Magnetism of very thin films

A brief introduction

by

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Preface

This document gives a brief introduction to the field of the magnetism of very thin films. It was originally submitted as part of the assessment process for the graduate course on magnetism held by Professor J.M.D. Coey in Trinity College, Dublin during the 1999/2000 academic year. It has been published by the author as a resource for those interested in the magnetism of thin films, and every effort has been made to ensure the accuracy of the contents. However, as with all scientific literature this may contain inaccuracies, and the reader is advised to refer to text books and other publications in this field to confirm that the statements and formulas contained here are correct. I hope that other people interested in the fields of surface science and magnetism will find this document useful.

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Chapter 1

Introduction

Thin films have been a topic of much interest over the last number of decades. With the movement towards greater data storage densities in computer disk drives, attention is being focused on the magnetic properties of these films. This article will give an overview of the magnetic properties of very thin films (also known as ultra thin films), which are between one and ten monolayers thick. The way in which film properties differ from those of bulk samples will be discussed. As the structure of ultrathin films has a strong influence on their magnetic properties, the manner in which ultrathin films grow is discussed initially. A detailed description of the theory behind the unusual magnetic anisotropies exhibited by thin films is then described. Following a discussion of experiments measuring these anisotropies in a number of systems, the related phenomena of magnetostriction is outlined. Finally, the temperature dependence of the magnetic order in thin films is also discussed in the context of spin waves or magnons (which are analogous to phonons in a crystal lattice).

Chapter 2

Structure and epitaxy

The magnetic properties of thin films are strongly influenced by their structure. Therefore it is useful to describe the manner in which they grow before discussing their magnetic properties. The thin films discussed here are grown epitaxialy, that is each crystal in the film grows in a unique orientation on a single-crystalline substrate. If both materials are the same then this is referred to as auto- or homo-epitaxial growth, and if they are different it is referred to as heteroepitaxial. Thin films rarely grow in a layer-by-layer manner because of the strains caused by depositing the film and substrate materials on top of one another.

Bauer [1] proposed that the growth modes of crystals could be classified into the modes outlined below:

1. **Frank-van der Merwe (FM) growth**

   Layer-by-layer growth where complete monolayers are formed before subsequent layers nucleate — the growth is two dimensional (2D).

2. **Volmer-Weber (VW) growth**

Small clusters nucleate on the substrate forming islands in a 3D manner.

3. **Stranski-Krastanov (SK) growth**

   Is a mode intermediate between VW and FM. Initial growth is 2D but after a critical thickness is reached, islands form on top of the monolayers. It is sometimes referred to as 2D $\longrightarrow$ 3D growth.

The growth modes can be considered as a wetting problem, governed by an equation based on the surface energies of the film (σ_A), substrate (σ_B), interface (σ^*) and lattice mismatch (σ_S).

$$\Delta\sigma = \sigma_A - \sigma_B + \sigma^* + \sigma_S \tag{2.1}$$

The growth begins as a monolayer if $\Delta\sigma < 0$ and as islands if $\Delta\sigma > 0$. Plane FM growth is very rare because of the strain energy or lattice mismatch term that must be included in the surface energies of Equation 2.1. However if the growth is induced by supersaturation (i.e. either low substrate temperature or high evaporation rates) then monolayer nucleation can occur and a forced layer or quasi-FM growth mode results. Kinetic principles govern the growth in most real growth processes and condensation at low temperatures results in small grain sizes while that at high temperatures results in large grains.

The lattice misfit, f, which plays an important role in determining the structure of films, can be defined (in a 1D model) as

$$f = \frac{(b-a)}{a} \tag{2.2}$$

Where, b and a are the lattice parameters of the film and substrate respectively. This misfit results in dislocations and elastic strain, which have important consequences for the magnetoelastic anisotropy of ultrathin films.

Chapter 3

Anisotropy

The unusual anisotropies of thin films are an important property both for applications (for example, as magnetic recording media) and as sources of long range magnetic order.

Anisotropy is defined as the contribution to sample free energy that depends on the direction of the magnetization vector **M**. Anisotropy results from the crystalline electrostatic field (reflecting the local symmetry of the crystal) influencing the orbits of the atoms, which in turn interact with the magnetization through spin-orbit coupling. Uniaxial anisotropy is the simplest example of anisotropy, and in this case it is favourable for **M** to lie along an *easy axis* denoted by z. This axis is the c-axis in hexagonal, tetragonal and rhombehedral crystals. In acicular (i.e. needle shaped) particles z is along the long axis. Ultrathin film structures exhibit strong uniaxial anisotropies linked with the uniaxial crystal-field interaction at their surfaces and interfaces.

The perpendicular magnetization often found in systems such as Fe/Ag(001), Ni/Cu(001) and Co/Pd can be understood qualitatively by con-

sidering the difference in the electronic structure when compared to the bulk, as discussed by [2]. In the bulk, the electrons can have components of momentum in any direction (although some directions are favourable based on the shapes of the orbitals). The magnetic anisotropy based on spin-orbit couplng in the bulk is given by $(\mathbf{r} \times \mathbf{p}) \cdot \mathbf{S}$. As it is unlikely to find d electrons outside the surface of the film, the components of electron momentum perpendicular to the surface are reduced. The velocity in the surface plane is linked to the angular momentum perpendicular to the surface and this causes the quantity $\frac{L_z^2}{L_x^2+L_y^2}$ to increase near the surface. In situations where the spin-orbit coupling is significant the component of the spin perpendicular to the surface will increase — consequently perpendicular magnetization is favoured.

Following the distinctions made by Gradmann [3], the various anisotropy contributions can be categorised as:

- shape anisotropy
- bulk magnetocrystalline anisotropy
- strain anisotropy
- magnetic surface anisotropy

In deriving equations to describe these contributions we will use the homogenous magnetization approximation, and assume a film thickness that is less than any relevant exchange length and the domain wall width. The notation used by Gradmann will also be used here to maintain consistency with the articles cited.

Shape anisotropy (also known as magnetostatic or stray field energy), results from the magnetization of the sample, which Gradmann denotes by J_s. This magnetization generates magnetic poles at the surfaces of the thin film, enclosing the stray fields in a small volume of homogenous magnetization. The volume density of this stray field energy is

$$f_m = \frac{J_s^2}{2\mu_0} \cos^2 \theta \tag{3.1}$$

This energy becomes a local property in the case of thin films, and the non-local character it has in the bulk disappears. Magnetic domains are formed in the bulk to minimize magnetostatic energy, but as f_m is large they cannot be formed in this way in thin films. A single domain equilibrium state results. It is only in the case where f_m is approximately equalled by the crystalline anisotropy energy that domains can form. As discussed by Gradmann [3] such domain creation has been observed in layers of Co on Au(111) magnetized perpendicularly to the plane of the film.

Equation 3.1 assumes a demagnetizing factor of $D = 1$, which is a good approximation for a plate-like magnet such as a thin film. The maximum magnetic field outside a magnet is $\frac{1-D}{M}$, indicating that it is very small outside thin films. In non-homogenous media such as thin films a thickness dependent D is required because of the atomistic structure of the films. This factor D is proportional to the surface. The magnetic surface anisotropy (i.e. the deviation as represented by a magnetostatic contribution to surface energy) is given by

$$\sigma_m = -k_s \delta (\frac{J_s^2}{2\mu_0}) \cos^2 \theta \tag{3.2}$$

Here δ is the lattice spacing and k_s is a correction factor that can be found in reference tables [3]. This correction factor is large for open surfaces like bcc(100) and fcc(100). For densely packed surfaces, such as fcc(111) and bcc (110) it is small.

It is also important to take bulk magnetocrystalline contributions, f_r, into consideration. The anisotropy energy density of a homogenously magnetized uniaxial sample (in units of Jm^{-3}) is given by [4]:

$$\frac{E_a}{V} = K_1 \sin^2 \theta \tag{3.3}$$

Here θ is the angle between $\mathbf{M}$ and the z-axis, and K_1 is the anisotropy constant. It follows from $\sin^2 \theta = 1 - \cos^2 \theta$ that:

$$\frac{E_a}{V} = -K_1 \cos^2 \theta \tag{3.4}$$

This formula is valid for non-cubic crystals. For cubic crystals however there is no unique z-axis and K_1 is small. In permanent magnets $K_1 > 0$. *Easy plane* anisotropy exists if $K_1 < 0$, and in this case there are many equivalent easy axes at $\theta = 90°$.

The contributions to the anisotropy caused by strain of density f_ε can also be strong. In pseudomorphic films elastic strains can be of the order of a few percent and are quite significant. In epitaxial films the strain can be caused by differences in the thermal expansion of the film and the substrate as well as defects caused in the growth process. The analysis of these strains is difficult and f_ε is found by experiment. Recent work [5] has helped to described the link between strain and magnetic anisotropy in more detail, and is discussed below.

The deviation from isotropy of the crystal surroundings of magnetic atoms is reflected in the magnetic surface anisotropy. It has been proposed by Néel [6] that the break in local magnetic symmetry in a surface must result in strong surface anisotropies. In a quadratic approximation the surface anisotropy is given by:

$$\sigma = K_s \cos^2\theta + K_{s,p} \sin^2\theta \cos^2\phi \tag{3.5}$$

The first term in this equation represents the out-of-plane surface anisotropy that is present in all magnetic surfaces. The second term represents the in-plane surface anisotropy and need only be considered in lower symmetry surfaces such as Fe (110).

Néel also proposed a model for magnetic anisotropies based on pair-bonding. This connects the magneto-elastic volume properties with the surface anisotropy constants. In this model, both the magnetic strain anisotropy and the surface anisotropies can be derived from a pseudo-dipolar pair interaction between neighbouring atoms given by:

$$w = l \cos^2\phi \tag{3.6}$$

Where ϕ is the angle between the magnetic moment and the axis of the pair, and l is the bond parameter deduced from magneto-elastic data. It has been shown [7] that this model can account for the role of surface roughness by demonstrating that for hcp(100) surfaces that the surface anisotropy per atom in atomic steps is reduced by a factor of 2 compared to a free surface.

Combining the contributions outlined above we get:

$$\frac{F}{V} = [(\frac{J_s^2}{2\mu_0})\cos^2\theta + f_k(\theta,\phi) + f_\varepsilon(\theta,\phi)] + \frac{1}{d}[\sigma^{(1)}(\theta,\phi) + \sigma^{(2)}(\theta,\phi)] \quad (3.7)$$

Here d is the film thickness, $\sigma^{(1)}$ and $\sigma^{(2)}$ are the surface anisotropies for both surfaces, F is the free energy, V is volume, θ is the polar angle of the magnetization direction with respect to the sample normal and ϕ is the azimuthal angle to some low symmetry direction in the plane.

In most cases, neglecting the in-plane contributions and using a quadratic approximation we can sum both the volume-type crystalline contributions with a common anisotropy constant K_v, and use K_s to represent the surface anisotropy constants of both surfaces. Equation 3.7 then becomes

$$\frac{F}{V} = L\cos^2\theta \quad (3.8)$$

where

$$L = [\frac{J_s^2}{2\mu_0} + K_v] + \frac{1}{d}[K_s^{(1)} + K_s^{(2)}] \quad (3.9)$$

The first term here is a real constant volume term and the second term is a surface term.

Chapter 4

Anisotropy in Experiments

In order to see how magnetic anisotropies are investigated in experiments, iron and cobalt films will be described.

Experiments showing the anisotropy behaviour of Fe films on Ag(001) have been carried out [8]. Films of a range of thicknesses between 0.8 monolayers (ML) and 10 ML thick were grown. It is unlikely that the Fe grows in a layer-by-layer way, and either layer-plus-island or island only growth mode is more probable at coverages below 3 to 4 ML. However, it is useful when analysing the results of the experiment to assume that complete layers were formed. The spin polarization of photoemitted electrons was measured on the films at a temperature of 30 K in order to determine their anisotropy, and a schematic of the setup is shown in Fig. 4.1 (a). A large field could be applied perpendicularly to the samples during the experiment. As can be seen in a graph of the results in Fig 4.1 (b), for thicknesses below 1.5 ML the magnetization is hard to saturate perpendicularly to the film, indicating no spontaneous magnetization in that direction. In the case of 3.5 ML and 5 ML thick films, the magnetization perpendicular to the sample increases

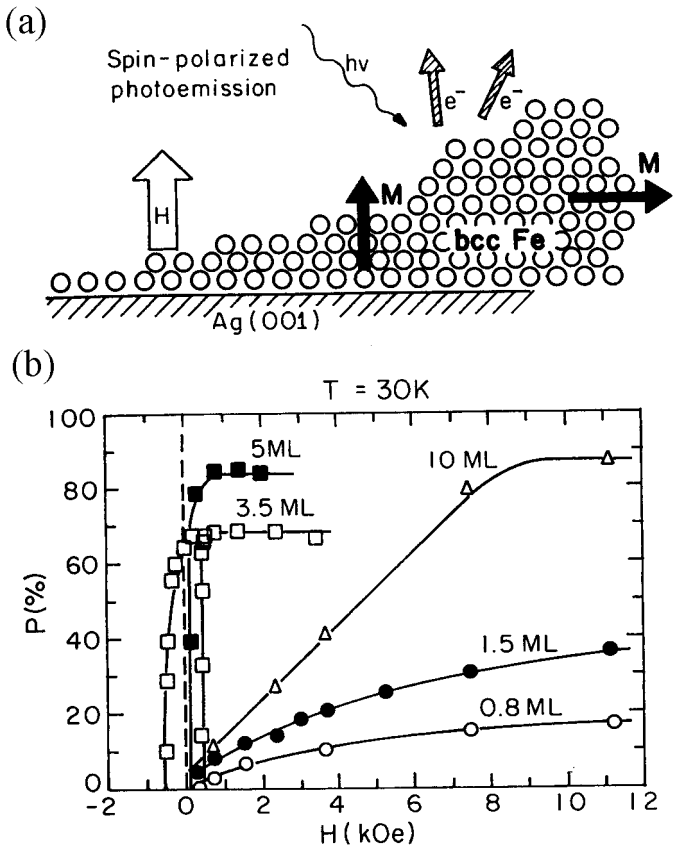

Figure 4.1: Anisotropy in Fe films. (a) Schematic of the experiment. (b) Polarization versus applied field. After Ref. [2]

rapidly with applied field and remanence is observed when the field is removed. However, when the thickness is increased to 10 ML magnetostatic energy in the film increases and the magnetization direction once again goes to its in-plane configuration. Taken together, these results indicate that a perpendicular surface anisotropy exists that produces a spontaneous perpendicular moment only when the magnetostatic energy does not dominate (as it does when the film becomes thicker).

The growth of Co on Au has been studied in a multilayer configuration [7].

By preparing multilayers with a periodicity of 1 nm using ion-beam sputtering, diffuse interfaces between the layers were formed. Recording M-H loops with the field alternately perpendicular and parallel to the sample indicated a clear preference for in-plane magnetization. If however the multilayers are annealed at $275°C$, the distinction between the layers is emphasized as the Au and Co separate out again. The magnetization loop then showed a preference for out of plane magnetization, reflecting the change in anisotropy caused by the sharp interface.

These experiments can provide valuable information on the anisotropy of a Co/Au film if one considers that only the number of surfaces measured has been changed by the multilayer structure. However it is also possible that the strain in the sample is changed by annealling it, and it has been pointed out [3] that a strain analysis by X-ray diffraction on similar Co(0001)/Au(111) superlattices could explain the magnetic anisotropies using a thickness-dependent strain only [9].

Chapter 5

Magnetostriction

As early as 1842, Joule observed an anisotropic strain associated with the direction of magnetization in iron. This effect appears when a sample has its magnetization aligned by an external magnetic field. Anisotropic magnetostriction (as opposed to isotropic effects like volume magnetostriction) can be characterized either by λ_S (the strain at magnetic saturation) or by the magnetoelastic coupling B_1 (which causes λ_S). Depending on the material λ_S can be between 10^{-7} and 10^{-3}. Like the piezoelectric effect, magnetostriction also has an inverse effect: the favoured magnetization direction in a material can be changed by stressing or straining it, leading to changes in the magnetic anisotropy.

This effect is important in the investigation of the magneto-elastic coupling constant of thin films. Recent experiments [5] have investigated the magnetostrictive bending of film-substrate composites. While bulk samples of Fe elongate by a factor of 10^{-5} when magnetized, ultrathin films bonded to a rigid surface do not exhibit magnetostrictive properties as the substrate suppresses them. However, if a thin substrate is used (of the order of $100\mu m$

thick) then the entire film-substrate composite is deflected slightly when magnetized. By measuring the radius of curvature of the composite using optical techniques, the magneto-elastic features of the film can be studied. For example, when 3 ML of Fe is deposited on $100\mu m$ of W (100), the radius of curvature of the composite is of the order of 200 km.

Chapter 6

Spin waves and the dependence of magnetic properties on temperature

The magnetization of a magnetic sample, $\mathbf{M}_s$, falls off as the sample temperature is increased until it reaches zero at a temperature known as the Curie temperature, T_C. At low temperatures, the rate at which $\mathbf{M}_s$ decreases in real samples deviates from that predicted by the Curie-Weiss function of mean-field theory. The Curie-Weiss function (which assumes random thermal fluctuations of the spins) drops more slowly. The temperature dependence of $\mathbf{M}_s$ is described better by Bloch's $T^{\frac{3}{2}}$ law:

$$\frac{\Delta M(T)}{M(0)} \propto -T^{\frac{3}{2}} \tag{6.1}$$

This model assumes spatially correlated thermal fluctuations. These fluctuations, which are analogous to phonons in a crystal lattice, are referred to

as magnons or spin waves. These spin waves form because an exchange coupled spin system can reduce its $\mathbf{M}_s$ by forming spatially correlated collective modes of demagnetization in which the adjacent spins are almost aligned.

In very thin films, both the ground-state magnetic moment (extrapolated from measurements at finite temperatures) and the temperature dependence of magnetic order are different from that found in the bulk. In addition properties such as magnetic anisotropy, surface effects, and exchange coupling, as well as the low temperature behaviour of films make it useful to measure spin waves and their frequency (which changes as the magnetic phase changes).

Bloch [10] attempted to model thin films using a 2D isotropic Heisenberg model. In his analysis, the spin-wave density diverged, and it was concluded that this indicated an absence of magnetic order. The magnetization in similar models is predicted to have a linear dependence on temperature at a wide range of low temperatures. However, anisotropy contributions could remove this linearity. The reduced magnetic coordination number of the atoms in a film also affects the temperature dependence of magnetic order, and theories of thin films in general are usefully compared to those of ferromagnetic monolayers. Although it is clear that the existence of long range magnetic order, including its dependence on temperature, is intimately linked to the magnetic anisotropies in the film, a theory of the temperature dependence that incorporates realistic anisotropies is not available at present.

Recent work [11] illustrates the approaches taken to the modelling of spin waves and magnetization dynamics in thin films. In thin films, spin wave frequencies can be used to find the exchange coupling in the films as the exchange effects become more important at low film thicknesses. With rela-

tively thick films, of over 100 ML, a continuum model is valid and Maxwell's equations can be used to treat the dipolar field of the film. The modes in a very thick film, i.e. the bulk modes, have a wavelength (perpendicular to the film plane) of approximately the thickness of the film, and a standing spin wave persists. In this extreme, neighbouring spins are to all intents and purposes parallel. But in thin films, the wavelength is decreased and spins next to one another need no longer be parallel. In very thin films, of thicknesses between $2 - 100$ monolayers, a discrete model where each layer is effectively independent should be used in place of the continuum model.

Experimental work on the dependence of T_C on film thickness (D, in monolayers) has been carried out on a variety of systems [3]. In the case of 48Ni/52Fe(111) and Co(111) grown on Cu(111), it was found that for a critical thickness the samples showed a perpendicular magnetization, and $\mathbf{M}_s$ was linear as a function of T. This implies the existence of flat islands at that coverage, and the enhanced decrease of magnetization agrees with the predictions of spin-wave theory. The dependence of T_C on D also agrees with the predictions of theory. Results for Fe(110) grown on W(110) are shown in Fig. 6.1. Again $T_C(D) \propto D$ at a growth temperature of 300 K. However if the sample was heated during growth, raising the temperature alternatively to 475 K and 800 K, a constant value of $T_C = 282$ K results. This indicates that extended monolayer patches are present at elevated temperatures, and that the Curie temperature is independent of the extent to which they cover the substrate surface. It can be concluded from the room temperature results that small monolayer patches are formed initially, and that T_C increases at greater coverages as these 2D islands coalesce.

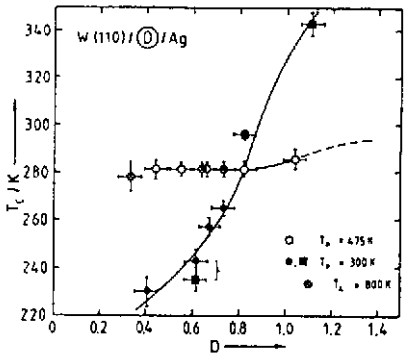

Figure 6.1: Curie temperature, T_C as a function of film thickness, D (in monolayers), for Fe(110) on W(110). Samples prepared at temperatures T_p as indicated, annealed at T_a and coated with Ag. After [3].

Chapter 7

Conclusions

Magnetic anisotropy plays a crucial role in determining the magnetic properties of thin films. This anisotropy is strongly influenced by the thickness of the layer, which can for example dictate whether the anisotropy is in the plane of the film or perpendicular to it. The stresses and strains in the film are also important factors. At low temperatures, spin waves play a strong role in determining the Curie temperature. It is important, therefore, when characterizing ultra thin magnetic films, that data on the anisotropy and on the dislocations in the films is gathered. Future work using scanning probe techniques may provide more information on the link between morphology and magnetic properties. This would open up the possibility of developing recording media of extremely high data density and provide new insights into the fundamental physics of magnetism.

Bibliography

[1] Bauer, E., 1958, Z. Kristallogr. **110**, 37

[2] O'Handley, R. C., 2000, Modern magnetic materials: principles and applications (John Wiley & Sons, Inc.)

[3] Gradmann, U., Magnetism in Ultrathin Transition Metal Films in Handbook of Magnetic Materials, Vol. 7 (Ed. Buschow, K. H. J., Elsevier Science Publishers B.V.)

[4] Skomski, R., Coey, J. M. D., 1999, Permanent Magnetism (Insitute of Physics)

[5] Sander, D., Enders, A., Kirschner, J., Journal of Magnetism and Magnetic Materials **200** (1999) 439-455

[6] Néel, L., 1954, J. Phys. Radium, **15**, 225

[7] den Broeder, F. J. A., Kuiper, D., van de Mosselaer, A. P., Hoving, W., 1988, Phys. Rev. Lett. **60**, 2769

[8] Stampanoni, M., Vaterlaus, A., Aeschlimann, M., Meier, F., 1987, Phys. Rev. Lett., **59**, 2483

[9] Lee, C. H., Hui He, F. J., Lamelas, Vavra, W., Uher, C., Clarke, R., 1990, Phys. Rev. B, **42**, 1066

[10] Bloch, F., 1930, Z. Phys., **61**, 206

[11] Camley, R. E., Journal of Magnetism and Magnetic Materials **200** (1999) 583-597