 1 T to -1 T back to 1 T. The obtained loops were processed manually to correct for the diamagnetic response of the substrate.

5.5.1 Mn_2Au (001)/Fe (001)

Figure 5.17 shows the corrected loops obtained from the Mn_2Au (001)/Fe (001) stack in the full field range between ± 1 T. The loops were measured, in order, at temperatures of 5 K, 50 K, 100 K, 140 K, 180 K, 200 K, 220 K and 270 K which are shown in the colours indicated in the graph legend. As expected there is a small increase in the FM magnetisation with decreasing temperature evidenced by the increasing saturation magnetisation from the green loops to the darker loop colours. Also of note is the paramagnetic response visible in the 5 K loop (black) indicating that the samples were likely exposed to paramagnetic impurities in the form of the marker ink initially used to preserve the FC direction. Although the sample was cleaned using acetone and IPA, clearly not all of the ink was removed as evidenced by the paramagnetic response in the 5 K loop. The coercivities of the loops appear to be smaller than the most minor tick on the graph (indicating 50 mT) and so are shown in a narrower field range below.

Figure 5.18 shows the low temperature loops of the Mn_2Au (001)/Fe (001) stack in the narrower field range of ± 100 mT to illustrate the coercive fields around magnetisation

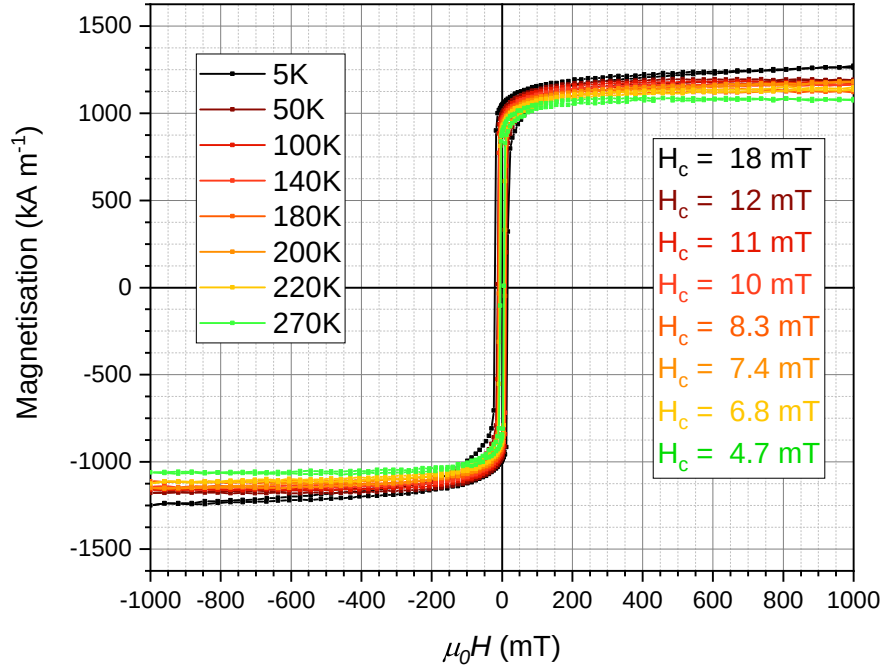


Figure 5.17: Low Temperature magnetisation vs. field loops, measured along $\varphi = 0^\circ$ for the Mn₂Au (001)/Fe (001) bilayer. The stacks were vacuum annealed at 350°C in an 800 mT field, along $\varphi = 0^\circ$, for 15 mins before being cooled in the PPMS from 300 K-5 K in a 1 T applied field, along $\varphi = 0^\circ$. The loops are colour coded according to the temperature of measurement which is displayed in the figure legend.

reversal. The coercive field of each loop is noted on the graph in the same colour which indicates the temperature at which the loop was measured. Looking first to the 270 K loop (green), the measured coercivity of the loop is 4.7 mT, which is much smaller than the coercivity measured at RT using the PMC Micromag VSM of ≈ 18 mT (see Figure 5.8). The origin of the discrepancy is not immediately clear and is difficult to explain. The FC cycles were performed with the black marker already on the samples. Given that marker inks typically use ferrous pigments to alter the dye colour it is possible that this was contributing to the coercive fields measured via RT VSM measurements as the vacuum environment of the FC procedure may have had a reducing effect on the ferrous pigments. Although measurement of a blank substrate coated with the same black permanent marker, using the PMC Micromag VSM only displayed a coercivity on the order $1\text{ mT} \pm 2\text{ mT}$. Between the two measurements, there was a considerable amount of time (on the order of 6 months), and the sample was subjected to a further 15 min FC cycle at 350°C . Although the sample was passivated with a 3 nm Ta layer, it is possible that this may have degraded over time. As the native Ta oxides, such as Ta₂O₅, which are initially protective, can become non-protective after an extended period of time and linear oxidation sets in [189].⁴ It is also possible that the Ta capping layer may not have been uniform resulting in the degradation of some parts of the stack while others remained unaffected. It could also be that the anneal caused degradation of the AFM domains due to diffusion, although that would be contradictory to what was

⁴This was not investigated due to time constraints.

observed in Chapter 4. There also may be a systematic element to the discrepancy, but this can't be said for certain without a comprehensive investigation of identical samples on both tools. Some of the systematic errors with the PPMS magnet will be listed below which make low field measurements difficult. As the magnetic field in the Micromag VSM is measured with a Hall probe, it can be considered, relatively, more accurate than the PPMS.

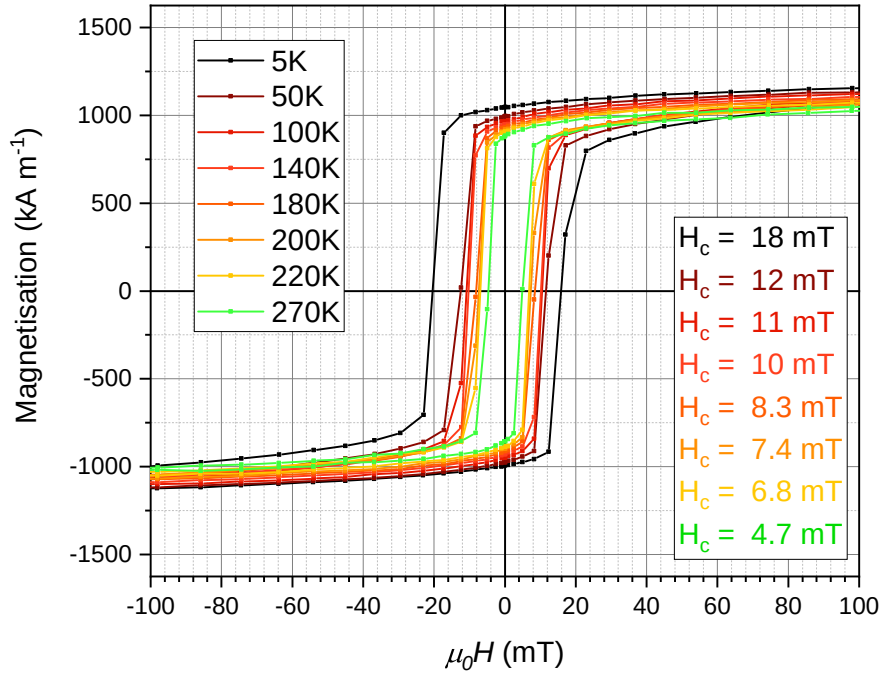


Figure 5.18: Reduced field range plot of the low temperature magnetisation vs. field loops Mn₂Au (001)/Fe (001) bilayer in the previous Figure for clarity of loops around magnetisation reversal. The loops are colour coded according to the temperature of measurement which is displayed in the figure legend.

The considerable coercive field, relative to that of uncoupled Fe, indicates that the FM/AFM layers are EC. The coercivities of the loops all appear to be relatively symmetric and there is no clear bias field apparent in the samples after FC. To get a better understanding of this, the temperature dependence of H_{c1} and H_{c2} and the H_{eb} (calculated according to Equation 17 in Chapter 1) are plotted in Figure 5.19. Before analysing the data there are some sources of error that first need to be considered. Defects in the superconducting wire windings which generate the magnetic field can cause magnetic flux to become pinned when the magnetic field is swept from a higher field value to zero field. This appears as a remanent field seen at the sample location, which can be as much as ± 12 mT in the 14 T superconducting magnet. The trapped flux may also escape over time causing a drift of the remanent field, which may appear as a bias field in a measurement where there is none.⁵ For field sweeps in a certain range (for example ± 1 T) this trapped flux should be consistent for all loops regardless

⁵Trapped flux value taken from following link, see for more information <https://www.qdusa.com/siteDocs/appNotes/1070-207.pdf>

of the temperature at which they were taken and so can be accounted for. Considering the value of the individual coercive fields now, the maximum difference in the values at higher temperatures is 0.5 mT indicating that there is minimal drift of the trapped flux in the magnet causing a bias field. To account for these errors any value for $H_{eb} \leq 1$ mT will be excluded.

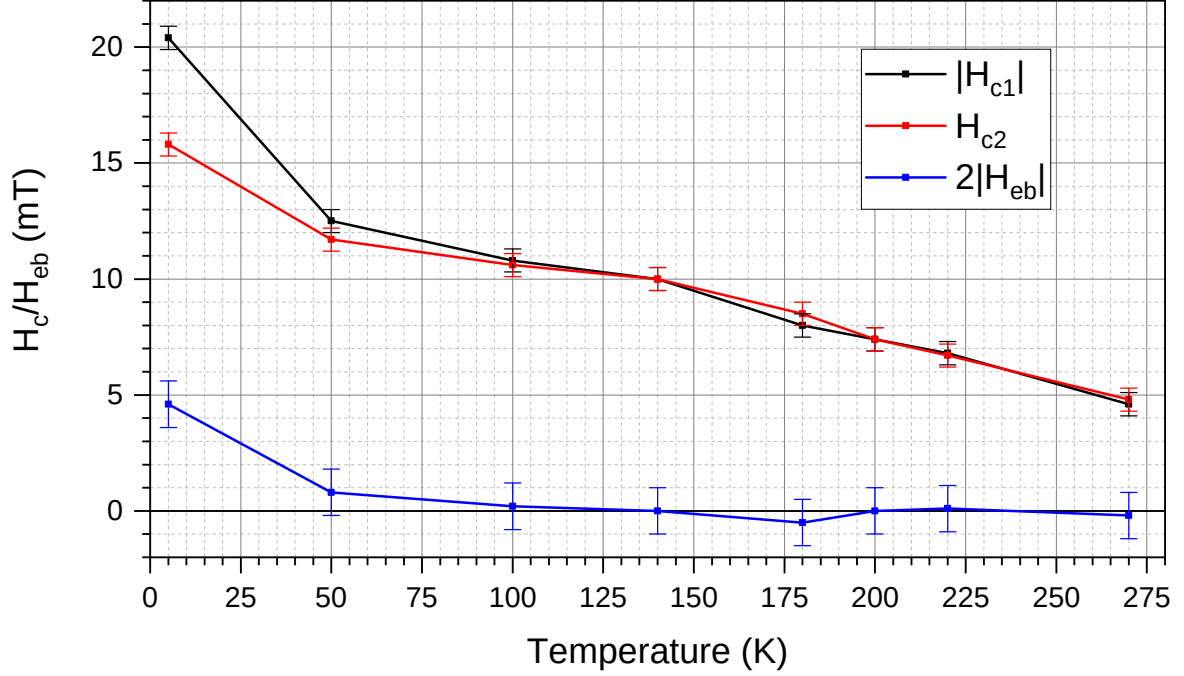


Figure 5.19: Temperature dependence of the coercive (H_{c1} and H_{c2}) and bias (H_{eb}) fields of the Mn_2Au (001)/Fe (001) after the two stage field cooling from 623 K-5 K. The modulus H_{c1} and of H_{eb} are displayed for the purposes of comparison, and the H_{eb} is doubled to make it easier to view the bias field, The lines through the data points are to guide the eye.

The loop taken at 5 K is the only loop where there is a bias field present, based on the restrictions set above and it has a nominal value of -2.3 mT. The negative sign of the bias is what is expected given the positive applied field during FC. This suggests that the blocking temperature of this stack is less than 50 K but given that there were no loops taken between 5 K-50 K is difficult to determine accurately. The low value for H_{eb} and ultra low blocking temperature suggest that the epitaxial Mn_2Au (001) layer has a low anisotropy caused by the reduced thickness of the AFM layer, meaning that the AFM moments at the interface only become pinned at ultra-low temperatures. This is in good agreement with previous work on epitaxial Mn_2Au (001) bilayers [32, 68]. The extremely low blocking temperature in comparison to Néel temperature of this stack is unusually low. One possibility is that the Mn_2Au (001) crystal structure is Au-terminated and there is an increased separation between the Fe moments and the FM Mn-sheets in the AFM Mn_2Au film, in comparison to traditional AFMs, such as MnO, giving rise to the low-anisotropy of the Mn_2Au layer. Another is that there is some small fraction of disorder in the Mn_2Au layer, evidenced by the modulation of

the Mn_2Au streaks observed in the RHEED shown in Figure 5.1. Finally, it is possible that the annealing temperature of 350°C was sufficient to induce the formation of an interfacial phase which is the source of the bias. FeMn is antiferromagnetic and forms in a wide stoichiometry range at 400°C [154] and there was a reduction in the magnetisation of the heterostructure after the FC procedure, suggesting the potential formation of an AFM alloy. It has a bulk Néel temperature of around 490 K, which is well below the FC temperature used. It is difficult to identify which scenario is most likely for this heterostructure without further characterisation.

5.5.2 Mn_2Au (110)/Fe (110)

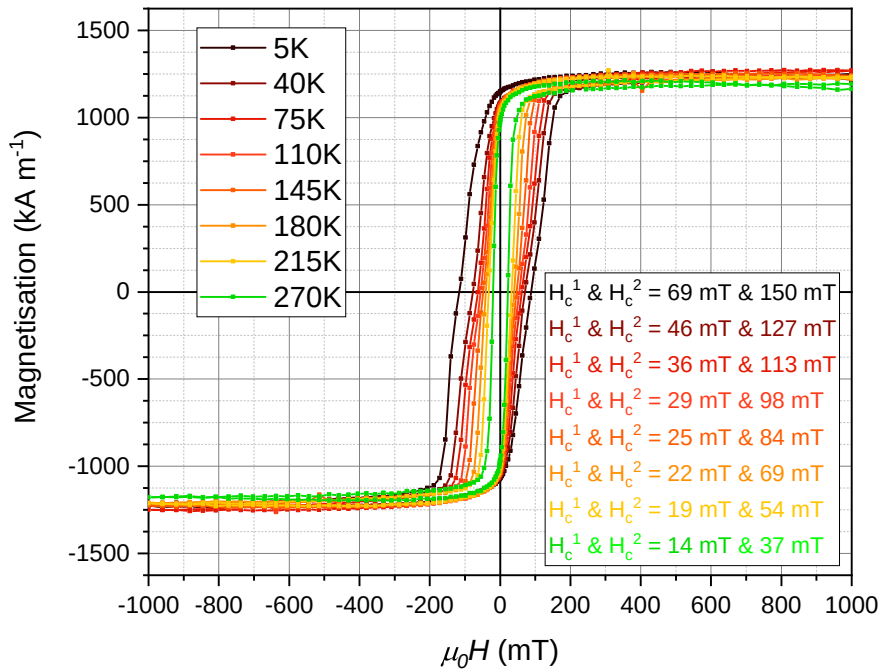


Figure 5.20: Low Temperature magnetisation vs. field loops, measured along $\varphi = 0^\circ$ for the Mn_2Au (110)/Fe (110) bilayer. The stacks were vacuum annealed at 350°C in an 800 mT field, along $\varphi = 0^\circ$, for 15 mins before being cooled in the PPMS from 300 K-5 K in a 1 T applied field, along $\varphi = 0^\circ$. The loops are colour coded according to the temperature of measurement which is displayed in the figure legend.

Figure 5.20 shows the corrected loops obtained from the Mn_2Au (110)/Fe (110) stack in the full field range between ± 1 T. The loops were measured, in order, at temperatures of 5 K, 40 K, 75 K, 110 K, 145 K, 180 K, 215 K and 270 K which are shown in the colours indicated in the graph legend. Similar to the Mn_2Au (001) loops in Figure 5.17, the Mn_2Au (110) loops show increasing saturation magnetisation with decreasing temperature as expected. And again there is a slight paramagnetic response visible in the loops at higher fields. This is particularly apparent in the lower temperature loops and is related to the marker ink used to mark $\varphi = 0^\circ$. As with the RT VSM, the measured values of the coercivities of the Mn_2Au (110)/Fe (110) stack are larger than the Mn_2Au (001)/Fe (001) stack. Again looking at the measured value of the coercivity

of the 270 K loop (green), it has a value of 21 mT which is less than the value of ≈ 26 mT observed at room temperature with the Micromag VSM. Similar to the Mn_2Au (001)/Fe (001) stack, there were approximately 6 months between the measurements at RT and those performed on the PPMS at low temperatures. The reduction is smaller than what was observed in the Mn_2Au (001)/Fe (001) stack, both in nominal terms and as a percentage. One could conclude that the change in the Mn_2Au (001)/Fe (001) stacks coercivities are unlikely to be entirely systematic and most likely indicates that the sample has been compromised through the additional FC cycle, degradation of the Ta capping layer or both. Looking at the loop taken at 5 K (black), there appears to be an asymmetry in the width of the descending and ascending branches of the hysteresis loop, even in the range of ± 1 T. To get a clearer view of the coercivities the loops must be plotted in a narrower field range.

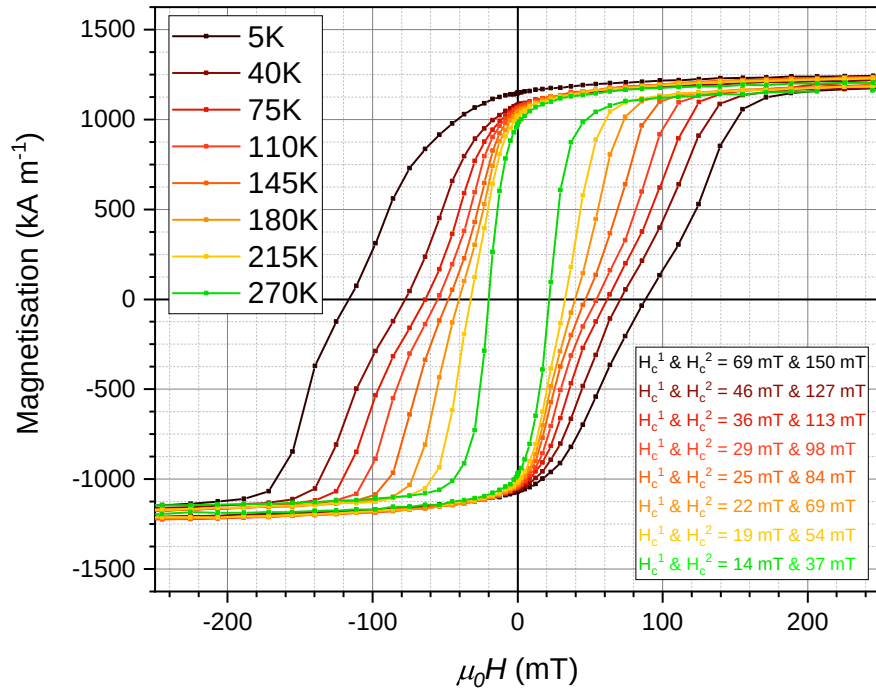


Figure 5.21: Reduced field range plot of the low temperature magnetisation vs. field loops Mn_2Au (110)/Fe (110) bilayer in the previous Figure for clarity of loops around magnetisation reversal. The loops are colour coded according to the temperature of measurement which is displayed in the figure legend.

Figure 5.21 shows the low temperature loops of the Mn_2Au (110)/Fe (110) stack in the narrower field range of ± 250 mT to illustrate the coercive fields around magnetisation reversal. It is clear that there are two coercive components to each of the loops; an outer coercivity H_c^2 and an inner coercivity H_c^1 . For reference, the outer and inner coercivities were determined by measuring the width of the loops along the 900 k A m^{-1} and the 500 k A m^{-1} Magnetisation lines. The coercive field of each loop is noted on the graph in the same colour which indicates the temperature the loop was measured at. The asymmetry of the zero magnetisation crossings, in the descending and ascending branches of the 5 K (black) hysteresis loop are clearly evident in this field range. If there

is asymmetry of the zero magnetisation crossings, in the descending and ascending branches of the other hysteresis loops it is not clearly evident to the eye, given the relatively large coercivity with respect to the small bias. One of the most prominent features of the loops in Figure 5.21 is the decreasing slopes of the descending and ascending branches with decreasing temperature. Intuitively, the increase in coercivity with decreasing temperature makes sense as the AFM moments become harder to rotate with decreasing temperature. The slope is more difficult to understand though; qualitatively it suggests that the reorientation of the FM magnetisation and thus the rotation of the AFM moments through the ECE becomes more gradual with decreasing temperature. This suggests that at lower temperatures, the AFM layer may display exchange spring-like behaviour, upon magnetisation reversal of the FM layer. These samples would benefit from the characterisation of the interfacial magnetisation dynamics under magnetisation reversal. Such characterisation is typically only possible using a combination of XMLD and, element-specific, XMCD measurements at synchrotrons. Typically PEEM is employed in conjunction with both techniques for visualisation of the magnetic domains [60, 89]. Another possibility is the use of polarised neutron reflectometry (PNR) to measure the magnetic depth profile of the AFM moments in this structure under different applied magnetic fields [190].

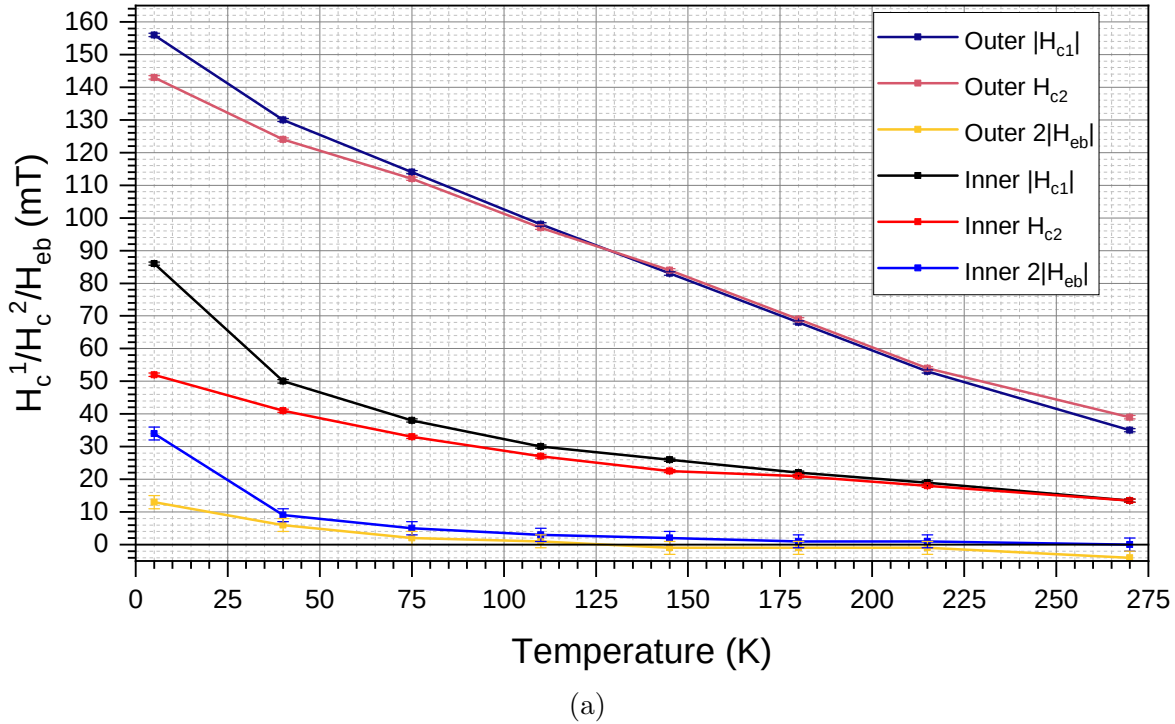


Figure 5.22: Temperature dependence of the coercive and bias fields of the Mn_2Au (110)/Fe (110) after the two stage field cooling from 623 K-5 K. The outer coercivity H_c^2 and an inner coercivity H_c^1 are both plotted as well as the resulting H_{eb} fields from each. The lines through the data points are to guide the eye.

Figure 5.22a show the temperature dependence of H_{c1} , H_{c2} and the H_{eb} field, for the outer coercivities H_c^2 and the inner coercivities H_c^1 . As with the Mn_2Au (001)/Fe

(001) stack, any bias field of ≤ 1 mT will be excluded. Under this framework, there are two points from H_c^2 and three from H_c^1 . For H_c^2 , these are the 5 K and 40 K loops and they each have H_{eb} values of -6.5 mT and -3 mT and for H_c^1 these are the 5 K, 40 K and 75 K loops and they each have H_{eb} values of -17 mT, -4.5 mT and -2.5 mT respectively. Again the sign of the bias is that which is expected for a positive applied magnetic field during FC. Exact determination of the blocking temperature is difficult again given the limited number of points, however, a linear fit of the bias field from H_c^2 , of the 5 K and 40 K points gives a value of T_b of 51 K. The temperature dependence of the bias field is typically not linear though [53], and so the actual blocking temperature is likely slightly greater than 51 K. The blocking temperature of the H_c^1 component is higher with the value a value greater than 75 K and an approximate value of 100 K. The blocking temperature of each component is higher than was found in the Mn_2Au (001)/Fe (001) stacks, but much lower than has been observed in other literature for disordered structures [31, 32].

The presence of two coercive and bias components is difficult to explain, but it suggests that there are two distinct thickness regions with different properties. Both biases are indicative of exchange spring type behaviour but suggest non-coherent rotation throughout the AFM layer. In other words, there may be two different angles of rotation for the AFM moments at different depth profiles in the AFM associated with the different thickness profiles. As noted previously, there was a reduction in the Fe magnetisation after the 350°C FC procedure, and that AFM FeMn forms in a wide stoichiometry range (30 %-50 % Mn at 400°C [154]) with a bulk Néel temperature of 490 K [20] well below the FC temperature used. As such the lower blocking temperature component may be from interfacial FeMn and the higher blocking temperature component is associated with the Mn_2Au layer. Another possibility is that there is an Mn-poor and an Mn-rich region in the Mn_2Au layer which has different exchange coupling properties. The origin of the larger blocking temperature component in this Mn_2Au (110)/Fe (110) heterostructure is not immediately clear, but a likely origin may lie in the disorder that was present in the Mn_2Au RHEED images after deposition, but this disorder disappeared from the surface of the Mn_2Au layer RHEED after the 450°C annealing cycle before the Fe layer was deposited.

Investigation of the micro-structure of the stack using a technique such as high resolution cross-sectional scanning tunneling electron microscopy may help elucidate which of cases above is the source of biases, as in other more disordered Mn_2Au structures. The role of the compensated moments at the AFM interface in Mn_2Au (110) is also unclear and the source of the bias could be interface roughness causing uncompensated moments at the interface, as described in Malozemoff's model for EB [61]. Investigation using XMCD and XMLD may elucidate the origin of the pinned moments at the interface for this structure. The higher blocking temperature bias field at 5 K is significant and is comparable to the bias fields observed in disordered Mn_2Au (001)/Fe

(001) structures, at similar temperatures and thicknesses [32, 68]. However it is smaller than the ≈ 35 mT bias field observed for a Fe (3 nm)/polycrystalline Mn_2Au (10 nm) structure [31].

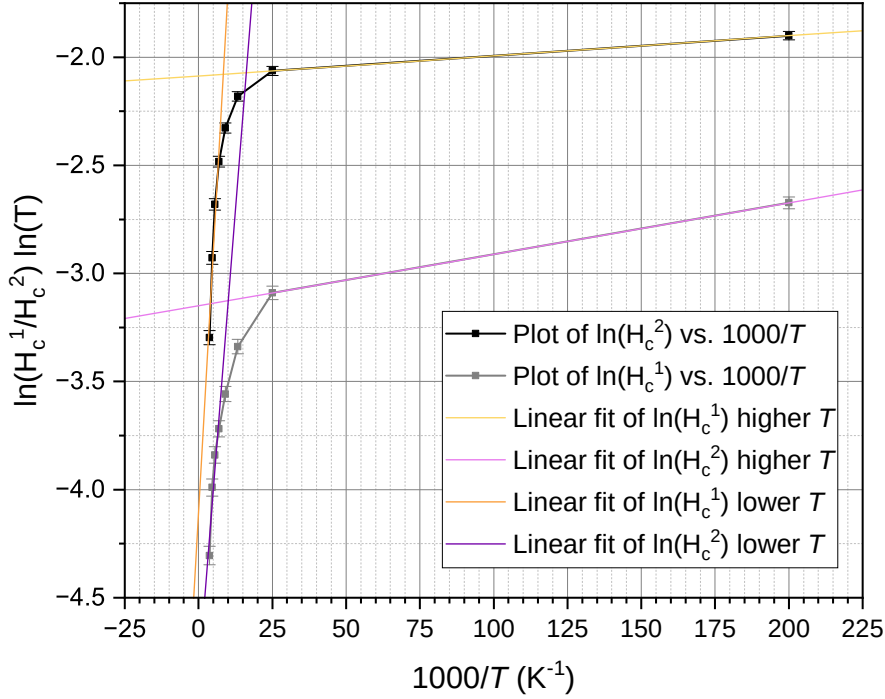


Figure 5.23: Arrhenius style plot of the two coercive phases, H_c^1 (grey) and H_c^2 (black), from the Mn_2Au (110)/Fe (110) bilayer in the form of $\ln(H_c)$ vs. $1000/T$. The plot shows two distinct slopes associated with above and below the blocking temperature for each coercive and bias phase. Linear fits of both H_c^1 and H_c^2 at low and high temperatures are shown in orange and purple respectively.

Figure 5.23 shows Arrhenius style plots of $\ln(H_c)$ vs. $1000/T$ using the values of coercivity from the two coercive phases of the Mn_2Au (110)/Fe (110) bilayer H_c^1 (grey) and H_c^2 (black). These are plotted using the same equations described for the flux in Chapter 2, substituting the flux with H_c in this case. Two distinct slopes can be seen in each plot, broadly correlated with the temperatures above and below the blocking temperature for each phase. Linear fits of both the lower temperature region and higher temperature region are shown for both H_c^1 and H_c^2 in orange and purple respectively. The fits of the lower temperature region can be considered to be more accurate as they incorporate four data points, while the higher temperature region only has two points due to the limited number of loops measured in this region. Using the slopes the characteristic anisotropy energy associated with each region can be extracted from the slope. Considering H_c^1 first; the anisotropy energy below the blocking temperature was found to be $20.8 \text{ meV} \pm 3.5 \text{ meV}$ while that above the blocking temperature was found to be $0.08 \text{ meV} \pm 0.05 \text{ meV}$. Similarly, for H_c^2 , the region above the below the blocking temperature was found to give an anisotropy energy of $14.8 \text{ meV} \pm 3.4 \text{ meV}$, while the region above the blocking temperature results in a value for the anisotropy energy of $0.21 \text{ meV} \pm 0.09 \text{ meV}$. Note that all the energies are per unit cell.

To summarise, exchange bias was successfully induced in the Mn₂Au (110)/Fe (110) heterostructure, with a significantly higher blocking temperature bias field and large coercivity of -17 mT and 65 mT at 5 K . The presence of both the bias and coercive field, in addition to the shape of the hysteresis loop, indicates exchange spring-like behaviour of the AFM moments in Mn₂Au upon magnetisation reversal. The blocking temperature for this component was determined to be approximately 100 K . There was also a lower blocking temperature component with a smaller bias field and extremely large coercivity of -7 mT and 150 mT at 5 K . The blocking temperature of this component was determined to be on the order of 50 K , but could not be determined exactly due to the limited number of loops displaying a bias field. The origin of both bias fields is unclear and requires further study.

5.5.3 Estimation of the Néel Temperature

The temperature dependence of the magnitude of the magnetic moments or magnetisation, will typically show a relationship where the magnitude decreases gradually until some critical temperature (T_{crit}) where it disappears entirely. An example of this is shown for a FM material in Figure 1.1 where the critical temperature is (T_C). This magnetic phase transition is typically described by a power law relationship between the magnitude of the magnetisation/individual moments and the critical temperature. A general form of this equation is shown below:

$$\frac{M}{M_0} = \left(1 - \frac{T}{T_{crit}}\right)^\beta \quad (1)$$

where M and M_0 describe the magnitude of the magnetisation at a temperature T and at a temperature of 0 K respectively. The exponent β typically ranges from $\frac{1}{2}$ to $\frac{1}{3}$ [191]. This relationship is also valid for the Néel temperature but it would use the magnitude of the magnetic moments and a modified version of Equation 1 above with $\beta = 0.3$ and $\alpha = 2$ as was done with Mn₂Au in [23] and can be seen below in Equation 2:

$$\frac{M}{M_0} = \left(1 - \left(\frac{T}{T_{crit}}\right)^\alpha\right)^\beta \quad (2)$$

Given that the EC relationship between FM/AFM bilayers results in a measurably increased coercivity, which in the absence of a bias will disappear at a temperature which approximates the Néel temperature of that particular AFM layer. Modifying the general equation above to reflect the temperature dependence of the coercive field of an EC FM/AFM bilayer results in the following equation:

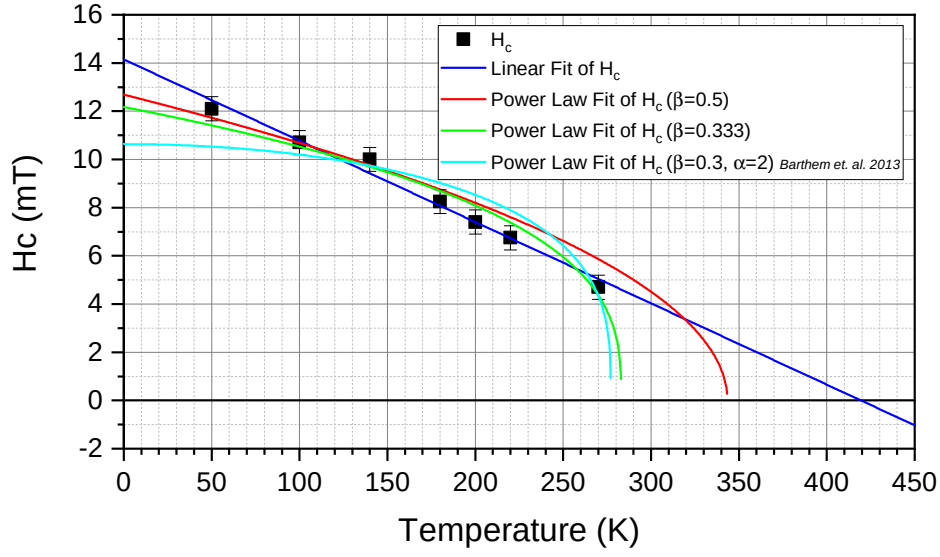
$$H_c(T) = H_c(0)\sqrt{1 - \frac{T}{T_N}} \quad (3)$$

Where $H_c(T)$ and $H_c(0)$ represent the coercivities of the bilayer at a temperature T and a temperature of 0 K respectively. The critical temperature from Equation 1 is replaced with the Néel temperature and the exponent β is set to $\frac{1}{2}$. This value of β is that which is given by Mean-field theory. This is an identical approach as was taken for the Néel temperature estimation in [68] and is done so only for comparison with the estimations for similar films in that work.

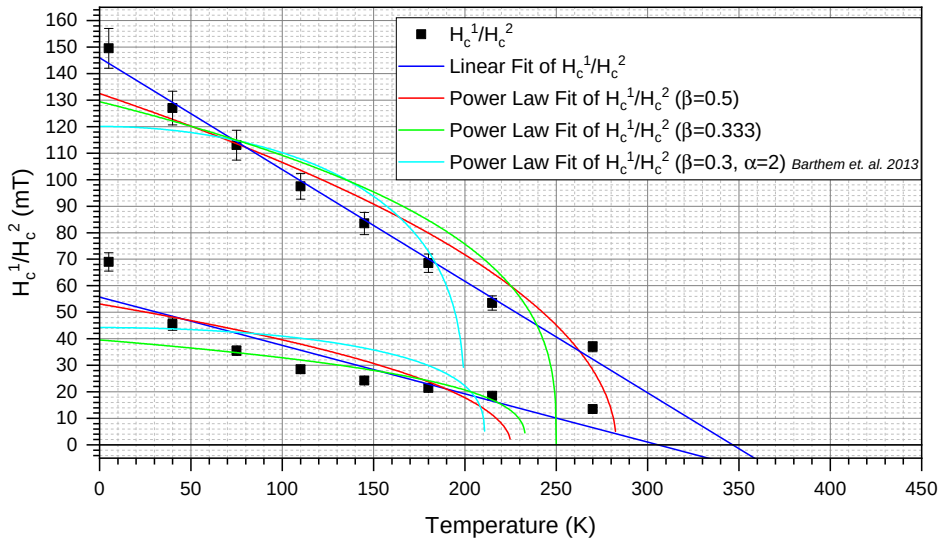
Using Equation 3 from above, the temperature dependent coercivity data which were shown in Figure 5.19 and Figure 5.22a can be fit to estimate the effective Néel temperature of the Mn₂Au layer. The coercive field values which result in a bias are excluded as they would distort the fit. Figure 5.24 shows the results of the fit using Equation 3 in red. The fits were performed in Origin Pro plotting software using the orthogonal distance regression iteration algorithm. A linear fit of each data set is shown also for contrast in blue. From Figure 5.24a the fit resulted in a value of 12.7 mT for $H_c(0)$ and 343 K for the Néel temperature of the Mn₂Au (001)/Fe (001) bilayer. For contrast the linear fit resulted in values of 14.1 mT and 418 K for the respective parameters. Similarly from Figure 5.24b the fit resulted values for $H_c(0)$ of 66.2 mT and 296 K for the Mn₂Au (110)/Fe (110) bilayer. The linear fit of this data results in values of 78.1 mT and 367 K for the respective parameters. The values produced using this method for similar Mn₂Au films in [68] were in the range of 470 K-550 K. The coercivities are also fit with Equation 2 (cyan) and for $\beta = \frac{1}{3}$ (green). For an increasing value of β the resulting fit gets quantitatively and qualitatively worse than those fit with $\beta = \frac{1}{3}$ and the linear fit.

The values for the fit which put the Néel temperature of the Mn₂Au (001) layer at a larger value than that of the Mn₂Au (110), are in good agreement with *in-situ* RHEED characterisation of the Mn₂Au layers from each stack. The power law and linear fits of the Néel temperature only serve to highlight that the field cooling temperature of 350 °C was well above the effective Néel temperature of both films. The fits using Equation 3 are generally poor for these datasets though, as highlighted by the much better linear fits of both datasets. This could partially be due to the limited number of values for the coercivity and temperature for each stack, but also the function just may not be a good approximation of the Néel temperature. The accuracy of the fit would be improved for a larger number of data points over a larger temperature range. It would be interesting to map the coercivity of an exchange coupled bilayer versus temperature, up to the point at which it was no longer exchange coupled. Then the validity of the function could be tested properly, or the value of β could be fit as a free parameter to improve the model, or the model disregarded altogether as Mean free theory does not appear to be a good approximation for the coercivity vs temperature

profile of an exchange coupled system.



(a)



(b)

Figure 5.24: Temperature dependence of the coercive fields of the (a) Mn_2Au (110)/Fe (110) bilayer and (b) Mn_2Au (110)/Fe (110) bilayer after field cooling. The Néel temperature of the Mn_2Au layers are estimated using the simple power law relation in Equation 3 (above) to fit the coercivities as a function of temperature (red). The data is also fit using Equation 1 for $\beta = \frac{1}{3}$ (green) and Equation 2 for $\beta = 0.3, \alpha = 2$ (cyan) as used for Mn_2Au in [23]. The temperature dependence of the coercivities are also fit linearly for contrast (blue).

5.6 Conclusion

In this chapter Mn_2Au (001) and Mn_2Au (110) based heterostructures were grown for determining the exchange coupling properties of each Mn_2Au orientation. The Mn_2Au layer was grown using the technique developed in [34] of deposition at 270°C

and a post annealing cycle of 1 hr at 450°C . The surface of the Mn_2Au layer was characterised using RHEED before and after the annealing cycle and was found to have minimal influence on this particular film evidenced by the near identical RHEED images for both. The Mn_2Au (001) heterostructures were grown with the form of $\text{r-Al}_2\text{O}_3/\text{Ta}/\text{Mn}_2\text{Au}/\text{Fe}/\text{TaO}_x$. Both $\theta - 2\theta$ and azimuthal ϕ XRD scans were used to determine the epitaxial relationship of Al_2O_3 ($1\bar{1}02$) $\parallel$ Ta (001) $\parallel$ Mn_2Au (001) $\parallel$ Fe (001) in the out-plane direction and Ta [100] $\parallel$ Mn_2Au [100] $\parallel$ Fe [100] in-plane, which was consistent with what was observed in a combination of works [32–34]. The thickness of each of the layers were 8 nm Ta, 5 nm Mn_2Au , 4 nm Fe, and a Ta capping layer of 3 nm which were all determined from known growth rates.

The Mn_2Au (110) heterostructure was of the form $\text{r-Al}_2\text{O}_3/\text{Pt}/\text{Mn}_2\text{Au}/\text{Fe}/\text{TaO}_x$, with the same nominal thicknesses for each of the layers as the (001) stack. The Mn_2Au layer was deposited at 270°C with a post annealing cycle of 1 hr at 450°C to be consistent with the Mn_2Au (110) stack. The Mn_2Au layer was found to be disordered after deposition, with evidence of the (110) phase and other polycrystalline phases present in the RHEED image; after the annealing cycle the surface of the film was noticeably smoother and the presence of the polycrystalline phases had disappeared from the surface of the film according to the RHEED image. Qualitatively, this indicated the Mn_2Au (110) layer was slightly more disordered than the Mn_2Au (001) layer. $\theta - 2\theta$ XRD scans were unable to directly detect the Mn_2Au (110) diffraction peak as the higher relative intensity Pt (111) peak obscured its presence. Azimuthal ϕ XRD scans were employed to detect the presence of the Mn_2Au phase, and the scan of the $\{101\}$ peaks showed the expected symmetry for an epitaxial Mn_2Au (110) layer grown on Pt (111). This is in contrast to the Mn_2Au (110) films grown on Pt (111) in Chapter 1, which showed that the films grew with three in-plane crystalline domains. This suggests that the additional annealing cycle used for this Mn_2Au (110) film, caused diffusion of the Mn and Au atoms allowing the Mn_2Au layer to form one crystalline in-plane domain. The reliability of this method in forming epitaxial Mn_2Au (110) layers on a Pt (111) seed layer will require further investigation.

The magnetic properties of both the Mn_2Au (001) and Mn_2Au (110) stacks were comprehensively analysed, before and after a 350°C vacuum anneal and cooling cycle to RT in an 800 mT permanent magnet, using RT VSM.

The Mn_2Au (001) stack was found to have an increased coercivity with respect to that of Fe thin films, for both the as-deposited and FC loops taken along the direction of FC. This was on the order of 18 mT for both loops indicating that there was exchange coupling between the $\text{Mn}_2\text{Au}/\text{Fe}$ layers. It was concluded that the deposition temperature of the Fe layer of 250°C was sufficient to induce EC between the Mn_2Au and Fe layers. However, it was unclear if the FC temperature was sufficient to overcome the effective Néel temperature of the films from the in-plane loops alone.

Azimuthal in-plane hysteresis loops were measured every 5° of in-plane rotation of the substrate. From these loops, the ratio of the remanent magnetisation to the saturation magnetisation of the loops showed that the exchange coupling was biaxial both before and after the FC cycle. The coercive profile of the azimuthal loops displayed 8 maxima before annealing. Four were found to point along the exchange coupling axes, which corresponded with the easy axes of the FM layer. The other four corresponded to the known positions of the Mn₂Au easy axes, which were at 45° to the Fe easy axes and it was speculated that there was a large percentage of re-switchable AFM moments at these positions which resulted in the maxima in coercivity observed at these positions. After the annealing cycle, the coercivity profile showed two primary maxima, which corresponded to the direction of the applied field during FC. There were six secondary maxima, two of which aligned with the Fe easy axes perpendicular to the FC direction. The other four were rotated on the order of 5°-15° away from the direction of FC. It was speculated that this indicated rotation of the Mn₂Au AFM easy axes, given the preference for AFMs to maximise $\chi_{\perp}$ over $\chi_{\parallel}$ in an applied magnetic field, excluding other factors. This would require further investigation to confirm, of course. From the overall change in the coercivity profile, it was concluded that the FC temperature of 350 °C was sufficient to overcome the effective Néel temperature of the Mn₂Au (001) layer. It was clear that there was no bias field to any of the loops after FC, suggesting that if the films would display exchange bias, it would only be present at lower temperatures.

The Mn₂Au (110) stack was also found to have an increased coercivity as-deposited indicating exchange coupling between the layers caused induced by the deposition temperature of the Fe layer. After the FC cycle, the coercivity measured along the direction of FC was found to be significantly increased from the as-deposited loop. From approximately 11 mT-26 mT and the shape of the loops were found to be different, suggesting that EC may be uniaxial. Both the anisotropy and coercivity profiles from the azimuthal loops indicated that the as-deposited Mn₂Au (110) stack displayed uniaxial exchange coupling. This correlated well with the XRD analysis suggesting that the Mn₂Au layer was epitaxial, but the crystalline direction of the exchange coupling relative to the expected easy axes of the AFM Mn₂Au moments was not able to be determined. This will be addressed in some future work. The anisotropy and coercivity profiles after FC were consistent with the reorientation of the FM and thus EC easy axes along the direction of the applied field. This conclusively demonstrated that the 350 °C FC temperature was sufficient to overcome the effective Néel temperature of the Mn₂Au (110) layer. From this, the coercivity along the direction of EC was determined to increase from approximately 16 mT-26 mT, which was significant. This was attributed to the presence of both the [110] and [1 $\bar{1}$ 0] Mn₂Au easy axes being present in the as-deposited stack, which was consistent with the literature for Mn₂Au (001) thin films [188]; which were reoriented by the FC process. Again there was no

bias field present in any of the samples, indicating that if this stack were to display exchange bias, it would be at temperatures below RT.

Hysteresis loops of both the Mn_2Au (001) and Mn_2Au (110) stacks were measured via low temperature VSM in a PPMS in a range of 5 K-270 K after cooling in a 1 T field applied along the direction of the FC from 623 K-300 K in the 800 mT permanent magnet.

The Mn_2Au (001) bilayers were found to display a minimal bias field of -2.3 mT at 5 K, which had disappeared at 50 K. The sign of the shift was consistent with the positive applied field during cooling. This indicated that the blocking temperature of the Mn_2Au stack was of the order of 10 K-15 K. Given that the Néel temperature is larger than 300 K, this implies weak anisotropy of the Mn_2Au moments in this 5 nm layer, meaning they only become pinned at ultra-low temperatures. This was consistent with results obtained from epitaxial Mn_2Au (001)/Fe (001) bilayers of similar thicknesses to those investigated here [32, 68]. An alternative source of the bias observed could be due to the formation of a thin interfacial AFM layer such FeMn. There was a slight reduction in the magnetisation post FC which lends credence to this suggestion, and the FeMn forms in a wide stoichiometry range at a temperature of 400°C [93] which is only slightly above the FC temperature of 350°C . To elucidate the exact origin of the bias would require the use of techniques such as XMCD and XMLD.

The Mn_2Au (110) bilayers were found to display two separate coercivity components each also displaying a bias at ultralow temperatures. The inner component H_c^1 displayed a significant bias and coercive field of -17 mT and 69 mT at 5 K. The sign of the bias was again consistent with the negative applied field during cooling. The bias field persisted in the loop taken at 40 K with a value of -5 mT, and the 75 K loops displayed a bias field of -2.5 mT suggesting that the blocking temperature of this component was approximately 100 K. The inner component H_c^2 displayed a smaller bias field and extremely large coercivity of -7 mT and 150 mT at 5 K. Which had an estimated blocking temperature of 50 K. As expected the coercivities of the loops increased with decreasing temperature indicating that rotation of the AFM moments via magnetisation reversal of the FM layer becomes more difficult. However, the slopes of the descending and ascending branches of the hysteresis loops decreased significantly with decreasing temperature also. This indicates a more gradual reorientation of the AFM moments upon reversal of the FM magnetisation. For the lowest temperature loops, where there is a bias present, this reorientation of the AFM may only be partial, suggestive of exchange spring-like behaviour of the AFM moments [12, 60]. The presence of two coercivity and bias components of varying magnitudes suggests that there is two distinct thickness regions with differing AFM moment rotation. Additionally, the origin of the two-phase exchange bias in this heterostructure was not immediately clear. Similar to the Mn_2Au (001) heterostructure a reduction in the

magnetisation of the loops was observed after the field cooling was observed. This suggests that an interfacial antiferromagnetic FeMn layer may have formed. Another possible reason for the two phases would be the formation of an Mn-rich and an Mn-poor region in the Mn_2Au thickness with different exchange coupling properties. To conclusively confirm this experiments at a large-scale facility, such as XMLD and XMCD at a synchrotron facility are needed. The anisotropy energies associated with each coercivity component below their blocking temperature were extracted from an Arrhenius-style plot. The anisotropy energy of H_c^1 was estimated to be $20.8 \text{ meV} \pm 3.5 \text{ meV}$, while that associated with H_c^2 was estimated to be $14.8 \text{ meV} \pm 3.4 \text{ meV}$. Both values are in energy per unit cell.

Finally, the Néel temperature of both exchange coupled bilayers was estimated by fitting the temperature dependent coercivities of each using a modified power law function, as was done for similar bilayers [68]. In general the fits produced based on Mean field theory resulted in qualitatively and quantitatively poor fits of the experimentally observed coercivities, suggesting that it is not suitable for modelling the temperature dependent coercivity profiles of exchange coupled bilayers. A linear fit of the data produced the best fit in each case. The Néel temperature of the Mn_2Au (001) bilayer was estimated to be on the order of 340 K, while the Mn_2Au (110) Néel temperature was estimated to be on the order of 300 K. These estimates with T_N (001) & T_N (110) correlated well with the structural analysis of each Mn_2Au layer via RHEED. They also serve to illustrate that the FC temperature of 623 K (350 °C) was sufficient for the reorientation of the AFM moments.

Chapter 6

Conclusion and Future Work

6.1 Conclusion

This thesis presents the growth and characterisation of Mn_2Au thin films and heterostructures and the work can be split broadly into two sections: (1) the development of a method for growing Mn_2Au thin films via MBE. (2) The integration of these Mn_2Au films into both FM/ Mn_2Au and Mn_2Au /FM based heterostructures working towards the future use of Mn_2Au in devices relying on the ECE.

Chapter 3 detailed the growth of thin film Mn_2Au on MgO (001) oriented substrates, using a co-deposition method where the ratio of the deposition rates for Mn:Au was 3:1. This yielded rough, polycrystalline films with excess Mn and were discontinuous for deposition temperatures above 400°C . Similarly, Mn_2Au films were grown on $\text{r-Al}_2\text{O}_3$ substrates with a refined flux ratio of Mn:Au atoms of 2:1. This was achieved through the careful measurement of the flux of the atoms as a function of k-cell temperature using a beam pressure monitor. This method yielded polycrystalline Mn_2Au films at a number of deposition temperatures, which were again discontinuous at deposition temperatures above 400°C . The latter half of this work utilised the epitaxial relationship between Pt (111) and Al_2O_3 (0001) for use of the Pt seed layer for Mn_2Au thin films [107, 133]. The Mn_2Au films were again deposited with a flux ratio of 2:1 for Mn:Au and yielded single out-of-plane (110) oriented Mn_2Au films. The Mn_2Au (110) films were analysed using XRD, XRR and the FWHM of the (110) rocking curve to determine the optimum deposition temperature, which was found to be 250°C . The films grown at this temperature were found to display Pendellösung fringes emanating from the Pt (111) and Mn_2Au (110) XRD reflexes, indicating that the crystalline domains from both films had continuous crystalline domains throughout the thickness of each layer. The optimum films also displayed sub nm surface roughness, with the FWHM of the Mn_2Au (110) rocking curve determined to be 0.011° , which is close to the resolution limit of the HRXRD used for the measurement. Azimuthal XRD

scans determined that the films displayed three in-plane crystalline domains, which were present in the films in roughly equal proportions. Analysis of the RHEED streak spacings, with respect to the reference Al_2O_3 values, indicated that the Mn_2Au films grew with minimal in-plane strain with respect to bulk values, while similar analysis of the (110) XRD reflex indicated minimal out-of-plane strain [92]. This work was, in part, published [136].

Chapter 4 dealt with the growth and characterisation of $\text{Co}/\text{Mn}_2\text{Au}$ and $\text{Fe}/\text{Mn}_2\text{Au}$ heterostructures. The $\text{Co}/\text{Mn}_2\text{Au}$ heterostructures were determined to have an out-of-plane epitaxial relation of Al_2O_3 (0001)||Pt (111)||Co (111)|| Mn_2Au (110) while the $\text{Fe}/\text{Mn}_2\text{Au}$ heterostructures were determined to have an out-of-plane epitaxial relation of Al_2O_3 (0001)||Pt (111)||Fe (110)|| Mn_2Au (110). Analysis of the Mn_2Au RHEED streak spacings in both types of heterostructures showed modulation in the width of the streaks which indicated that there were multiple in-plane rotational domains. Given the hcp nature of the Mn_2Au (110) surface and the Co (111) surface and the pseudo-hcp nature of the Fe (110) surface, suggests that there are up to 6 possible in-plane crystalline domains, and that Mn_2Au (110) has no preferential in-plane growth direction on either fcc Co (111) or bcc Fe (110). Strain analysis was performed on the RHEED streak spacings relative to the known spacings of the Al_2O_3 substrate. The Mn_2Au layer was found to grow with an expansion of the possible in-plane interatomic spacings, over a range of Mn_2Au thicknesses (2.5 nm-10 nm), in both types of heterostructures. In the $\text{Co}/\text{Mn}_2\text{Au}$ heterostructures the in-plane expansion was accompanied by a concomitant contraction in the out-of-plane inter-layer spacing along the [110] direction.

Both types of heterostructures were subjected to annealing under vacuum conditions at 350 °C and 500 °C and were subject to further crystallographic characterisation post-anneal. The Mn_2Au layers in each heterostructure improved in crystalline quality after annealing at both temperatures, as evidenced by the increasing relative intensity of the Mn_2Au (110) reflex. The samples annealed at 500 °C showed the highest relative increase in the intensity of the Mn_2Au (110) peak. The Pt/Co and Pt/Fe seed layers in both types of heterostructures displayed alloying in the post-anneal XRD patterns. In the case of the Pt/Co heterostructures, the thickness ratio of Pt to Co of 1:4 resulted in the formation of Co_3Pt at the interface. In the Pt/Fe seed layers, the thickness ratio was 1:1.2 which even at the lower temperature anneal resulted in the formation of some L1_0 ordered FePt at the interface.

During the anneal under vacuum conditions, an 800mT field was applied arbitrarily along one in-plane axis of the heterostructures. The magnetic properties of each of the stacks were investigated in their as-deposited state, and after the 350 °C and 500 °C vacuum anneals. For the as-deposited $\text{Co}/\text{Mn}_2\text{Au}$ heterostructures, the 7.5 nm and 10 nm samples showed an increased coercivity, beyond what was expected for Co thin

films, which indicated that there was EC between the Co/Mn₂Au bilayer that was induced by the 200 °C growth temperature used for the Mn₂Au layer. The 2.5 nm and 5 nm samples showed a coercivity representative of an uncoupled Co layer, which when combined with the data from the thicker heterostructures, suggests that the room temperature measurements were above the effective Néel temperature of the 2.5 nm and 5 nm Mn₂Au layers. There was an increase in the coercivity of each heterostructure after the 350 °C annealing cycle and again after the 500 °C annealing cycle, which was attributed to the increasing crystalline quality of the Mn₂Au layer observed in the XRD scans. With the increasing thickness of the AFM Mn₂Au layer for a fixed thickness of the FM Co layer, the trend in coercivity correlated well with what was observed in other FM/AFM exchange coupled systems [12, 52]. No exchange bias was observed in any of the heterostructures after the annealing cycles. The reason for this could not be identified within the scope of the experiments shown in this work. The Fe/Mn₂Au heterostructures were found to be unsuitable for studying the ECE in Mn₂Au due to the formation of L1₀ ordered FePt, which has a coercivity much larger than what would be expected from the EC effect.

Chapter 5 investigated the ECE in both Mn₂Au (001)/Fe (001) and Mn₂Au (110)/Fe (110) based heterostructures. The Mn₂Au layers in both heterostructures were grown according to parameters reported in [34], which consisted of a deposition temperature of 270 °C and a post annealing cycle at 450 °C for 1 hr. The thicknesses of the Mn₂Au and Fe layers were 5 nm and 4 nm respectively. The Mn₂Au (001) structure consisted of r-Al₂O₃/Ta (001)/Mn₂Au (001)/Fe (001)/TaO_x with the out-of-plane orientation confirmed via $\theta-2\theta$ XRD scans. Azimuthal XRD scans determined that the heterostructure had the same in-plane epitaxial relationship as was reported elsewhere [32–34]. The Mn₂Au (110) stack structure consisted of c-Al₂O₃/Pt (111)/Mn₂Au (110)/Fe (110)/TaO_x as was determined using a combination of $\theta-2\theta$ and azimuthal XRD scans. The azimuthal XRD scans revealed that the Mn₂Au (110) layer had a single in-plane orientation, in contrast to those shown in Chapter 3 which consisted of three in-plane crystalline domains. This was likely driven by the additional annealing step at 450 °C post-deposition of the Mn₂Au (110) layer in this work. Qualitative analysis of the Mn₂Au RHEED images post-deposition and post-annealing revealed that the Mn₂Au (110) layer was more disordered than the Mn₂Au (001) layer.

The magnetic properties of both stacks were comprehensively analysed using room temperature VSM measurements, both as-deposited and after a 1 hr vacuum anneal at 350 °C, cooled to room temperature, all in an 800 mT applied magnetic field. Both stacks were characterised using azimuthal in-plane VSM hysteresis loops taken every 5° of in-plane rotation. For the Mn₂Au (001) stack the coercivity of the loops was found to be on the order of 18 mT before and after the FC cycle, when measured along the direction of the anneal. This indicated EC between the FM and AFM layers, which appeared to be unchanged by the FC procedure. From the azimuthal loops,

profiles of the azimuthal magnetocrystalline anisotropy and the coercivity of the stacks were investigated. The anisotropy profile indicated biaxial exchange coupling between the layers which was unaffected by the FC procedure. The as-deposited coercivity profile displayed eight maxima, four of which aligned with the expected Fe easy axes which lay along the same directions indicated by the anisotropy profile. The other four maxima lay along the FM hard axes which were 45° rotated from the easy axes. These maxima corresponded to the reported positions of the AFM moment easy axes of $[110]$ and $[1\bar{1}0]$ for Mn_2Au [188]. Post-FC the coercivity profile consisted of two primary maxima, which were along the direction of FC, and six secondary maxima. Two of the six secondary maxima lay perpendicular to the primary maxima along the direction of FC and corresponded with the position of the FM easy axis. The other four maxima were rotated by 5° - 15° from the corresponding maxima in the as-deposited profile; the rotation was away from the direction of the applied field. It was suggested that this may indicate a rotation of easy axes, given the preference for AFMs to maximise $\chi_\perp$ over $\chi_\parallel$ in an applied magnetic field. Further investigation would be necessary to experimentally confirm this suggestion. In the Mn_2Au (110) stack, there was an increase in the coercivity from 11 mT-26 mT, between the as-deposited and FC-loops along the direction of FC. This indicated EC between the FM/AFM layers. Investigation of the anisotropy and coercive profiles indicated that the stack has uniaxial anisotropy of the EC in the as-deposited state, which was reoriented by the FC process. This revealed that the increase in coercivity along the easy axis of the EC was in the range of 16 mT-26 mT, which was a significant increase. The uniaxial anisotropy of the FM layer and the EC was in good agreement with the XRD suggesting that the Mn_2Au (110) layer was epitaxial. This suggested that both of the Mn_2Au easy axes of $[110]$ and $[1\bar{1}0]$ were present in the layer after deposition, causing the FM moments to align preferentially with a uniaxial easy axis. This large increase in the EC coercivity post FC, was ascribed to the reorientation of both sets of easy axis moments so that they both contributed to the EC between the FM and AFM layers. This analysis clearly indicated that the FC temperature of 350°C was above T_N^* for each Mn_2Au layer. No bias field was present in either stack at room temperature.

Low temperature VSM loops were measured in the range of 5 K-270 K, after both of the stacks were field cooled; first for 15 minutes from 623 K-300 K in the 800 mT field, and then from 300 K-5 K in a 1 T applied field. The Mn_2Au (001) stack was found to only have a small bias field of -2.3 mT at 5 K, which suggested that the blocking temperature was in the region of 10 K-15 K. This was consistent with similar work on epitaxial Mn_2Au (001)/Fe (001) bilayers [32, 68]. Given the larger than RT T_N^* of this layer, as evidenced by the EC at room temperature, this suggests the presence of a weak anisotropy of the AFM moments in this thin Mn_2Au layer; such that the AFM moments only become pinned at ultra-low temperatures. The low temperature loops of the Mn_2Au (110) bilayer revealed two separate coercivity components each also displaying

a bias at lower temperatures. The inner component H_c^1 displayed a significant bias and coercive field of -17 mT and 69 mT at 5 K. The sign of the bias was again consistent with the negative applied field during cooling. The bias field persisted in the loop taken at 40 K with a value of -5 mT, and the 75 K loops displayed a bias field of -2.5 mT suggesting that the blocking temperature of this component was approximately 100 K. The inner component H_c^2 displayed a smaller bias field and extremely large coercivity of -7 mT and 150 mT at 5 K. Which had an estimated blocking temperature of 50 K. The presence of both large coercivities and bias fields coupled with the shape of the loops was indicative of exchange spring-like behaviour of the AFM Mn_2Au moments at this temperature for each of the distinct phases. The direction and sign of the bias were preserved through the FC and measurement processes by marking the direction of the applied magnetic field on the back of the substrate. Which was replaced by a scratch in the back of the substrate by a diamond-tipped pen, before the marker was removed and the low T magnetometry measurements performed. The origin of the bias in the Mn_2Au stack could not be directly determined but one suggestion was that it may arise from the disorder of the Mn_2Au layer as evidenced in the RHEED images.

The anisotropy energies associated with each coercivity component below their blocking temperature were extracted from an Arrhenius-style plot. The anisotropy energy of H_c^1 was estimated to be $20.8 \text{ meV} \pm 3.5 \text{ meV}$, while that associated with H_c^2 was estimated to be $14.8 \text{ meV} \pm 3.4 \text{ meV}$. Both values are in energy per unit cell.

Finally, the Néel temperature of each stack was estimated using a modified power law function to fit the temperature dependent coercivities of each exchange coupled stack. The power law model based on Mean field theory resulted in fits which were a poor approximation of the temperature dependent profile observed for the coercivities. A linear fit of the coercivities appeared to have the best fits and resulted in the most sensible values of the Néel temperature in relation to the experimentally observed data. The Néel temperature of the Mn_2Au (001) layer was estimated to be on the order of 340 K, while the Néel temperature of the Mn_2Au (110) layer was estimated to be on the order of 300 K. These estimates correlated well with the RHEED analysis of each layer, with the Mn_2Au (110) layer indicated to be more disordered than the Mn_2Au (001) layer. These estimates also highlighted that the FC temperature used of 623 K was well above the effective Néel temperature of both layers.

6.2 Future Work

Firstly considering the growth of Mn_2Au (110) films grown on Pt (111) in Chapters 3 and 5; the deposition of the Mn_2Au layer at 250°C resulted in three in-plane rotational crystalline domains, while the Mn_2Au layer which was annealed for 1 hr at 450°C produced an epitaxial Mn_2Au (110) layer with a single in-plane crystalline

domain. One future experiment is to repeat the growth of Mn_2Au (110) on Pt (111) for a thick layer to explore the repeatability of the anneal in producing a single in-plane crystalline domain. The epitaxial relationship between the layer could also be elucidated. Similarly, the Mn_2Au films grown directly on $\text{r-Al}_2\text{O}_3$ substrates in this work produced polycrystalline films, which was in contrast to the epitaxial (001) films produced by magnetron sputtering [28] on the same substrates. The role of the annealing cycle in the deposition of Mn_2Au layers directly onto Al_2O_3 needs investigation, as if the films produced were epitaxial, with smooth morphology and high crystallinity they would be ideal for probing the magnetotransport properties such as SOT and the intrinsic hall effect in Mn_2Au , for example. This applies for both the deposition of Mn_2Au on $\text{r-Al}_2\text{O}_3$ and $\text{c-Al}_2\text{O}_3$, as different epitaxial orientations will be key for the advancement of AFM spintronic effects in Mn_2Au . For example, if single in-plane orientation epitaxial (110) Mn_2Au thin films could be fabricated, either directly on $\text{c-Al}_2\text{O}_3$ or via a Pt (111) seed layer as discussed above, there is the prospect of reducing the complexity needed in Mn_2Au devices to display the NSOT effect. Existing Mn_2Au (001) NSOT devices have 6 terminals (4 writing, 2 reading) and require e-beam lithography to achieve the small device size necessary to create the current densities necessary to switch the Néel vector. A (110) Mn_2Au device may only need 4 terminals (2 writing, 2 reading, each orthogonal to each other) where the AFM moments are switched between the in-plane and out-of-plane easy axes, which may be re-written by switching the polarity of the switching current along the writing terminals. This would offer easier device fabrication and the potential to layer other spintronic on top of the NSOT and create more complex devices, by reducing the space needed for the writing terminals.

There are many future experiments planned to continue the work presented in Chapter 5 on the ECE in Mn_2Au (110)/Fe (110) bilayers. The origin of the bias field was not clear, although one suggestion is that it may lie within the disorder of the layer that was evident in the RHEED images. Additionally, there was evidence of exchange spring-like behaviour of the Mn_2Au moments in this sample at low temperatures. Some experiments to address these questions would be a microstructure characterisation of the stack using high resolution Z-contrast high angle annular dark field Scanning TEM, which would elucidate the nature of the interfaces between the layers and discern any parasitic crystalline disorder at the Mn_2Au interfaces. Additionally, the magnetisation dynamics of the exchange spring under magnetisation reversal need confirmatory experiments, such as X-ray synchrotron techniques like XMLD and XMCD; which would also help clarify the origin of the bias field in this stack. Similarly, a neutron technique such as PNR could be used to determine the magnetic depth profile of the structure under a saturating field, and an applied field around the point of magnetisation reversal.¹

¹Time at the NCNR had been granted for PNR experiments exploring the exchange-spring effect in Mn_2Au , but could not be taken up due to a reactor leak at the facility.

The experiments on the ECE in Mn_2Au presented in this work and elsewhere [31, 32, 68] suggest that the role of crystalline disorder is essential in obtaining any appreciable bias field. In particular, the low anisotropy of the AFM moments in thin epitaxial Mn_2Au (001) layers coupled with their large effective Néel temperatures [68] does not bode well for the integration Mn_2Au (001) films into MTJs which seek to exploit the TAMR effect; such a device would rely on thin Mn_2Au layers that display both an appreciable coercive and bias field to rotate the AFM moments. Similarly, there appears to be difficulty in creating a uniaxial anisotropy of the EC in Mn_2Au (001), even when FC from above Néel temperature. An interesting experiment would be to investigate the role of the direction of FC, with respect to the in-plane crystalline axes of Mn_2Au (001)/Fe (001) on the EC properties of the system. For example, a FC along one of the AFM easy axis directions may produce a different reorientation of the AFM moments than the FC performed at a 45° angle to both AFM easy axes presented in this work and in [32, 68]. Conversely, the induction of uniaxial EC appears to be much more achievable, likely originating in the fact that there is only a single AFM in-plane easy axis for an epitaxial Mn_2Au (110) layer. The bias field that was generated in the Mn_2Au (110) bilayers suggests that they may not display the same issues relating to the weak anisotropy of the AFM layer as the Mn_2Au (001), and the reasons for that are unclear in this work but may be originated in the disorder evidenced in the RHEED post-deposition. This could be investigated in two ways: Firstly, the EC in the Co (111)/ Mn_2Au (110) bilayers which were investigated at room temperature in Chapter 4, could be investigated using low temperature magnetometry; as these stacks qualitatively contained a less disordered Mn_2Au layer, as evidenced by the RHEED images. The second method would be through the introduction of intentional disorder into bilayers such as these by varying the ratio of the Mn:Au flux to produce intentionally off-stoichiometric Mn_2Au layers and mapping that against observed bias fields and blocking temperatures that this might produce. Either work, in combination with that already presented here, would elucidate if TAMR in Mn_2Au is achievable via the exchange spring effect or if another means of AFM moment manipulation to drive the TAMR effect is necessary. One such example of which is, the TAMR effect driven by NSOT in a device similar to what was described above for the Mn_2Au (110) NSOT, but with a tunnel junction style MgO barrier and NM top contact layer such as Pt to read the TAMR current. Such a junction would require the reduced number of terminals potentially offered by a Mn_2Au (110) NSOT device than is currently achievable with the 6-terminal Mn_2Au NSOT devices.

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