Amorphous, Nanocrystalline, Single Crystalline: Morphology of Magnetic Thin Films and Multilayers

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Abstract

Properties of magnetic thin film devices cannot be understood without detailed knowledge of their structure. For this purpose, a variety of thin film and multilayer systems have been studied. Both reciprocal space (low energy electron diffraction, reflection high energy electron diffraction, X-ray diffraction and reflectometry) and direct space (transmission electron microscopy) as well as Rutherford backscattering spectrometry have been applied.

To gain understanding of an oxidation procedure for the growth of magnetite layers, thermal stability of iron layers on molybdenum seed layers has been investigated.

Following the mosaicity and the out-of-plane coherence length over different ratios between the constituting layers allowed a deeper understanding of the limits of metallic superlattices. This, together with an approach to use hydrogen in the process gas during magnetron sputter epitaxy, opens routes for the growth of metallic superlattices of superior quality.

A non-isostuctural multilayer/superlattice system, Fe/MgO, has been investigated. In turn, this gave more understanding how superlattice diffraction patterns are suppressed by strain fields.

As an alternative route to single-crystalline superlattices, amorphous multilayers present interesting opportunities. In this context, crystallization effects of iron/zirconium layers on aluminium oxide were studied. Understanding these effects enables significant improvement in the quality of amorphous multilayers, and allows avoiding these, growing truly amorphous layers.

Both the substantial improvement in quality of metallic superlattices, approaching true single-crystallinity, as well as the improvements in the growth of amorphous multilayers give rise to opportunities in the field of magnetic coupling and superconducting spin valves.

Keywords: Multilayer, Superlattice, X-ray diffraction, X-ray reflectometry, electron diffraction, Rutherford backscattering spectrometry, Interdiffusion, thin film growth, transmission electron microscopy, Epitaxial growth

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I believe there is no philosophical high-road in science, with epistemological signposts. No, we are in a jungle and find our way by trial and error, building our road behind us as we proceed.  
Max Born
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  **Thermal stability of Fe/Mo layers**
Liebig, A., Hjörvarsson, B., Rüdiger, U.

II  **Hydrogen assisted growth of Fe/V superlattices**
Remhof, A., Nowak, G., Liebig, A., Zabel, H., Hjörvarsson, B.

III  **Stability limits of superlattice growth: The example of Cr/V**
Liebig, A., Andersson, G., Hjörvarsson, B., Birch, J.
in manuscript

IV  **Resistivity changes in Cr/V(001) superlattices during hydrogen absorption**
Eriksson, A.K., Liebig, A., Ólafsson, S., Hjörvarsson, B.

V  **The influence of weak links on magnetic ordering in layered structures**
accepted by Europhys. Lett.

VI  **Structural coherence and layer perfection in Fe/MgO multilayers**
Raanaei, H., Liebig, A., Lidbaum, H., Leifer, K., Hjörvarsson, B.
submitted to *J. Phys.: Condens. Matter*

VII  **Morphology of amorphous Fe$_9$Zr$_9$/Al$_2$O$_3$ multilayers: Dewetting and crystallization**
Liebig, A., Korelis, P., Lidbaum, H., Andersson, G., Leifer, K., Hjörvarsson, B.

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Publications not included

The following publication is not included in this thesis, since it is not relevant to the present subject.

**Onset of spin-density-wave antiferromagnetism in Cr/V multilayers**

Comments on my participation

The level of my participation is somewhat reflected by my position in the author list. The following is a brief statement of the level of my involvement in the different papers:

I  Initiated the project. Rebuilt vacuum system. Grew the samples, performed the measurements, and wrote the paper.
II Assisted with the modification of the growth system and the growth of the samples.
III Initiated the project, as a follow-up of IV. Grew the samples, performed the measurements, conceived the model, and wrote the paper.
IV  Grew the samples.
V   Grew the samples
VI  Participated in the experimental planning, was responsible for the growth system.
VII Participated in the growth and the X-ray measurements, conceived the model and wrote the paper.
1. Introduction

Ten years ago, one doctoral thesis in this research group started with the words "Over the past decade there has been an enormous growth of interest in the magnetic properties of thin film structures, which presently form the technological bases for a large industry" [1]. This was nine years after Grünberg and Fert had discovered the giant magnetoresistance effect [2, 3], and in the same year IBM employed this effect for the first time in a commercial hard drive.

As of 2007, there seems to be no sign of waning interest, and the same words could be said today. The data density stands now at 70 gigabit per square inch, a database search for "magnetic" and "thin films" shows no less than 25478 publication on this topic in the last decade, and Grünberg and Fert have been awarded the Nobel prize.

Yet, this development would have been impossible without continuous improvements in the controlled deposition of the films and multilayers, on which these structures are based. Thin layers can be grown by a variety of methods: materials can be evaporated and condensed on surfaces, chemical methods can be used to precipitate layers, compounds can be broken up by heat or plasma in chemical vapour deposition, and materials can be sputtered. Some of the physics involved is rather general, and applies to many methods.

In some way, this can also be seen as an analogy to how research works: some things are unique to very specialized projects, but many things – equipment and knowledge – are shared, and most projects would not work without the contribution of many people, often also from different groups.

Consequently, this thesis concerns itself mostly with the growth of magnetic layers (papers I, II, VI, and VII), but most of the magnetic studies were done by colleagues, whereas other theses in our research group have more emphasized the magnetic properties.

Across the board were other interesting themes – hydrogen in metals not the least of them. And here we have the connection between some of the different fields of research: for the hydrogen uptake measurements a comparison between Fe/V and Cr/V superlattices was needed (paper IV), but this turned out to have some major implications for our understanding of the growth of superlattices (paper III), which in turn gave rise to a new project on magnetic coupling, and so on.

The thesis is organized as follows: in chapter 2 the most important experimental methods are reviewed. Since my own work was mostly concerned with the growth and the structural characterisation, magnetic characterization
methods are excluded here. Chapter 3 deals with the mechanisms of layer growth in general, although magnetron sputter epitaxy is considered most. The discussion starts from the growth of a single crystal, and then goes on to compositionally modulated crystals – superlattices – to non-isostuctural superlattices, where the crystal structure changes between the constituent layers. After the crystalline samples, amorphous multilayers are discussed in chapter 4. Since metallic glasses are a relatively new topic in our group, some of the background on glasses and glass formers is reviewed. Naturally, it is impossible to give a full review of the extremely rich field of amorphous materials in general in a single chapter, and some references for the interested reader are given. Finally, in chapter 5 a review over the papers constituting this thesis is given. An outlook to future experiments and questions opened concludes the text.
2. Experimental Methods

A multitude of methods was used to prepare and analyze the specimens on which this thesis is based. This chapter focusses, so to speak, on the machine part. The physics of the sample growth itself will be covered in chapters 3 and 4. The term epitaxy – growth of crystalline layers, where the crystal structure is governed by the substrate – will be discussed in more detail in chapter 3.

Molecular beam epitaxy (MBE) was only used for the samples in paper I. Since the mode of operation was quite different (very few layers grown, with a different substrate temperature for each and with postannealing steps) to the sputter deposited samples – a rapid succession of up to 120 layers, keeping the substrate temperature constant, the two methods will not be compared in detail. It seems useful however, since I was involved in work on several different sputter systems, to note some of their advantages and disadvantages.

X-ray characterization – both X-ray Reflectometry (XRR) and X-ray diffraction (XRD) – are standard methods in our group, applied to nearly every sample. For the electron diffraction we have to distinguish between the in-situ methods, LEED (low energy electron diffraction) and RHEED (reflection high energy electron diffraction), which were extensively used for papers I and IV, where the instruments are built into the growth systems,
and the electron diffraction in an electron microscope. Due to the more demanding specimen preparation for electron microscopy, diffraction and microscopy was only done on selected samples.

2.1 Deposition and sample preparation

2.1.1 Molecular Beam Epitaxy - MBE

Thermal evaporation of metals in high vacuum is already known for many decades. Advances in vacuum technology made it possible in the 1960ies to refine the process, using better vacuum, and lower, better controlled growth rates, to achieve metallic or semiconducting layers of high crystalline quality, with thicknesses in the monolayer range [4, 5].

Ultra-high vacuum and in-situ preparation tools, and very often also in-situ characterization possibilities, are the features that distinguish MBE from simple thermal evaporation. But pure MBE systems use also only thermal evaporation of the source materials. There are different thermal sources: so-called Knudsen cells can be seen as small furnaces, which are in thermal equilibrium with the evaporant. The deposition rate can be finely regulated, due to the (known) vapour pressures at given temperatures. Electron-beam evaporators, on the other hand, use an electron gun, projecting a focussed electron beam into the evaporant. They can reach extremely high temperatures and can evaporate all metals, and also many ceramics. On the other hand, the deposition rate is much less well defined. Deposition with an electron beam evaporator has normally to be continuously monitored by either a quartz crystal microbalance, or, for example RHEED or Auger spectrometry. It should be mentioned that there are combinations of these two approaches available: small, cell-like electron beam evaporators. To deposit compounds, normally separate sources for the elemental materials have to be used, since only very few compounds evaporate congruently.

2.1.2 Oxidation

To prepare the half-metallic Fe$_3$O$_4$(111) surface, it suggests itself to use the close lattice match to the Fe(110) surface. By oxidation of crystalline Fe(110), crystalline films of Fe$_3$O$_4$(111) have been obtained [6, 7, 8, 9, 10]. The iron film is simply exposed to an oxygen atmosphere at high temperature. For pressure and temperature different recipes have been used by different groups, see for example [6, 9, 10]. For our experiments, we tried to follow the recipe of Fonin and coworkers [9], which had been found to yield magnetite layers of high crystalline quality. There, the iron layer is exposed to $5 \times 10^{-6}$ mbar oxygen at 700°C for 30 minutes.
2.1.3 Magnetron Sputter Epitaxy

The principle of magnetron sputtering is very simple – the material to be deposited is connected as the cathode in an electrical discharge. Anode rays – ionized gas atoms or molecules – hit the cathode, sputtering the cathode material out, which then deposits on a suitably positioned substrate.

However, the gas pressures needed to sustain a glow discharge are relatively high (for vacuum applications), and the process gas interferes with the deposit reaching the substrate. Also, in a higher pressure, the sputtered material will completely thermalize with the process gas, which is not always desired.

![Schematics of a magnetron with a non-magnetic target. The dashed lines indicate the magnetic field. The pits in the target depict the cross-section of the wide, relatively shallow erosion track typical for non-magnetic targets.](image)

A standard way to sustain an electrical discharge at lower pressures is the use of a magnetic field. The schematic layout can be seen in Fig. 2.2: a ring-like\(^1\) outer magnet (either really a ring, or an assembly of smaller magnets) and a smaller central magnet create a field which extends into the space in front of the target. Electrons, passing from the cathode – the target – to the anode ring experience a Lorentz force, guiding them on a spiral trajectory. The path of the electrons is therefore increased, and thereby the probability to ionize gas atoms on their way. The geometry of the field effects the uneven erosion of the target and gives the typical circular “race track”. The working pressures are then in the range of 0.5 Pa.

The process gas depends on the system to be grown: oxides and nitrides can be grown by an addition of oxygen or nitrogen respectively. Argon, as the most abundant noble gas, and with an atomic mass of 39.9 u effecting a good sputtering yield, is the obvious choice for a non-reactive process gas. To keep the amount of impurities as low as possible, Ar with a purity of 99.9999\% was used for the samples described herein. With the working pressure given above this results in an impurity level of 10\(^{-7}\) Pa. So, if the background pressure in the process chamber would be higher than this, these efforts would be squandered. If high-purity samples are to be achieved, ultra-high vacuum is therefore necessary.

\(^{1}\)Industrially, also rectangular magnetrons are used. The principles are similar.
From Fig. 2.2 one might immediately infer a problem: many of the samples described in this work consist of magnetic materials. A ferromagnetic target would close the magnetic flux between the centre and the outer magnets, and little, if any, magnetic flux would permeate into the space in front of the target. Magnetic targets have therefore to be much thinner than nonmagnetic ones. Careful arrangement of the magnet sizes and strengths allows, as shown in Fig. 2.3, to saturate the target close to the rim of the central magnet. The magnetic flux is then pressed out of the target. Since the saturation of the target is only possible in a comparably small area, racetracks on magnetic targets are smaller in diameter (following the central magnet) and narrower than on nonmagnetic ones.

![Diagram of a magnetron with magnetic target](image)

**Figure 2.3:** Schematics of a magnetron with a magnetic target. The magnetic flux is short-circuited through the target. Only around the rim of the central magnet significant flux extends before the target. The sputter track is rather deep and narrow.

Since the magnetic field confines the plasma of the discharge, changing the field geometry will influence the growth rate and energy distribution of the sputtered material. The field sketched in Fig. 2.2 indicates a "balanced" configuration – the flux lines from the outer magnet close through the inner magnet and the yoke. The magnetron has no net dipole moment. This configuration yields a very localized plasma and a medium sputtering rate. It is also suitable for magnetic targets. In our sputtering systems "Binford" and "Odin", this configuration is employed.

An unbalanced magnetron yields a more spread out plasma and a higher growth rate. This can be used to draw argon ions from the plasma to the sample to influence the growth mode. For an example see the work by Birch and coworkers on Cr/V multilayers [11].

If more than one magnetron is used in a system, which is nearly always the case, regard has to be taken to the interaction between the magnetrons. Fig. 2.4 shows a case ("Odin", initial configuration) where four magnetrons had identical polarity, with the ones visible to the left and right in unbalanced configuration. The repulsion between the magnets bent the plasma streams apart. This resulted in an unexpectedly low growth rate.
2.2 Characterization and Analysis

Most of the work described in this thesis concerns the structure of the samples – crystallinity or absence of crystallinity as well as the quality of the layering. To this end, a variety of techniques has been used. It seems logical, to distinguish between direct and reciprocal space techniques. However, an essential part of papers VI and VII is done by electron microscopy – and a modern transmission electron microscope (TEM) equipped with components for a multitude of operation modes serves at the same time for imagining, diffraction, chemical and even magnetic analysis. It would therefore be incomplete to list it just as a "direct space" technique. Therefore, the techniques and instruments will be discussed according to their accessibility and their dependence on separate preparation steps:

1. the in-situ instruments of the surface physicist, integrated into the growth system.
2. Our most common technique, X-ray characterization, which is done for virtually all samples in our group. In this category we include also measurements at the Tandem laboratory at the Ångströmlab and the "big science", at synchrotron facilities, where normally no further sample preparation is required.
3. The transmission electron microscopy. Since special specimen preparation is necessary, only a small part of the sample is accessible – but this in unprecedented detail.

Nevertheless, it is necessary to start with a short discussion of some concepts common to all scattering techniques. With some exaggeration, one could say that the entire solid state physics was conceived in reciprocal space – electron
wave functions, yielding the band structure and thereby optical, acoustic and mechanical properties of a solid, are calculated as Bloch waves in reciprocal space. However, we will introduce the concept here from the scattering point of view.

2.2.1 Reciprocal space and Laue equations

In the following an approximative expression for the scattering intensity is given, the so-called kinematic approximation. There, inelastic scattering and multiple scattering events are neglected. We follow in the deduction mostly [12].

![Figure 2.5: For the illustration of the scattering geometry. The source S is distant enough, that the incident beam can be viewed as plane wave. Compare [12].](image_url)

The (position dependent) scattering of a body is described by a scattering density $\rho(\vec{r})$. This is a complex number, describing amplitude and phase of the scattered wave relative to the incident one.

We assume that the source is sufficiently distant that the incident wave can be described as a plane wave. Its amplitude at $P$ (see Fig. 2.5)

$$A_P = A_0 \rho(\vec{r}) e^{i\vec{k}_0 \cdot (\vec{R} + \vec{r}) - i\omega_0 t}.$$  \hspace{1cm} (2.1)

The emitted wave is, using the scattering density $\rho(\vec{r})$:

$$A_O = A_P(\vec{r}, t) \rho(\vec{r}) \frac{e^{i|\vec{R}'|}}{|\vec{R}' - \vec{r}|}.$$ \hspace{1cm} (2.2)

Since $\vec{k}$ is parallel to $\vec{R}' - \vec{r}$, we can replace the absolute product by the inner product. Furthermore, for large $\vec{R}'$, we can neglect $\vec{r}$ in the denominator:

$$A_O = A_P(\vec{r}, t) \rho(\vec{r}) \frac{1}{|\vec{R}'|} e^{i\vec{k} \cdot (\vec{R}' - \vec{r})}.$$ \hspace{1cm} (2.3)

Using $A_P$ (equation 2.1):

$$A_O = \frac{A_0}{|\vec{R}'|} e^{i(\vec{k}_0 \cdot \vec{R}' + \vec{k} \cdot \vec{r})} e^{-i\omega_0 t} \rho(\vec{r}) e^{i(\vec{k}_0 - \vec{k}) \cdot \vec{r}}.$$ \hspace{1cm} (2.4)
The overall intensity at point $O$ is given by the integral of $\rho(\vec{r})$ over $\vec{r}$:

$$A_O(t) \propto e^{i\omega t} \int \rho(\vec{r}) e^{i(\vec{k}_0 - \vec{k}) \cdot \vec{r}} d\vec{r}. \quad (2.5)$$

From this amplitude we get the intensity:

$$I(\vec{K}) \propto |A_O|^2 \propto \left| \int \rho(\vec{r}) e^{-i\vec{K} \cdot \vec{r}} d\vec{r} \right|^2. \quad (2.6)$$

Here we introduce the scattering vector $\vec{K} = \vec{k} - \vec{k}_0$. The intensity is therefore the absolute of the Fourier transformation of $\rho(\vec{r})$ respective to $\vec{K}$. If the structure we are dealing with is periodic, we can expand $\rho(\vec{r})$ as Fourier series:

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad (2.7)$$

From the periodicity follows, that $\rho(\vec{r})$ must be invariant under translations respective to lattice vectors:

$$\vec{G} \cdot \vec{r}_n = 2\pi m \quad m \text{ integer}. \quad (2.8)$$

The condition (2.8) can generally only be fulfilled for

$$\vec{g}_1 \cdot \vec{a}_j = 2\pi \delta_{ij}. \quad (2.9)$$

To meet this condition, we construct $\vec{g}_1$ as:

$$\vec{g}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}. \quad (2.10)$$

This is the definition for a reciprocal lattice vector (sometimes the factor $2\pi$ is neglected). We put now the Fourier transform (2.7) into the intensity (2.6):

$$I(\vec{K}) \propto \left| \frac{A_0}{R^2} \right|^2 \left| \sum_{\vec{G}} \rho_{\vec{G}} \int e^{i(\vec{G} - \vec{K}) \cdot \vec{r}} d\vec{r} \right|^2. \quad (2.11)$$

Constructive interference occurs, if the integral is real, which happens for

$$\vec{G} = \vec{K}. \quad (2.12)$$

This condition is known as the Laue equation. It is quite a restrictive condition: for a monochromatic incident beam, diffraction will only seldom be observed.

The Laue condition can be depicted using Ewald’s sphere: Let $\vec{k}_0$ point to the origin in the reciprocal lattice. Draw a sphere with radius $r = |\vec{k}_0|$ around the starting point of $\vec{k}_0$. Diffraction will only occur for those $\vec{K}$ which touch a reciprocal lattice point. See Fig. 2.6 for an illustration.
2.2.2 In situ – LEED, RHEED, AES

In situ methods do not play a huge role in our group. Since the focus of the work is mostly on materials properties of the bulk of the films, not on the surface structure, in situ measurements are not always necessary. Some of the methods, like X-ray diffraction or magneto-optical measurements, could only with considerable effort be integrated into the growth systems – with little benefit. Measurements that are easily done ex situ would also take up time for the growth chamber, which in this way can be used otherwise. Furthermore, most samples are grown by magnetron sputter epitaxy, and the process gas makes "online" measurements during the deposition, like in MBE, impossible.

Nevertheless, thin films grow on surfaces, and it is difficult to understand growth processes without some understanding of the processes on the surfaces. In the multi-step process of deposition, annealing and oxidizing described in paper I, electron diffraction was an indispensable tool to control the individual steps.

In the sputtering system "Freyja" [1] a reflection high energy electron diffraction (RHEED) system is integrated. "Binford" [13] is a pure growth system, but medium energy electron diffraction (MEED), low energy electron diffraction (LEED) and Auger electron spectroscopy is accessible through the connected MBE system "MössPAC" [14].

Low energy electron diffraction – LEED

The principles of low energy electron diffraction (LEED) go back to the earliest scattering experiments involving particles. In the early 1920s Davisson and Germer investigated the angular dependence of electrons backscattered from a Ni surface. For a crystalline surface, they were surprised to measure distinct
peaks in the angular distribution. As is well known, eventually they found the explanation in diffraction of electron waves, resulting in the Nobel prize 1937. But already in their initial publication [15], they put the new method to use to study adsorbed gas layers.

Nowadays, Davissons and Germers Faraday cup detector has made way for a fluorescence screen, allowing the acquisition of the entire diffraction pattern at once (see Fig. 2.7). Since the electron energy is normally insufficient to yield fluorescence, a system of two to four grids is used to accelerate the scattered electrons before the screen. The grid system is also used to repel electrons at lower lower energy, thereby reducing the inelastic background. The electron energies used are in the range 10 to 500 eV [4], where the de Broglie wavelength is of the order of the interatomic distances.
Since electrons in this energy range penetrate only a few Ångström deep into the crystal, they do not see the ”depth” coordinate of the reciprocal lattice, and this component of the Laue equation (2.12) looses virtually its meaning: the diffraction becomes nearly purely two-dimensional. The remaining contribution of the depth coordinate can be observed as a variation in intensity, when the primary energy is varied.

If the surface structure shows a modification against the bulk structure, i.e. reconstruction, additional spots appear between the main ones.

**Reflection electron diffraction – MEED and RHEED**

For electrons with higher energies (5-10 keV), the diffraction angles become small. The backscattering geometry of Fig. 2.7 is no longer possible. Therefore, a grazing incidence geometry is used, see Fig. 2.9.

![Figure 2.9: Schematics of a RHEED/MEED setup.](image)

Medium energy electron diffraction (MEED) and reflection high energy electron diffraction (RHEED) can be used to obtain different information about the sample due to the shorter wavelength compared to LEED. However, the most common reason for the use of RHEED/MEED is geometrical: as seen in Fig. 2.9, both electron gun and fluorescence screen stand sideways of the sample. The space before the sample can be used otherwise, for example for deposition sources. Therefore RHEED/MEED setups are relatively easy to integrate into growth systems.

In Fig. 2.9 the appearance of a RHEED pattern is sketched. Since the reciprocal lattice is now essentially two-dimensional, it consists of rods, instead of points. As depicted in Fig. 2.10, the reciprocal lattice rods intersect Ewald’s sphere under very small angles. So any non-ideality, like a energy distribution of the incident beam, or surface disorder, will lead to a finite thickness Ewald’s sphere or to a finite diameter of the rods. In reality, therefore, the spots are elongated, and form streaks. An example is depicted in Fig. 2.11. For further discussion see [16].
Figure 2.10: Schematics of the Ewald construction for the RHEED geometry. The reciprocal lattice rods intersect Ewald’s sphere under very small angles.

It should be mentioned, that the appearance of a Laue type of diffraction pattern – spots due to ordinary, three-dimensional diffraction – is entirely possible: in this case the sample surface is so rough that the electron beam has penetrated islands and hills, yielding a three-dimensional transmission pattern.

Due to the strong interaction of the electrons with the sample, and the grazing incidence, which leads to a rather large scattering volume, multiple scattering can no longer be neglected. The Ewald picture then does not hold any longer. Multiple scattering events lead to the appearance of curved, relatively weak lines in the diffraction pattern: the Kikuchi lines. A pronounced Kikuchi pattern is an indication of high crystalline order in the sample [16]. For a more detailed discussion of these effects see [17].

**Auger electron spectroscopy – (AES)**

If, by impact of high energy ions, electrons or photons, an atom loses a core electron – a core hole is formed – there are different recombination processes: the hole might be filled by an electron from an outer shell under emission of an (X-ray) photon. Alternatively, when the electron from the outer shell fills the hole, the energy difference might be taken up by another electron, which is then ejected from the atom. The interaction involved is purely electrostatic, so there are no selection rules for photon emission to be fulfilled. The transition rate is given by

\[
\sigma_{fi} = \left| \frac{e^2}{r_{1,2} 4 \pi \varepsilon_0} \left\langle \Psi_1 \Psi_2 \right| \Psi_A \Psi_0 \right|^2
\]  

(2.13)
where $\Psi_0, \Psi_1, \Psi_2$ are the wavefunctions of the energy levels involved ($\Psi_0$ the one of the hole) and $\Psi_A$ the wavefunction of the emitted electron. This is the Auger process. The transitions are noted using the involved levels: a KLM transition is the emission of an M-electron, using the energy of an L-electron filling a K-hole. Since the initial states had defined energy levels, the energy of the emitted electron is characteristic for the transition, and can be used to identify the atom concerned.

The finite lifetime of the initial state (the core hole) and the end state (two interacting holes) lead to a line broadening. So, Auger lines are rather broad, compared to other electron spectroscopy methods like X-ray photoelectron spectroscopy.

An Auger electron spectrometer is relatively simple: an electron gun for excitation, a spectrometer – which does not need high energy resolution – and a detector, usually a channeltron, or secondary electron multiplier. While this provides a quick and easy method to check sample surfaces for contamination, it is not without problems: using an electron beam for excitation yields a strong contribution of secondary electrons. The measured spectrum consists of a wide distribution of these secondary electrons, superimposed on the small Auger peaks.

To obtain a reasonable signal, the transmission energy of the spectrometer is modulated, and the signal processed with a lock-in amplifier. Classically, all Auger spectra are therefore represented as differential spectra. An example is shown in Fig. 2.12. Three types of spectrometers are often used [4]:

**hemispherical analyzer:** the standard instrument for photoelectron spectroscopy, can very well be used for Auger, although its high resolution is unnecessary here.

**cylindrical mirror analyzer (CMA):** two concentric cylinders, the electrons enter through an annular aperture in the inner cylinder and are repelled...
MössPAC is equipped with a 100 mm single stage CMA. For single-stage CMAs even small shifts in the sample position will lead to changes in the recorded electron energy and the peak widths [18]. Since the recorded spectrum is differentiated, a change in peak widths would also affect the recorded intensities. For this reason, the spectrometer would be set on the energy of a major peak (for the samples in paper I normally the Fe peak at 703 eV) and then the sample position would be optimized for the maximum signal.

Charging effects due to the primary electron beam are a further complication: if the sample is charged, electrons will be further accelerated, and measurements are impossible. For semiconducting samples this effect can often be suppressed by tilting the sample [19]. However, for metal films on insulating substrates, this proved to be insufficient. The solution was to directly ground the metal film over the clamp that holds the sample on the sample plate. During deposition the clamp would shadow the substrate, and therefore have no contact to the film. It was therefore necessary to move the clamp slightly using the wobble stick, after the first metal layer was deposited.
The intensity of an Auger line depends not only on the concentration of that element, but also on overlayers, which absorb Auger electrons, as well as underlayers, which might give effectively a higher primary intensity by backscattering of primary electrons. Since the mean free path of the Auger electrons is in the order of 20 Å, AES is extremely surface sensitive. Therefore a detailed knowledge of the mean free paths $\lambda$ of electrons in the specimen is necessary for the quantitative analysis of an Auger spectrum. In the past, often a so called universal curve [20] had been used, where the mean free path is only dependent on the energy:

$$\lambda(E) = \frac{1430}{E^2} + 0.54\sqrt{E} [\text{Å}]$$

(2.14)

However, this equation gives significantly too low values. For further details (and a careful distinction between ”attenuation length” and ”mean free path” which have been used synonymously here) the reader is referred to the work of Jablonski and Powell [21].

2.2.3 Ex situ – X-ray, RBS

X-ray analysis

X-ray diffraction (XRD) is a surprisingly old tool in crystallography – indeed, diffraction from crystalline lattices was also a very important proof of the wave nature of X-rays themselves [4].

Since the principles of scattering have already been reviewed in section 2.2.1, only some points about the application to thin films and multilayers will be discussed here. Detailed discussion can be found in the earlier theses of Inna Soroka [13] and Matts Björck [22], thus this part is kept rather short here.

Few X-ray measurements are done in transmission geometry: photons of the often used X-ray wavelengths 1.54 Å (Cu K$_{\alpha}$) and 0.71 Å (Mo K$_{\alpha}$) have
penetration lengths in the range of \( \mu \text{m} \). Fig. 2.13 depicts the situation in reciprocal space: \( \omega \) is the incidence angle, \( 2\theta \) the scattering angle. Since the radiation cannot penetrate a macroscopic sample, a measurement is only possible if both source and detector are above the horizon. The most common scans, the radial or ”coupled” scan, and the transversal scan, or ”rocking curve” correspond to a radius in Fig. 2.13 and a circle around the origin, respectively. For very thin films, we have to take also some other effects into account:

**X-ray reflectivity**

As electromagnetic waves, X-rays are refracted according to Snell’s law when they pass a boundary between optically different materials. However, for X-rays, the refractive indices are very close to unity, and significant effects are only observed for very low angles of incidence. A curious feature is, that the index of refraction for most materials is actually smaller than unity. Therefore, X-rays can undergo total reflection on the surface of a solid up to a critical incidence angle, which is typically lower than \( 1^\circ \).

In the early 1930ies Kiessig [23] investigated the X-ray reflectivities of thin Ni films. He observed fringes, a series of maxima and minima, for angles higher than the critical one. These *Kiessig fringes* are interferences between reflections from the surface and the film/substrate interface.

![Figure 2.14: X-ray reflectivity of a Fe/MgO multilayer, bilayer thicknes 45 Å, 15 repetitions.](image)

If not only a single layer, but a stack of (generally) two different layers is deposited and repeated several times, interference from all interfaces can be observed. The reflectivity curve will still show the Kiessig fringes, but for positions corresponding to a constructive interference of all bilayers, much higher peaks will be observed. An example is shown in Fig. 2.14 (as common in X-ray analysis, the scattering angle \( 2\theta \) is used for the abscissa, instead of the incidence angle \( \omega \)): after the critical angle, the intensity drops nearly three decades, before rising again to the first multilayer peak at \( 2\theta = 2^\circ \). The position of the \( n \)-th peak can be calculated from the X-ray wavelength \( \lambda \), the
bilayer thickness \( \Lambda \) and the average real part of the index of refraction \( 1 - \delta \) as [24]:

\[
\sin^2 \theta = \left[ \frac{n\Lambda}{2\Lambda} \right]^2 + 2\delta. \tag{2.15}
\]

Beware that the angle in this equation is \( \theta \), not \( 2\theta \)! From equation 2.15, \( \Lambda \) can be obtained by linear regression of \( \sin^2 \theta \) versus \( n \).

The small oscillations in between the multilayer peaks are the Kiessig fringes. There are \( n - 2 = 13 \) maxima in between the main maxima, showing that the sample consists of \( n = 15 \) repetitions. The third and the sixth multilayer peak seem to have lower intensity than one would expect – in fact, they are lower than the respective next peaks in the series. Such changes in intensity reveal the thickness ratio of the constituent layers. A complete absence of the third (and sixth) peak would indicate a sample where the thickness ratio is close to 1:2. For the sample depicted in Fig. 2.14, the thickness ratio is between 1:1 and 1:2.

Interestingly, in this angular range, the atomic structure of the sample plays only a small role - as long as they have flat interfaces, amorphous multilayers can show exactly the same reflectivity as ideal, single-crystalline superlattices.

The reflectivities can be calculated from a model, which is then refined. Following Parratt [25], one can work out the reflectivity of a multilayer by a recursive procedure, taking multiple reflections and absorption into account. Since the Parratt procedure is very tedious, the recursion is normally evaluated numerically, not algebraically. If non-ideal interfaces with a finite width are allowed for, the fitting becomes unwieldy, involving many parameters for a highly non-linear problem. Several fitting algorithms have been developed to obtain a stable optimization [24, 26]. A differential evolution algorithm is used in the program GenX [22, 26], written by Matts Björck. It has become standard in our group.

### X-ray diffraction from superlattices

The diffraction pattern of a layered structure, where the crystalline coherence length is much larger than the bilayer thickness, will show more than one relevant length scale, and therefore more than one peak. For an idealized superlattice, with perfect interfaces and an integer number of monolayers per layer, the diffraction intensity for out of plane scattering can be written as [27]:

\[
I(Q_z) = L_N(\Lambda)^2 \left\{ |f_A|^2 L_{n_A}(d_A)^2 + |f_B|^2 L_{n_B}(d_B)^2 \right\}
+ 2|f_B||f_A|L_{n_B}(d_B)L_{n_A}(d_A) \cos(Q_z\Lambda/2) \tag{2.16}
\]

where the Laue function

\[
L_N(x) = \frac{\sin(Q_n x/2)}{\sin(Q x/2)} \tag{2.17}
\]

and \( f_A, f_B \) the scattering lengths of the two materials, \( d_A, d_B \) the lattice spacings, and \( n_A, n_B \) the number of monolayers in each layer. We get a product of
two terms: the superlattice term $L_N(\Lambda)^2$, representing a unit cell of the thickness of one bilayer, and an envelope function. The envelope function consists of three summands, one from each constituent layer, and a cross term. If the layers are thin, and the lattice spacings $d_A, d_B$ are rather close, the cross term will dominate. This is the case for most Mo/V, Fe/V and Cr/V superlattices. An experimental example is given in the next chapter, Fig. 3.7. We observe an ”average Bragg peak” for an average lattice spacing $d$, with superlattice satellite peaks. Written in angular scale:

$$2 \sin(\theta)/\lambda = \frac{1}{d} \pm \frac{n}{\Lambda}. \quad (2.18)$$

However, if the individual lattice spacings are far apart, and the layers relatively thick, the single layer terms overlap little, the cross-term becomes small, and single layer terms have more weight. An ideal, simulated case is depicted in Fig. 2.15.

![Simulated X-ray pattern of an ideal Fe/MgO superlattice](image)

**Figure 2.15:** Simulated X-ray pattern of an ideal Fe/MgO superlattice. The MgO 002 peak would be expected at $2\theta = 42.9^\circ$, the Fe 110 at $2\theta = 65.1^\circ$. The wavelength used is 1.54 Å.

**Rutherford backscattering spectrometry**

If high-energetic, light ions, like He$^+$ hit a solid, they will be scattered by the electrons in the solid, however, since the electron mass is small, the trajectory of the ions does not change significantly. The ions will, however, lose energy. Larger scattering angles can be effected by the electrostatic potential of the nuclei. For a major change in direction a close approach to a nucleus is necessary, where the scattering can be basically described in terms of classical mechanics: the larger the scattering angle, the higher the momentum transfer to the target nucleus must be. If one now uses a fixed incident energy, and uses a detector at a fixed scattering angle, for example 160°, the momentum transfer must be related to the mass of the target atom: the heavier the target, the less momentum and energy will be transferred. Thereby the mass of the
target atom can be determined by the energy of the backscattered atom – a heavier target atom will appear at higher energies.

Since the ions lose energy while travelling through the sample, a thick layer will give a broadened peak – the highest energy from the surface, the lowest from the lower interface. Since the stopping powers for most elements are well known, it is possible to simulate the expected spectrum numerically and compare to the experiment. An example is presented in Fig. 2.16.

![RBS spectrum of an Fe/Mo bilayer](image)

*Figure 2.16: RBS spectrum of an Fe/Mo bilayer, Taken at 2 MeV primary energy, scattering angle 160° (from paper I).*

From the description above it might seem impossible to deduce the true composition of a sample: is a given peak now from a layer at the surface or from a buried layer of a much heavier material? However, RBS is rarely employed without any idea of the sample composition. For the spectrum in Fig. 2.16 it is known for example that it was from an iron/molybdenum bilayer. What can now be learned from the spectrum? First, the areal densities of the constituent materials: thin films can show densities that deviate strongly from the bulk. Together with XRR, which gives the thickness, the atomic density can be exactly determined. Therefore, the stoichiometry of compounds can also be specified in absolute numbers. Furthermore, the initial model of the sample will be refined during the analysis, yielding more information about the buildup of the sample. In Fig. 2.16, we see a distinctive shoulder at the high-energy side of the Mo peak. This indicates that some Mo must be ”higher up” in the sample than the remainder of the Mo layer. Since there is no separation between the shoulder and the main peak, it is unambiguously proven that there is Mo in the Fe layer above the Mo layer. See paper I for more details.

### 2.2.4 Transmission Electron Microscopy

A structure with a lengthscale $d$, for example a grating, will diffract light. Resolving this structure in a microscope is only possible if at least the first
diffraction order falls into the microscope objective, since the zeroth order (direct beam) does not contain information about the object (resolution criterion of E. Abbe [28]). The minimum length, that can be resolved by a microscope is therefore

$$d_{\text{min}} = \frac{\lambda}{n \sin \alpha}$$  \hspace{1cm} (2.19)

where $\lambda$ is the wavelength, $\alpha$ half the angle under which the objective appears from the object, and $n$ the refractive index of the medium before the objective. Since $n \sin \alpha$, the numerical aperture, cannot be driven much higher than 1, the resolution of a microscope is inherently dependent on the wavelength.

If the light optics are replaced by an electron optics system, the wavelength can become many orders of magnitude smaller (for 100 keV this corresponds to $\lambda = 0.037 \, \text{Å}$), but due to nearly incorrectable aberrations of magnetic electron lenses, $\alpha$ is limited to the millirad range. Balancing these two factors, an electron microscope has at least three orders of magnitude higher resolution than an optical microscope.

![Figure 2.17: Schematic view of a transmission electron microscope.](image)

The principal setup (Fig. 2.17) is similar to an ordinary transmission light microscope. There are, however, operation modes possible that have no analogy in optical microscopy. Before these are discussed, some requirements for TEM samples have to be discussed.

**TEM sample preparation**

For use in transmission microscopy, a sample has obviously to be transparent. For use in a TEM, specimens should be of a thickness in the order of 100 nm or less. There are different ways to achieve that, the procedure described in
the following has been used in the investigations described in papers VI and VII.

There the sample is thinned first by mechanical dimple grinding, and then, in a second step, by ion milling. The two step procedure is advisable, since the ion milling cannot take much material away, while the mechanical polishing does not reach the necessary precision. Normally, the ion milling is done until a small hole appears in the sample. There will then be, in the rim of the hole, a zone where the specimen has the appropriate thickness.

Figure 2.18: Edge of the sputtered hole in a TEM specimen. Two FeZr/AlO multilayer samples seen on the right. See text for details.

Cross-sectional samples, of especially high interest for multilayers can be produced in a similar manner: two multilayer samples are glued face to face, and a hole is ground and sputtered, so that the hole transects the glueline. An example – a specimen two FeZr/AlO samples – can be seen in Fig. 2.18. The (crystalline) Si substrates shows thickness fringes. The lower of the multilayer was grown on an oxidized Si wafer, and the (amorphous) SiO$_2$ can be seen as a uniform grey layer underneath the multilayer. Also, the different sputtering rates for the different materials can be seen: the glue between the samples has already been removed, while the preferential sputtering of the SiO$_2$ creates an undercut under the multilayer.

It goes without saying that the preparation technique should affect the sample as little as possible. Curiously, transfer through ambient air from the sputter-chamber to the microscope presents seldom a problem: the sample is still thick enough that the vast majority of the signal comes from the unoxidized "bulk". Care has to be taken that the lubricants in the mechanical grinding do not affect the sample. Often, a water-based lubricant is used. However, this
affects MgO layers and substrate, they form hydroxides, expand, and crack. Replacing the water by propylene glycol solved these problems, as seen in Fig. 3.9.

**Different operation modes**

As in an optical microscope, there will be a diffraction pattern of the sample in the rear focal plane of the objective. In this position, an aperture can be placed, to select a certain part of the diffraction pattern for generating the image. Selecting a field around the central spot gives the standard *bright field* mode. According to the discussion about resolution, this will preclude atomic resolution, since the information about the atomic structure is contained in the diffraction spots. So, this mode gives not the highest resolution, but good contrast.

Selecting another spot, not the direct one, in the focal plane gives a *dark field* image, and using a larger area, containing several spots, yields the *high resolution* mode, where atomic resolution becomes possible.

For Fig. 4 in paper VI a fundamentally different operation mode was used: „scanning transmission electron microscopy” STEM, where the electron beam is focussed in the specimen and scans the sample linewise. This mode allows the use of different detectors to enhance contrast. For example, local chemical analysis is now possible, by using an X-ray detector and measuring the X-ray spectra for each point (*EDX*).

However, in paper VI we were mostly interested in contrast between elements with different $Z$-numbers: So a ring-like detector is used, where the primary beam passes through, and only electrons scattered in a certain angle are counted. If this angle is kept large, signal of heavy elements is maximised, since the probability of high deflection angles goes with $Z^2$. We have therefore an *high-angle annular dark-field* image: HAADF.

An electron spectrometer (under the fluorescence screen, which can be swivelled away) can be used to acquire energy filtered images.

For a more detailed discussion of TEM techniques, see [29].
3. Crystalline Layers and Superlattices

Today, there are few areas in daily life where we do not meet products from thin film deposition techniques – sometimes comparatively crude ones like the coatings on window panes – but also sophisticated ones, consisting of many deposition steps with lithography steps in between, finally creating for example the board of a wrist-watch.

Let us first have a look at the last example: the growth and fabrication of semiconductor devices. Nearly without exception, silicon structures for use in electronic applications are grown on silicon substrates. In this technique, the intrinsic conductivity of the substrate can be problematic, and much effort has been spent to replace the semiconducting Si substrates with an insulator, for example sapphire. This approach is known as silicon-on-sapphire (SOS) or silicon on insulator (SOI). Despite huge commercial interest, the devices are still in the prototype stage [30, 5]. The obstacle in the way to industrial application seems to be a trifle: the upscaling of laboratory processes (where SOS devices can be fabricated in high quality and low numbers) to industrial size.

This example, well outside the scope of this work, shows that the physics of structural properties and growth related phenomena needs to be taken into account when designing thin film systems. Using them, on the other hand, allows to grow materials which do not exist in the bulk, in the form of thin films and multilayers. For example iron, which appears at room temperature in a bcc structure, can be stabilized in a fcc-like structure [31], while normally hexagonal cobalt can be prepared in a bcc-like structure [32].

Before we discuss the details of thin films, we will have first a look at bulk crystals for comparison: if a crystal is grown, say, from a solution or melt, the entire process is kept near thermal equilibrium. To crystallize a material out of a solution, the solution is cooled down, so that the solution becomes saturated. During further cooling the solute will exceed the solubility. If a seed crystal is now put into the supersaturated solution, it will grow. Care is taken that the supersaturation becomes not so large that other crystallites can nucleate.

Since, in a crystal, the surface energies will not be isotropic, the different facets of the crystal will grow with different speeds, higher-indexed surfaces with large surface energies will grow faster than facets with lower surface energies, since the change in free enthalpy is given by both the increase of surface (by the growth) and the change in the chemical potential. If a crystal
grows by \( n \) monomers, the change in free enthalpy \( \Delta G \) is given by [33]

\[
\Delta G(n) = -n\Delta \mu + \sum_{j=1}^{k} \gamma_j A_j
\]  

(3.1)

where \( \mu \) is the chemical potential, \( \gamma \) the surface energy, and \( A \) the area of a given facet, denoted by the index \( j \).

To obtain the macroscopic shape of the crystal, the surface tensions \( \gamma \) are plotted versus the angle in a polar diagram. The planes normal to the radius vectors are the *Wulff planes*. Their involute is the equilibrium shape of the crystal.

\[ \gamma_{B} \]

\[ B \]

*Figure 3.1:* Equilibrium shape of a free crystal. \( A_j \) denotes the area of facet \( j \), \( \gamma_j \) the orientation dependent surface energy.

In equilibrium, the distances of the facets to the centre of the crystal \( h_i \) are then given by

\[
\frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = \cdots = \frac{\gamma_k}{h_k}.
\]  

(3.2)

This relation is known as *Wulffs theorem* [33, 34]. It must, however, be noted, that real crystals can strongly deviate from the Wulff shape, depending on the growth conditions.

Deposition in a vacuum system, whether by thermal evaporation or by magnetron sputtering, has only little in common with this – nearly without exceptions the substrate temperatures are several hundred kelvin below equilibrium. An atom impinging on the surface might recoil, but it nearly never reevaporates. The process is far from thermodynamic equilibrium. This brings some disadvantages and some advantages with it:

- On the negative side, a nearly defect free crystal – the lowest energy state for the metals and oxides considered here – is close to impossible to achieve.
Figure 3.2: Overview of different processes possible on a surface, compare [35]. At ordinary substrate temperatures desorption is a very improbable process.

- On the positive side, structures which are by themselves non-equilibrium now become possible. This is especially important for layered structures. There are many classes of naturally layered crystal structures – the perovskite structure of the high-$T_C$ superconductors probably being the most well known example – but if focus is on thickness dependent properties, for example the oscillatory magnetic exchange coupling [36, 37] over non-magnetic spacer layers, non-equilibrium structures can hardly be avoided. Vacuum deposition technology has gone a very long way from the simple tungsten ”boat”, heated by electrical current in a more or less uncontrolled manner.

### 3.1 Nucleation and the three classical growth modes

If a crystal is grown on a substrate (”epitaxy” if the crystal structure and orientation is governed by the substrate), which is generally of a different material (heteroepitaxy), but not necessarily (homoepitaxy), the properties of the interface between crystal and substrate become important. Given the success of Wulff’s description for the equilibrium shape of a crystal, it is not surprising that a similar model has been tried for epitactic growth. If the macroscopic surface and interface energies are valid on the length scales considered, we can distinguish between wetting, dewetting and intermediate growth:

- **wetting** also known as the Frank-van-der-Merwe [38] type of growth: The deposit grows as a flat layer, completely covering the substrate.

- **dewetting** Volmer-Weber growth [39]. The adsorbate dewets, and forms islands, leaving parts of the substrate uncovered until a nominal thickness of several monolayers is reached. The islands themselves can have a truncated Wulff shape, as discussed below.

- **intermediate** or Stranski-Krastanov growth. This growth mode is difficult to explain in a continuum picture: the adsorbate initially forms a thin (just a few monolayers) wetting layer, on top of which islands are formed.
The binding energy for an atom bound to the surface will in general be much less than the bulk binding energy, since the adsorbed atom can not form the full number of bonds. Surface diffusion is therefore normally possible. The diffusing atoms either get trapped at surface steps and defects (heterogeneous nucleation), or they can agglomerate to stable nuclei (homogeneous nucleation). When an island with radius \( r \) is formed, binding energy is gained, at a cost in surface energy \( \gamma \) (three-dimensional nucleation) or line tension energy \( \gamma_l \) (two-dimensional nucleation) [40]. The Free Energy \( F \) takes then the form:

\[
F_{2D} = 2\pi \gamma_l r - \pi \Delta \mu r^2 \tag{3.3}
\]
\[
F_{3D} = 2\pi \gamma r^2 - \frac{4}{3} \pi \Delta \mu r^3. \tag{3.4}
\]

Qualitatively, both expressions show the same behaviour: the free energy increases up to a certain island size, then the binding energy term takes over, and the free energy decreases again. If a nucleus is too small it will decay before it has the possibility to grow further. There will be a certain size of a nucleus, that has equal probability to decay or to grow further. This is the critical nucleus. For a high growth rate, the nucleus has little time to decay before the next atoms agglomerate to it. For very low growth rates it would have, on the other hand, nearly infinite time to decay. Therefore the critical nucleus is smaller for higher deposition rates. For standard conditions in vacuum deposition, the critical nucleus can be as small as ten atoms [41, 42]. The continuum approximation in the formulas given above is therefore questionable.

For a known critical island size \( i \) the distribution of island sizes can be calculated by dynamical scaling theory [43]. Thereby a relation between deposition rate \( F \), island density \( N \), diffusion coefficient \( D \) and the size of the critical nucleus \( i \) is obtained:

\[
N \propto \left( \frac{D}{F} \right)^{-\frac{i}{\pi \Delta \mu}} \tag{3.5}
\]

This is an approximation that necessitates \( N \) to be nearly time independent, which is valid for coverages between roughly 0.05 monolayers and 0.33 monolayers.

Since the early stages of nucleation have only been of limited relevance to this work (except for paper VII, which will be discussed in the next chapter), we will not take the discussion further, coming back to the shape of the islands instead.

Equation 3.2 can be modified to take the interface to the substrate into account. One facet \( (A_A, \gamma_A) \) of the growing crystallite touches the surface \( (A_B, \gamma_B) \) on an area \( A_{AB} \). For this interface there is also an energy gain by substrate-adsorbate interaction. With the specific free adhesion energy \( \beta \), equation 3.1 takes the form:

\[
\Delta G(n) = -n\Delta \mu + (\gamma_A - \beta)A_{AB} + \sum_{j=1}^{k-1} \gamma_j A_j \tag{3.6}
\]

36
In equilibrium we get:

\[
\frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = \ldots = \frac{\gamma_A - \beta}{h_{AB}} \quad (3.7)
\]

One beautiful example are metal islands on WSe₂ or WS₂, where the low interaction with the substrate (only van-der-Waals forces) allows the islands to form clear crystal facets [44, 45].

In this discussion we have focused purely on the interface energies, without referring to lattice mismatch between substrate and adsorbate. Obviously, the lattice mismatch gives a major contribution to the interface energy, but it is not the only relevant parameter. Often, a prediction whether Volmer-Weber or Frank-van-der-Merwe growth will occur is just made on the basis of the lattice mismatch. This is, however, often too simple, as evidenced by the above given example of the growth on van-der-Waals surfaces [45].

### 3.2 Dynamical Effects and the Ehrlich-Schwoebel barrier

In the equilibrium picture of the previous section, a growing layer would always have the truncated Wulff shape. So, if a layer wets completely, a monolayer would be filled up completely, before the next one can start. Atoms that land on top of islands have therefore to traverse step edges to reach their equilibrium position. However, as Ehrlich and Hudda [46] found, diffusing atoms can be repelled by step edges.

This can for high-symmetry surfaces lead to a destabilisation: Atoms impinging on top of the islands nucleate there instead of filling the gap between the islands. In extreme cases growth of pyramid-like structures becomes pos-
sible [47]. This type of instability occurs mostly at lower temperatures, since the diffusion barrier can be overcome by higher thermal energy.

3.3 Higher coverages and critical layer thickness

If the adsorbate layer becomes thicker than several monolayers, the "classical" growth modes described above lose their meaning. If the layer is just thick enough, islands will coagulate. Coagulation of islands can either introduce dislocations [48], or grain boundaries and therefore columnar growth.

On the other hand, for completely coherent growth on the interface between two materials with different lattice parameters, the elastic forces will become large, necessitating a relief mechanism. There are two basic types of strain relief possible, albeit combinations are often found. The film might change its surface structure, in a sort of 2D-3D transition, where the film surface is not longer plane, but becomes wavy (Asaro-Tiller-Grinfeld instability) [49]. The more common way, however, is the introduction of dislocations in or close to the interface. Frank and van der Merwe [38, 50] introduced the concept of a critical layer thickness, above which the introduction of dislocations becomes energetically favourable. The theoretical framework has been expanded by many authors [51, 52, 53, 54, 55, 56] and a review is given by Politi and coworkers [49].

The introduction of misfit dislocations reduces the strain energy, but a core energy term is introduced. Also important is the type of dislocations: perfect dislocations – where the Burgers vector is a lattice vector – yield relatively high core energies. So, for many materials, partial dislocations, where the Burgers vector is a fraction of a lattice vector, can be energetically favourable in a certain thickness range [57]. A partial dislocation is the edge of a two-dimensional defect, for example a stacking fault. Partial dislocations can easily nucleate in materials where the stacking fault energy is low. Other dislocations might be emitted from the substrate, glide as a misfit dislocation (mathematically similar to an edge dislocation) near the interface, and pass through the layer as a threading dislocation.

If the substrate is of high quality, the number of threading dislocations might be very low. On the other hand, nucleation of new dislocations can be a rather improbable event, if it involves a high energy barrier. Therefore layers might grow coherently for thicknesses exceeding the critical thickness by far. Also, introduction of dislocations does not necessarily lead to complete strain relaxation. Under ordinary growth conditions [49], only glide of dislocations is possible. Since the Burgers vector has to lie in the glide plane, and the glide plane cannot be the interface, it follows that misfit dislocations have an out-of-plane component which does not contribute to the strain relief.

The models developed have different complexity. Starting from a single dislocation dipole, one can derive the Matthews-Blakeslee expression for the
critical thickness [52, 53, 49]

\[ h_c = \frac{b}{8\pi f} \left( \frac{1 - \nu \cos^2 \beta}{1 + \nu} \sin \beta \cos \phi \right) \left( \ln \frac{h_c}{b} + 1 \right), \]  

(3.8)

where \( b \) is the length of the Burgers vector of the activated dislocations, \( f \) the misfit between the layers, \( \nu \) Poisson’s ratio, \( \beta \) the angle between the Burgers vector and the dislocation line on the interface, and \( \phi \) the angle between the glide plane and the surface.

The rather simple calculations for the critical thickness \( h_c \), based on a single dislocation dipole, have often revealed their predictive power [58]. However, critics have pointed out [55] that the interaction between dislocations will change the results. Also, the classical derivation of the \( h_c \), going back to Frank and van der Merwe, assumes equal elastic constants for layer and substrate – otherwise the misfit dislocation could not lie directly in the interface, but a certain distance above or below. Using Head’s solution for an edge dislocation in an elastically inhomogenous medium [59], Dynna and coworkers [60] have derived a closed form expression for the total elastic energy.

### 3.4 Multilayers and Superlattices

We will now extend the above discussion to systems with more than one layer. In some way one can treat a multilayer in two stages: first, the relation between the layers themselves; second, the multilayer as a single entity in relation to the substrate [54].

The classic work on superlattices, by Matthews and Blakeslee [52, 53, 54], focuses on semiconductors on a semiconducting substrate. Lattice mismatch is small, not to say tiny in comparison to the systems described in this thesis. Strong directionality of the bonds and high energies of dislocation lines, together with the small lattice mismatch, often result in highly coherent growth.

The focus of our group has long been on metallic systems. Here, it is more difficult to achieve a high degree of coherence. Furthermore, as metallic single crystals are very expensive, and also in other ways not always preferable, we use oxidic substrates. We have therefore to deal first with the growth of the first metal layer on the oxide and then with the constituent layers growing on each other.

Relatively recently we started to investigate systems consisting of oxidic and metallic layers, as detailed in Paper VI. Since here the constituent layers have different structures, and we have always oxide-metal interfaces, this system – Fe/MgO – will be treated separately in section 3.4.2.
3.4.1 Metallic Superlattices

In this thesis, two types of metallic superlattices have been studied: Fe/V and Fe/Cr. Paper I deals with Fe on Mo, grown on a sapphire substrate. While high structural coherence was there also achieved, these layers are repeated only once and count therefore not as superlattices.

For the superlattices, which were all grown in the (001) direction, magnesium oxide (MgO) substrates were used. The epitaxial relationship for all of the metals used is $[100]_{\text{metal}} \parallel [110]_{\text{MgO}}$.

![RHEED pattern of a 10 Å thick Cr film on MgO(001). Spotty pattern with broad peaks indicates rough surface of low quality.](image)

The growth of, for example, iron on magnesium oxide is not straightforwardly one of the ideal growth modes. A strong Ehrlich-Schwoebel barrier gives rise to dynamic effects. Depending on the temperature [61, 47] iron films can grow in pyramid-like structures, or – at higher temperatures – a sort of Stranski-Krastanov growth. Indeed, the RHEED pattern for a seven monolayer thick Cr film on MgO, Fig. 3.4, shows a broadened, spotty pattern. The streaks of the two-dimensional diffraction pattern are still visible, but the major features are round, nearly blurry spots. The surface is clearly not of very high quality with respect to flatness and crystalline order.

The layer whose diffraction pattern is shown in Fig. 3.4 served as an underlayer for a superlattice with sixteen repetitions. After this, another RHEED pattern was acquired. This time – Fig. 3.5 – the streaks are much more pronounced and narrow. Even a Kikuchi pattern is visible, indicating high quality of the stacking of the crystal [16].

If we grow another monolayer of Cr on top of this sample, the picture stays nearly unchanged (Fig. 3.6). Although the lattice mismatch between bulk Cr and V is much larger than between either metal and MgO, taking into account the epitaxial relationship, the growth is pseudomorphic and completely coherent.
Figure 3.5: RHEED pattern of a 14 ML Cr/14 ML V superlattice, at the top of the 16th V layer. Streaks are narrower and more pronounced than in Fig. 3.4. Appearance of a Kikuchi pattern indicates high quality of the stacking.

Figure 3.6: RHEED pattern of one monolayer Cr grown on top of the sample depicted in Fig: 3.5. Figure from paper III.
So, from the in-plane view, the growth of a superlattice apparently suppresses the 3-dimensional growth of the first layers and leads to well defined crystalline structure. However, the main reason to grow a superlattice was to have a structure modulated in the out of plane direction – and this is not accessible by surface sensitive methods like RHEED, as mentioned in chapter 2. XRR and XRD are therefore used to access the out-of-plane periodicities. In Fig. 3.7 an X-ray diffraction pattern of a very well defined Cr/V superlattice is shown. Sharp superlattice peaks to the (-4) and (+7) order indicate a sharp chemical modulation, and the Laue fringes between the (-1) and the fundamental 002 Bragg peak show complete out-of-plane coherence throughout the entire layer thickness.

![X-ray diffraction pattern of a Cr/V superlattice](image)

*Figure 3.7: X-ray diffraction pattern of a Cr/V superlattice with 20 repetitions of 3 ML Cr, 25 ML V, acquired at the high-resolution diffractometer at the beamline W1.1, HASYLAB. The inset shows the Laue fringes between the 002 peak and the (-1) superlattice peak. Also visible are the MgO 002 (42.9°) and Pd 002 (46.7°) reflections. Figure from paper III.*

The sample yielding the pattern in Fig. 3.7 is, however, of exceptional quality. Fig. 3.8 compares the rocking curves over the fundamental 002 Bragg peak of different samples. The width of the rocking curves – the mosaicity – shows huge differences. We therefore have to have a look at the various imperfections that might appear in a sample.

**Interdiffusion versus crystalline quality**

We have mentioned above that growth of high quality bulk crystals is a near equilibrium process. However, most of the transition metals we use for superlattice growth are miscible over a wide composition range, so the equilibrium crystal structure would be an alloy layer without any chemical modulation.
Therefore, the sample has to be kept at relatively low temperatures during growth and thereafter. On the other hand, preventing the material to reach its equilibrium alloy state prevents also the formation of large crystallite grains and therefore higher temperatures are desirable. Generally, a higher growth temperature will lead to larger grains with less misalignment, thereby reducing mosaicity. Growth of high-quality superlattices is thus always a trade-off between crystallinity and interdiffusion, and careful optimisation is necessary to find a temperature window in which samples of sufficient crystallinity with an acceptable level of interdiffusion can be grown.

However, the crystalline quality depends on surface diffusion on the growth front, while the interdiffusion depends on the bulk diffusion. Increasing or decreasing the substrate temperature during growth will obviously affect both. Therefore, any parameters in the growth process that affect only one of the diffusion coefficients can open routes for enhanced sample quality.

For not purely thermal growth methods, like magnetron sputtering, variation of other parameters is also possible. Collisions between atoms of the sputtered material and the process gas lead to a partial thermalisation of the first, and higher gas pressures will lead to lower impact energy of the deposited material. The process gas pressure is therefore one parameter more that can be optimized.

The observation of Horch and coworkers [62] that adsorbed hydrogen can enhance the self diffusion of Pt atoms on Pt surfaces opens an interesting route. Hydrogen as a surfactant during growth had been studied by several groups for semiconductors [63, 64, 65] before, but not for metals. We have explored that route in paper II. For Fe/V superlattices growth temperatures could indeed be lowered without loss of crystalline quality. An additional ben-
efit could be chemical purification, in that the hydrogen reduces metal oxides, removing oxygen impurities from the deposit. Later experiments on Fe layers on germanium, however, showed ambiguous results. It seems that for this system, the addition of hydrogen actually makes the crystallinity worse. For the Cr/V superlattices described in paper III it was found that the crystalline quality is mostly determined by the vanadium layers. So, if adsorbed hydrogen enhances the growth of vanadium, but not of iron, these results can be easily reconciled with that of paper II. On the other hand, it is also possible that the hydrogen has different effects on the germanium substrate.

Formation of misfit dislocations
The discussion in section 3.3 applies obviously also to superlattices. As we mentioned above, Matthews and Blakeslee [54] have pointed out that for completely coherent growth of a superlattice the critical layer thickness condition has to be fulfilled twice: one time for the growth of the individual layers on the already grown superlattice, and a second time for the entire superlattice on the substrate. In general, superlattices with shorter periods can therefore be grown with a higher degree of coherence [53, 54, 66]. Since \( h_c \) for the individual layer strongly depends on the misfit, it depends on the average lattice parameter in a superlattice. Asymmetric superlattices, where one layer is significantly thicker than the other, can therefore show superior crystalline coherence. The thicker layer has bigger influence on the average lattice parameter, yielding less misfit and a larger \( h_c \). For the thinner layer the misfit is larger, but here the thickness is anyway small. This relation is discussed in paper III for Cr/V superlattices.

While \( h_c \) seems to be an inherent property, it is nevertheless interesting to discuss whether there are routes around it. One observation [48] is that iron films up to more than 50 nm thickness are not fully relaxed – the film is still strongly strained. Apparently, the introduction of misfit dislocations is an energy costly process. Are there now any ways to avoid the formation of misfit dislocations? Two processes have to be considered here: the glide of threading dislocations, and the nucleation of ”new” dislocations. The nucleation of new dislocations is nearly impossible to avoid and will set an upper limit. On the other hand, threading dislocations, which are emitted from the substrate, have been observed in Fe/V superlattices [67]. These can now glide sideways, and provide a misfit dislocation at an interface. A mechanism that prevents dislocations from the substrate to thread through the multilayer, could therefore be interesting. Since a dislocation experiences a force close to an interface, where the elastic constants change [59, 68], an interface from a softer to a stiffer material can repel a dislocation. Matthew and Blakeslee [54] discuss how this can lead to the escape of dislocations – they cannot end inside the sample, but they can be pushed out to the edges, instead of threading to the surface. For multilayers, the mathematical treatment can become quite complex [69], especially as we would now deal with mathematically more demanding
edge dislocations. Nevertheless, it could be interesting to study whether it is possible to find a dislocation blocking layer combination.

**Instability of the growth front**

From the discussion of Wulff’s theorem follows that it is in no way necessary that the growth front, parallel to the substrate plane, is also thermodynamically favourable. For fully developed island growth, side facets often appear [45]. This is also not yet the full picture: in the equilibrium description, we neglected strain terms. Nevertheless, already from this simple argument we can see that we should not take flatness of the growth front for granted.

While the introduction of misfit dislocations is a common way to relieve misfit, there are other mechanisms, and the most import is the transition from a flat surface to a wavy one. This process is known as the Asaro-Tiller-Grinfeld instability [49, 70] and it is common in III-V semiconductors. An interesting point is that the transition to a wavy surface is also dependent on a critical thickness [70].

Birch and coworkers [71] have observed this transition for vanadium layers in Mo/V superlattices – a system very similar to the Cr/V and Fe/V superlattices in this work. Indeed we see in the samples described in paper III that the diffuse scattering part in the XRR increases strongly for V layers thicker than around 35 Å, indicating that this transition occurs also for V layers under compressive strain. Instability of the growth front is therefore a mechanism not to be neglected in metallic superlattices. A related work by Sridhar and coworkers [72] discusses the stability of the interfaces between the layers against in-plane diffusion.

### 3.4.2 Metal/Oxide Superlattices

Paper VI describes an entirely different system: superlattices consisting of iron and magnesium oxide layers. The Fe/MgO system has attracted interest due to theoretical predictions of very high tunneling magnetoresistance values [73]. There have been many experimental realizations of tunneling junctions based on Fe/MgO/Fe trilayers, for example by Yuasa and coworkers [74]. However, as their high resolution micrographs show, such layers are rarely free of dislocations. The formation of an FeO layer on the interface between Fe and MgO has also been reported [75, 76]. Since XRR is one of our standard methods, it was natural to use a superlattice to increase the signal and thereby the sensitivity to interface related phenomena.

From the discussion above about the growth of transition metals on MgO, one can infer that this would not be trivial. Island or Stranski-Krastanov growth is not reconcilable with flat superlattice structures, and the desired, relatively thin iron layers would not have the volume necessary to compensate for the initial roughness.
We succeeded nevertheless to grow flat multilayers, as seen by XRR, with very high crystal coherence, as evidenced by the high resolution TEM micrograph, Fig. 3.9. Although intermixing was no problem in this system, the growth temperatures had to be kept significantly lower than for comparable metallic superlattices: at higher temperatures, accumulative roughness would destroy the layering. At very high growth temperatures, the four-fold in-plane magnetic anisotropy was less pronounced, suggesting that the deposited iron showed diminished registry with the substrate.

Despite the fact that the XRR showed a well defined layered structure with extremely sharp interfaces, comparable to the best metallic superlattices, and near complete structural coherence, as seen in the micrograph, the sample did not show the diffraction pattern of a superlattice. In fact, the iron peak was rather broad, indicating a short crystalline coherence length. In paper VI these seemingly contradictory observations were explored. We found that the strain fields originating from steps are destroying the coherence, making the iron layers effectively independent scatterers.
4. Amorphous Multilayers

As we have seen in the previous chapter, crystalline systems have, despite or even because of their symmetries, some disadvantages. Crystalline layers can seldom be grown free of defects, which can act as pinning centers for domain walls, changing the magnetic properties of the layers. Introduction of dislocations will also change the elastic properties.

Moreover, if the growth is not phase-locked, multilayers will always contain atomic steps, leading to strain fields and variation in the layer thicknesses. An extreme case can be seen in Paper VI, where the induced strains actually destroy the typical X-ray signature of superlattices.

These problems can be removed by removing the crystallinity entirely, and using amorphous layers as building blocks. We have therefore to look at amorphous metals, or "metallic glasses".

4.1 Glasses and the glass transition

Now we have in one line introduced two concepts - "glass" in a different meaning than the mostly amorphous silicon dioxide in window panes, and metals not in the crystalline structure found in the basic text books of solid state physics. In the next paragraphs we will first deal with some general properties of glasses, before we come back to the metals.

It must be mentioned that the theoretical description of glasses and the glass transition is not yet concluded. Although there has been huge progress over the entire 20th century, even the basics are still under discussion [77, 78, 79].

First, the definition of a glass - in a wider sense one could define a glass as an amorphous solid. If we take this one step further, an amorphous solid would be something that failed to crystallize when cooled down from a liquid state, staying in a state of higher energy than the equilibrium crystal\(^1\). To describe such behaviour, Ostwald introduced in 1910 the concept of a metastable state. The energy of the system increases for all small displacements of the particles, but can decrease for certain large displacements. Ostwald gave as a conceptual example the picture of a marble in a bowl above a table. For small displacements, the marble will return to the bottom of the bowl, but for larger

\(^1\)Atactic polymers and similar systems, which cannot crystallize, go beyond the scope of this work and are not considered
displacements, the marble is thrown out of the bowl, coming to a state of lower potential energy on the table.

In the formulation of Kauzmann [80], we can say that a system is in a metastable state if small isothermal changes in the independent thermodynamical variables result in an increase of its free energy, while larger changes can result in a state with lower energy. Examples of metastable states can be found in the daily life in supercooling water in a freezer, or superheating water in a microwave oven. Therefore it is tempting to see a glass just as a supercooled liquid, which due to its low temperature has a viscosity so high that it appears as a solid. However, the "daily life" examples of superheating and supercooling are limited to a few kelvin. Silicon dioxide, forming the the archetypical "glass", however has a melting point of 1650°C. In this picture, an ordinary windowpane would be a liquid nearly one and a half thousand kelvin beneath its melting point. The driving force for crystallization would be enormous. So, there must be something more to it.

If we now consider the entropy of a system in the crystalline and molten states, the entropy in the crystal is dominated by vibrational contributions, whereas the entropy of the melt is dominated by the configurational part. Since the configurational entropy increases with the free volume, the larger thermal expansion of a melt as compared to a solid leads to a much steeper increase of the entropy with temperature for the melt than for the crystal. Extrapolating the entropy of crystal and melt from the melting point to lower temperatures would therefore lead to a point where the entropy of the liquid is first equal (at a "Kauzmann temperature" $T_K$) and then lower than that of the crystal. This would lead to a violation of the third law of thermodynamics, and is known as the Kauzmann paradox [80].

Experimentally, however, it is determined that the specific heat and the thermal expansion coefficient, for example, drop suddenly at a temperature $T_G$ which is roughly two-thirds of the melting point. The entropy shows a sudden change of slope, to roughly the same as for the crystal. The exact temperature of this transition is not only system-dependent, but depends on the cooling rate - the slower the cooling proceeds, the lower the apparent transition temperature.

Theories that describe this glass transition can be roughly divided into three classes [77]: the first class – free volume theories – assume that the diffusive transport in a liquid will become impeded by backscattering, and that the backscattering probability increases sharply if the density exceeds a certain value [81]. In other words, to flow, molecules need space, and if a liquid becomes too dense during cooldown, its properties become that of a solid.

The observation that the glass-transition temperature depends on the cooling rate leads to the second class of theorie, the kinetic ones. A change of conformation can be described by a (formal) activation energy, which increases for decreasing temperature and diverges at $T_G$. This point of view can be related to the description using the free volume, but it leads to a different defi-
tion of the free volume. Although both descriptions are closely related, they cannot yet be unified.

As discussed previously, the entropy versus temperature curve shows a sudden change of slope at $T_G$. Thermodynamically, the glass transition can therefore be interpreted as a second-order phase transition. There are some difficulties with that approach, namely the cooling-rate dependence of $T_G$. Using a quasi-lattice theory for linear molecular chains, Gibbs and DiMarzio [82] deduced the existence of a thermodynamic second-order transition, masked by kinetic effects. The configurational entropy decreases while approaching $T_G$, but the system relaxations become increasingly slower, exceeding the experimentally available timescales, and the system stops in a glassy state with a remaining configurational entropy. If kinetic restrictions would not apply, the configurational part of the entropy would vanish at a temperature $T_2$, the transition temperature of the theoretical second-order phase transition.

Adam and Gibbs [83] developed this picture further, introducing a "cooperatively rearranging region", the minimum size of a subsystem which can undergo a conformation change without affecting the rest of the system. For liquids this region is quite small, but it diverges when the temperature approaches zero. However, this picture has recently been criticised by Stillinger and coworkers first by showing that a Kauzmann point does not necessarily lead to a third law violation [78], and later by showing the non-existence of a thermodynamic glass transition in binary hard sphere mixtures [84].

It seems surprising, that more than forty years after the properties of a thermodynamic transition were believed to be found, the bare existence of it is doubted. This shows the richness of the underlying physics and also the difficulty to abstract the common properties of such different systems as polymers, hard sphere, molecular, ionic and metallic glasses.

4.2 Glass-forming ability and metallic glasses

In the section above we have discussed the formation of a glassy phase under conditions approaching thermal equilibrium. However, in many glass forming system crystallization prevails under such conditions. Strong directional bonds – as in silica or alumina – or steric inhibitions – as in polymer glasses – can suppress crystallization. This shows the fundamental difficulty of obtaining glasses in metallic systems: metallic bonds show no strong directionality, and metals crystallize by simple rearrangement, without involving folding and conformation changes as polymers.

It has been suggested by Rawson (1967, cited after [85]) that the glass forming ability scales with the ratio of the bond strength to the melting temperature $B/T_m$, since crystallization involves rearrangement and thereby breaking of bonds. This is evidenced by the easy glass forming of, for example, silica
with very strong Si-O bonds. However, while this criterion is useful, there are many factors involved, and it is difficult to predict whether certain materials are good glass formers or not [86].

We therefore do not expect metals in general to be very good glass formers. It is difficult to produce amorphous elemental metals, and indeed they tend to recrystallize easily.

From the above we can deduce that anything that lowers the melting point or increases the glass-transition temperature by slowing down relaxation processes might facilitate glass forming. Since elemental metals are unsuited, binary alloys come to mind. In the phase diagrams of these, eutectic points are especially interesting, since they yield the lowest available melting points, increasing $B/T_m$. Eutectic points mean immiscibility in the solid phase. We have therefore a look at the well-known Hume-Rothery rules for the formation of solutions [87]:

1. The solute should not differ in its atomic diameter by more than about 15% from that of the host. If not, it is likely to have low solubility.
2. The solute should not have a large difference in electronegativity, compared to the host.
3. A metal with a lower valence is more likely to dissolve on which has a higher valence than vice versa

Searching for desired deep eutectica, we have to look for conditions where these rules are not fulfilled. It seems obvious that we have to look into compounds of quite different metals. Pure metallic glass formers are found in the following systems [85]:

- early transition metal (TE) - late transition metals (TL) (e. g. NbNi, ZrFe)
- rare earth metals (RE) - late transition metals (TL) (e. g. GdNi)
- alkaline earth metals (AE) with either simple metals (S) (MgZn), transition metals or rare earth metals.
- actinides (AC) - transition metals (e. g. UCr)

Most studied, however, are alloys of transition metals with semimetals – ”metalloids” – such as Si, B, P. Transition metal-metalloid glasses show mostly metallic behaviour. Among the frequently studied systems are ternary glasses in the Fe-Co-B system, that have also shown interesting technological potential [88]. Quaternary glasses (e. g. Fe-Ni-P-B) are also commercially available. High metalloid contents, however (good glass formers contain approximately 20% metalloid), have adverse effects on magnetic, elastic and plastic properties [89].

Since, in general, metals are much worse glass formers than many oxides or polymers, glassy phases can nearly only be obtained by employing very high cooling rates (the alternative approach of solid state amorphization will be considered in connection with multilayer systems). Cooling rates of $10^6 - 10^8$ Ks$^{-1}$ can be obtained by melt-spinning, a technique where a fine jet of melt is cast on a rapidly turning, cooled copper wheel. Thereby thin (ap-
proximately 30-50 µm) ribbons of up to several centimetres width and several hundred metres length can be produced.

While the effective cooling rates of vacuum deposition are difficult to assess, they are several orders of magnitude higher than those of melt-spinning and comparable techniques. Many materials, that cannot be obtained in an amorphous state by other techniques, may be grown as amorphous thin films.

4.2.1 Iron-zirconium based glasses

In this work we have focussed on a pure metallic, binary system, accepting lower glass-forming ability than in the metalloid based systems. Neither pure boron nor phosphorus are well suited for deposition in a vacuum system without special precautions. This would make the use of compound targets necessary, which has some advantages, but makes it more difficult to tailor magnetic and chemical properties by adjusting the stoichiometry. Given these, the iron/zirconium system around the eutectic point of 11.2 at.% Zr\(^2\), at 1583.1 K [91] was chosen.

In the Fe-Zr system there is another eutectic, at 72.5 at.% Zr, at a lower temperature of 1206.5 K. Since, however, our interest is mainly in magnetic properties, we had to use the iron rich eutectic point. Using melt-spinning, metallic glasses can be fabricated in the range of 7-12 at.% Zr [92]. Using vacuum deposition, this range can be extended significantly, at least to lower zirconium contents [93].

Magnetically, the system is believed to be Heisenberg-like, although modified by anisotropy terms, leading to frustration and, at low temperatures, spin-glass behaviour [92, 94]. However, it has been found difficult to completely remove crystallinity in the iron-rich FeZr glasses [94].

The FeZr glasses exhibited therefore several points of interest for us. Vacuum deposition was supposed to easily overcome problems with remaining crystallinity and polarized neutron studies could therefore address the magnetic behaviour of a pure glassy system. Magnetic coupling over non-magnetic interlayers has often been studied [95] but only rarely over amorphous interlayers.

As described in Paper VII, we found that, despite the enormous effective cooling rates during the deposition process, the material was partly crystallized. This was taken as a reason to have a closer look at crystallization processes, especially related to surfaces.

\(^2\)The Fe-Zr phase diagram, and especially the stoichiometries of intermetallic phases has undergone some revisions in the past years. Older sources [90] give the eutectic at lower Zr content.
4.3 Crystallization on surfaces

There are several studies about crystallization in the FeZr system [96, 93]. Zárubová and coworkers [96] investigated the crystallization of melt-spun samples by differential scanning calorimetry. As mentioned above, melt-spun FeZr samples are rarely entirely free of crystallites, and indeed the crystallization behaviour was found to be dominated by quenched-in crystallites.

An entirely different route, somewhat closer to our approach, was chosen by Herr and coworkers [93]. They studied the crystallization of FeZr amorphous layers for compositions with less than 7% Zr. The $\alpha$-iron phase can incorporate this amount of Zr, therefore these alloys can crystallize without undergoing a phase separation. Herr et al. used a Zr underlayer to ensure initial amorphicity - they found no trace of crystallinity before annealing.

And indeed it is often found that incongruent interfaces stabilize the amorphous state [97], instead of facilitating crystallization. Yet the micrograph, Fig. 4.1, shows the grains preferentially at the interface. Electron diffraction revealed them to consist of $\alpha$-iron, with a somewhat expanded lattice parameter, due to the incorporation of Zr. However, $\alpha$-iron cannot incorporate more than 7% of Zr [91, 93]. So, there had to be a phase separation involved, creating areas of lower Fe content.

In order to get a better understanding of the differences between our work and that of Herr’s group [97], we reviewed some general aspects of metallic and other glasses. Although some parts of them are rather distant to the subject of this work, they are nevertheless presented here to show some connection to different fields of physics.
4.3.1 Stability of the glassy state

We have discussed above several theories for the formation of glasses. There have been many works on abstracting general criteria from the multitude of experimental results. A very useful criterion has been suggested by Egami [98]. To work out the limits for a local topological instability, he starts from the stability of a crystal against melting.

In a cubic close packed structure, the coordination number is 12. So, if thermal expansion lowers the density, so that a thirteenth neighbouring atom is allowed, the structure will collapse. Egami calculates now how much the structure must expand, to allow the same atomic density on the sphere defined by the nearest neighbor atoms $\eta_{2D}$, with 13 atoms instead of 12. This expansion $\varepsilon_V$ is then:

$$\frac{12}{13} = \frac{1}{(1 + \varepsilon_V)^{2/3}}, \quad \varepsilon_V = 0.128$$  \hspace{1cm} (4.1)

However, already when half of the sites can accept an additional neighbor, the structure will collapse. From this simple argument follows, that for a critical expansion of

$$\varepsilon_{V}^{crit} = 0.064$$  \hspace{1cm} (4.2)

a metal will melt. And indeed it is found that the majority of metal melts, irrespective of their actual melting temperature, their atomic radius, or even their crystal structure, melt at between 6 and 8% thermal expansion. This argument can be expanded to cover a dense random packing model, yielding a slightly lower $\varepsilon_{V}^{crit}$ of 0.0554. Melting of the glass now occurs when for a majority of the sites this condition is continually fulfilled. For a glass, distinguishing it from the treatment for the crystal, local fluctuations have to be taken into account. Egami uses the local atomic pressure to describe these fluctuations. The structure will collapse – or even be in state of constant collapse, and therefore liquid – when the percolation limit for the sites, where the instability condition is fulfilled, is reached. If the distribution of the local atomic strains is gaussian, the percolation limit (15 %) is reached when the root mean square of the local strains equals $\varepsilon_{V}^{crit}$:

$$\varepsilon_{V}^{crit} = \sqrt{\langle \varepsilon_{V}^{2} (i) \rangle}.$$  \hspace{1cm} (4.3)

However, it proved difficult to expand Egami’s criterion to our system. Getting hold of the local strains in the near-surface region would probably have required an extensive molecular dynamics study.

4.3.2 Surface nucleation

Since the crystallites seen in Fig. 4.1 are seemingly related to the interface, another look at the nucleation on surfaces as described in chapter 3 seemed worthwhile.
As discussed previously, for the formation of a nucleus the gain in binding energy has to compensate the expended surface energy (See equation 3.4). Since the bulk energy for a crystalline state is lower than for the glassy state, the critical nucleus for the crystalline state would be smaller than that for the amorphous one. It seemed obvious that the system, given the availability of both routes, would preferentially form crystalline nuclei.

However, as discussed in the previous chapter, the critical nucleus under ordinary sputter deposition conditions is very small – 10 atoms or less. Especially if we also take surface relaxations for the small cluster into account, ”crystalline” or ”amorphous” is simply not yet defined on such length scales. We therefore abandoned the size of the critical nucleus as an explanation for the crystallites.

4.3.3 Entropically: hard-sphere model

Could it be, that some sort of order is introduced just by the flat surface of the substrate? If the deposited atoms have to arrange in two dimensions, but have no freedom in the third, could that be already enough ”order” to preclude an amorphous phase?

Figure 4.2: The depletion effect. The area marked by the dashed lines is unavailable for the smaller spheres. The shaded area is excluded by two particles (or the wall) together – if they were further apart, they would exclude the area separately [99].

A simple model for a fluid – actually the most simple possible – consists of hard spheres, without any additional attractive interaction. Crystallization seems at the first look impossible without an attractive force, holding the crystal together. However, the entropy of the crystalline phase can, for sufficiently high densities, be higher than that of the liquid phase, and the system will crystallize [100, 101].
For binary mixtures of hard sphere particles with different sizes, there is an entropic driving force favouring phase separation [102, 103]. Simply put, a small particle cannot approach another particle nearer than the sum of their radii (the definition of a hard sphere). Therefore a certain part of the system volume is inaccessible to the particles, lowering the entropy. As Fig. 4.2 illustrates, it is possible that the excluded volumes around particles overlap, in effect reducing the overall excluded volume, thereby increasing the space available and the configurational entropy. Thereby in binary mixtures, the bigger particles might cluster together, to ”make space” for the smaller ones.

As also seen in Fig. 4.2, walls of the system also exclude volume, and thereby there exists an effective attractive potential pulling the larger particles to the wall [104], which can lead to preferred crystallization close to the wall [105]. Dinsmore and coworkers [106] have followed this process from the first wetting liquid layer to the crystallization on the walls of the system. However, to see such a phase separation, the size ratio between the particles needs to be rather large ($r_1/r_2 \approx 0.15$).

Even though the phase separation appears similar to our metallic glasses, the differences are huge: entropic potentials are several orders of magnitude smaller than chemical interactions, and the size ratio between Fe and Zr is also by far smaller than necessary for a phase separation, even if the chemical interaction would not exist.

4.3.4 Phase-separation by dewetting

The film growth can be viewed as proceeding in three steps: first, nucleation of small clusters by agglomeration of single atoms; second, formation of island grains, and third, formation of a continuous film after complete metal coverage. As discussed in more detail in paper VII, the separation into an iron rich and an iron poor phase must occur during the first, or possibly the first two, steps.

As we have seen above, the size of the critical nucleus cannot be related to the question whether it is amorphous or crystalline. However, the nucleation can be related to the segregation of an iron-rich phase: the surface diffusion, and thereby the growth rate of the initial cluster $\Gamma_n^+$, depends exponentially on the activation energy (see e. g. [41]):

$$\Gamma_n^+ = \sigma_n N_1 a \nu \exp \left( \frac{Q_D}{kT} \right)$$

(4.4)

where $\sigma_n$ is the capture width of the cluster, $N_1$ the number of single atoms on the surface, $a$ the separation between the clusters, $\nu$ the attempt frequency and $Q_D$ the activation energy for surface diffusion.

In paper VII this relation is used to explain the preferred nucleation of iron-rich clusters. However, the thermal diffusion is also an equilibrium process – and the deposited atoms impinge on the surface with much higher energy,
which they quickly lose on the surface. How can this process be accounted for? In principle, the atom has to be followed from the impact on the surface until it comes to rest. The energy loss during impact on a crystalline surface has been studied theoretically by McCarroll and Ehrlich [107]. The main results are that impinging atoms lose their energy very fast (in the order of $10^{-14}$ s). Conceptually, this is easy to understand: if the atom is impinging with an energy corresponding to a temperature of several thousand kelvin, it must loose it very quickly, otherwise it would simply reevaporate. Here the main difference between metallic and oxidic surfaces comes into play: On the metallic surface, the diffusion lengths are short, since the impinging metal atom can immediately form the chemical bonds. On an oxidic surface, the binding energy is less, and the diffusion lengths are larger. The exponential term in equation 4.4 will dominate.

Outgoing from the study in paper VII, we have used metallic interlayers, in particular AlZr alloys. On these, we have, as expected from the above, not seen any crystallization in the FeZr.
5. Results and Conclusion

In this chapter the results from the papers are briefly collected. The backgrounds to the methods used have been reviewed in the previous chapters, and although occasionally an example from the papers was highlighted, all results are brought together here. Since this thesis concerns itself with a variety of subjects, there are interesting points that the author would like to follow up at some point in several areas – technical, experimental, and some also theoretical. Implications for future research are thus discussed, and a short outlook concludes the chapter.

5.1 Summary of the appended papers

The papers constituting this thesis, although all concerned with the growth of thin film materials, nevertheless cover a range of subjects. It was therefore found advantageous to account for their content separately.

5.1.1 Paper I

Paper I concerns itself with the interdiffusion of an iron/molybdenum bilayer. This system serves as a basis in the preparation of magnetite layers by oxidation of iron. Magnetite (Fe$_3$O$_4$) has been found to be a half-metallic ferromagnet [8], where only one spin state exists at the Fermi level. This would be of extreme interest for spintronics applications, since there would be no "spin leakage". The preparation method suggested by Fonin and coworkers [9] consists of the preparation of a high quality Fe(110) layer on a Mo(110) seed layer, grown on a sapphire substrate. As we have later tested ourselves, it is not possible to grow Fe(110) directly on Al$_2$O$_3$ (11$ar{2}$0) with high quality, since the mismatch is too high. A Mo or W seed layer can therefore be used to take up the misfit.

To get a comparatively thick ($\approx$ 200 Å) magnetite layer, the sample has to be heated to high temperatures ($\approx$ 700°C) for tens of minutes. Barbieri and coworkers [10] have described an alternative route, where the oxidation occurs at room temperature, but they prepare only a single atomic layer, oxidze, anneal, and grow the next monolayer of iron.

We decided for the high temperature approach, in order to reduce the number of preparation steps. Investigation of the resulting film, however, showed that Mo had interdiffused with the iron, up to thermal equilibrium. This basi-
cally excludes this approach to the growth of magnetite layers, and offers an explanation for the observation of Fonin and coworkers [9] that magnetite layers grown on molybdenum show less spin polarisation than such grown on W. Tungsten seed layers seem, due to the lower solubility of W in Fe, possible, although the lattice match to Fe is worse.

5.1.2 Paper II

In paper II, hydrogen assisted growth of Fe/V superlattices, the effects of hydrogen in the process gas during growth were studied. As already mentioned in chapter 3, hydrogen is supposed to enhance surface diffusion, thereby opening a route to improved crystalline quality.

The sample stack chosen for these experiments, 30 repetitions of 2ML Fe/16 ML V, is, as we saw in the work reported in paper III, in a window where excellent crystal quality can be achieved even without hydrogen. The changes in crystalline quality were therefore only accessible with high-resolution diffraction. This was done at the six-circle diffractometer of the beamline W1.1 at HASYLAB. It was found that the substrate temperature during growth could be lowered by 50 K without any unfavourable changes in mosaicity, while for the hydrogen free process the mosaicity nearly doubled. For the growth temperature optimized for the hydrogen free process, the in-plane correlation length, determined by the diffuse scattering around the reflectivity peaks, doubled from 150 nm to 300 nm.

The superconducting properties of pure vanadium samples were also studied. There it was found that the defect-related part of the electrical resistance was significantly reduced for layers grown under hydrogen pressure, and the coherence length of the Cooper pairs increased.

Besides the improved surface diffusion, hydrogen can also reduce impurities, since it removes oxygen. The improvement in superconducting properties indicated that no hydrogen impurities remain in the film.

5.1.3 Paper III

It has been observed earlier [71], that V layers in Mo/V superlattices can be grown coherently only to a thickness of 16 ML. However, in this study of Cr/V superlattices it was found that the crystalline quality in a series of samples actually seemed to improve with the V thickness even beyond the limit of 16 ML. A systematic study revealed a maximum in mosaicity and a minimum in out-of-plane crystalline coherence length for symmetric superlattices, i.e. superlattices where both constituent layers have the same thickness.

Application of the Matthews-Blakeslee [53] expression for the critical layer thickness for a relaxed superlattice yields an explanation of the development of the mosaicity over the changing ratio between Cr and V. The only major deviation is the extreme case for nearly pure vanadium superlattices, where
the Asaro-Tiller-Grinfeld instability appears, and the roughness of the layers increases.

In between these structural instabilities, there exists an optimum where superlattices of surprising quality can be grown. An out-of-plane coherence length equal to the sample thickness and a mosaicity of less than 0.02° are achieved for a sample with 3 monolayers Cr and 25 monolayers V.

5.1.4 Paper IV

If a metal, in this case V, absorbs H to interstitial sites, the resistivity changes. In the simplest case, hydrogen acts as a point scatterer and the resistivity increases with hydrogen content for low concentrations. For high hydrogen contents the resistivity decreases again, as the hydrogen vacancy density decreases. In superlattices, interface effects cannot be neglected. In particular, following from the previous, there should be a maximum of the resistivity – this is observed for Mo/V, but not for Fe/V, where the V layers are under compressive strain [108].

A recent theoretical study [109] suggested that interface effects in Mo/V and Fe/V can be completely explained by elastic effects, and electrostatic effects could be neglected. To verify this point, Cr/V superlattices were used. Since Cr has a similar lattice parameter to Fe, V layers can be prepared in the same strain state for Cr/V and Fe/V superlattices. However, the sample behaved more like a comparable Mo/V superlattice, with a distinct maximum, than like an Fe/V sample. Therefore, elastic effects are not sufficient to explain both the hydrogen uptake and the resistivity changes in superlattices.

5.1.5 Paper V

Paper V deals with interesting aspects of the magnetic ordering on different length scales in superlattices. Fe/V is again used as a model system, and the inherent ordering temperatures of the layers are adjusted using the thickness. An Fe/V superlattice, where the thickness of the V layers ensures antiferromagnetic coupling at low temperatures, has been prepared in such way that every second Fe layer has, due to finite size effects, a lower ordering temperature than the ones between. Thereby an additional lengthscale is introduced.

5.1.6 Paper VI

Paper VI is also about multilayers/superlattices. However, the Fe/MgO samples described therein are not isostructural, metallic superlattices. Here, we have the difference between the rock-salt structure of MgO and the α-Fe structure. The huge difference in lattice parameter must lead to a different superlattice diffraction pattern (chapter 3). However, the superlattice pattern is, despite carefully optimized growth, not found. The diffraction pattern of the
samples was more consistent with that of a single iron layer – the coherence length being only comparable to one layer thickness.

So, there is a question whether the samples described in paper VI are superlattices or not. From the high resolution TEM image, lattice coherence seems evident, seemingly contradicting the diffraction measurement, where this is not the case. Since the monolayer thicknesses of the Fe and MgO are largely different and incommensurate, layer edges lead to strain fields, giving rise to a continuous variation in the distance between the iron and MgO layers, thereby destroying coherence.

5.1.7 Paper VII

In paper VII the growth of Fe$_{91}$Zr$_{9}$/Al$_{2}$O$_{3}$ multilayers was studied. Amorphous magnetic layers would avoid anisotropy terms from atomic steps at the interfaces. Also the low magnetic coercivity would be of high interest.

However, the samples were not free from crystallites. High-resolution TEM pinpointed the crystalline impurities at the lower interfaces. As it has been discussed in section 4.3.4, this showed a dewetting induced phase separation. This can have large implications for the growth of amorphous metal-insulator heterostructures.

5.2 Concluding Discussion and Outlook

The aim of the present work was to optimize thin film structures for several purposes – hydrogen uptake, measurements of magnetic coupling and phase transitions – as well as opening a route to amorphous magnetic multilayers. Of the papers discussed, I-III, VI, and VII deal nearly exclusively with the structural part, while IV and V represent the application of the grown structures.

On the metallic superlattices, Cr/V and Fe/V, the previous line of action was continued. It could be shown, that there is still possibility for improvement in crystalline quality. The approach pursued in paper II, use of hydrogen in the sputter gas, seems to be validated for the Fe/V system, and possibly also for Cr/V. However, the baseline for the samples in the hydrogen study was already rather high, with mosaicities in the range of $0.03^\circ - 0.04^\circ$, so the change in diffraction was not huge. The superconducting properties of V grown under hydrogen, on the other hand, show quite a dramatic enhancement. This would make the hydrogen approach appealing for samples where the detailed electrical transport properties play a role. For magnetic superlattices, this could become important for thick V layers, in higher order transitions between ferromagnetic and antiferromagnetic coupling.

As already mentioned in chapter 3, the hydrogen assisted growth studies have been continued with iron layers on germanium. However, until now
these results have been ambiguous. As paper II implies, the hydrogen assisted growth might have great potential. Therefore it will be very interesting to follow up this line and hopefully understand the different results on the Ge substrates.

With regard to thicker V layers also the approach in paper III, mapping out the critical layer thickness in dependence on the in-plane lattice parameter gives also new insight. It should be mentioned that the 28 monolayer repetition length of the Cr/V samples detailed in paper III is comparatively high, thereby coming close to or even exceeding the limits of the critical layer thickness. The best ratio for Cr/V superlattices found in paper III was 3/25, which is relatively close to the 2/16 for the Fe/V samples in paper II, giving an explanation of the high base line quality of the samples in the hydrogen experiments.

With the Fe/MgO samples in paper VI, an interesting case on the borderline of a superlattice was observed: the crystalline coherence length measured by X-ray diffraction is close to the thickness of one Fe layer, and thereby diffraction does not yield a superlattice pattern. If a coherent superlattice is desired, paper VI seems to exclude Fe/MgO for this purpose, albeit Fe/MgO/Fe tunnel junctions have been grown to high perfection by several groups - but there the crystal coherence is of limited importance.

While paper VI shows limits for insulator/metal superlattices, at least for lower metal thicknesses, it could be nevertheless interesting to try other systems, possibly including sapphire layers. The lattice match of Fe(110) to Al₂O₃(11\overline{2}0) seems to preclude this, but a magnetic iron/tungsten alloy could be interesting. Also the Fe/MgO system has not yet been explored for much thicker Fe layers, which might take up the strain, thus allowing true superlattice properties. Unfortunately, these would be for many applications too thick.

The study of amorphous multilayers is still ongoing: paper VII presents only the first step. The FeZr layers showed a crystalline precipitate at the interface to the substrate or the underlying oxide layer. This crystallization is now understood as a dewetting effect on the surface, as described in chapter 4. The implications have already been followed up: metallic interlayers, where the surface diffusion is much less, have given promising results, with well defined magnetic transition temperatures, indicating only one magnetic compound. Unfortunately, that is then not a ”metal/insulator” structure. But there might be ways around it. It has been observed by other groups that tunnel junctions using amorphous FeCoB electrodes with polycrystalline MgO layers have a higher tunneling magnetoresistance ratio than such with amorphous aluminium oxide layers. This could imply that these aluminium oxide junctions are also plagued by crystallization effects (although these authors have not seen any crystallization). This could open a route for the FeZr also. Or, since FeZr is not a strong glass-former compared to metalloid glasses like FeCoB, it might be that the crystallization problem is smaller in FeCoB.

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The magnetic data on the partially crystallized FeZr/AlO samples, especially the magnetization versus temperature, are at the moment not understood. It seems, however, that the crystalline, and ferromagnetic, precipitate polarizes the amorphous matrix. It will be interesting, to see whether this allows samples, which are macroscopically ferromagnetic, but due to the low crystalline fraction and the random angular distribution of the nanocrystals, still of vanishing coercivity.
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7. Svensk Sammanfattning

Amorft, nanokristallint, enkristallint: magnetiska tunnfilms och multilagers morfologi

För tio år sedan började en doktorsavhandling i just vår forskargrupp med meningen ”Over the past decade there has been an enormous growth of interest in the magnetic properties of thin film structures, which presently form the technological bases for a large industry” [1] – ”Under de senaste tio åren har intresset för magnetiska egenskaper hos tunnfilmstrukturer, som nu bildar basen för en stor industri, ökat enormt”. Det var nio år efter Grünberg och Fert hade upptäckt jättemagnetoresistansen [2, 3], och samma år använde IBM effekten första gången i en kommersiell hårdisk.

År 2007 ser det inte så ut att intresset minskar, och samma ord kunde sägas idag. Minnesdensiteten på hårdiskytan är nu på 70 gigabit per kvadrattum, databassökning för ”magnetisk” och ”tunna filmer” ger inte mindre än 25478 publikationer i detta område, och Grünberg och Fert har tilldelats årets Nobelpris.

Denna utveckling har bara varit möjlig genom kontinuerliga framsteg i vakuumteknik och deponering av tunna filmer och multilager, på vilka dessa strukturer är baserade.

Tunna filmer tillväxtes med hjälp av olika metoder: material kan förångas och kondenseras på ytor, kemisk metoder kan bilda lager, föreningar kan tvingas ihop genom värme eller plasma i CVD (chemical vapour deposition – gasfasreaktioner), och i stället för förångning kan man använda en process som kallas katodförstoffning – engelska ordet ”sputtering” är vanligare – i en elektrisk urladdning. Delar av den iblandade fysiken är relativt generella och passar in på många metoder. Andra är mer speciella och har mer begränsad tillämpning.

På något sätt kan man se det som en analogi till hur forskning fungerar: några saker tillämpas bara för mycket specialiserade projekt, men flera, både utrustning och kunskap, är gemensamma, och de flesta projekt skulle inte ha någon framgång utan bidrag av många människor, oftast från olika forskargrupper. Därför behandlar den här avhandlingen till största delen tillväxten av magnetiska lager (artiklar I, II, VI och VII), men det mesta av de magnetiska mätningarna gjordes av kollegor (till exempel i artikel V). Andra avhandlingar i vår forskargrupp har mer betonat magnetiska egenskaper.

Det finns många andra intressanta områden också, och varje i metaller är inte det minsta. Väteatomer kan lagras i mellangitterplatser i många metaller.
Till skillnad från andra ämnen som går in på mellangitterplatser, som kol eller kväve, är väte relativt mobilt, och kan under relativt moderat värmebehandling pressas in i eller ut ur proven. Möjliga framtida användningar finns inom energiteknik, men för grundforskningen är ordning av väte i en metall och påverkan av elektriska och magnetiska egenskaper intressant.


I den andra artikeln undersöktes en möjlig rutt för förbättring av kristallens tillväxt. Om man växer supergitter är temperaturen mycket viktig. För låga temperaturer betyder att atomer inte alltid hittar rätt plats i kristallstrukturen, och kristallkvaliteten minskas. För höga temperaturer betyder att lagren blandas, och man hittar inte skarpa mellanytor. Om där finns möjligheter att öka diffusionen av deponerade atomer på ytan utan att höja temperaturen, skulle det vara möjligt att få bättre supergitterprover. En möjlighet är användningen av väte i processgasen, då väte har setts öka ytdiffusionen i några system. I artikel II finns en jämförelse av prover växta i ren argon och i en argon-väteblandning. Tillsatt väte sänker den optimala tillväxttemperaturen och förbättrar också de supraleddande egenskaperna hos ett ensamt vanadinlager.


I artiklarna IV och V används prover som jag hade tillverkat. Artikel IV är ett samarbete med Islands universitet och behandlar påverkan av väte på


Vid första anblicken ser det så ut att den sista artikeln bara stänger vissa rutter, men vidare undersökningar visar att användning av ett metalliskt mellanlager undviker kristallisation, och erfarenheter från detta arbete möjliggör fortsatt utveckling i amorfa multilager. Projekten ska fortsättas också efter min avhandling, och det är spännande att se den vidare utvecklingen. Preliminära resultat antyder att järn-vanadinsupergitter visar likadant beteende som krom-vanadinproverna i artikel III - och därmed öppnas helt nya möjligheter för undersökningar av magnetisk koppling.
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