Functional Modification in Ultrathin Films: from Metastable Magnets to Molecular Materials

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Abstract

Ultrathin films have become an area at the frontier of materials science due to their novel properties and new applications. In particular, ultrathin magnetic films and ultrathin organic films are drawing more and more attention. The former is associated with a series of new phenomena such as giant magnetoresistence and oscillatory exchange coupling which enable fabrication of new devices and applications, while the interest in the later is ignited by the promise prospect of molecular optoelectronics and molecular electronics. To make a full use of these films, it is important to learn how to manipulate their growth and how to tailor their properties. The aim of this work was to explore methods efficient for functional modification of these films.

(Fe, Ni) bilayers with different individual thickness and different deposition sequences have been investigated experimentally with special attention to the temperature dependence of their magnetic parameters. It is unequivocally found that in (Fe, Ni) bilayers the spin reorientation transition shifts to larger Ni film thicknesses compared with Ni/Cu(100) films. This result is explained by an enhanced demagnetization field when the two magnetic layers with unequal magnetization are put together and possibly by a Fe/Ni in-plane interface anisotropy. The non-monotonic temperature dependence of the coercivity observed in the bilayers strongly suggests the existence of an in-plane anisotropy at the Fe/Ni interface. Magnetic live layers of Fe have been found at the Fe/Ni interface. The magnetic structure of the surface layer of 9-ML Fe on Ni on Cu(100) is closely related to the thickness of the underlying Ni film. A magnetic live layer with Curie temperature around 230 K is observed when the thickness of Ni layer is chosen to be 10 ML, while it is absent when the Ni thickness increases to 15 ML. The structural relaxation of the Ni layers with thickness is thought to be responsible for the observations. These results provide a further evidence for a sensitive correlation between the structure and magnetism in fcc Fe. The single domain state is not stable for the (Fe, Ni) bilayer with small perpendicular anisotropy. With the withdrawal of the external field, the single domain state gradually relaxes to a multi-domain state, resulting in a decay of remanent magnetization with time. The relaxation behavior disappears.
when the perpendicular anisotropy is large.

An exchange biasing in ultrathin Fe films on Ni/Cu(100) has been observed when the (2×1) and (4×1) phase coexist. This biasing could be attributed to the coexistence of AFM and FM domains as observed previously in granular systems. However, with all the direct experimental result objecting the existence of a AFM phase at the studied temperature, a new model is proposed to account for this unusual biased coupling phenomenon. It is based on the assumption that the strong biquadratic exchange coupling results in an orthogonal coupling between the (2×1) Fe domains and their underlying Ni layer.

By measuring and analyzing the hysteresis loops of Ni/Cu(100) films with several thicknesses at different temperatures, the magnetization reversal mechanisms have also been investigated for Ni/Cu(100) films with perpendicular magnetic anisotropy. The magnetization reversal procedure consists of the nucleation of the reversed domains and the following motion of the domain wall. Which process is the dominant mechanism depends on the temperature and the film thickness. For thick films with large perpendicular anisotropy, the nucleation field, which is correlated to the anisotropy, is greater than the pinning field of most pinning centers. The magnetization reversal is dominated by the nucleation and the reversal procedure can be described by the nucleation followed by the viscous motion of the wall without obstacles, resulting in a high squareness in the shape of the hysteresis loops. With decreasing film thickness, the effective anisotropy field becomes comparable with the effective pinning field. Then the role of temperature becomes important. At high temperature, the motion of the domain wall is thermally assisted and thus easy, so the nucleation of the reversed domain is still the dominant process. At low temperature the pinning effect of the wall motion is visible. Therefore the shape of the hysteresis loop changes from rectangular at high temperature to inclined and round at low temperature. In this case the adsorbed residual gases have a pronounced effect on the reversal procedure acting as pinning centers. The high stability of the magnetic properties of Ni/Cu(100) films with perpendicular anisotropy upon multiple magnetization reversals has been measured and is confirmed by a theoretical analysis.

AFM and x-ray diffraction have been used to investigate the growth behavior of perylene films on a (111)-oriented polycrystalline Au substrate, as well as on the same substrate but additionally coated with a self assembled monolayer (SAM) of 1-Octadecanethiol molecules. It has been found that the perylene molecules have a smaller diffusion coefficient on the SAM than on the Au surface. An additional self-assembled monolayer of 1-Octadecanethiol molecules on an Au-substrate greatly modifies the properties of the subsequently vacuum deposited perylene films. The grain size becomes smaller and a strong c-axis texture is introduced. Both factors tend to reduce the roughness of the perylene films. These
effects are attributed to the changes in the perylene molecule-substrate interaction by the additional self assembled monolayer.

To further reveal the unique growth behavior of molecular crystals, perylene have been evaporated on a oil film. The growth speed along the crystallographic [100] axis is found to be dramatically different from that along its opposite [-100]. The ratio of two growth speed is around 2.3, and does not show an obvious dependence on supersaturation. This asymmetric growth is believed to has a steric origin, which is special for organic crystals. An organic molecule, which is the unit building block of a organic crystal, consists of a number of atoms and shows a finite size and specific shape. These features complicate the growth behavior of organic crystals. For the growth of perylene crystals on an oil film, the steric environment for a perylene molecule to be incorporate to a crystal is different for [100] and [-100], resulting in a difference in the growth speed. Interesting growth patterns have also been observed for perylene crystals grown on a oil film. Though it is preliminary, our study indicates that the stress field at the growth interface and especially around a step has significant effects on the growth behavior.
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Introduction to this Dissertation

Engineers always dream that they can have an infinitely long list of components with various properties for their product design. Material scientists always dream that they have countless kinds of phases of materials to deal with. They even wish that there would be double the number of elements in the periodic table of the element. However, the reality is that, the number of stable element on the earth is fixed, and the discovery of a new substance becomes scarer and scarer. This situation have forced the material scientist to explore novel methods to broaden the scope of modern materials science, which are not based on the discovery of new substances. These endeavors at least lead to two progresses in thin film materials for electronic and recording media applications. The first is to employ metastable structures as a component of electronic devices. The basic idea is to surmount the limitations imposed by the restriction of using only the equilibrium phases of materials and start to design metastable structures with custom-chosen properties. Epitaxial growth provides an effective method to stabilize metastable structures as ultrathin films. The second progress is to use molecular films and polymeric films to compose organic or organic-inorganic composite electronic devices and optoelectronic devices. Because the number of organic substances is overwhelmingly larger than that of inorganic materials, and also because the properties of organic materials can be tailored by molecular engineering with less difficulty than inorganic materials, incorporation of organic thin films in devices provides unique versatility for the designers. Metastable metal films and molecular films are just the subject that this dissertation is concerning.

As the work of semiconducting metastable structures opened vast prospects for electronic band engineering [1], new magnetic phases have been observed in ultrathin metastable 3d metal films [2]. Furthermore, a close correlation has been found between growth, structure, and magnetic properties for these metastable films. This enables tailoring the film properties by the control of the film growth. One of the most studied film systems showing such features are iron films on Cu(100). Fe/Cu(100) films show richness in structure and magnetic phase depending on the film thickness and preparation conditions [3]. In addition, with the dimensions of
technological devices reaching a few atomic constants, the interface effects can not be ignored anymore in device design. In another way, interface coupling and interface effects have also been important tools to tailor the film properties to meet the device requirements. Against this background, ultrathin Fe/Ni bilayer have been prepared in an ultrahigh vacuum chamber and their magnetic properties have been investigated mainly using the magneto-optic Kerr effect (MOKE). The first part of this dissertation is composed by the topics concerning the growth and magnetic properties of ultrathin Fe and Ni films and their bilayer. In order to clarify the interface induced effects, the fcc nickel films are first studied. The results are presented in Chapter 3. Then, based on the known correlation between growth, structure and magnetism of Fe/Cu(100) films [3] and the results of Chapter 3, the magnetic properties of Fe/Ni bilayers are investigated in Chapter 4. In Chapter 5, an interesting exchange anisotropy observed in Fe/Ni bilayers is discussed. Additionally, a review of the basic aspects of the growth and magnetism of metal thin films is presented in Chapter 1. A simple description of the experimental set-up and measurement techniques can be found in Chapter 2. A brief summary of the experimental results is given in Chapter 6.

As it is mentioned above, organic films are playing a more and more important role in technology. Organic light emitting devices have been successfully fabricated and the flexible large-area display screens made from organic materials are expected to be commercialized in the near future. Organic electronics is also attracting our attention, which shows the advantage of low cost. These applications are all associated with the growth of organic films. However, compared to inorganic films, especially to semiconductor and metal films, our understanding of the growth of organic films is rather limited. In the second part of this dissertation, attempts have been made to add to the knowledge of organic film growth. Perylene, a regularly shaped molecule, whose numerous derivatives are important organic semiconductors with extensive applications, is chosen to study as a typical organic material. The growth behavior of perylene on (111)-orientated polycrystalline gold substrate and on the same substrate but covered with a self-assembled monolayer (SAM) is investigated in Chapter 8, with an emphasis on the effects of the SAM on the film growth and morphology. In order to obtain a comprehensive understanding of the growth behavior for this important molecule, the crystal growth on a liquid film has also been investigated. The results are presented in Chapter 9 and Chapter 10. Theoretical basis which is needed for the discussion in Chapter 9 and Chapter 10 is introduced in Chapter 7. Chapter 11 summarizes the results for the growth of perylene film and crystals.
Part I

Magnetic properties of ultrathin Fe and Ni films and their bilayer on Cu/(100)
Chapter 1

Magnetic Metal Films:
Theoretical Basis

Ultrathin magnetic films, as a low dimensional magnetic system, have attracted a great amount of attention in the past decades because, as expected, the lowered symmetry and coordination number offer a variety of opportunities for inducing new phenomena that are not present in bulk materials. For example, the abrupt termination of the lattice or change of composition in the surface or interface can lead to localized electronic states, enhanced magnetic moment, magnetocrystalline anisotropy and complex magnetic ordering, etc. On the other hand, when several ultrathin films are put together and compose multilayers, the magnetic layers will be coupled to each other by a variety of mechanisms. Magnetic coupling become a very important aspect of film magnetism, by which the properties of the magnetic multilayers can be tailored. A typical example is the oscillatory coupling between two ferromagnetic layers separated by a nonmagnetic layer. The giant magneto-resistance device based on this oscillatory coupling has been successfully commercialized as magnetic field sensor.

In this chapter, the basic aspects of film growth and magnetism are first reviewed simply, then the motivation of the work present in Part I of this dissertation is explained.

1.1 Growth of Ultrathin Metal Films

Driven by many technological applications of thin films, our understanding of the atomic processes involved in thin film growth and the principles governing these processes has progressed tremendously in the last century. Growth of thin films has changed from an art to a science. In this section, the different growth modes are first introduced and described from the viewpoints of thermodynamics and kinetics.
The growth parameters, such as growth temperature, growth rate and application of a surfactant, are discussed in some length as possible tools to modify the growth and thus the film properties.

1.1.1 Growth Modes

Here I will focus on ultrathin epitaxial films on metallic single crystal substrates, which are prepared from the vapor phase under ultra high vacuum (UHV) conditions. The structure of such films can be described on the atomic level. This facilitates an investigation of the correlation between the film properties and the film structure and enables us to explore the limits of the property modification. The term epitaxy describes the oriented growth of one crystal on another crystal. Sometimes a distinction is made between homoepitaxy, where film and substrate are of the same material and heteroepitaxy where this is not the case. While homoepitaxial systems are usually studied as simple model systems with the goal of achieving a fundamental understanding of the growth kinetics, heteroepitaxial growth is of more practical relevance. For ultrathin magnetic films, film and substrate need to differ from each other so that the properties of the film can be tailored by epitaxial growth. Therefore homoepitaxial growth is seldom used to produce ultrathin magnetic films.

Depending on the specific application, different surface morphologies are required for the films. For example, in the production of magnetic storage devices atomically smooth films are desired, whereas rough films with well-defined island sizes and densities are pursued for heterogeneous catalysis. Manipulating the morphology of the epitaxially grown films through detailed control of the growth conditions has always been a challenge. In reaching such a goal, the primary concern is to control the growth mode. The growth mode characterizes the nucleation and growth processes, and there is a direct correspondence between the growth mode and film morphology. Three growth modes are frequently encountered. They are: Frank-van der Merwe mode, Stranski-Krastanov mode, and Volmer-Weber mode.

- **Frank-van der Merwe growth** [4] is defined by the sequential occupation of the layers. The growth of the (n+1)-th layer only starts after the n-th layer has been completed. Therefore it is also called layer-by-layer growth. Clearly, two-dimensional nucleation is a prerequisite for the layer-by-layer growth. Frequently, imperfect layer-by-layer growth is found in which growth of the (n+1)-th layer already begins before the n-th layer is completed. In cases which aim to produce smooth films, the layer-by-layer growth mode is most favorable.

- **Volmer-Weber growth** [5] is defined by the growth of three-dimensional is-
lands on the substrate.

- *Stranski-Krastanov growth* [6] is encountered for systems that initially grow in a layer-by-layer fashion but then develop three-dimensional islands above a certain thickness. It can be simply described as a layer-by-layer plus island mode.

The three modes mentioned above phenomenologically describe the different growth behavior observed on perfectly flat substrates. In fact, real substrates always contain steps and other defects. At high temperature and low deposition rate, the mobility of the adatoms can be very high, so that on a real surface all the deposited adatoms reach the pre-existing step edges and are captured there before they meet to form stable nuclei. In this case, the growth is characterized by the absence of nucleation and the advancement of steps over the lower terraces. This growth mode is called *step-flow mode* [7]. For heteroepitaxy, elevated growth temperatures must usually be avoided due to the risk of massive interdiffusion. Therefore we will exclude the step-flow growth in our further discussions.

In general, whether the epitaxial film undergoes layer-by-layer growth, island growth, or layer-by-layer plus island growth is determined by both the surface energetics and kinetics. While the surface energetics predict the thermodynamic equilibrium limit for the growth mode, the film growth is by definition a non-equilibrium kinetic process. The actual growth mode is determined by the growth condition, such as growth rate and temperature, and the material parameters of the film/substrate combination. In the following, various contributions which influence or even control the growth mode will be discussed.
1.1.2 Thermodynamic Criterion of Growth Modes

Bauer has developed a thermodynamic criterion for the growth mode which neglects the strain energy of the film [8]. The criterion states that under equilibrium conditions the growth mode is determined by the following energy difference

$$\Delta \sigma = \sigma_f + \sigma_i - \sigma_s$$  \hspace{1cm} (1.1)

where $\sigma_i$ is the surface free energy of the substrate, $\sigma_i$ the free energy of the interface, and $\sigma_f$ the surface free energy of the film. If $\Delta \sigma \leq 0$, the adatoms are more strongly bound to the substrate than to each other and the film tends to extend on (wet) the substrate to minimize the total energy. Under this condition, complete wetting of the substrate is favorable and the Frank-van der Merwe (layer-by-layer) growth should be observed. The inequality has the opposite sign when the atoms (molecules) are more strongly bound to each other than to the substrate. In this case, one usually obtains the Volmer-Weber growth (island growth), i.e., no wetting of the substrate. The film energy may have a contribution such as, for example, the strain energy, which increases linearly with increasing film thickness. After adding this energy to $\Delta \sigma$, it is possible for $\Delta \sigma$ to be smaller than zero until a certain thickness is reached and then larger than zero above this coverage. In this case, the Stranski-Krastanov growth generally occurs.

1.1.3 Surface Free Energy and Interfacial Free Energy

In order to apply Bauer’s criterion to any film-substrate pair, one needs to know the surface free energy and the interface energy of the materials considered. The surface free energy can be defined by the work $W$ which is required to break a crystal so that these surfaces are left exposed. Let $S$ be the area of the fracture section, then the surface free energy for unit area or the surface tension is $\sigma = W/(2S)$. 

---

**Figure 1.2:** Bauer’s thermodynamic criterion for growth mode: $\sigma_f + \sigma_i - \sigma_s < 0$ favors layer-by-layer growth. The island growth is observed if the film does not wet the substrate, i.e., $\sigma_f + \sigma_i - \sigma_s > 0$.
On the other hand, the interfacial free energy is defined by Dupre’s relation [9]

\[ \sigma_i = \sigma_s + \sigma_f - \beta \]  

where \( \beta \) is the adhesion energy, which is equal to the work required to separate the film from the substrate along the interface plane. Experimentally, it is rather difficult to determine surface free energies and interfacial energies precisely. Surface free energies of solid metals have been estimated from liquid surface tension measurements [10] and directly measured by quantitative cleavage experiments [11], but the errors were reported to reach as much as thirty percent [12]. Therefore theoretical models have been proposed to calculate the surface free energies and interfacial energies from physical quantities that can be easily measured, such as the heat of sublimation [13, 14] and the internal free enthalpy of atomization [15]. An empirical relation [16] between the surface free energy per atom \( \sigma \), the lattice constant \( a \) and the heat of vaporization \( \Delta H \) (also expressed in energy per atom), is frequently used to roughly estimate the surface free energy.

\[ \frac{\sigma a}{\Delta H} \sim 0.3 - 0.4 \]  

Recently, a number of endeavors have been undertaken to develop reliable theoretical models to calculate the surface free energy. These attempts include the jellium model pioneered by Lang and Kohn [17, 18] and improved by Perdew and coworkers [19, 20, 21], the embedded atom method developed by Daw and Baskes [22] and modified by Baskes and coworkers [23, 24, 25], and ab initio calculations using different techniques [27, 28, 29, 30]. However, the calculated values of surface free energies differ considerably from method to method [31] and even from group to group [32]. The data on surface free energies, both from experimental measurements and from theoretical calculations, are listed in Table.1.1 for the magnetic and nonmagnetic metals, which are commonly involved in the preparation of ultrathin magnetic films. Magnetic materials always exhibit a relatively high surface energy, owing to their partially filled d shell, while noble metal substrates have smaller surface free energies and insulating substrates have even smaller ones. The surface free energy does not only depend upon the material considered but also on the orientation of the surface. As a general rule, the surface free energy decreases with increasing atomic layer spacing, i.e., increasing number of nearest neighbors of the surface atoms. For example, bcc crystals show the following sequence in layer spacing: \( d_{(110)} = \frac{\sqrt{2}}{2} a > d_{(100)} = \frac{1}{2} a > d_{(111)} = \frac{\sqrt{3}}{6} a \). Correspondingly, the surface free energy obeys the order: \( \sigma_{(110)} < \sigma_{(100)} < \sigma_{(111)} \). For fcc crystals, the spacing sequence is \( d_{(111)} = \frac{\sqrt{3}}{2} a > d_{(100)} = \frac{1}{2} a > d_{(111)} = \frac{\sqrt{2}}{4} a \), resulting in a different order in surface free energy, which is \( \sigma_{(111)} < \sigma_{(100)} < \sigma_{(110)} \). This order of surface free energies is clearly seen in Table. 1.1. The relationship between the surface free energy and the layer spacing explains why a crystal is easy
to cleave along the most densely packed crystal face, where the layer spacing is larger, since in this case the fewest bonds need to be broken.

If we conclude that the precise determination of the surface free energy is still a challenge, the situation for interface free energies is even worse. Interfaces in essence present the next step in complexity in comparison to the surface problem. The possible occurrence of inter-diffusion and epitaxy induced strain add further intricacy to the problem. Up to now, ab initio calculations of interface free energies have been performed only in a very limited number of cases, such as a metal-ceramic interface [33] and a semiconductor interface [34].

1.1.4 Strain Energy and Stranski-Krastanov Growth

In the above discussion on the thermodynamic criterion of growth modes, we have ignored the effect of the strain energy upon the growth mode. Now we return to this point. In heteroepitaxy, the substrate and the deposited film generally have different equilibrium lattice constants. We say there is a misfit between the film and the substrate. The misfit is defined as the relative difference in the equilibrium lattice constants of the substrate \( a_s \) and film \( a_f \) respectively, i.e.

\[
f = \frac{a_s - a_f}{a_f}
\]

(1.4)

The basic feature of the role which a misfit plays can be described as follows. For a film-substrate system with \( \Delta \sigma < 0 \) (see (1.1)), the film grows in layer-by-layer mode if there is no misfit. When the effect of misfit is added, the film is initially forced to register with regard to the substrate lattice, resulting in a strain equal to the misfit \( f \). With increasing film thickness, dislocation-free islands will form, because the strain energy can be reduced by the nonuniform strain field induced by island arrays, compared to a uniformly stressed flat film [36]. Hereby the growth mode changes to Stranski-Krastanov growth. If the island volume exceeds a certain critical size, the inclusion of a mismatch strain relieving edge dislocation is favorable. In fact, the detailed misfit effect is much more complicated for at least two reasons. First, the strain field and thus the total energy of the system is sensitive to the properties of the islands such as island shape, island size and island density. Secondly even the surface free energy and the interface free energy are film thickness dependent, in particular for ultrathin films.

Grabow and Gilmer [39] have investigated the influence of strain upon film growth using molecular dynamics simulations for a particular film-substrate system, where all particles in the film and the substrate interact with pair potentials such as the Lennard-Jones potential for molecular crystals and the Stillinger-Weber potential for silicon. Their result is shown in Fig. 1.3. The relative adlayer interac-
### Table 1.1: Surface energies $\sigma (Jm^{-2})$ for magnetic and non-magnetic materials.

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$^a$Derived from the surface tension of liquid metals. See [26].
$^b$Calculated from the internal free enthalpies of atomization. See [15].
$^c$Ab initio calculation results. See [27] and also compare [28] for Fe, Co and Ni.
$^d$Calculated by second nearest-neighbor modified embedded atom method. See [25].
$^e$Calculation results from [29].
$^f$Ab initio values from [30] and [35].
**Table 1.2:** Lattice parameter in Å of magnetic transition metals and the commonly used substrates for their epitaxial growth [37, 38]

<table>
<thead>
<tr>
<th></th>
<th>Cr(bcc)</th>
<th>Fe(bcc)</th>
<th>Co(bcc)</th>
<th>W(bcc)</th>
<th>Mo(bcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>√2a</td>
<td>4.080</td>
<td>4.053</td>
<td>3.99</td>
<td>3.165</td>
<td>3.15</td>
</tr>
<tr>
<td>a</td>
<td>2.885</td>
<td>2.866</td>
<td>2.82</td>
<td>2.238</td>
<td>2.227</td>
</tr>
<tr>
<td>Al(fcc)</td>
<td>4.041</td>
<td>4.086</td>
<td>4.078</td>
<td>3.924</td>
<td>3.890</td>
</tr>
<tr>
<td>a</td>
<td>2.885</td>
<td>2.866</td>
<td>2.82</td>
<td>2.238</td>
<td>2.227</td>
</tr>
<tr>
<td>Fe(fcc)</td>
<td>3.59</td>
<td>3.55</td>
<td>3.52</td>
<td>3.61</td>
<td>3.57</td>
</tr>
<tr>
<td>a</td>
<td>2.507</td>
<td>2.698</td>
<td>2.752</td>
<td>2.755</td>
<td></td>
</tr>
<tr>
<td>Co(hcp)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>2.507</td>
<td>2.698</td>
<td>2.755</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The interaction strength $W$ is defined as

$$W = \frac{\epsilon_{fs}}{\epsilon_{ff}}$$  \hspace{1cm} (1.5)

where $\epsilon_{fs}$ and $\epsilon_{ff}$ are the well depth of the potential between a film particle and a substrate particle and between two film particles respectively. When $W$ is smaller than one, Volmer-Weber growth is always observed. Only for stronger film-substrate interaction, i.e. $W > 1$, can Stranski-Krastanov growth be observed. It should be noted that this transition shifts to higher values of $W$ with increasing misfit.

### 1.1.5 Atomistic Processes in Film Growth

So far, we have discussed the energetics of film growth, i.e., the equilibrium properties of the growing film. However, growth is by definition a non-equilibrium phenomenon. In most practical cases, growth inevitably occurs very far from equilibrium. In this case the growth is strongly influenced by kinetic processes. The final macroscopic state of the film is not necessarily the most stable but the kinetically most favorable. Therefore a comprehensive understanding of film growth should cover both the thermodynamic principles and the atomistic processes. In this section the kinetic aspects and microscopic models of growth will be discussed. The experimental parameters such as substrate temperature and growth rate, which are known to have a pronounced influence on film growth and film quality, will enter our discussion.
Figure 1.3: Influence of misfit on the growth mode. The dependence of the equilibrium growth mode upon misfit \( f \) and relative adlayer interaction strength \( W \) is shown for the epitaxial growth on an fcc(100) surface. Stranski-Krastanov growth can only be achieved for \( W > 1 \) (after [39]).

The atomistic processes in film growth are schematically illustrated in Fig. 1.4. The growth of films always starts with the arrival of atoms from the vapor. These atoms (adatoms) keep on migrating on the substrate surface until one of the processes described below occurs. These processes include re-evaporation into the vacuum, capture by existing steps and clusters, and nucleation into clusters. For metal film growth on a metal substrate, re-evaporation is negligible at relevant growth temperatures. Before we go to discuss the nucleation and the capture, let’s first take a look at the migration properties of the adatoms on the substrate surface.

On a surface, the potential for adatoms (binding energy) shows a modulation due to the atomic arrangement of the underlying substrate. The minima of the potential are the adsorption sites. Adatoms may migrate on the surface by jumping from one adsorption site to the neighboring site. If the density of adatoms is low and there is no interaction between adatoms, the adatoms’ migration can be characterized by an individual random walk. The statistical displacement \(|\vec{\Lambda}|\) of an adatom after \( n \) random jumps is given by [40]

\[
|\vec{\Lambda}|^2 = na^2
\]

assuming the adsorption sites consist of a two-dimensional square lattice with a
lattice constant $a$. It follows that the statistical movement $\lambda$ along a given direction, say $x$-direction, is

$$\lambda^2 = \frac{1}{4} |\Lambda^2| = \frac{1}{4} na^2$$  \hspace{1cm} (1.7)

To describe the velocity of the adatom migration, the diffusion coefficient $D$ is defined by

$$\langle (r(t' + t) - r(t'))^2 \rangle = 2dDt$$ \hspace{1cm} (1.8)

where $r(t)$ is the position of an adatom as a function of time $t$ and $d$ is the dimension of the diffusion path considered. Hence $d = 2$ for surface migration. Comparing (1.6) and (1.8), $D$ should be proportional to the number of the realized jumps within unit time. To move from an adsorption site to a neighboring one, the adatom must jump over an energy barrier $E_d$. According to the Gibbs-Boltzmann formula, the probability of an adatom in equilibrium overcoming this energy barrier is proportional to $\exp(-E_d/k_BT)$. Usually the frequency of the successful jump is expressed as

$$f = \nu_0\exp(-E_d/k_BT)$$ \hspace{1cm} (1.9)

The prefactor $\nu_0$ is often assumed to be of the order of a typical vibrational frequency of the atom, say, $10^{13}$ s$^{-1}$, and depends only weakly on temperature. Since a theoretical determination of $\nu_0$ is still a challenge, it is usually taken as an experimental fit parameter. Applying (1.6), (1.8) and (1.9), the diffusion coefficient on a square surface lattice can be further expressed as

$$D = \frac{a^2}{4} \nu_0\exp\left(\frac{-E_d}{k_BT}\right)$$ \hspace{1cm} (1.10)
FIGURE 1.5: Side view of a stepped fcc(100) surface and the corresponding schematic potential showing a decreased barrier near an ascending step due to the step-adatom attraction and the Ehrlich-Schwoebel barrier at the descending step.

The diffusion barrier $E_d$ at the surface is much smaller than in the bulk (see Fig. 1.12). The bulk diffusion takes place mainly through the motion of defects, especially vacancies and interstitial atoms. From (1.10), one can see that the migration properties of adatoms strongly depend on temperature. The diffusion coefficient defined above is called tracer diffusion coefficient, to distinguish it from the Fick diffusion coefficient $D_f$. The latter is defined by Fick's law

$$\frac{d\rho(r,t)}{dt} = D_f \nabla^2 \rho(r,t)$$ (1.11)

where $\rho(r,t)$ is the particle density. While the tracer diffusion coefficient purely reflects the rapidness of the migration, Fick’s diffusion coefficient also takes the mutual influence of migrating particles into account [41].

The random-walk motion of the adatom will be disrupted when the adatom encounters a step along the diffusion path. When an adatom migrating over a terrace strikes an ascending step, it will be incorporated into it. It is even found that an adatom on the lower terrace is subject to a short-range attractive interaction when it approaches an ascending step. This adatom-step attraction has been observed by field-ion-microscopy on the Ir(111) surface [42], and is confirmed by the calculated smaller diffusion barriers near a step [43]. In contrast, an adatom approaching a descending step has to overcome an additional potential barrier to roll over the edge before it can attach itself to the step, since the adatom will pass through a position in which it possesses fewest nearest neighbors. The effects of this potential barrier on diffusion and crystal growth were first studied by Ehrlich using Field-ion-microscopy [44] and theoretically by Schwoebel [45]. Therefore
Figure 1.6: Schematic side view of an adatom descending a step. (a) Adatom rolls over the step. (b) Adatom exchanges place with a step atom.

This barrier is now called Ehrlich-Schwoebel barrier. The Ehrlich-Schwoebel barrier plays an important role in film growth. It prevents the adatoms from diffusion to the lower terrace. With a large Ehrlich-Schwoebel barrier, nucleation of new islands on top of existing islands may occur before coalescence of the islands of the previous layer, resulting in an island growth even though the energetics favor a layer-by-layer growth mode. Instead of the rolling-over mechanism, an alternative mechanism has been found for the interlayer diffusion, i.e., the exchange process (See Fig 1.6). In this process, the adatom approaching a descending step can descend the step by pushing a terrace atom at the step edge further onto the lower terrace and sinking into its initial position. The kinks at step edges and corners are believed to be the preferred sites for the exchange process. For the Al(111) surface, exchange diffusion is favored over direct hopping. The activation energy for interlayer diffusion is found to be dependent on the type and roughness of the step [46, 47]. Thus the interlayer mass transport would be dependent on island size, island shape and even the island orientation if the exchange process is an efficient diffusion pathway. Exchange processes have been observed at room temperature for Co on Pt(111) [48] using atomically resolved scanning-tunnelling microscopy. It is also proposed [49] to be responsible for the reentrant layer-by-layer growth at low temperature observed in the Pt/Pt(111) system [50, 51], since at low temperature the increased kink density of the smaller island promotes the interlayer diffusion due to the smaller barrier. Recently, the Ehrlich-Schwoebel barrier has been found to be correlated with the occupation of surface states [52, 53]. By analyzing the ripening of multilayer islands on Cu(111), Giesen et al. have revealed that the Ehrlich-Schwoebel barrier is independent of the terrace width $w$ until a critical value $w_c = 14 \pm 2 \text{ Å}$ is reached. When the terrace width is smaller than $w_c$, the Ehrlich-Schwoebel barrier vanishes abruptly [53]. The critical width $w_c$ corresponds to the terrace width below which the surface state is pushed above the Fermi level due to quantum confinement. The modification of charge density in the
surface state by quantum confinement leads to a reduction of the binding energy at steps and hence to the Ehrlich-Schwoebel barrier.

The migration of adatoms has been for long time considered as the basic atomic process for mass transport. The migrating adatoms perform a random walk on the terrace. An adatom would be reflected by the step or attached to it after overcoming the Ehrlich-Schwoebel barrier when it meets a descending step. When the adatom approaches an ascending step, it will be incorporated into the step edge. On a simple metal surface, there is no obvious additional barrier for this incorporation. That is to say, the barrier for diffusion on the terrace will be the same as or larger than the barrier associated with this incorporation. However, the adatoms are not always the diffusing species. It has recently been found that the diffusion of Mn atoms incorporated in the Cu(100) surface was mediated by vacancies [54]. Furthermore also the surface self-diffusion on Cu(100) was shown to be mediated by single atom vacancies on the terrace [55, 56]. In other words, vacancies are the prevailing

**Figure 1.7:** The surface self-diffusion on Cu(100) mediated via single atom vacancies rather than adatoms. The left panel shows a vacancy being incorporated into a step edge at a kink site: Atom B moves into the vacancy and atom A drops down to replace B. The right panel shows the diffusion barriers experienced by a vacancy as it approaches a kink [55]
mass transport carrying species on Cu(100). This conclusion was based upon the experimentally observed constant decay rate of small islands and its independence of the environment [55, 56], and has been confirmed by theoretical studies [43, 57]. Both the diffusion energy and the formation energy are calculated to be smaller for a vacancy than for an adatom (see Fig.1.7). The creating mechanism of a vacancy at steps has been discussed by Ibach et al. [58]. The vacancies and the atomic exchange processes in the vicinity of kinks are also responsible for the formation of surface alloys [54, 59, 60, 61, 62, 63].

An adatom striking a step will be attached to the step. The attached adatom will remain mobile along the step edge until it finds a kink position to rest in. The migration of an attached adatom along the periphery is called edge diffusion. The edge-diffusing adatoms still have a non-vanishing probability to re-evaporate onto the terrace but it is small for a metal/metal system. The energy barriers for an edge-diffusing atom to pass a corner (kinks and island corners) are usually larger than those on a smooth step edge. The edge diffusion and corner-crossing processes, which are generally dependent on the step direction, have a decisive effect on the evolution of the island shape [64, 65].

Up to now, we have discussed the migration of adatoms on a terrace as well as the motion across a step edge. On the other hand, the migrating adatoms may meet and form a cluster. These clusters may disappear again by decaying into single adatoms or alternatively develop into a stable nucleus. The stable nuclei will grow further by capturing single adatoms. Thus the atomic processes involved in the initial stage of film growth are quite complicated. The kinetic rate equations allow a quantitative description of these relevant processes. This is the subject that we will discuss in the next subsection.

1.1.6 Kinetic Rate Equations for Nucleation and Growth

The atoms deposited from the vapor will diffuse on the substrate surface. The diffusion process will be terminated when the adatoms are captured by an existing step or by clusters, as we have discussed in the previous subsection. Alternatively, as the adatoms diffuse over the surface, they may encounter other adatoms with whom they can combine to form clusters. These clusters can also decompose and by this process release adatoms. It is only above a critical cluster size ($n_i$) that growth becomes much more important than decay. These stable clusters grow by further capture of adatoms. The relationship between the atomistic processes included in nucleation and growth is illustrated in Fig. 1.8.

Let’s consider the situation after atoms are evaporated onto a step-free substrate with constant rate $R$. Initially, the evaporation leads to a steady increase in adatom density $n_1$. After some time stable clusters are formed and their density
Figure 1.8: Competition between nucleation and growth. Different processes that govern nucleation and growth are depicted. Unlikely processes are denoted by dashed lines. The single adatom density \( n_1 \) is determined by the arrival rate \( R \), and the characteristic times for nucleation (\( \tau_n \)) and diffusion capture (\( \tau_c \)) by stable clusters \( n_x \). These stable clusters are formed from addition of one more adatom to a critical cluster \( n_i \). The capture of single adatoms by stable clusters leads to their growth. The subcritical clusters \( n_j \) may decay via dissociation or develop into stable nuclei by further capture of adatoms. After [66]

\( (n_x) \) increases with time. Since the stable clusters act as adatom sinks, there exists a time \( \tau_c \), the capture time, above which the adatom density starts to decrease. \( \tau_c \) is inversely proportional to the adatom diffusion coefficient \( D \) and the density of stable clusters \( n_x \) [67]. The total number of stable clusters \( (n_x) \) always increases up to the coverage at which cluster coalescence becomes important. Therefore one has time-dependent densities of adatoms and stable clusters as shown in Fig. 1.9. Nucleation and growth are two competing processes which reduce the number of adatoms. Usually nucleation dominates in the early stage and growth in the later stage of film formation.

To gain a quantitative description of nucleation and growth, a set of kinetic equations incorporating the main atomistic processes has been developed by Zinsmeister [68], Logan [69], and Frankl and Venables [70]. These equations are called kinetic rate equations or simply rate equations. Here we will discuss the rate equations following the approach given by Venables et. al. [67]. Assuming only single atoms are mobile on the surface, the rate equations have the following general form of

\[
\frac{dn_1}{dt} = R - \frac{n_1}{\tau_n} - 2U_1 - \sum_{j=2}^{\infty} U_j
\]

(1.12)

\[
\frac{dn_j}{dt} = U_{j-1} - U_j \quad (j \geq 2)
\]

(1.13)
Figure 1.9: Evolution of the density of single adatoms and stable clusters. The density of adatoms $n_1$ increases linearly with time until the capture time $\tau_c$ is reached. Then a pronounced increase in the density of stable clusters $n_x$ is encountered. The number of stable clusters only decreases after longer deposition times when coalescence becomes important. Modified after [67]
where \( n_1, n_j \) are the surface densities (per unit area) of adatoms and clusters consisting of \( j \) atoms respectively, and \( U_j \) describes the net rate of capture of single atoms by the \( j \)-atom clusters. \( \tau_a \) is the lifetime of an adatom, i.e., the time between its arrival and re-evaporation. \( \tau_a \) is related to the adatom’s adsorption energy \( E_a \) and the substrate temperature by

\[
\tau_a = \frac{1}{\nu_0} \exp\left(\frac{E_a}{k_B T}\right)
\]

(1.14)

with \( \nu_0 \) being a constant. The physical meaning of (1.12) and (1.13) is straightforward. The terms on the right side of (1.12) describe the processes of adsorption from the vapor at a deposition rate \( R \), re-evaporation, formation of two-atom clusters, and capture by other clusters, respectively. Accepting that a local equilibrium exists between the subcritical clusters leads to a further simplification of the rate equations. In thermodynamic equilibrium, the subcritical clusters have a steady distribution, i.e.

\[
dn_j/dt = 0 \quad (1 \leq j \leq i)
\]

(1.15)

The densities of the subcritical clusters have been derived from statistical principles and are given by the so-called Walton relation [71]

\[
\frac{n_j/N_0}{n_1/N_0} = \sum_m c_j(m) \exp\left[\frac{E_j(m)}{k_BT}\right],
\]

(1.16)

where \( n_j \) is the density of the \( j \)-atom cluster \((j < i)\) and \( N_0 \) is the density of adsorption sites. \( E_j(m) \) denotes the binding energy of the \( j \)-atom cluster in \( m \) configuration and the coefficients \( c_j(m) \) are statistical weights. In case that the subcritical cluster is in local equilibrium, by summing all stable clusters via

\[
n_x = \sum_{j=i+1}^{\infty} n_j,
\]

(1.17)

the rate equation can be simplified to

\[
dn_1/dt = R - n_1/\tau_a - d(n_x w_x)/dt
\]

(1.18)

\[
dn_j/dt = 0 \quad (2 \leq j \leq i)
\]

(1.19)

\[
dn_x/dt = U_i - U_c.
\]

(1.20)

\[
d(n_x w_x)/dt = (i + 1)U_i + \sigma_x Dn_1 n_x + RZ
\]

(1.21)

In (1.18) the last term represents the loss of adatoms to \( n_x \) stable clusters with an average of \( w \) atoms per cluster. The last term in (1.20) describes attempts to deal with coalescence. If stable clusters impinge on each other by growth with a rate
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$U_c$, then the number of stable clusters will be reduced. The first term in (1.21) is the nucleation rate, which can be expressed as

$$U_i = \sigma_i D n_1 n_i,$$

(1.22)

with $D$ being the single atom surface diffusion coefficient and $\sigma_i$ the capture number of the critical clusters. The other two terms on the right side of (1.21) represent, respectively, the contributions of capture by surface diffusion and of direct impingement on growing clusters which cover a fraction $Z$ of the surface.

In general, the rate equations enable a numerical solution for the stable cluster density $n_x$, once the associated parameters such as $R$, $D$, $\sigma_i$ and $\sigma_x$ are known. However, useful analytical formulae can also be deduced from the approximate treatment of the rate equation under specific conditions. For a metal/metal system, if the temperature is not too high, re-evaporation does not take place. The single-atom concentration $n_1$ is hence only limited by the growth of clusters. If it is further assumed that cluster coalescence does not occur, and the dominant term in (1.21) is the middle term, i.e. the capture by the stable cluster, then the steady state condition $dn_1/dt = 0$ gives

$$n_1 = \frac{R \sigma_x}{D n_x}$$

(1.23)

Using (1.20), (1.22) and (1.23), as well as the Walton relation (1.16), one can obtain the following relationship

$$n_x^{i+1} dn_x = \frac{1}{N_0-i} \frac{\sigma_i}{\sigma_{x+1}} \left( \frac{R}{D} \right)^i c_x \exp(\frac{E_i}{k_B T}) R dt.$$  

(1.24)

Since $\int R dt = \Theta$, integrating (1.24) gives

$$n_x \propto \frac{\sigma_i}{\sigma_{x+1}} \Theta \frac{1}{i+1} \left( \frac{R}{D} \right)^{i+1} \exp(E_i/[i+2]k_B T),$$

(1.25)

where $\Theta$ is the total coverage. Equation (1.25) contains several important results: the island density depends on the two most important experimental parameters $R$ and $D$ by a scaling law $n_x \propto (R/D)^\kappa$ and the scaling exponent is determined by the size of the critical cluster. With (1.10), (1.25) can be rewritten as

$$n_x \propto \frac{\sigma_i}{\sigma_{x+1}} \Theta \frac{1}{i+1} R^{i+1} \exp(E_i + iE_d)/[(i + 2)k_B T].$$  

(1.26)

(1.26) allows the determination of the energy term in the exponential function, i.e., $((E_i + iE_d)/(i + 2))$, by experimentally measuring the density of stable clusters at a given coverage for different temperatures. With this knowledge, one can draw some conclusions about the magnitude of the activation energy for adatom diffusion and the binding energy of the critical nucleus. The situation is simplified when
i = 1 and therefore $E_i = 0$. In this case the energy in the exponential term simply equals $E_d/3$.

The theory of nucleation and growth based on the rate equations is usually called an atomistic theory, to distinguish it from classical theories, which are based on the continuum thermodynamic properties of clusters and diffusion equations. Detailed discussions of classical theories on nucleation and growth can be found in the books by Lewis [40] and Pimpinelli [41].

1.1.7 Manipulating the Growth by Variation of Temperature and Deposition Rate

After we have gained a detailed understanding of the elementary processes involved in film growth and the principles governing these processes, we are capable of manipulating the film growth. To manipulate film growth requires to choose the appropriate growth conditions and thus guide the non-equilibrium growth in the required direction. This goal can be reached by choosing the substrate temperature, tuning the growth rate, and applying a surfactant. Ion beam bombardment has also been used to modify film growth.

In typical growth experiments, it is very easy to vary the diffusion coefficient over several orders of magnitude by simply changing the substrate temperature. The variation of the deposition flux can also span two or three orders of magnitude, though it is more difficult to modify than the diffusion coefficient. We will see that the film growth can be effectively manipulated by changing the growth temperature and the growth rate.

In MBE growth, the growth mode usually changes from three-dimensional growth at low temperature to layer-by-layer growth at higher temperature. As we have seen in (1.10), all the diffusion processes show an exponential dependence on temperature, though the characteristic energies vary with the specific type of diffusion process. At higher temperature, the adatoms become more mobile so that they can jump over local energy barriers, including the barriers at step edges, the so-called Ehrlich-Schwoebel barrier. This barrier can suppress the interlayer transport at low temperature. Hence the arriving adatoms nucleate on the top of clusters and give rise to the growth of three-dimensional islands with pyramid-like features. This kind of mode transition with temperature has been clearly shown by Stroscio et al. for Fe growing on Fe (100) (Fig. 1.10) [72]. It should be pointed out that, upon further increasing the substrate temperature and using a very low deposition rate or a substrate with high step density, film growth could follow the step-flow mode, where the adatoms can diffuse to the nearest steps and are captured there. This is another mode to produce smooth films apart from layer-by-layer growth, but it is seldom exploited for heteroepitaxial film growth due to the elevated in-
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...diffusion between substrate and film. Nevertheless, when high melting point substrates are used, such as W(110), Mo(110) etc., the step-flow mode provides an alternative pathway to manipulate the growth [73, 74]. A detailed discussion on interdiffusion will be given later in this subsection.

The role that temperature can play in manipulating film growth by regulating the adatom mobility is already described above. Another less direct influence of temperature on growth lies in its capability to determine the nuclei density and nuclei size. As shown by (1.25), the density of nuclei increases with deposition flux and inversely with diffusion coefficient in a power law. Therefore the density of nuclei is quite sensitive to temperature. On the other hand, a number of atomistic processes, for example, the inter-layer diffusion and edge diffusion, are strongly affected by the nuclei density and nuclei size. Tersoff et al. pointed out that the onset of the second layer nucleation on top of the island is associated with a critical island radius $R_c$ [75], which is dependent on the Ehrlich-Schwoebel barrier at the step edge. This provides a simple criterion for layer-by-layer versus island growth: for a given island spacing $L_n$ (determined by the density of nuclei), if $R_c < L_n$ the islands will nucleate a second layer before coalescence, resulting in multilayer growth. The existence of the critical island radius has been confirmed by experiments [50, 75, 76] and simulations [77]. It can be qualitatively understood by considering that for small islands the adatoms have a high probability to reach the step edge and thus have a high probability to reach the lower terrace. The increased kink density for small islands could also contribute to the interlayer diffusion [50, 51]. The existence of a critical island radius provides another means to obtain layer-by-layer growth by increasing the density of nuclei. This can be realized by using a large deposition flux, the application of a surfactant, and/or by decreasing the growth temperature. A possible phase diagram for growth given by Tersoff is shown in Fig. 1.11, which takes the effect of interlayer diffusion on the island density into account. The reentrant layer-by-layer growth mode at low temperature is of particular importance for systems with strong interdiffusion at high temperature. It has been observed in a number of systems [50, 76] including ultrathin Co films on Cu(001) [78].

Up to now, we see two conflicting effects of adatom mobility on the growth mode. To obtain a layer-by-layer growth, on the one hand we wish the adatom diffusion to be small in the nucleation stage so that a large density of nuclei is obtained. In this case the island size could remain below the critical size for second layer nucleation until coalescence is reached and thus the island growth is suppressed even in the presence of an Ehrlich-Schwoebel barrier. On the other hand, to reach the same goal we wish to have a high adatom mobility in the growth stage so that the adatoms can effectively roll over the steps. Faced with this dilemma, Comsa et al. proposed the “concept of two mobilities” to manipulate the film...
Figure 1.10: Change of growth mode from layer-by-layer at high temperature to three-dimensional island growth at lower temperature for Fe growing on Fe(100) as seen by STM and RHEED. From [72]
growth [79]. The basic idea is that the experimental parameters can be varied deliberately in the different stages so that a high density of nuclei is obtained in the nucleation stage and a high mobility is employed in the growth stage. To realize this strategy, complexity in deposition technology is inevitably introduced.

When we exploit the growth temperature to manipulate heteroepitaxial growth, much attention should be paid to inter-diffusion, i.e., the diffusion of adatoms into the bulk of the substrate or vice versa the diffusion of substrate atoms into the film. These processes are highly unwanted if chemically sharp interfaces are to be grown. Therefore interdiffusion sets an upper limit to the manipulating temperature. The interdiffusion has been estimated by Flynn using the concept of the penetration depth [80]. The penetration depth \( L_b \) is defined as the length over which the concentration of substrate atoms in the film decreases by \( 1/e \). This depth corresponds to \( L_b = \sqrt{D_b t} \), where \( D_b \) is the bulk diffusion coefficient of the substrate atoms in the film. If \( L_b \) is smaller than a typical nearest neighbor spacing of 2.5 Å, interdiffusion is negligible. On the other hand, pronounced interdiffusion is found when \( L_b \) is considerably larger than the nearest neighbor distance and \( t \) is the typical time of a growth experiment. Using a deposition time of \( 10^4 \) sec, Flynn’s model gives a temperature limit \( T = 3/8 T_M \) for the onset of interdiffusion. In this derivation, an empirical formula \( D_b(T) = 10^{-1/2} \times 10^{-7T_M/T} \text{ cm}^2\text{s}^{-1} \) is used to relate the bulk diffusion coefficient to the melting temperature of the film material \( (T_M) \). Using another empirical formula \( D_s(T) = 10^{-3} \times 10^{-3T_M/2T} \text{ cm}^2\text{s}^{-1} \) for the surface diffusion, Flynn could also obtain a lower temperature limit for step flow growth and nucleation-growth-type layer-by-layer growth as \( 3/8 T_M \) and \( 1/8 T_M \), respectively. Here the reentrant layer-by-layer growth is not included.

**Figure 1.11:** A possible phase diagram for film growth. SF, LBL, ML, and RLBL, respectively, denote the regime of step flow, layer-by-layer, multilayer, and reentrant layer-by-layer growth. \( \theta \) is the angle of surface miscut, which determines the step density. \( T_s \) corresponds to the onset of step flow at a given angle of miscut. Boundary lines indicate a smooth crossover between regimes, not an abrupt transition. From [75]
Figure 1.12: Temperature dependence of bulk diffusion $D_b$ and surface diffusion $D_s$. The temperature dependence has been calculated using an empirical formula which relates the diffusion coefficient for bulk and surface diffusion to the melting temperature of the film material. The dashed-dotted line and the arrow denote the temperature limit above which interdiffusion between substrate and adsorbate atoms is observed ($T > 3/8 T_M$), while the dotted and dashed lines, respectively, identify the low temperature limits for nucleation-growth-type layer-by-layer growth ($T > 1/8 T_M$) and step flow growth ($T > 1/4 T_M$). From [80]
in the consideration. The main results of Flynn’s estimation are shown in Fig. 1.12, which can act as a rough guide for choosing a growth temperature.

1.2 Magnetism of Metal Films

In this section, the basic aspects of film magnetism will be the focus. At first theoretical models to describe the ferro- and antiferromagnetism of 3d metals are introduced. Then, the relationship between structure and magnetism for bulk phases is discussed. Next, magnetic properties of surfaces and thin films and the coupling between magnetic thin layers receive attention. Finally, attention is turned to a specific ultrathin film system, i.e., Fe films on Cu(100), which shows an interesting correlation between structure and magnetism.

1.2.1 Itinerant Electron Magnetism

The characteristic feature of a ferromagnet is the existence of a spontaneous magnetization below the Curie temperature $T_c$. The energy involved in the transition from the ferromagnetic to the paramagnetic state is of the order of $k_B T_c / \text{atom} \approx 0.1 \text{ eV/atom}$. This shows that ferromagnetism is not the consequence of a magnetic dipole interaction which would only give an orientation dependent energy difference of the order of $10^{-4} \text{ eV/atom}$. The responsible mechanism is the exchange interaction which is a consequence of the Pauli principle and the Coulomb interaction between electrons. The Pauli principle forbids two electrons with parallel spins to occupy the same orbital state. Thus the effective Coulomb repulsion between a pair of electrons with parallel spins is different from that between a pair of electrons with antiparallel spins. In some cases the former is weaker than the later. This favors a parallel alignment of spins and is the origin of ferromagnetism.

Depending upon the degree of localization of the electrons which carry the magnetic moments, two different models are applied to explain the ferromagnetism of solids. The Heisenberg model is well suited to describe magnetism of mostly localized electrons found in materials such as 3d metal oxides, 4f metals and their compounds. Upon increasing delocalization of the electrons which carry the magnetic moment, the Heisenberg model becomes less applicable. Thus, the itinerant (delocalized) magnetism of the 3d metals (Fe, Co, Ni, Cr, Mn) is better explained by the band model which was introduced by Stoner [84]. As a theoretical basis, we will outline the Stoner model in this section. Since the Stoner model is based on the electronic band structure, we will first introduce a density functional theory, the local density approximation (LDA), which is extensively used to calculate the electronic and magnetic properties of ultrathin metal films.
Local Spin Density Approximation

Solving the Schödinger equation for an interacting many-particle system is impractical for most cases so that approximative treatments need to be adopted to reduce the problem to the solution of single-particle equations. LDA provides such a formalism [85]. In 1964, Hohenberg and Kohn showed that the ground-state properties, particularly the total energy \( E[\rho_0] \) of a system of interacting electrons are unique functionals of the electron density of the ground state \( \rho_0 \). This forms the theoretical basis of the LDA. Since \( \rho_0 \) is a single particle density, the problem of determining the ground state energy of a \( N \)-particle system is reduced to the problem of a single particle in an effective potential. The total energy can be decomposed into different contributions [86]:

\[
E[\rho(r)] = T_0[\rho(r)] + \int d\vec{r} V(\vec{r}) \rho(\vec{r}) + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho(\vec{r})]
\]

(1.27)

where \( V(\vec{r}) \) describes the interaction of the electrons with the ion cores. \( T_0[\rho(r)] \) is the functional for the kinetic energy of non-interacting electrons and the double integral describes the electron-electron interaction within the Hartree-approximation which neglects the contribution of exchange and correlation. These two terms describe contributions to the Coulomb interaction beyond the Hartree-approximation which arise as a consequence of the Pauli principle. This can cause electrons of the same spin to stay spatially apart while electrons of opposite spin come more closely together. Therefore the average repulsion energy between two electron of the same spin orientation is reduced by the intrinsic tendency of these electrons to avoid each other. The corresponding reduction of energy is called the exchange energy. This average quantity still neglects electron correlations, which are included in the correlation energy. The contribution of exchange and correlation to the electron-electron interaction as well as the contribution of correlation to the kinetic energy is contained in \( E_{xc}[\rho(\vec{r})] \), assuming that the electrons move independently. Once (1.27) is established, the ground-state electron density and energy of an interacting many-electron system can be determined in a self-consistent procedure using the following formulae:

\[
\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r})\right) \psi_j(\vec{r}) = \epsilon_j \psi_j(\vec{r})
\]

(1.28)

\[
\rho(\vec{r}) = \sum_{j=1}^{N} |\psi_j(\vec{r})|^2
\]

(1.29)

\[
v_{eff} = V(\vec{r}) + \frac{1}{4\pi\varepsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}(r)
\]

(1.30)
where $v_{xc}(r)$ is the local exchange-correlation potential, defined as

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}$$  (1.31)

The expression for $v_{eff}$ is obtained from (1.27) by applying a variation principle. The essential difficulty of solving the above equations arises from the fact that $E_{xc}$ is unknown. Thus the main challenge for reducing the N-particle problem to a one particle problem is a suitable approximation for the exchange correlation functional. Usually the Local Density Approximation (LDA) is chosen. In this approximation:

$$E_{xc} = \int d\vec{r} n(\vec{r}) \epsilon_{xc}(n(\vec{r}))$$  (1.32)

where $\epsilon_{xc}(n(\vec{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas with the local density $n(\vec{r})$. Thus the effective potential of (1.30) becomes local. The simplest approximation for $\epsilon_{xc}(n(\vec{r}))$ is the so-called $X\alpha$ approximation, where $\epsilon_{xc}(n(\vec{r}))$ is obtained by perturbation theory for a free electron gas with density $n$.

$$\epsilon_{xc}(n) = -\alpha \frac{3}{4} \left( \frac{3}{\pi} \right) \frac{1}{2} e \frac{2}{3} n^{\frac{1}{3}}$$  (1.33)

where values between 2/3 and 1 are assumed for $\alpha$.

This approximation includes the exchange energy but neglects the correlation energy. Therefore, more reliable forms of the exchange-correlation energy are necessary for a successful description of the properties of solids [87]. With such improved expressions for $\epsilon_{xc}$, the crystal structure, lattice constants, cohesive energy and bulk moduli are fairly well described. Lattice constants calculated by the LDA are underestimated by 3-4% for most metals. This is due to the fact that the exchange-correlation contribution to the electron-electron interaction favors overbinding.

To apply the LDA to magnetic materials, one has to consider spin densities instead of electron densities [88]. The total electron density can be decomposed into two parts, $n^+$ and $n^-$, the electron densities for up and down spins respectively.

$$n(\vec{r}) = n^+(\vec{r}) + n^-(\vec{r})$$  (1.34)

If $m(\vec{r})$ is defined as

$$m(\vec{r}) = n^+(\vec{r}) - n^-(\vec{r})$$  (1.35)

then the local magnetization density is $\mu_B m(\vec{r})$. Since the magnetic anisotropy is irrelevant for the following discussion, the representation of the magnetization by a scalar quantity is justified. One can reformulate (1.28-1.30) for the spin densities $n^+$ and $n^-$. The important new feature of a description using spin densities rather than charge densities is a spin dependent contribution of the exchange-correlation
potential for spin up and spin down electrons. When only the effects of first order are considered, \( v_{xc}(\vec{r}) \) can be expanded with respect to \( m(\vec{r}) \) as [89]

\[
v_{xc}^{\pm}(\vec{r}) = v_{xc}^{0}(\vec{r}) \mp \tilde{v}[n(\vec{r})]m(\vec{r}), \quad \tilde{v}[n(\vec{r})] > 0
\]

where \( v_{xc}^{0} \) is the exchange-correlation contribution for the nonmagnetic case. As a consequence, spin-up electrons experience a more attractive potential than spin-down electrons. Once it is feasible to calculate \( v_{xc}^{\pm}(\vec{r}) \) from a given spin-density distribution, the spin-specific band structure can be obtained self-consistently and a number of magnetic properties can be subsequently derived.

**Stoner Model**

In the Stoner model [84, 90], the potential shift in (1.36) is represented by a constant:

\[
v_{xc}^{\pm}(\vec{r}) = v_{xc}^{0}(\vec{r}) \mp \frac{1}{2} IM = \int_{V_{atom}} m(\vec{r})d\vec{r}
\]

where \( \mu_B M \) is the local atomic moment and \( I \) is the so-called Stoner parameter assumed to be independent of wave vector \( \vec{k} \). \( I \) can be considered essentially as the exchange energy. As a consequence of the constant potential difference, (1.28) can be expressed as

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) \right)\psi_{jq}(\vec{r}) = (\epsilon_{jq} \pm \frac{1}{2} IM)\psi_{jq}(\vec{r})
\]

where the eigenvectors that solve (1.28) in the nonmagnetic case \( \psi_{k\nu}^{0}(\vec{r}) \) also solve the magnetic case:

\[
\psi_{k\nu}^{\pm}(\vec{r}) = \psi_{k\nu}^{0}(\vec{r})
\]

where \( \psi_{k\nu}^{\pm}(\vec{r}) \) is the solution for the magnetic case and subscripts \( \vec{k} \) and \( \nu \) denote the wave vector and the band index, respectively. The eigenvalues \( \epsilon_{k\nu}^{\pm} \), however, show a symmetric energy splitting:

\[
\epsilon_{k\nu}^{\pm} = \epsilon_{k\nu}^{0} \mp \frac{1}{2} IM
\]

This results in a spin-split band structure where the density of states for up and down electron is only shifted by \( IM \) but the functional form remains unchanged.

If, starting from the non-magnetic band structure (no spin-splitting), a transfer of electrons from the spin-down band to the spin-up band is energetically favorable, spin-splitting will occur, resulting in a non-zero \( m(\vec{r}) \). A sufficient condition for a metal to show ferromagnetism at \( T = 0 \) K is [90]

\[
IN_{0}^{0}(\epsilon_F) > 1
\]

This Stoner criterion states that metals, for which the product of the Stoner parameter \( I \) and the nonmagnetic density of states at the Fermi level \( N_{0}(\epsilon_F) \) is larger than one, should show ferromagnetism.
Table 1.3: Density of states at the Fermi level $N^0(\epsilon_F)$, the Stoner parameter at the Fermi level $I(\epsilon_F)$ and the product of both quantities for different metals [91, 92]. Only Fe, Co and Ni fulfill the Stoner criterion, i.e., $I(\epsilon_F)N^0(\epsilon_F) > 1$

<table>
<thead>
<tr>
<th>Element</th>
<th>$N^0(\epsilon_F) [\text{eV}^{-1}]$</th>
<th>$I(\epsilon_F) [\text{eV}]$</th>
<th>$N^0(\epsilon_F)I(\epsilon_F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.23</td>
<td>1.82</td>
<td>0.41</td>
</tr>
<tr>
<td>Al</td>
<td>0.21</td>
<td>1.22</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr</td>
<td>0.35</td>
<td>0.76</td>
<td>0.27</td>
</tr>
<tr>
<td>Mn</td>
<td>0.77</td>
<td>0.82</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe(bcc)</td>
<td>1.54</td>
<td>0.93</td>
<td>1.43</td>
</tr>
<tr>
<td>Co</td>
<td>1.72</td>
<td>0.99</td>
<td>1.70</td>
</tr>
<tr>
<td>Ni</td>
<td>2.02</td>
<td>1.01</td>
<td>2.04</td>
</tr>
<tr>
<td>Cu</td>
<td>0.14</td>
<td>0.73</td>
<td>0.11</td>
</tr>
<tr>
<td>Pd</td>
<td>1.14</td>
<td>0.68</td>
<td>0.78</td>
</tr>
<tr>
<td>Pt</td>
<td>0.79</td>
<td>0.63</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Discussions

The Stoner model provides a simple way to calculate the magnetic properties. The parameter $I$ can be derived from the LDA formulae with the correlation energy taken into account [91]. Hence, an explicit expression is obtained for $I$, which depends upon the electron energy $\epsilon$. Thus $I(\epsilon)$, as well as $N^0(\epsilon_F)$, can be calculated by the LDA. Table 1.3 lists calculation results for the Stoner parameter, the nonmagnetic density of states and their product for a number of metals. This table shows that the Stoner criterion is only fulfilled for Fe, Co and Ni, precisely those metals that show itinerant ferromagnetism.

As mentioned before, the LDA is also able to reproduce the magnetic moments of these 'bandmagnets' quite well. Fig. 1.13 shows the density of states of spin-up and spin-down electrons for Fe and Ni. It can be seen that the density of states of spin-up and spin-down electrons are exchange split but otherwise their form remains very similar. This shows that the approximation made in the Stoner model holds quite well. The difference between iron and nickel is that the spin-up bands of Ni are filled and only 0.6 electrons are missing in the spin-down band, while for iron neither the spin-up nor the spin-down bands are completely filled. This property makes iron a weak ferromagnet, while Ni, as well as Co, which also has a filled spin-up (majority) band, are so-called strong ferromagnets.

The Stoner criterion also allows a straight-forward discussion under which conditions magnetism is favored. Certainly, a large Stoner parameter favors ferromagnetism. This parameter is element specific and in a first approximation, an intratomic quantity. Thus it is independent of the local atomic environment. For the
Figure 1.13: Density of states of spin-up and spin-down electrons for Fe and Ni: The density of states for the spin-up and spin-down electrons are exchange split but otherwise their forms are very similar. This shows the validity of the approximation made in the Stoner model. The solid lines describe the density of states and the dotted line the integrated density of states, i.e., the number of electrons for a given spin direction. From [93]
Magnetism of Metal Films

3d, 4d and 5d metals, the following global trend for the Stoner parameter is found [91, 92]:

\[ I_{3d} > I_{4d} > I_{5d} \]  \hspace{1cm} (1.42)

The most important quantity in most cases is the nonmagnetic density of states. For transition metals, the density of states close to the Fermi energy is dominated by the contribution of the d-band. This density of states has pronounced structures as shown for example by photoemission measurements. Nevertheless, in a first approximation, the density of states of the d-band is inversely proportional to the band width:

\[ n_d^0 \sim \frac{1}{W_d} \]  \hspace{1cm} (1.43)

where \( W_d \) is the band width of the d electrons [94]. This width can be described within the nearest neighbor tight binding approximation as:

\[ W_d = 2\sqrt{N_n h_d} \]  \hspace{1cm} (1.44)

Thus \( W_d \) depends on both the hopping matrix element to the nearest neighbors \( h_d \), i.e. the hopping rate, and the number of nearest neighbors. The hopping rate decreases with increasing localization of the d-electron. For transition metals, the following trend is found:

\[ h_{3d} < h_{4d} < h_{5d} \]  \hspace{1cm} (1.45)

Correspondingly, one has

\[ W_{3d} < W_{4d} < W_{5d} \]  \hspace{1cm} (1.46)

leading to smaller band widths for 3d than for 4d and 5d metals. This is schematically depicted in Fig. 1.14 where the band widths of 4f and 5f electrons are also shown for comparison. From Fig. 1.14, one can see that the tendency towards magnetism is more pronounced in the later 3d metals, the 5f and 4f metals. 3d and the early 5f metals shows a trend towards band magnetism (itinerant electron magnetism) while the other rare earths are examples of localized magnets that can be described best by the Heisenberg model.

With this picture in mind, one can also understand the influence of increasing (decreasing) atomic spacing. Upon increasing the lattice spacing, the band width \( W \) decreases, thus ferromagnetism becomes more favorable and the atomic moment per atom increases. This can be seen from Fig. 1.15 where calculations for the ground state of fcc Co are presented as a function of lattice spacing. Above a lattice spacing of 3.35 Å, fcc Co is found to be ferromagnetic in this calculation. With increasing lattice spacing of the solid, the magnetic moment increases towards the atomic limit of 3 \( \mu_B \).

Unfortunately, it is experimentally impossible to expand a crystal lattice which would correspond to applying a negative hydrostatic pressure. Even the small
CHAPTER 1. THEORETICAL BASIS

Figure 1.14: Schematic representation of the band width $W$ of transition metals, rare earths and actinides. After [89]

Figure 1.15: Magnetic moment and ground state energy as a function of lattice spacing: Ground-state properties of fcc Co vs cubic lattice constant in Å. Energy changes in eV per atom and the magnetic moment in Bohr magnetons are depicted. NM and FM denote the nonmagnetic and ferromagnetic solution, respectively. The stability limits of these two phases are shown by dashed lines. From [95]
Figure 1.16: Crystal structure of transition metals as a function of d-band filling: In the upper portion of the figure, the predicted structure of transition metals is depicted [96]. This prediction only depends on the d-band filling. The actual crystal structure observed at room temperature is shown below. The open square for Mn denotes the complex cubic structure of this element. In general, the theory reproduces the observed structures quite well. It should be noted that magnetic 3d elements (Mn, Fe and Co) show deviations from the structure of their 4d and 5d counterparts. This indicates the strong influence of the magnetic ground state on the crystal structure. After [93]

range of lattice compressions that are accessible by applying high pressures are insufficient to really probe the dependence of magnetism on interatomic spacings. Nevertheless, there is other indirect experimental evidence which points towards a pronounced correlation between magnetism and structure. In Fig. 1.16, the crystal structure of the 3d, 4d and 5d metals is shown together with the predictions based on the tight binding method.

First of all, it is pleasant to note that the tight binding method correctly predicts the structure of most solids but it can also not be overlooked that it fails for elements such as Fe and Mn, which show magnetic behavior. Clearly, Fig. 1.16 gives only indirect evidence for a correlation between structure and magnetism. Support for this claim comes from the fact that typically the structural phase diagrams of magnetic metals are richer than their nonmagnetic counterparts. Finally in Fig. 1.17, the atomic densities of 3d, 4d, and 5d metals are depicted. It can be seen that the atomic densities for those 3d metals that show magnetism (ferro- or antiferromagnetism) are considerably smaller than the atomic densities of their nonmagnetic 4d and 5d counterparts.
Figure 1.17: Atomic density of different transition metals: For 3d, 4d and 5d metals, the atomic concentration of the element is graphed. The magnetic elements Cr, Mn, Fe, Co and Ni have a smaller atomic density than their nonmagnetic 4d and 5d counterparts. These elements are denoted by broken bars. To make the presentation easier, the densities of 4d and 5d metals have been normalized by setting the densities of Cu, Ag and Au equal. After [97]

1.2.2 Itinerant Antiferromagnetism – Spin Density Wave in bcc Cr

Among the 3d transition metals, Fe, Co and Ni show ferromagnetism, while three other metals, namely bcc Cr, fcc Fe and α-Mn with a complex crystal structure, show antiferromagnetism. In contrast to the few investigations of Mn and Fe, the antiferromagnetism of bcc Cr has been studied extensively. The antiferromagnetism in Cr is characterized by a static incommensurate spin density wave (SDW) as shown in Fig. 1.18. The spin density \( m(\vec{r}) \) shows a sinusoidal variation with position. The amplitude of the spin density oscillation was found to be 0.62 per atom at 4.2 K [98]. The wave vector can be in one of the 6 equivalent \( <100> \) directions, resulting in the formation of a domain structure. Cr shows a Néel temperature of 311 K, which is the highest among the three antiferromagnetic metals. At 123 K, there exists a spin-flip transition, through which the spin polarization direction changes from that perpendicular to the wave vector at high temperature to parallel to it at low temperature. This change in magnetic ordering has been observed by polarized neutron scattering.

The SDW antiferromagnetism is explained in the framework of band theory, hence it is also called itinerant antiferromagnetism. The Stoner criterion tell us whether the ferromagnetic state or the paramagnetic state is energetically favorable, but it does not take the SDW state into account. Overhauser pointed out that there exists an instability of the paramagnetic state with respect to the formation
**Figure 1.18:** Schematic incommensurate spin density wave in bcc Cr. The wave vector in the \(<100>\) direction has a length of \(\frac{2\pi}{1.04a}\). The arrows indicate the amplitude of the spin density wave at the lattice sites.

**Figure 1.19:** Electronic structure of bcc Cr. (a) Energy bands along lines of high symmetry. (b) Three dimensional sketch of the Fermi surface. An electron Fermi ”pocket” is centered at the origin \(\Gamma\) of the Brillouin zone, while four hole ”jacks” are centered around the H points. See text for more details. (c) (001) cross section of the Fermi surface through the origin of the Brillouin zone. From [99, 100]
of an SDW for an electron gas [101]. This instability occurs for an SDW having a wave vector \( q \simeq 2k_F \), where \( k_F \) is the diameter of the Fermi sphere. Let us illustrate this instability for a one-dimensional solid. Once an SDW with a wave vector of \( 2k_F \) is introduced, a periodic potential \( V_{\pm \|}^\perp \) with period \( \pi/k_F \) is established for spin-up and spin-down electrons. This potential would produce an energy gap at the Fermi level. The energy of the occupied states near the Fermi level is lowered and that of the unoccupied states near the Fermi level is raised, so that the overall energy of the electron system decreases. The situation is quite analogous to energy gaps that open at \( k = \pm n\pi/a \) for a one-dimensional free electron gas when the lattice induced periodic potential is considered. On the other hand, such a spin-specific periodic potential will result in periodically varying spin density, as we can see from the formulae of local spin density functional theory. This is an instability, which would lead to an SDW ground state.

Specifically for bcc Cr, the situation is much more complicated than the one-dimensional case discussed above. Generally, the antiferromagnetism in bcc Cr arises from its particular electronic structure of its paramagnetic state – the so-called nesting structure. A nesting structure is encountered when two different sections of the Fermi surface can be brought into almost perfect coincidence by a rigid translation in \( k \)-space. The electronic structure of bcc Cr is shown in Fig.1.19. Cr has 6 valence electrons per atom (3d\(^5\)4s\(^1\)). The first two bands are completely filled. Band three has a hole Fermi surface around \( H \) and \( N \). We call it a hole Fermi surface because the states inside the "jack" centered at \( H \) are unoccupied while those outside of it are occupied. Band four presents an electron Fermi "pocket" centered at the origin of the Brillouin zone. On the contrary to the hole Fermi jack, the states inside the pocket are occupied by electrons and those outside the pocket are unoccupied. The Fermi surface mainly consists of the states of band three and band four. The two pieces of Fermi sections, the hole "jack" and the electron "pocket" are separated by vectors \( \vec{Q} \), which are approximately equal to the reciprocal vector \( \vec{G}_{100} \), or its two equivalent vectors \( \vec{G}_{010} \) and \( \vec{G}_{001} \).

This nesting structure favors a SDW ground state [102]. Basically, a periodic modulation of spin density will lead to a mixing of the two one-electron states whose spin wave functions are opposite and whose \( \vec{k} \) vectors differ by the wave vector \( \vec{q} \) of the spin density modulation. This mixing modifies the electron wave functions and their one-electron energy parameters, and is especially important when \( E_{\vec{k}} = E_{\vec{k}+q} \) for then the interaction produces a first-order energy change

\[
E_{\vec{k}} = E_{\vec{k}+q} \rightarrow E_{\vec{k}} \pm V_{\vec{k}+\vec{q}}
\]

(1.47)

In addition, if \( E_{\vec{k}} \) is close to the Fermi energy, the sum of the energy of the occupied states is lowered, and the total energy of the system is reduced. That is to say, the nesting structure for bcc Cr favors a SDW state with an wave vector corresponding
to the nesting vector $\vec{Q}$.

### 1.2.3 Magnetism of Ultrathin Films

After the general concepts of magnetism for 3d transition metals have been discussed in the last section, we now turn to the characteristic features shown by ultrathin films. These new features discussed here mainly include dimensionality effects, the modification of magnetic moments at surfaces and interfaces, and the contribution to the magnetic anisotropy arising from surfaces and interfaces.

**Dimensionality Effects**

When the thickness of a magnetic film decreases to the monolayer range, a dimensionality crossover from 3-dimensional (3D) to 2-dimensional (2D) behavior is expected. Statistical mechanics predicts different critical exponents for systems of different dimensionality. The critical exponent $\beta$, for example $\beta$, describes how the magnetization $M$ vanishes near $T_C$:

$$M \propto (1 - \frac{T}{T_C})^{\beta}, \quad T \to T_C$$

(1.48)

Different $\beta$ values are predicted when different models are used, but they are independent of specific details of the chosen system. In the *Heisenberg model*, the orientation of the spins is not restricted. In this model, long-range magnetic ordering is expected only for three dimensional systems. The predicted $\beta$ value is about 0.365. If the spin orientation is confined in a plane, one obtains the *xy model*. In this case, $\beta \approx 0.34$ for 3D system and $\beta \approx 0.23$ for finite 2D systems \(^1\). In the *Ising model*, a preferred spin orientation exists so that there are only two choices for the spins, parallel or opposite to the given direction. For this case, the critical exponents are 0.325 for a 3D system and 0.125 for a 2D system.

The critical exponents have been measured for a number of ultrathin films. These data, compiled by Himpsel [38], are listed in Table 1.4. The measured exponents fall into two groups, which are corresponding to the 2D Ising model and the finite xy model, respectively.

By measuring the critical exponent, Li and Baberschke [110] have demonstrated that a dimensionality crossover from 3D to 2D takes place with decreasing film thickness for Ni(111) films on a W(110) substrate. The critical exponent $\beta$ as a function of thickness is shown in Fig. 1.20. The gradual decrease of $\beta$ from 0.38 at 20 ML to 0.29 at 7.5 ML is interpreted as a crossover from 3D Heisenberg to 3D

\(^1\)At finite temperature and zero applied field, an infinite isotropic 2D xy system can not sustain long-range order but exhibits a Kosterlitz-Thouless phase transition to a state with infinite correlation length at low temperature.
Table 1.4: Experimentally measured critical exponents $\beta$ for ultrathin metal films. Values close to 0.125 are characteristic for Ising like systems, while values around 0.23 are indicative for 2D $xy$ models.

<table>
<thead>
<tr>
<th>System</th>
<th>$\beta$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Pd(100)</td>
<td>0.127</td>
<td>[103]</td>
</tr>
<tr>
<td>Fe(110)/Ag(111)</td>
<td>0.137</td>
<td>[104]</td>
</tr>
<tr>
<td>Fe/W(11)</td>
<td>0.123</td>
<td>[105]</td>
</tr>
<tr>
<td>Fe/Au(100)</td>
<td>0.22</td>
<td>[106]</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
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<td>[107]</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
<td>0.28</td>
<td>[108]</td>
</tr>
<tr>
<td>Ni/Cu(100)</td>
<td>0.24</td>
<td>[108]</td>
</tr>
<tr>
<td>Fe/W(100)</td>
<td>0.22</td>
<td>[109]</td>
</tr>
</tbody>
</table>

Figure 1.20: Critical exponent $\beta$ as a function of film thickness for Ni(111)/W(110). The dashed lines show the theoretical values for a 3D Heisenberg, 3D Ising, and 2D Ising system. The shaded regime marks the crossover from 3D to 2D. From [110]
Magnetism of Metal Films

Figure 1.21: Scaling behavior of Curie temperature as a function of film thickness. The Curie temperatures are normalized to their respective bulk values $T_C(\infty)$. The data are collected for a number of systems: open squares for Ni(111)/W(110), open circles for Fe(110) Ag(111), open triangles for Ni(111)/Re(0001), solid squares for Ni/Cu(100), solid circles for Ni$_9$Co$_1$/Cu(100), and solid triangles for Ni$_3$Co$_1$/Cu(100). From [108]

Ising behavior, due to an increasing anisotropy energy. A dimensionality transition from a 3D Ising system to 2D a Ising system is responsible for the dramatic reduction of $\beta$ between 7 and 5 ML. Accompanied by the dimensionality crossover is a reduction of Curie temperature $T_C$ with decreasing thickness. As shown in Fig. 1.21, the reduction of $T_C$ displays finite-size scaling. When the Curie temperatures are normalized to their respective bulk values, the thickness dependence for a variety of films can be scaled to two curves, one for the 2D Ising system with strong uniaxial magnetic anisotropy and the other for 2D xy films. As we mentioned before, these two group of films show critical exponents of 0.125 and 0.23, respectively. The Ising films show higher $T_C$ values than the xy films. For xy films, $T_C$ is reduced to half its bulk value at a thickness of about 5 ML and it decreases to zero at about one ML for both systems.

Magnetic Moments at Surfaces and Interfaces

For 3d transition metals, the itinerant magnetism leads to a magnetic moment that is determined by the electronic band structure. A positive exchange interaction splits the valence band into the majority band and the minority band. The difference in the number of occupied states between these two bands gives rise to the average magnetic moment per atom. At a metal surface, the broken symmetry and the reduced coordination number lead to a narrowing of the d band and localized surface states or surface resonance states, which affect the magnetic properties in
the near surface region. Several ab initio methods (mainly the full-potential linearized augmented plane wave method) based on the local spin density functional theory have been developed to calculate the electronic and magnetic structure of materials [111]. One of great successes of these theoretical studies is the prediction of the magnetic moment enhancement at the surface of 3d transition metals. It is well recognized that the magnetic moment enhancement comes from the reduced number of nearest neighbors and hence weaker interatomic hybridization, as we have discussed in the last section. The calculated results for the magnetic moment of 3d transition metal atoms at the surface and, for comparison, the respective bulk values are summarized in Table 1.5. In each case, the magnetic moment at the surface is enhanced. In accordance with the tight binding model, the enhancement for a given bulk material is larger the smaller the number of nearest neighbors. Thus, for fcc Ni, the more open (110) surface has a larger magnetic moment than the (100) surface which has one more nearest neighbor at the surface. For bcc crystals, the reverse situation is found. In this case the (100) surface is more open than the (110) surface and thus shows the larger increase of the magnetic moment. What is more difficult to explain within the tight binding model is that the magnetic moment at the Cr and Fe surface have a much more pronounced enhancement than at the Ni and Co surface. In principle, this is due to the fact that for Ni and Co, the majority d-band is completely filled while for Cr and Fe, both the minority and the majority band contain unoccupied states. In the latter situation, a d-band narrowing can change magnetic moment more easily. For Co and Ni, it is more difficult to change the magnetic moment since these metals are strong ferromagnets [94].

Spin polarized low energy electron diffraction (SPLEED) provides an experimental method to test the theoretical predictions. Qualitative agreement has been obtained for Fe(110), Ni(100) and Ni(111) surfaces [112, 113].

In the calculation of the magnetic moments, the atomic distances at the surface are usually assumed to be identical to the corresponding bulk distance. This is very often not the case. Relaxations, a change of interlayer spacing in the vicinity of the surface, or even reconstructions, a change of the structural arrangement of the topmost layer(s), are the rule rather than the exception. Both would modify the results on magnetic moment of surface atoms. On clean metal surfaces, commonly an inward relaxation of the first interlayer spacing is found [114], which has been attributed to a smoothing of the electron density at the surface [115]. Such a relaxation will influence the magnetic moment, as is shown in Fig. 1.22 for the Fe(100) surface [111]. An inward relaxation leads to a decrease of magnetic moment. Theoretically an inward relaxation of 4% is determined for Fe(100) [116] which leads to a 6% decrease in the magnetic moment. Nevertheless, the resulting magnetic moment is still considerably larger than the bulk value of about 2.2\(\mu_B\) [111]. This example demonstrates that for an understanding of magnetic properties of surfaces,
Magnetism of Metal Films

Table 1.5: Magnetic moment ($\mu_B$) at the surface and in the center layer and the corresponding enhancement (in percent) for the surface atom (from A. J. Freeman et al. [111]).

<table>
<thead>
<tr>
<th>System</th>
<th>Surface</th>
<th>Center</th>
<th>Enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Fe(001)</td>
<td>2.96</td>
<td>2.27</td>
<td>30</td>
</tr>
<tr>
<td>bcc Fe(110)</td>
<td>2.65</td>
<td>2.22</td>
<td>19</td>
</tr>
<tr>
<td>bcc Fe(111)</td>
<td>2.70</td>
<td>2.3</td>
<td>17</td>
</tr>
<tr>
<td>hcp Co(0001)</td>
<td>1.76</td>
<td>1.64</td>
<td>7</td>
</tr>
<tr>
<td>fcc Ni(001)</td>
<td>0.68</td>
<td>0.56</td>
<td>23</td>
</tr>
<tr>
<td>fcc Ni(110)</td>
<td>0.63</td>
<td>0.56</td>
<td>13</td>
</tr>
<tr>
<td>fcc Ni(111)</td>
<td>0.63</td>
<td>0.58</td>
<td>9</td>
</tr>
<tr>
<td>fcc Fe(001)</td>
<td>2.85</td>
<td>1.99</td>
<td>43</td>
</tr>
<tr>
<td>bcc Co(001)</td>
<td>1.95</td>
<td>1.76</td>
<td>11</td>
</tr>
<tr>
<td>bcc Co(110)</td>
<td>1.82</td>
<td>1.76</td>
<td>3</td>
</tr>
<tr>
<td>fcc Co(001)</td>
<td>1.86</td>
<td>1.65</td>
<td>13</td>
</tr>
<tr>
<td>bcc Cr(001)</td>
<td>2.49</td>
<td>0.59</td>
<td>322</td>
</tr>
</tbody>
</table>

A detailed knowledge of the structure is desirable.

At the interface of two materials, the magnetization is influenced by the mutual perturbation of these two materials. The mutual perturbation may give rise to an enhanced or decreased interface magnetism and even to an oscillatory magnetization profile in the interface region. Niklasson et al. have calculated the magnetic spin moments of magnetic 3d bilayer interfaces for a variety of systems using the local spin-density approximation [117]. It was found that the magnetic moment of atoms at the interface is quite different from the bulk value. How the interface magnetic moment deviates from the bulk value depends on the adjacent material. To illustrate this effect, their results are given in Fig. 1.23.

Interface magnetism has also been experimentally studied during the last decade. A number of techniques have been applied to detect the interface magnetic moment. They are mainly spin polarized electron spectroscopy (SPEP), polarized neutron reflection, ferromagnetic resonance (FMR), conversion electron Mössbauer spectroscopy (CEMS), and x-ray magnetic circular dichroism (XMCD). The combination of XMCD and conventional magnetometry such as superconductor quantum interference device (SQUID) measurements and vibrating sample magnetometry (VSM) has proven to be a powerful tool to study interface magnetism. The later measures the absolute value of the magnetization and the former separates the contribution of the two materials at the interface. Therefore the atomic magnetic moment of the interface element can be determined. Pd/Fe and Cr/Fe are the most frequently studied systems. The Fe moment was found to be enhanced at the Pd/Fe
interface and a ferromagnetically coupled Cr bilayer with huge moment has been reported in agreement with the theoretical prediction. Induced magnetic ordering has also been found in “nonmagnetic” transition metals such as V and Pd when they are next to a ferromagnetic layer at the interface. We summarize the experimental results on the interface magnetic moments in Table 1.6.

The properties of ultrathin epitaxial films can be discussed in a very similar manner to surface moments. For a monolayer on a substrate, an equation similar to (1.44) can be used. However, one has to distinguish between the hopping of d-electrons within the monolayer $h_{∥}$ and the hopping element to the substrate $h_{⊥}$. Furthermore, the coordination number in the plane $N_{∥}$ and to the substrate $N_{⊥}$ has to be considered [94]. While the coordination numbers only depend on the structure of the surface, the hopping matrix elements will be specific for the chosen film-substrate pair. Hopping and therefore the film magnetism can thus be influenced by the choice of substrate. In particular, the use of noble metal substrates with their low-lying d-band should result in a small d-d hybridization between film and substrate and therefore leads to a small $h_{⊥}$. The monolayer films then show almost two-dimensional behavior. This is favorable to induce or enhance magnetism. Indeed, it has been demonstrated by total energy calculations within the local spin density approximation that even monolayers of 4d and 5d metals on Ag(100) show ferromagnetism [128]( see Fig. 1.24). On the contrary, if a nonmagnetic transition metal is chosen as a substrate, the strong interaction between film and substrate
Figure 1.23: The profiles of magnetic moments in the vicinity of the interface for different magnetic bilayers. Two different lattice constants, corresponding to the bulk lattice constants of the two materials forming the bilayer, have been assumed in the calculations and are given in parentheses in the figures. From [117]
Fig. 1.23 continued
**Table 1.6:** The measured magnetic moments (in Bohr magnetons) of interface atoms are obviously different from the bulk values as demonstrated in this table. The bulk values are 2.3 $\mu_B$ for Fe, 0.6 $\mu_B$ for Ni, and 0.59 $\mu_B$ for Cr. V and Pt are nonmagnetic metals.

<table>
<thead>
<tr>
<th>Element</th>
<th>System</th>
<th>interface moment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Pd/Fe multilayers</td>
<td>2.8</td>
<td>[118]</td>
</tr>
<tr>
<td>Fe</td>
<td>Pd/Fe multilayers</td>
<td>2.3～3.2$^a$</td>
<td>[119]</td>
</tr>
<tr>
<td>Fe</td>
<td>Ag/5.5MLFe/Ag(001)</td>
<td>2.58$^b$</td>
<td>[120]</td>
</tr>
<tr>
<td>Fe</td>
<td>Cu/5.7MLFe/Ag(001)</td>
<td>2.50$^b$</td>
<td>[120]</td>
</tr>
<tr>
<td>Fe</td>
<td>Pd/5.7MLFe/Ag(001)</td>
<td>2.6$^b$</td>
<td>[120]</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe/V superlattice</td>
<td>1.34～2.12$^a$</td>
<td>[121]</td>
</tr>
<tr>
<td>V</td>
<td>Fe/V superlattice</td>
<td>-0.27～-1.06$^{a,c}$</td>
<td>[121]</td>
</tr>
<tr>
<td>V</td>
<td>V/Fe(100)</td>
<td>-0.3$^c$</td>
<td>[122]</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr/Fe(100)</td>
<td>4</td>
<td>[123]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni/Cu(100)</td>
<td>0.30～0.35$^a$</td>
<td>[124]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni/Fe(001)</td>
<td>0.69</td>
<td>[125]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni/Pt multilayers</td>
<td>0.24～0.54$^a$</td>
<td>[126]</td>
</tr>
<tr>
<td>Pt</td>
<td>Ni/Pt multilayers</td>
<td>0.09～0.21$^a$</td>
<td>[126]</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt/Co multilayers</td>
<td>0.21</td>
<td>[127]</td>
</tr>
</tbody>
</table>

$^a$average total moment, which varies from sample to sample, depending on the thicknesses of the component layers.

$^b$average total moment.

$^c$the minus signal denotes that the V moment is antiparallel to the moments of the Fe substrate.
Figure 1.24: Predicted magnetic moment of 3d-, 4d- and 5d-metals on Ag(100): These calculations show that epitaxial monolayers of 4d and 5d elements can develop a magnetic moment on a noble metal substrate [128].

diminishes the ferromagnetism of the monolayer film [111].

To close this subsection, we would like to briefly discuss the orbital magnetic moment. It is well known that the orbital moments are strongly suppressed in the bulk by the crystal splitting and by the hybridization with the neighboring atoms, resulting in an almost complete quenching of angular momentum. Calculations yield very small orbital moments for 3d ferromagnetic bulk metals: 0.082 $\mu_B$ for bcc Fe, 0.123 $\mu_B$ for hcp Co, and 0.058 $\mu_B$ for fcc Ni [129]. Therefore the total moments mainly come from the spin contribution. However, the quenching of orbital moment can be partly lifted on the surface, resulting in enhanced surface orbital moments. The orbital moment of the fct Fe surface layer on Cu(100) has been measured to be three times larger than the bulk value by x-ray magnetic circular dichroism, which allows one to separate the spin and orbital contribution to the total moment [130]. Similarly, a two times larger orbital moment is found in ultrathin Co film grown on Cu(100) [131].

Magnetic Anisotropy in Ultrathin Films

In the preceding discussion, the direction of the magnetization with respect to the crystal axes was not considered. In reality however, the total energy of a film is dependent on the spin orientation. The change in free energy for a crystal or film upon rotation of the magnetization is called the anisotropy energy. Though the magnitude of the anisotropy energy is of the order of $10^{-4}$ to $10^{-3}$ eV/atom only, the total anisotropy energy of a crystal or a film consisting of a huge number of atoms is much larger than $k_B T$. Therefore the preferred magnetization direction is
usually dictated by the anisotropy energy.

Two major contributions dominate the anisotropy energy—the spin-orbit coupling and the dipole-dipole interaction. Due to the long range character, the dipole-dipole interaction leads to a contribution to the anisotropy which depends upon the specimen shape and is also called the shape anisotropy. The spin-orbit coupling relates the magnetization to the crystal lattice and results in a so-called magnetocrystalline anisotropy. If the sample is stressed, the spin-orbit coupling is modified by the strain. This modification to the magnetocrystalline anisotropy is called magneto-elastic anisotropy, though it has the same microscopic origin as the the magnetocrystalline anisotropy, i.e., the spin-orbit interaction. In the following these three anisotropies will be discussed in more detail.

**Shape Anisotropy** The shape anisotropy comes from the long range magnetic dipolar interaction. The shape effect of the dipolar interaction in ellipsoidal ferromagnetic samples can be described via an anisotropic demagnetizing field, $H_d$, given by $H_d = -N\vec{M}$. Here $\vec{M}$ is the magnetization vector and $N$ is a shape-dependent demagnetizing tensor. For a thin film, all tensor elements are zero except for the diagonal element corresponding to the direction perpendicular to the film plane, which is equal to unity. Since the magnetostatic energy can be expressed as

$$E_d = \frac{-\mu_0}{2V} \int \vec{M} \cdot \vec{H}_d \, dv$$

the shape anisotropy energy per unit volume of a film reads as

$$E_d = \frac{1}{2} \mu_0 M^2 \cos^2 \theta.$$ (1.50)

Here $\theta$ is the angle of the magnetization $\vec{M}$ with respect to the film normal. According to this expression, the shape anisotropy favors an in-plane orientation for the magnetization. Since the film thickness does not enter into the expression, the shape anisotropy is a bulk quantity and is proportional to the number of atoms.

**Magnetocrystalline Anisotropy** As early as 1954, Néel proposed a phenomenological description of the magnetic anisotropy [132]. In Néel’s model, the spin-orbit interaction introduces an angular-dependent magnetic interaction. The interaction between two atomic magnetic moments separated by a vector $\vec{r}$ can be written as

$$E(r) \sim l(r) \cos^2 \phi + q(r) \cos^4 \phi,$$ (1.51)

where $l(r)$ and $q(r)$ are expansion coefficients and $\phi$ is the angle between the interatomic distance $r$ and the parallel magnetic moment of the two atoms considered.

It should be pointed out that Néel’s model is based on the localized moment approximation and therefore is not well suited for itinerant magnets. Within the
model of delocalized electrons, the magnetocrystalline anisotropy is explained as a modification to the band structure induced by the spin-orbit coupling. Spin-orbit coupling can be interpreted as the coupling between the spin of the electron and the magnetic field created by its own orbital motion around the nucleus. The orbital motion is coupled to the lattice via the electron potential of the ions. For ferromagnetic 3d metals (Fe, Co, Ni), the electronic states are degenerate for the 3d band. Spin-orbit coupling lifts the degeneracy. The splitting of the degenerate states at the Fermi level decreases the density of the states (DOS) at the Fermi surface and increases the DOS below the Fermi level. Hence the total energy of the electrons decreases. The amplitude of the band splitting depends on the spin direction. The direction, in which the spin-orbit coupling produces the maximum splitting and thus the minimum system energy, gives rise to the easy axis.

The crystalline anisotropy energy can be expanded in successive powers of \( \alpha_x \), \( \alpha_y \) and \( \alpha_z \), where \( \alpha_i \) are the direction cosines of the orientation of the magnetization with respect to the crystal axes. Due to the time-reversal symmetry, only even orders of \( \alpha_i \) appear in this expansion. Furthermore, the expression can be simplified by the crystal symmetry. For a cubic crystal, the second order term \( (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) \) is constant and does not give an anisotropy. In this case, the bulk crystalline anisotropy energy is expressed as:

\[
E_K = K_0 + K_1 (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) + K_2 \alpha_x^2 \alpha_y^2 + K_3 (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2)^2 + \ldots
\]  

(1.52)

The coefficients are both temperature dependent and vary from material to material. For Fe at 4.2 K, \( K_1 = 4.02 \times 10^{-6} \) eV/atom, \( K_2 = 1.44 \times 10^{-8} \) eV/atom and \( K_3 = 6.6 \times 10^{-9} \) eV/atom. For a hexagonal crystal, the anisotropy energy has the form of

\[
E_K = K_0 + K_{u1} \sin^2 \theta + K_{u2} \sin^4 \theta + K_{u3} \sin^6 \theta + K'_{u3} \sin^6 \theta \cos^6 \phi
\]  

(1.53)

where \( \theta \) is the angle between the magnetization vector and the hexagonal axis and \( \phi \) is the azimuthal angle of the magnetization. For a tetragonal lattice,

\[
E_K = K_0 + K_{u1} \sin^2 \theta + K_{u2} \sin^4 \theta + K_{u3} \cos^2 \alpha \cos^2 \beta
\]  

(1.54)

where the magnetization vector makes an angle of \( \theta \) with respect to the tetragonal axis and it forms angles of \( \alpha \) and \( \beta \) with the other two axes.

At a surface, the transition symmetry is broken in the direction of the film normal, resulting in an uniaxial anisotropy [133]. It is termed surface anisotropy. Using the pair-potential of (1.51), Néel derived this surface anisotropy energy for fcc(111) and fcc(100) surfaces

\[
E = K_s \cos^2 \theta,
\]  

(1.55)
with $K_s$ differing for (111) and (100) surfaces. $\theta$ is the angle of the magnetization away from surface normal. In general, the surface anisotropy energy can be written as

$$E = K_s \cos^2 \theta + K_{s,p} \sin^2 \theta \cos^2 \phi,$$  \hspace{1cm} (1.56)

with $\phi$ being the azimuthal angle [134, 135]. For $K_s < 0$, the surface normal is an easy axis. For $K_s > 0$, the film plane is an easy plane of the surface anisotropy. $K_{s,p}$ is the constant for the additional in-plane anisotropy. $K_{s,p}$ disappears if the surface normal is an n-fold rotation axis with $n > 2$. If $K_{s,p}$ does not disappear, the x-axis is the easy axis when $K_{s,p} < 0$ and the hard axis when $K_{s,p} > 0$.

The effect of the symmetry reduction at a surface on the anisotropy energy has also been examined within band theory. It is concluded that a large surface contribution can be expected due to the narrowed d band [136, 137].

[**Magneto-elastic Anisotropy**] The magneto-elastic anisotropy is nothing else than a strain-induced modification of the magnetocrystalline anisotropy. Strain in ultrathin films is mainly induced by the lattice mismatch between the film and the substrate, which is $\eta = (a_f - a_s)/a_s$. $a_f$ and $a_s$ are the lattice parameter of the film and the substrate, respectively. The strain state is film thickness dependent. This has been discussed in the previous chapter.

How the strain modifies the magnetocrystalline anisotropy can be analyzed by expanding the magnetocrystalline anisotropy energy in a Taylor’s series with respect to the strains.

$$E_K = (E_K)_0 + \sum (\partial E_K/\partial e_{ij})_0 e_{ij} + \cdots.$$  \hspace{1cm} (1.57)

As an example, for a cubic crystal [138],

$$(E_K)_0 = K(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2)$$  \hspace{1cm} (1.58)

and the first order term in the Taylor’s expansion can be written as

$$E_{ME} = B_1(\alpha_1^2 e_{xx} + \alpha_2^2 e_{yy} + \alpha_3^2 e_{zz}) + B_2(\alpha_1 \alpha_2 e_{xy} + \alpha_2 \alpha_3 e_{xz} + \alpha_1 \alpha_3 e_{zz}).$$  \hspace{1cm} (1.59)

Here $K$ is the first order cubic magnetocrystalline anisotropy constant. $\alpha_i$ is the direction cosine of the magnetization vector and $e_{ij}$ denotes the strains. $B_1$ and $B_2$ are the magneto-elastic coupling constants and they are related to the first order partial derivative through:

$$\partial E_K/\partial e_{ii} = B_1 \alpha_i^2 \quad \partial E_K/\partial e_{ij} = B_2 \alpha_i \alpha_j.$$  \hspace{1cm} (1.60)
When the strains are known, the strain-induced modification $E_{ME}$ is easy to calculate according to (1.59).

As has been pointed out above, atoms at the surface and interface have a different atomic environment from the bulk atoms. Hence additional magnetoelastic coupling coefficients might be necessary to take this surface and interface effect into account. Therefore the effective magneto-elastic coupling constant should be written as $B_{\text{eff}} = B_{\text{bulk}} + B_s/t$, where $t$ is the film thickness [139, 140].

From the above discussions we know that the dipole-dipole interaction has a bulk contribution to the free energy, i.e., the induced anisotropy energy is shared by all the atoms. However, the distinction should be made for the magnetocrystalline anisotropy between the surface/interface atom and the interior atoms, due to the different atomic environments. For a cubic crystal, a square-term appears in the expression of the anisotropy energy due to the broken symmetry for the atoms at surface and interface, while for bulk atoms, the lowest term is the quartic term. Therefore the surface/interface magnetocrystalline anisotropy could be much larger than the bulk contribution. To reflect this difference between interfacial atoms and bulk atoms, the magnetic anisotropy energy $K$ can be phenomenologically separated in a volume contribution $K_v$, interface and surface contribution, $K_{in}$ and $K_s$, respectively. The relation between them can be written as

$$K = K_{\text{eff}} = K_v + \frac{K_s + K_{in}}{t}$$  \hspace{1cm} (1.61)

where $t$ is the film thickness. This relation represents the averaged value of the magnetic anisotropy energy of the interface atoms, surface atoms and the inner atoms. In this way, $K$ becomes an explicit function of film thickness. It is possible that the lowest energy state for the magnetization changes with film thickness, for example, from in-plane to out-of-plane. This is to say, a spin reorientation transition could occur upon variation of film thickness. On the other hand, the anisotropy coefficients are a function of a number of parameters, such as temperature, chemical composition and stress state. Spin reorientation transitions can also be induced by changes in these quantities. Spin reorientation transitions and a perpendicular magnetic anisotropy have been observed for a number of ultrathin films and have been intensively investigated.

### 1.2.4 Magnetic Coupling

The magnetic coupling between different magnetic layers is of importance both for practical application and for theoretic aspect. It is well-known, for an ultrathin bilayer consisting of two ferromagnetic layers, the magnetic properties of each layer are interwoven through the interface exchange coupling. It has been shown that for strongly exchange-coupled layers some of the bilayer magnetic properties can
be given by a linear combination of the magnetic properties of the individual layers, with coefficients for each layer given by the product of the magnetic moment per atom and the number of the atoms [141]. In this way the magnetic properties of the bilayer can be tailored by adjusting the thickness of the individual layers. The exchange coupling between a antiferromagnetic layer and its neighboring ferromagnetic layer is of special interest, since it result in the so-called exchange anisotropy. Exchange anisotropy exhibits itself by a shift of the hysteresis loop after cooling the system with an ordered ferromagnetic layer below the Neél temperature of the antiferromagnetic layer. The spin-valve devices are designed basing on this exchange anisotropy. In contrast with the above direct exchange coupling at the interface of two magnetic layers, a novel coupling phenomena has been found between the magnetic films separated by a nonmagnetic spacer layer [142, 143]. It is usually called interlayer exchange coupling and tightly associated with the giant magnetoresistance (GMR) effect observed in the ferromagnetic-nonmagnetic multilayer structure [144]. GMR refers to large change in resistance obtained in modest magnetic field. The change in resistance correlates to a change in a relative orientation of the magnetization in adjacent magnetic layers upon the application or withdraw of a external field. The GMR effect has opened a possibility for applications in a variety of areas, such as magnetic recording, nonvolatile memories, and magnetic sensors.

In the coming subsection, the experimental phenomena and their physical origins will be addressed for interlayer exchange coupling and the exchange anisotropy.

Interlayer exchange coupling

[General description] Grünberg et al. first found that an antiferromagnetic exchange coupling exist between the Fe films separated by a Cr spacer [142]. Later Parkin et al. discovered the oscillation of the interlayer exchange coupling in Fe/Cr/Fe and Co/Ru/Co multilayers between ferromagnetic (parallel magnetization) and antiferromagnetic (antiparallel) as a function of spacer thickness [143]. Furthermore, Parkin showed that the oscillatory exchange coupling occurs with almost any metal as the spacer material [145]. Stimulated by Grünberg and Parkin’s discoveries, a huge number of studies have been done on the subject of interlayer coupling and more detailed characteristics have been specified. Some important results are listed below.

- There exist two kinds of oscillatory period, the long period and the short period. The long oscillatory period is also called as the common period, which is around 1 nm and does not depend much on the species of the spacer element. The short oscillatory period is only 2 or 3 atomic layers.
• Besides the co-linear Heisenberg type coupling (parallel or antiparallel), non-co-linear coupling orientation has also been observed. For example, the magnetic moments of the FM layers were found to be orthogonal to each other in Fe/Cr/Fe [146] and Co/Cu/Co [147] sandwich structures. Therefore the coupling interaction is usually phenomenologically expressed as

\[ E = -J_1 \cos \theta + J_2 \cos^2 \theta, \]  

(1.62)

where \( \theta \) is the angle between the magnetic moments of the neighboring ferromagnetic layers, and \( J_1 \) and \( J_2 \) are constants. The first term describes the bilinear exchange interaction of a Heisenberg nature. Depending on the sign of the constants \( J_1 \), this term leads to a co-linear parallel or antiparallel ordering of the neighboring magnetic moments. The second term, which characterizes the biquadratic exchange, gives a preferential 90-degree ordering. Obviously, \( J_1 \) would oscillate with the spacer thickness.

• In the theoretic aspects, there have been mainly two parallel models, the quantum-well (QW) model and the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory based model, to explain the oscillatory interlayer coupling. The RKKY theory describes an indirect exchange interaction between local magnetic moments mediated by conduction electrons. It has successfully explained the magnetism of rare-earth metals, in which the magnetic moment comes from the localized f electrons and the s electrons are delocalized conduction electrons. The QW model focuses on the electron confinement induced electron standing waves, i.e., the quantum well states. Both models predict the same oscillation periods, which is given by the Fermi wave vector. However, other measurements rather than oscillation period support more the QW model. For example, the coupling interaction was found to be dependent on the FM layer thickness [148, 149]. Moreover, the coupling was found even to oscillate with the thickness of a cap Cu layer on top of a Co/Cu/Co sandwich [150, 151]. These can be explained within the QW model as a result of quantum interference effect.

**Quantum well states model** [152, 153] It is well known, when the size of a physical system is reduced to nanometer range, electron confinement is expected to generate quantum well states. With the QW model, the oscillatory exchange coupling arises because the energy that takes to fill the electron states up to the Fermi level oscillates as a function of the well width.

The essential physics can be illustrated by a one-dimensional QW. Let’s first consider a single step of the well, Fig. 1.25 (a) shows the probability for an electron incident from the well to reflect at this step as a function of the electron energy. The
energy origin is chosen to be the band minimum in the outside-well region. This is also the threshold for the states of the well material to be able to transmit across the step. At energies below the threshold, a state incident from the left reflects with unit probability; while above the threshold the reflection probability decreases from one to zero as the energy increases. When the second step is introduced, there are two types of states in the well region, bound states at negative energies, and scattering states at positive energies. The bound states result from the constructive interference in the multiple reflection of electrons. The scattering states consist of a plane wave incident on the QW from either side, a reflected wave with reduced amplitude on the same side of the well, waves scattering in both directions in the well, and a transmitted wave on the other side of the well. Fig. 1.25(b) show the probability for a electron to reflect from the QW structure. The oscillatory component to the reflection probability is caused by transmission resonances. At energy close to those at which an integer number of wavelengths fit inside the well the state undergoes increased multiple scattering in the well, and transmits with unit probability.

By making a well structure, the density of states is changed compared to the bulk material (see Fig. 1.25). Importantly, the change in density of states is well thickness dependent. Followed is an interesting result that the energy required to fill the states up to the fermi level dampingly oscillates with the well thickness. The change in energy relative to the bulk state is shown in Fig. 1.26 as a function of well thickness. In the limit of small reflection probability and large well thickness, the change in total energy is given by

\[ \Delta E(t) = \frac{\hbar}{\pi} \frac{v_F}{2} |R|^2 \frac{1}{t} \sin(2k_F t), \]  

(1.63)

where \( k_F \) is the Fermi wave vector and \( v_F = \hbar k_F / m \) is the electron velocity at the Fermi level. \( t \) is the well thickness and \( R \) is the reflection probability. One can see the oscillation period is \( 2\pi/2k_F \).

For magnetic sandwich structures the oscillatory exchange coupling arises for the same reasons as the oscillatory energy in a QW. In magnetic structures, each spin system experiences a different potential. Model potentials for both spins are shown in Fig. 1.27 for the cases of ferromagnetic and antiferromagnetic alignment of the magnetizations.

For each spin system the energy oscillates for the different magnetic configurations. The difference in these oscillatory energy is the oscillatory exchange coupling. All of the oscillatory energies have the same period because the period is determined by the Fermi surface of bulk spacer-layer material. Since the potential barriers are different, the reflection probability are different, and the amplitudes of the oscillatory energies are different from one magnetic configuration (for exam-
Figure 1.25: Properties of a QW. (a) shows the probability for an electron incident from the wall to reflect from a single step as a function of the energy. (b) shows the probability for an electron to reflect from a QW structure. Inset in both panels schematize the processes. (c) shows the change in the density of states for QW structure, the curve has been reduced by a factor of 10 to fit it in the figure. The arrows represent the $\delta$ function contribution to the density of states due to the presence of bound states. (from Stiles [152])
**Figure 1.26:** Total energy of the quantum well filled to the Fermi level. The solid line shows exact calculation result and the dashed line is calculated using eq. (1.63). (from Stiles [152])

**Figure 1.27:** Quantum wells for exchange coupling. The top left (right) quantum well shows the potential seen by spin-up (-down) electrons in a ferromagnetically aligned quantum well structure. The bottom left (right) quantum well shows the potential seen by spin-up (down) electrons in antiferromagnetically aligned quantum well structure. (from Stiles [152])
Mechanisms of biquadratic coupling

As it gradually comes to consensus that the quantum well mechanism produce the bilinear exchange coupling $J_1$ (see eq. (1.62)) between two ferromagnetic layers separated by a nonmagnetic spacer, several mechanism have been proposed to explain the biquadratic coupling.

Slonczewski first proposed the thickness fluctuation mechanism [154, 155]. He pointed out that the thickness fluctuation of the spacer layer produces an inhomogeneous bilinear coupling $J_1$, since $J_1$ oscillates with the spacer thickness as is addressed above. He found by micromagnetic calculation that the sum of coupling and exchange-stiffness energies is minimized when the mean moments of the ferromagnetic layers are orthogonal. Let $\pm 2\Delta J$ denotes the difference in $J_1$ of a monolayer-high terraces with width $L$, the effective biquadratic coupling can be deduced as

$$J_{2\, eff} = \left[2L(\triangle J)^2/\pi^3\right] \sum_{i=1,2} A_i^{-1} \coth(\pi D_i/L),$$

where $A_i$ is the exchange stiffness within the ferromagnetic layer of thickness $D_i$ (see Fig. 1.28). Since $J_1, A_1, A_2$ are temperature dependent, eq. (1.65) predicts a modest temperature dependence for $J_{2\, eff}$.

To explain the strong temperature dependence of $J_{2\, eff}$ in the samples with Au and Al as spacer layers, again Slonczewski proposed the loose-spin model [156].
Magnetic Coupling

It postulates magnetic impurities with spin $S_i$ located inside or at the interface of the spacer. The underlying mechanism is an indirect exchange, such as RKKY, coupling each localized spin $S_i$ to other spins through the polarizability of the conduction electrons. Such localized spins inside the spacer or at the interface of the spacer are termed as loose spins. Because it interact with both magnets, any loose spin contributes an effective exchange coupling between the ferromagnetic layers. In concreteness, a loose spin with spin quantum number $S$ at position $z$ is subject to exchange-coupling fields induced by the two ferromagnets through the non-local spin polarizability of the conduction electrons (see Fig. 1.28(b)). The vector sum of these fields can be conveniently parametrized as $\vec{U} = U_1(z)\vec{M}_1 + U_2(z)\vec{M}_2$, which give rise to a effective local-spin Hamiltonian $H = (U_1 + U_2) \cdot \vec{S}/S$. The energy levels of the loose spin are $\epsilon_m = -Um/S$ with $m = -S, -(S-1), ... S$. Here $U = |U_1 + U_2| = (U_1^2 + U_2^2 + 2U_1U_2 \cos \theta)^{1/2}$, where $\theta$ is the angle between $\vec{M}_1$ and $\vec{M}_2$. From conventional statistics, the free energy per loose spin is

$$f(T, \theta) = -K_B T \ln\left\{ \frac{\sinh\left[ (1 + (2S)^{-1})U(\theta)/K_B T \right]}{\sinh\left[ U(\theta)/2SK_B T \right]} \right\} \quad (1.66)$$

By expanding the free energy of the loose spin in the form of $f(\theta) = J_0 - J_1 \cos \theta + J_2 \cos^2 \theta + J_3 \cos^3 \theta + ...$, the contribution of the loose spins to the bilinear coupling and biquadratic coupling are obtained as $J_1$ and $J_2$. Loose spin model has successfully explained the strong temperature dependence of $J_2$. In practice, the loose spins are frequently produced by atomic mixing and atom diffusion at the interface.

Exchange biasing

The term “exchange biasing” describes a phenomenon associated with the interface coupling between ferromagnetic (FM) and antiferromagnetic (AFM) materials. This interface coupling leads to a shift ($H_e$) of the magnetic hysteresis loop away from $H = 0$ when the composite system is cooled through the Néel temperature of the AFM material in the presence a external field or already ordered FM component. This effect was discovered four decades ago [157] and it is also termed as unidirectional exchange anisotropy since the effective anisotropy energy can be written as $E_{eff} = -K \cos \theta$ with $\theta$ to be the angle of the FM magnetization from the cooling field axis. The recent applications of exchange biased films to magnetoresistive sensors have renewed interest in the effect and its underlying physics. However, the microscopic mechanism to exchange biasing has not been well established. Up to now several mechanisms have been proposed in attempt to explain how the coupling between the AFM and the FM leads to a unidirectional anisotropy [158].
For an uncompensated perfectly flat interface, the existence of a coupling between the AFM and FM is straightforward to understand. Because of the magnetocrystalline anisotropy in the AFM, the interfacial AFM spins maintain their initial orientation, while those of FM reverse following the external field. Therefore the initial and final configuration, before and after the reversal of the applied field, will have different energies due to the interfacial exchange interaction $J\vec{S}_1 \cdot \vec{S}_2$, which results in the unidirectional exchange anisotropy (see Fig. 1.29(a)). However the value of $H_e = 2JS_1S_2/a^2Mt$ predicted in this way is by several orders of magnitude larger than the observed. Here $S_1$ and $S_2$ are the spins of the AFM and the FM respectively.

Neél and Mauri et al. have shown that the realistic value for $H_e$ can be obtained when a domain wall forms in the AFM during the reversal of the FM magnetization. This is the domain wall model [159, 160]. The physical core of this model is that a domain wall can be built in the AFM reversing the spins at the interface when the FM magnetization is reversed from the initial direction (see Fig. 1.29(b)). In this case the difference in energy between the states before and after reversal is $2\sqrt{AK}$ instead of $2JS_1S_2$ so that $H_e$ is now determined by $H_e t M = \sqrt{AK}$, where $A$ and $K$ are the exchange stiffness and crystalline anisotropy in the antiferromagnet respectively. ¹

It should be noticed that, according to the domain wall model, the exchange anisotropy is not obvious when the FM/AFM interface is compensated. ² On the other hand, experiments indicate that the loop shift is of similar magnitude for compensated and uncompensated interfaces. In addition, exchange anisotropy has also been observed in FM/AFM bilayer whose AFM thickness is much smaller than the domain wall. Based on these facts, Malozemoff proposed the random-field model of exchange anisotropy for rough interface [161, 162]. In this model, the interface is considered to be random on a atomic scale due to interface roughness or chemical inhomogeneity. That is to say, the interfacial exchange interaction is also random. Therefore a random field exists and the AFM would break up into a domain state as local regions reorient to minimized the interfacial random-field energy [163, 164]. Here the random-field can be understood as a statistical fluctuation induced interfacial exchange interaction. For an infinitely large irregular AFM/FM interface, the statistical fluctuation is zero, so the total interfacial exchange interaction is also zero if the AFM and the FM are both in single domain state, since the number of parallel-coupled interfacial spin pairs equals to that of the antiparallel-coupled

¹The expression of the domain wall energy $2\sqrt{AK}$ is only valid for cubic system. For uniaxial crystal, it reads as $4\sqrt{AK}$. Some confusion exists in [160].

²In a compensated AFM interface the net spin averaged over a microscopic length scale is zero. In contrast, if the spin arrangement is such that the surface magnetization is non-zero, the surface is uncompensated.
Figure 1.29: (a) Schematic diagrams of the spin configuration at the FM/AFM interface before and after the magnetization reversal. The difference in exchange interaction between these two configurations is expected to give rise to an shifted hysteresis loop. (b) The domain wall model for the interface of a thin FM film on a thick AFM substrate. The uniaxial anisotropy of the AFM is along the z-axis. The figure depicts a situation in which a external magnetic field is applied opposite to z and in which the exchange coupling across the interface with thickness $\xi$ is positive. The spin of only one sublattice of the AFM are shown (from Mauri et al. [160]).
spin pairs. However, when the AFM breaks into many domains, the atomic number of each domain which exchange-coupled with the FM atoms becomes limited and the statistical fluctuation also becomes important with the size of the domains decreasing. Assuming the local magnitude of the interfacial exchange interaction is on the average \( \varepsilon_I = \pm zJ/a^2 \) for unit interfacial area, the random-field energy of a domain with an area of \( L^2 \) is \( \varepsilon \sim \varepsilon_I / \sqrt{N} \), according to the random statistics theory. \( N = L^2 / a^2 \) is the number of sites projected onto the interface plane. \( J \) is the exchange constant and \( z \) is a constant depending on the concrete structure.\(^3\) Like the domain wall model, now the magnitude of the exchange anisotropy is reduced by a factor of \( 1 / \sqrt{N} \) and becomes comparable with the experimental value. In contrast to the parallel configuration between domain wall and the interface in the domain wall model, here the walls are perpendicular with the interface.

The mechanism of exchange anisotropy is now still an intensive research topic. New theories are being proposed continually. For example, Sulh and Shuller have recently proposed the spin wave theory [165]. They use a quantum mechanical description of the spins and show that the emission and reabsorption of virtual spin wave leads to an exchange anisotropy. Hinchey and Mills [166] and recently Koon [167] demonstrated that, due to frustration of interfacial spins, the FM magnetization will align perpendicular to the AFM easy axis when the AFM interface plane is compensated. This establishes the coupling between the FM and the AFM when the interface is compensated and is referred to as spin-flop coupling.

### 1.3 Complex Correlation between Structure and Magnetism in Epitaxially Grown Metastable Phases

The magnetic properties and the structural properties are strongly correlated in ultrathin films. Magnetic quantities such as magnetic moment, magnetic anisotropy and Curie temperature are closely linked to structural parameters such as lattice constants, strain, roughness etc. Lattice mismatch induced strain would produce additional magnetic anisotropy, which may result in a spin reorientation transition, for example, in Ni/Cu(100). Surface steps, which is associated with the surface roughness, also have their influence on magnetic anisotropy by changing the surface symmetry. The atoms in the steps and kinks might show larger moment as a result of reduced magnetic coordinations. However, the correlation between the structure and magnetism is no more clearly shown than the epitaxially grown metastable phases.

By epitaxially growth, the high temperature phases such as bcc Co and fcc Fe may be stabilized on certain substrates. Due to their metastable property, they

\(^3\)refer to [161] for the further explanation of \( z \)
**Figure 1.30:** Correlation between magnetism, structure and growth of Fe/Cu(100) ultra-thin films. In the upper portion the magnetic moment extrapolated to $T = 0$K are depicted as a function of film thickness. Filled and open circles represent data recorded when external field is applied perpendicular ($\perp$) and parallel ($\parallel$) to the film plane, respectively. In the first two regions the magnetization is perpendicular to the film surface and parallel in region III. In the lower portion the intensity of the (00) MEED beam is depicted during Fe deposition showing the three different regions. The corresponding surface reconstructions for each region ($4 \times 1$, $5 \times 1$ in region I, $2 \times 1$ in region II, and $3 \times 1$ in region III) are denoted as well. Between 4 and 11 ML in region II, the film is in fcc structure with (100) orientation (fcc(100)). Above 11 ML the films transform from the fcc(10 0) structure to a bcc structure (bcc(110)). (from [168])
usually show structural instability upon increasing thickness. The structural instability is accompanied by the magnetic instability. Fe/Cu(100) is a prototypical system to illustrate this interplay between structure and magnetism. As shown in Fig. 1.30, the system can be divided into three regions in each of which the structure and magnetism are distinguished from the others. In region I (below 4 ML), the film surface show \((4 \times 1)\) or \((5 \times 1)\) reconstruction and have a uniform high-spin ferromagnetic phase as indicated by the linear increase of magnetic moments as a function of thickness [169]. The ferromagnetic phase in region I has been confirmed by Mössbauer effect measurements [170, 171]. This high-spin ferromagnetic phase was understood to be linked with increased atomic volume of Fe due to the tetragonal expansion [172]. In region II (\(4 \sim 11\) ML), the magnetic moment of the film is nearly one thirds of the 4 ML film, and kept nearly constant for all thicknesses in region II. More careful experimental measurements indicate that the moment of the film actually oscillates with increasing thickness [173, 174]. The current understanding of such interesting magnetic behavior is that the top one or two layers of the films have a high-moment ferromagnetic phase [169], and the layers underneath have some sort of antiferromagnetic structure or they are paramagnetic. As the high-spin ferromagnetic phase at the top layer(s) is well established [175, 176, 177], the magnetic phase of the underlying layer is still in controversy [178]. It was extensively assumed to be antiferromagnetic with a Néel temperature around 200 K based on the anomalous magnetic behaviors with an onset at this temperature, but this antiferromagnetic transition has not seen up to now directly by any atomistic measurement. Recently the spin density wave state has been proposed to be responsible for the magnetic behaviors in region II [174]. The structural origin of the transition from region I to region II has been discussed mainly based on the fact that the films undergo a structural transition from fct (tetragonally distorted fcc) to fcc for all layers except the top two in region II, although the real structure of the films is more complex due to a fcc to bcc Martensitic structural transformation [179, 180]. In region III (> 11ML), the fcc to bcc structural transformation completes and as a result, the bcc films become again uniformly magnetized with an easy magnetization being parallel to the film plane. The precise location of the transition regions on the thickness scale is in addition influenced by adsorbates, e.g. carbon monoxide and hydrogen [169, 181, 182].
Chapter 2

Experimental Methods

2.1 The Apparatus

All the experiments in chapter 3-5 were performed in an ultra-high vacuum chamber as schematically shown in Fig. 2.1. The chamber has a base pressure of \(6 \times 10^{-9}\) Pa as measured by an ionization gauge. The vacuum is obtained by a combined use of a mechanical pump, a turbomolecular pump, and a titanium sublimation pump. A quadrupole mass spectrometer is employed to determine the component of the residual gas, which typically consists of H\(_2\), H\(_2\)O and Ar.

The chamber is equipped with all facilities necessary to prepare the substrate and films as well as analyze the growth, structure, and magnetic properties of the film. The sample can be heated by thermal radiation or cooled using liquid nitrogen. A sample manipulator enables the sample translation and to change its polar and azimuthal angle precisely. An Ar-ion gun was operated at 2 kV to clean the substrate. The surface cleanliness was checked using an Auger electron spectrometer (AES) with cylindrical mirror analyzer. The evaporator includes two water cooled Knudsen cells, which are parallelly arranged, so that bilayer samples can be conveniently prepared. To analyze the structure of the surface, a three-grid back-view low-energy electron diffraction (LEED) system was employed providing electron energies up to 500 eV. Medium-energy electron diffraction (MEED) was also used to monitor the film growth. The MEED measurement uses 3-keV electrons from the Auger system to impinge on the sample with a maximum angle of 5° against the surface plane. The diffraction beams were displayed on the fluorescent LEED screen. To investigate the magnetic properties using the surface magneto-optic effect (SMOKE), a pair of Helmholtz coils is installed in the chamber to apply a magnetic field up to 1050 Oe.
Figure 2.1: Schematic diagram of the chamber, which is equipped with an ion gun, an evaporation source, a LEED system, and an Auger spectrometer. A pair of coils is also installed in the chamber, which is not shown in this diagram.
2.2 Sample Preparation

In this work, Ni/Cu(100) film, Fe/Cu(100) film, and (Ni,Fe) bilayers on Cu(100) have been investigated. The typical sample preparation procedure is described as follows.

A polished Cu(100) single crystal disk with a diameter of 7.5 mm and a thickness of 2.5 mm was used as substrate for all the experiments in this work. The substrate was cleaned by 2 keV Ar-ion sputtering. During the sputtering the Ar flow is adjusted in such a way that the pressure of the chamber is kept at $5 \times 10^{-5}$ Pa. The typical sputtering time is one hour. Subsequently the sample was annealed at 900 K for 5 minutes to smoothen the surface. This cycle was repeated for several times until no trace of impurities were detected by AES. High-purity Ni (99.98\%) and Fe (99.99\%) was evaporated from thin disks of 10 mm diameter and 0.2 mm thickness, heated by the radiation of a tungsten filament. A deposition rate of about 0.3 ML/min was chosen for both Ni and Fe. During the deposition, the pressure did not exceed $3 \times 10^{-8}$ Pa. All depositions were performed at room temperature. The growth of the films was monitored by MEED, employing an electron energy of 3 keV at an angle of 5° against the surface plane. For the preparation of the bilayer samples, the second film was grown after the first film had been deposited without subsequent annealing to avoid or at least reduce interfacial mixing. LEED was used to determine the crystal order of the substrate and the film.

2.3 Thickness Calibration

Since the structure and the magnetic properties of the studied films are sensitively dependent on the film thickness, it is of key importance to control and measure the film thickness precisely. In this work the film thickness is mainly determined by MEED oscillations.

MEED (or RHEED: reflection high energy electron diffraction) is a very convenient method to monitor the film growth in real-time. For many growth systems, the MEED intensity shows oscillations with coverage when a suitable electron energy and incident angle are chosen (the anti-phase condition). The intensity oscillation comes from the destructive interference between the electron beam reflected from adjacent terraces. For layer-by-layer growth regular oscillations result as either the difference in area between the odd and even terraces or the step density oscillates with coverage, depending on whether the detection area is comparable with the correlation length of the sample surface or much greater than it. MEED intensity oscillations sometimes also occur for films with a morphology far from layer-by-layer growth. In this case the correlation between the oscillation and the coverage becomes complicated and other kinds of measurement, e.g., STM (scan-
The growth of both Ni and Fe on Cu(100) has been investigated carefully. Ni on Cu is a good epitaxial system since both materials have the same fcc crystal structure with only 2.5% lattice mismatch. It was found that a good layer-by-layer growth persists up to 3.5 ML and subsequently multilayer growth starts and becomes dominant when the Ni thickness is above 6 ML [183]. All of these growth characteristics are reflected by the MEED curves. Fig. 2.2 show a typical MEED measurement on Ni/Cu(100). For the curve of \((3, 2)\) beam, the first four oscillations have almost the same amplitude, suggesting a perfect layer-by-layer growth. Above 4 ML, both the oscillatory amplitude and the average intensity decreases with film thickness, indicating that a multilayer growth mode has developed. Though multilayer growth is dominant for Ni films with a thickness greater than 6 ML, the MEED oscillation keeps the same period as for the first 4 ML. Therefore for the Ni/Cu(100) system, it is straightforward to calibrate the film thickness using MEED oscillations. The clear MEED intensity oscillations enable a precise thickness determination to within 2%.

The situation is somewhat more complex for Fe grown on Cu(100). Its MEED and RHEED curves have been reported in several papers [169, 184, 185]. The general features have been summarized in Ref. [184]: a rapid decrease in intensity between 0 and 1 ML, a increase in intensity around 4 ML, regular oscillations between 4 and 14 ML \(^1\), and a drastic decrease of intensity starting at 14

\(^1\)The transition thickness from oscillation to the final decrease was found to be dependent on the precise surface contamination. For example, a CO background pressure of \(7 \times 10^{-8}\) shifts it from 11 to above 13 ML [169].
Figure 2.3: Typical MEED curves of the growth of Fe on Cu(100). The indices of the diffraction spots are also labelled on the figure. The shape of (0,0) curve is slightly different from that reported by Thomassen et al. [184] but quite resembles the RHEED curve reported by Escorcia-Aparicio et al. [185]. The absence of clear oscillations between 5 and 11 ML could result from thickness inhomogeneity.
ML. The interpretation of the MEED results had been tightly associated with the understanding of the growth mode for the Fe/Cu(100) system. Based on the combined measurements of Auger-electron spectroscopy and He$^+$ Rutherford back-scattering spectroscopy (RBS), Glatzel et al. first proposed the bilayer-by-bilayer growth mode for the first two bilayers [186]. However STM measurements contradict this bilayer growth mechanism [187, 188, 189, 190]. STM observations reveal a poor layer-by-layer growth mode for room-temperature growth of Fe on Cu(100). Atom exchange was suggested to occur in the first two monolayers and Fe inclusions are formed for the same thickness [187]. Chambliss et al. [191] have shown that a kinematic calculation using the STM results as inputs can reproduce the MEED curves measured by Thomassen et al. [169] after taking into account the atomic intermixing in the initial stage and the effect of change of the effective correlation length of the sample. Despite the complexity shown by the Fe/Cu(100) growth, the features of the MEED curves are clear enough to determine the film thickness. Fig. 2.3 shows a typical MEED measurement. Though the concrete shape of the curve differs from experiment to experiment, the main characteristics remain similar. For example, the (2, 1), (3, 1) and (0, 0) spots show local maxima of intensity at the completion of the first and second monolayer and their average intensity keeps constant after the growth of the forth layer is finished. Shallow oscillations sometimes appear between 4 and 11 monolayer but it does not always happen. Slight inhomogeneity in film thickness and poor substrate quality will hinder the appearance of MEED oscillations. In this case the evaporation rate is determined by the features of the growth of the first four monolayers. Generally, the film thickness for Fe on Cu(100) can be determined using MEED curves to within 4%.

The situation is less favorable when a second film is deposited, i.e., when Fe is deposited on a Ni film or vice versa (see Fig. 2.4). Then, weaker and short-lived oscillations are observed only, which most likely have to be attributed to the rougher surface formed after deposition of the first film. As a consequence, a larger error bar of roughly 10% exists in the film thickness determination from the MEED data for the second film, especially for Ni deposition on Fe. Presumably, however, this error bar overestimates the true error, since we have used parameters for the evaporation source identical to previous runs, where Fe and Ni had been deposited separately, and the deposition rate could be determined with high precision.

2.4 SMOKE

Since the middle of the 1980s, the surface magneto-optic Kerr effect (SMOKE) has been extensively applied to study the magnetism in low-dimensional systems.
Figure 2.4: MEED curves of the (1,0) beam of Fe growing on 11 ML Ni on Cu(100) and of (2,-3) beam of Ni growing on 9 ML Fe on Cu(100). E=3 keV. Ts=320 K.
because of its simplicity and convenience. In this work all the data on magnetic properties were obtained by this method. Therefore a brief introduction to SMOKE is given in this section [192].

2.4.1 Operation Principle

The magneto-optic Kerr effect (MOKE) describes such a phenomenon where a plane polarized beam of light becomes elliptically polarized upon being reflected from a polished ferromagnet with its major axes rotated with respect to the plane of polarization of the incident beam. For the transmission case the effect is referred to as Faraday effect.

As it is well known, the optical properties of a medium are determined by a dielectric tensor which is determined by the motion of the electrons in the medium. Microscopically, a different response of the electrons to left- and right-circularly polarized electromagnetic waves, into which a beam of plane polarized light can be decomposed, gives rise to the magneto-optic Kerr effect. As a beam of light propagates through a medium, the electric field of the light generates the motion of the electrons in the medium. Without an external magnetic field, it is obvious that a left-circularly polarized electric field will drive the electrons into left circular motion, and a right-circularly polarized electric field will drive the electrons into right circular motion. The radius of the electron orbit for left and right circular motion will be the same. After an external magnetic field is applied in the propagation direction of the light, there will be an additional Lorentz force acting on each electron. This force points towards or away from the circle’s center for left and right circular motion. Thus, the radius for left circular motion will be reduced and the radius for right circular motion will expand. The difference in the radii of the left- and right-circularly polarized modes will give different dielectric constants correspondingly. The magneto-optic effect is quite large in ferromagnetic materials, since there exists an extraordinarily large effective magnetic field, which originates from the spin-splitting and spin-orbit interaction. The latter couples the magnetic moment of the electron with its motion, thus, connecting the magnetic and optical properties of a ferromagnet.

Using an one-electron Hamiltonian including both the spin-orbit interaction and the magnetic field vector potential in the kinetic momentum operator, Argyres deduced the conductivity tensor and the polarizability tensor of a ferromagnet for polar configuration [193], which are both antisymmetric tensors. Usually, the magneto-optic effect is treated using an antisymmetric dielectric constant tensor
SMOKE

Figure 2.5: Three geometries for SMOKE measurement. From left to right they are polar, longitudinal, and transverse geometry.

\[ \epsilon = \begin{pmatrix} 1 & iQ_z & -iQ_y \\ -iQ_z & 1 & iQ_x \\ iQ_y & -iQ_x & 1 \end{pmatrix}. \] (2.1)

Q = (Q_x, Q_y, Q_z) is called the Voigt vector [194]. The two normal modes in the medium with such a dielectric tensor are left-circularly polarized light with refraction index \( n_L = n(1 - \frac{1}{2} \vec{Q} \cdot \hat{k}) \), and right-circularly polarized light with refraction index \( n_R = n(1 + \frac{1}{2} \vec{Q} \cdot \hat{k}) \) (see appendix 1 for the deduction). Therefore the magneto-optic effect can be equivalently described by two different complex indices of refraction for light of right- and left-handed circular polarization. From this viewpoint, two effects are easy to imagine for light propagating in a magnetized medium. First the two circularly polarized modes gain different phase shifts due to their different propagating velocities, resulting in a rotation of the polarization plane. Second, the different absorption rates of the medium for the two circularly polarized modes affect the ellipticity. Thus two parameters are used to describe the Kerr effect, the Kerr rotation \( \phi' \) and the ellipticity \( \phi'' \). Argyres showed that for normal incidence both parameters are proportional to the magnetization component along the normal of the reflecting surface [193]. The proportionality also remains valid for other configurations [195] (see Fig. 2.5). However the proportionality constant is sensitive to a number of external factors. It depends on the frequency of the light and it also depends on the direction of magnetization and the incident angle, i.e. the configuration, but it does not depend on temperature. Theoretical predictions of the proportionality constant are so complicated that it actually becomes impossible for most cases. So the magneto-optic effect can not give the absolute value of the magnetization. This is a disadvantage. Starting from the above dielectric constant tensor, Zak et al. developed a general expression for the Kerr signal by solving the Maxwell equations with satisfied boundary conditions.
which was deduced for the case of a multilayer and covers arbitrary incident angles and magnetization orientation.

2.4.2 Experimental Setup

An actual experimental SMOKE setup usually takes an as simple form as possible. The incident plane, applied magnetic field and the sample are arranged in one of the three configurations shown in Fig. 2.5. Before discussing the experimental setup, it is necessary to first discuss the working principle of the experimental method. Consider linear p-polarized light reflected from a sample surface. If the sample is nonmagnetic, the reflected light is purely p polarized. If the sample is ferromagnetic then the reflection beam should consist of an s component \(E_s\) in addition to the dominant p component, with \(|E_s|/|E_p|\) being the Kerr rotation. Experimentally, the measurement of the s component could be realized by placing a linear polarizer in front of the photodetector to eliminate the p component. However, this measurement geometry has disadvantages. First the quantity measured by the photodetector \(|E_s|^2\) is proportional to the square of the magnetization rather than the magnetization itself. Second, it is difficult to quantify the absolute value of the Kerr rotation. The disadvantages can be circumvented by setting the polarizer (the analyzer) at a small angle \(\delta\) from the p axis. In this way the intensity measured by the photodetector after the polarizer is

\[
I = |E_p \sin \delta + E_s \cos \delta|^2 \approx |E_p \delta + E_s|^2
\]  

(2.2)

Since \(E_s/E_p = \phi' + i\phi''\) gives the Kerr rotation \(\phi'\) and ellipticity \(\phi''\), eqn. 2.2 becomes

\[
I = |E_p|^2 |\delta + \phi' + \phi''|^2 \approx |E_p|^2 (\delta^2 + 2\delta \phi') = I_0 (1 + \frac{2\phi'}{\delta})
\]

(2.3)

with

\[
I = |E_p|^2 \delta^2
\]

(2.4)

representing the intensity at zero Kerr rotation. Since both \(\phi'\) and \(\phi''\) are linearly proportional to the magnetization, the measured intensity as a function of H yields the magnetic hysteresis loops. The saturation Kerr rotation \(\phi'_m\) can be determined by the relative change of the Kerr intensity \(\Delta I\) obtained upon magnetization reversal. From eqn. 2.3 and eqn. 2.4, it is easy to get

\[
\phi'_m = \frac{\delta}{4} \cdot \frac{\Delta I}{I_0}
\]

(2.5)

The actual SMOKE setup used in this work is schematically described in Fig. 2.6. A He-Ne laser (laser) operating in single mode is used as a light source.
Figure 2.6: Scheme of the SMOKE setup. See the text for the explanation of the components.
Figure 2.7: A illustration of magnetization hysteresis loop of 3 ML Fe on Cu(100) measured by SMOKE at 237 K.

The light becomes p linearly polarized after it goes through the first polarizer (\(P\), and it is reflected from the sample surface (\textit{sample}) and its intensity is detected by the photodiode (\textit{PD}). The second polarizer (\(A\)) is put between the sample and the photodiode and its polarization plane is adjusted \(\delta\) degrees away from the extinction position. Two Helmholtz coils (\textit{coils}) are used to produce the magnetic field. The current which drives the coils is controlled by a computer (\textit{computer}), and simultaneously the data for the light intensity from the photodiode are collected by the computer. In addition two lenses are applied to focus the light on the sample and on the photodiode. An \(\lambda/4\) wave plate is inserted into the light path to cancel the birefringence effect produced by the UHV windows, through which the light passes. Fig. 2.7 illustrates a magnetic hysteresis loop of 3 ML Fe on Cu(100) measured by the SMOKE.
Chapter 3

Perpendicular Magnetic Anisotropy of Ultrathin Ni Films on Cu(100) and its Stability

In recent years, substantial effort has been focused on the preparation and characterization of ultrathin magnetic films with perpendicular magnetic anisotropy because of their potential application as high density storage media [197]. A vast number of studies has discussed the origin of the perpendicular anisotropy, its thickness and temperature dependence, and related properties [198, 199]. Several film systems have been found to possess a perpendicular magnetic easy axis. A popular example are CoCr films grown in the c-axis orientation, where the anisotropy has a magnetocrystalline origin [200]. Epitaxial superlattices of Co/Pt, Co/Pd, and Co/Au have also been studied extensively since they offer a large Kerr rotation. Their perpendicular anisotropy is believed to originate from the interface anisotropy due to the reduced coordination number of the interface [201]. The reduced coordination number also makes ultrathin Fe and Co films exhibit a magnetic anisotropy with an easy-axis perpendicular to the film plane. For these films, there exists a critical thickness below which the surface anisotropy is sufficient to overcome the demagnetization field and the films are preferentially magnetized in perpendicular direction [169, 202, 203]. However, the critical thickness is usually only a few monolayers (MLs). This thickness limitation is disadvantageous for practical applications.

The ultrathin Ni film grown on Cu(100) is another system with perpendicular anisotropy. It shows a peculiar behavior regarding the magnetic anisotropy. For a film thickness between 7 ML and 8 ML, a sharp spin reorientation transition from in-plane at low thickness to out-of-plane at high thickness is observed. At much larger film thicknesses between 37 ML and 70 ML, the preferential magnetization

77
direction gradually rotates back to the film plane. Hence in the range from 9 ML to 37 ML, the films show a perpendicular easy axis. The large thickness range within which the films show perpendicular anisotropy is favorable for practical application. Using ferromagnetic resonance, Schulz and Baberschke [204] found that this unusual behavior results from the competition between the perpendicular magneto-elastic volume anisotropy due to mismatch induced strain and the sum of shape anisotropy plus surface and interface anisotropy. The latter favors in-plane magnetization. In the pseudomorphic region, Ni films have an in-plane lattice constant expanded by 2.5 % to match that of the Cu substrate, causing a corresponding contraction of 3.2% in the perpendicular direction [172]. The tetragonal stress induced perpendicular uniaxial anisotropy is determined by

\[ K_u = \frac{3}{2} \lambda_{100}(c_{11} - c_{12})(\varepsilon_2 - \varepsilon_1). \]  

(3.1)

Here \( \lambda_{100} \) is the magnetostriction constant, \( c_{11} \) and \( c_{12} \) are the cubic elastic constants, and \( \varepsilon_2 \) and \( \varepsilon_1 \) are the in-plane compressive strain and tensile strain in perpendicular direction, respectively [204]. Therefore the strain state directly determines the value of the perpendicular anisotropy and is closely correlated to the preferential magnetization direction. When the thickness increases beyond the pseudomorphic region, strain relief by dislocation formation begins and the perpendicular anisotropy is gradually reduced. At last, the easy axis returns back to the plane.

On the other hand, the stability of magnetic properties upon multiple magnetization reversals is a fundamental requirement for data storage materials, since their magnetic properties should have high stability under their working conditions. Magnetic recording media undergo a large number of rewrite and erase processes. Therefore, if their magnetic properties, including the perpendicular anisotropy, the remanent magnetization, and the coercive field, change with the number of magnetization cycles, recording failure or data loss can occur. It is hence of key importance to check the magnetic stability of Ni/Cu(100) thin films that are prospective recording media. In this chapter the magnetic properties of Ni/Cu(100) films have been studied with emphasis on their temperature dependence and the stability of the perpendicular anisotropy upon multiple magnetic reversals.

### 3.1 Temperature Dependence of \( M_s \), \( M_r \) and \( H_c \) of Ni/Cu(100)

Films with Perpendicular Anisotropy

Many works have been concerned with the perpendicular anisotropy and its unusual spin reorientation transition with thickness observed in the Ni/Cu(100) system [108, 204, 206, 207, 209]. In the present work, Ni/Cu(100) films with several
thicknesses, all of which show perpendicular anisotropy at room temperature, have been studied with an emphasis on the temperature dependence of the hysteresis loop properties such as saturation magnetization, remanent magnetization, the coercive field, and the shape evolution.

### 3.1.1 8 ML Ni/Cu(100)

The 8 ML thick Ni/Cu(100) film is an interesting candidate for temperature dependent measurements, since its thickness is located sharply at the edge of the spin reorientation region (7-8 ML). Therefore the anisotropy field $H_{an}$ is small and nearly close to zero. In other words, the contributions which favor in-plane magnetization are almost in balance with those favor out-of-plane orientation. Generally all contributions change with temperature but each contribution has an individual temperature dependence. In this case the magnetic properties of the film are subject to the slight change in the anisotropy field with temperature.

Bearing this in mind, extra attention was paid to controlling the film thickness and making the film homogeneous. The homogeneity in thickness is confirmed by the clear MEED intensity oscillations persisting until the end of the evaporation (see Fig. 3.1). On the other hand the thickness can be directly determined by counting the oscillations within an error smaller than 2%.

Fig. 3.2 shows the temperature dependence of the magnetization and the coercive field of the 8 ML Ni/Cu(100) film. $M_{meas}$ denotes the magnitudes of the magnetization measured at an applied field of 20 Oe for polar geometry and 380 Oe for longitudinal geometry. $M_r$ is the remanent magnetization. The polar magnetization hysteresis loops at typical temperatures are illustrated in Fig. 3.3. According to the shape of the hysteresis loops, three temperature regimes can be distinguished. Within a temperature range between 160 K and 345 K, rectangular hysteresis loops are observed, indicating the magnetic anisotropy is dominated by the perpendicular component. That is to say the film shows perpendicular anisotropy within this temperature range. Above 355 K, there is no hysteresis loop recorded. The magnetization curve evolves from a curved shape at 355 K to an inclined line at 365 K accompanying with a rapid decrease in $M_{meas}$. $M_{meas}$ drops to zero at 375 K. This temperature is taken as the Curie temperature. The reported Curie temperature of 8 ML Ni on Cu(100) varies from group to group. Early a Curie temperature around 450 K was reported by Huang et al. [108]. However, Poulopoulos measured the Curie temperature to be 390 K for 8.4 ML Ni on Cu(100) [210]. The present result

---

1The anisotropy field $H_{an}$ is defined by $H_{an} = \mu_0 - 2K_{eff}/M$. The first term is the demagnetizing field that always favors in-plane magnetization. The second term arises from the intrinsic magnetic anisotropy. $K_{eff} = K_\perp - K_\parallel$. A positive $K_{eff}$ represents a perpendicular intrinsic anisotropy. Hence, if $H_{an} > 0$, an in-plane magnetization is favored, whereas $H_{an} < 0$ gives rise to out-of-plane magnetization.
Figure 3.1: MEED intensity of ($\bar{3}$, 2) for the growth of 8 ML Ni/Cu(100) (solid circles) and 10 ML Ni/Cu(100) (open circles).

Figure 3.2: Temperature dependence of $M_{\text{meas}}$, $M_r$ and $H_c$ of 8 ML Ni/Cu(100) in polar geometry. $M_{\text{meas}}$: magnetization measured in an applied field of 20 Oe; $M_r$: remanent magnetization; $H_c$: coercive field. Inset: temperature dependence of the longitudinal Kerr rotation measured in an applied field of 380 Oe.)
Figure 3.3: Polar magnetization hysteresis loops for an 8-ML Ni/Cu(100) film at typical temperatures
Figure 3.4: Magnetization hysteresis loops measured at four temperature by longitudinal SMOKE.

on Curie temperature coincides quite well with Poulopoulos’ measurement. It can also been seen in Fig. 3.2 that starting from 345 K the remanent magnetization $M_r$ rapidly drops to zero in advance of the measured magnetization $M_s$. A spin re-orientation transition, from perpendicular direction to in-plane, has been proposed to explain this phenomenon [210]. The transition could be driven by increasing magnetization entropy with temperature, since the in-plane spin orientation has a larger magnetization entropy than the perpendicularly magnetized state [211]. Below 160 K, $M_{meas}$ turns to decreases with sample cooling. At the same time, the polar hysteresis loop evolves from the rectangular shape into a round shape. In contrast, the longitudinal SMOKE signal increases with decreasing temperature in this temperature range (see the inset of Fig. 3.2). At 98 K the longitudinal SMOKE measurement displays a rectangular magnetization hysteresis loop (see Fig. 3.4), indicating that the in-plane anisotropy has developed. All the phenomena described above consistently reveal that the preferred spin orientation gradually rotates from perpendicular direction to in-plane with decreasing temperature below 160 K.

The results on 8 ML Ni/Cu(100) presented here are in good agreement with Farles’s measurement on 7.6 ML Ni/Cu(100). Farle et al. found by in situ ferromagnetic resonance that the spontaneous magnetization measured from the film normal changes continuously from $90^\circ$ at 200 K, i.e. in-plane, to $16^\circ$ at 250 K, to $0^\circ$ above 300 K [213]. The continuous reorientation of magnetization from in-plane at low temperature to perpendicular direction at high temperature is described by a tem-
Figure 3.5: The calculated magnetization hysteresis loops for single-domain grain with an uniaxial anisotropy $K_u$. The numbers on the loops denote the angles which the applied field makes with the easy-axis. If this angle is zero, the coercive field $H_c$ is given by $2K_u/\mu_0M_s$ [212].

Temperature dependence of the volume and interface anisotropy. The volume magnetoelastic anisotropy favors a perpendicular magnetization and both the surface and the shape anisotropy favor an in-plane magnetization. They are all dependent on temperature but the surface anisotropy increases faster than the magneto-elastic anisotropy when the temperature is reduced. Therefore the magnetization rotates to in-plane with decreasing temperature. Since the surface anisotropy does not depend on film thickness while the magneto-elastic anisotropy is proportional to the film thickness, the reorientation transition shifts to lower temperature when the film thickness increases from 7.6 ML to 8 ML. It should be pointed out that a continuous spin-reorientation transition can not be theoretically predicted without taking the high order (for example, the forth-order) term of the anisotropy constant into account.\(^2\)

The coercive field shows an unusual behavior. With decreasing temperature, it increases first, then presents a local minimum around 150 K and at last starts to decrease. Clearly the coercive field is not controlled by the magnetic anisotropy like a single domain particle (see Fig. 3.5). Otherwise the coercive field would decrease with reduced temperature and approaches zero at the reorientation transition temperature in the same way as the anisotropy field changes with temperature. Therefore the coercivity is associated with the formation of the reversed nuclei and

\[^2\]The uniaxial magneto-crystalline anisotropy of a crystal with cubic symmetry can be generally written as $[-K_2\cos^2\theta - \frac{1}{2}K_{\perp}\cos^4\theta - \frac{1}{2}K_{||}(3 + \cos 4\phi)\sin^4\theta]$. $\theta$ and $\phi$ are the polar and azimuthal angles respectively.
The motion of the domain wall. This is in agreement with the established fact of the existence of magnetic domains with Bloch walls in Ni/Cu(100) films [215, 216]. In the following, the author tries to give a reasonable explanation to this unusual temperature dependence.

In some way the coercive field is not a well-defined parameter since the mechanisms determining it vary from sample to sample depending on the concrete reversal procedure. Therefore, the first question to answer here is what process determines the coercive field for the 8-ML Ni/Cu(100) film, the nucleation of the reversed domain or the motion of the domain wall? To the author’s opinion, the reversal mechanism differs from temperature range to temperature range. At high temperature, the motion of the domain walls is thermal-assisted and thus easy. The nucleation could be the dominating process. Resultantly the hysteresis loop shows high squareness. With decreasing temperature, the thermal activation becomes weaker and on the other hand the pinning energy could become larger. The effect of the domain expansion on the magnetization reversal becomes important. In this case an inclined reversal magnetization curve could be observed. This argument is supported by the shape evolution of the hysteresis in the temperature range from 220 K to 320 K. With decreasing temperature, the rectangular-like hysteresis gradually develops round corners. This also explains why the coercive field increases with decreasing temperature. However this trend is perturbed by the spin-reorientation transition. When the temperature approaches the reorientation transition point, the nucleation field, as well as the wall energy decrease to near zero, resulting in a rapid drop in the domain size. The domain size is found to decrease by more than 1 order of magnitude within a very small thickness range in
the vicinity of the transition thickness in Co/Au(111) system [214]. A remarkable
decrease in domain size has also been observed for Cu/Ni/Cu(100) when the film
thickness enters the second reorientation transition range [215]. Under this circum-
stance, the pinning of the motion of the domain wall becomes less important for
determining the coercivity, since the reversal of one half of spins can be easy to
reach by nucleation and growth in the areas free of pinning centers. The point is
that, with the domain size decreasing, the total area where a reversed domain can
occupy increases. This can be understood by analogy with coins that are put to
cover a board with irregularly distributed nails protruding on it. A coin can be put
on the board only when a similar area free of nail is found on the board. More areas
would be covered if one-cent coins are used rather than the 50-cent coins, when the
average area which a nail occupies is smaller than the 50-cent coin but larger than
the 1-cent coin. The author thinks that the first decrease of the coercivity, which
occurs in advance of the decrease of the magnetization, can be traced to the de-
crease of domain size near the reorientation transition. When the temperature is
reduced further, the coercivity turns to increase again. At the same time the mag-
netization start to decrease. Hence the author associates this increase in coercive
field with the gradual rotation of the easy axis away from the perpendicular direc-
tion. To confirm this link, calculations involving high-order anisotropy constants
are needed. The final drop of the coercivity is easy to understood. it is due to the
easy axis rotating into the film plane and thus the hysteresis disappears at last.

3.1.2 10 ML Ni/Cu(100)

Interesting phenomena have also been observed in the temperature-dependent mea-
surement for the 10 ML Ni/Cu(100) film. The MEED curve of the growth of this
film has already been shown in Fig. 3.1. Like for the 8 ML film, intensity oscilla-
tions persist during the whole growth procedure which facilitate the film thickness
being controlled with high precision. For this film the temperature dependence of
the saturation magnetization and the coercive field have been measured both upon
cooling and heating. The film shows a Curie temperature around 430 K. Again it is
lower than the 500 K reported by Huang [108]. In contrast with the coincidence in
saturation magnetization between the cooling measurement and the heating mea-
surement, the coercive field presents a thermal hysteresis between 260 K and 100
K. The author ascribes this thermal hysteresis of the coercive field to the adsorp-
tion and desorption of residual gas. It was reported that the adsorption of hydrogen
strongly changes the magnetocrystalline anisotropy so that the critical thickness
for spin orientation transition is also modified [217]. The existence of the thermal
hysteresis only in the $H_c - T$ curve suggests that the adsorbed gas could play an
Figure 3.7: Temperature dependence of the saturation magnetization and coercive field (inset) of 10 ML Ni/Cu(100). The measurements were performed upon both heating and cooling.

important role in the magnetic reversal procedure rather than modifying the intrinsic magnetic moment. Since a higher coercive field was observed during the heating cycle, which followed the cooling cycle, the adsorbed gas possibly acts as a pinning mechanism to the domain wall motion. Resultantly the coercive field would be enhanced by adsorbed gases. More evidence will be supplied latter for this pinning effect of adsorbed gases.

A close check of the magnetic hysteresis loop (see Fig. 3.8) at various temperatures reveals another interesting phenomenon. At high temperature, the film of 10 ML Ni/Cu(100) shows a rectangular loop. With temperature decreasing, the rectangular hysteresis gradually evolves into a "hourglass" shape. Spoken more concretely, this particular loop shape can be characterized by a vertical part followed by a round part upon magnetization reversal. This kind of hysteresis has been frequently observed in magnetic films whose thickness or temperature is close to the spin-orientation transition. Fe/Cu$_3$Au(100) films with thicknesses of 3.4 and 3.5 ML show similar loop shapes at 160 K for which a spin-orientation transition from perpendicular direction at low temperature to in-plane at high temperature occurs within a thickness range of 3.5-4 ML [218]. The "hourglass" shaped hysteresis loops have also been measured for 3.8 ML low-temperature grown Fe/Cu(100) [219] and 3.8 ML Fe/Ag(100) [220]. For both systems a similar spin-reorientation transition exists and the film thicknesses are both located near the transition thickness. Therefore it can be concluded that this particular shape is associated with the spin-reorientation transition, or in other words, the small anisotropy field.

The mechanism beneath the "hourglass" loop has not yet been addressed. It
can not be explained by a deviation of the easy axis from the direction of the applied field, since in this case the reversal magnetization curve should be a round curve followed by a vertical segment rather than vice versa. Baudelet et al. [218] paid much attention to this special hysteresis early in 1995. They thought of the loops as composed from a contribution of two independent mechanisms of moment reversal. The first contribution is due to the perpendicular anisotropy, causing the high remanence and initial steep slope of the loops after field reversal. The second contribution is responsible for the round off of the loops and may be due to an easy axis which is no longer aligned with the surface normal. They excluded the possibility of inhomogeneity in coverage as a mechanism for the coexistence of two kind of domains with different easy axis by comparing size of the probing laser spot and the sample. Without information from domain imaging experiments, they could not give a definite conclusion but suggested to link the loop to the nucleation and growth process of the reversed domain.

Mentz et al. studied the magnetization reversal of a 3.8 ML low temperature grown Fe/Cu(100) film using a combined technique of SMOKE and Kerr microscopy (see Fig. 3.9). They observed a fractal domain structure, suggesting that the activation energy for domain nucleation and motion is not homogeneous. Unfortunately they did not extent the Kerr microscopic observation into the inclined

Figure 3.8: Polar magnetization hysteresis loops for 10 ML Ni/Cu(100).
Figure 3.9: Polar SMOKE hysteresis loops for 3.8 ML and 4 ML Fe/Cu(100). The approximate points at which domain images were recorded are indicated. (b) and (c): Growth of magnetic domains (dark areas) for 3.8 ML Fe/Cu(100). (d) After a domain state similar to that in (c) had been established, the external magnetic field was reduced to $H \leq 0$ resulting in less magnetic contrast in the dark areas. (e)(g): Domain images during magnetization reversal at 4-ML Fe/Cu(100). In the upper-right corner the nonmagnetic sample holder is seen. Copy from [220].
part. Up to now the detailed magnetization reversal procedure behind the “hourglass” loop is still unclear.

In hope to obtain some clues to the magnetization reversal, the change of the ratio $R(M_{\text{vertical}}/M_{\text{total}})$ of the vertical part to the total reversed magnetization ($2M_s$) with temperature has been investigated, which is plotted in Fig. 3.10. The magnitudes of the external field at which the magnetization reversal starts ($H_{\text{start}}$) and completes ($H_{\text{comp}}$) are also plotted in Fig. 3.11 as a function of temperature for both heating and cooling cycles. Several striking features drawn from Fig. 3.10 and Fig. 3.11 are summarized as follows:

- The portion of the vertical part in the total reversed magnetization changes with temperature. As an overall trend, it decreases with reduced temperature. However, it is not a monotonic function of temperature. Local fluctuations are observed for both cycles.

- The above ratio in the cooling cycle is uniformly larger than that in the heating cycle within the whole temperature range.

- $H_{\text{start}}$, the external field at which the magnetization reversal starts, does not depend much on whether the measurement is done in cooling cycle or heating cycle, while $H_{\text{comp}}$, the external field at which the magnetization reversal is completed, is strongly dependent on the type of the cycles. This feature is clearer when the hysteresis loop at 217 K during cooling is compared with that at 215 K during heating (Fig. 3.12).
Figure 3.11: Temperature dependence of $H_{\text{start}}$ (bottom) and $H_{\text{comp}}$ (top) for magnetization reversal of 10 ML Ni/Cu(100).
Based on the above findings, a model is proposed here to explain the "hourglass" hysteresis loop and its evolution with temperature. The core of the model is that $H_{\text{start}}$ is determined by the nucleation coercivity and the round part of the reversal magnetization curve is dominated by the inhomogeneous pinning of the domain wall motion. For thicker Ni/Cu(100) films the perpendicular anisotropy is large enough and thus the nucleation coercivity is larger than the coercivity determined by domain wall motion. Resultantly, the domains grow by viscous motion of the wall and the hysteresis loop shows height squareness as will be shown in the next subsection. In this case, once the nuclei are created at a certain applied field, they continue to grow without further hindrance. When the film thickness is close to the critical thickness for spin-reorientation, the anisotropy field becomes small. Consequently, the nucleation coercivity becomes comparable with that determined by wall motion. After the nuclei are formed at a certain external field, the reversal domains grow rapidly until their growth front encounters a pinning center whose pinning energy (an energy barrier) is greater than the released energy by the pinning center during magnetization reversal at the given applied field. This is the vertical part of the reversal magnetization curve. Depinning occurs when the applied field increases further. To some extent, the round part of the reversal magnetization curve reflects the population distribution of pinning centers with pinning energy. This model is in agreement with the fractal growth mode of the domain observed by Mentz et al. [220].

Based on the above model, several conclusions can be drawn from the temperature-
dependent measurement: (1) the adsorbed residual gas has a strong effect on the
pinning of the domain wall. They either act as new pinning centers or increase the
pinning energy of the existed pinning centers. Therefore both $R(M_{vertical}/M_{total})$
and $H_{comp}$ are larger for the heating cycle, which followed the cooling cycle and
thus has the higher density of the adsorbed gases at the same temperature. (2) On
the other hand, the nucleation field $H_{start}$ keeps intact upon residual gases adsorp-
tion, so that $H_{start}$-T curves of the heating and cooling cycle are identical. (3)
The pinning strength has a trend to increase with decreasing temperature, which
is reflected in the $R(M_{vertical}/M_{total})$-T curves both for the heating cycle and for
the cooling cycle. The local fluctuation reflects the statistical characteristics of the
motion of the wall.

3.1.3 Thicker Ni/Cu(100) Films

Two thicker Ni/Cu(100) films, 18-ML and 30-ML, have also been investigated in
this work. Common features are found for these thicker films: (1) Both the satura-
tion magnetization and the coercivity monotonically increase with decreasing tem-
perature (see Fig. 3.13). (2) within the whole range of measurement temperature,
the hysteresis loops show large squareness (see Fig. 3.14). The author thinks that
nucleation dominates the magnetization reversal process. Due to the large thick-
ness, the films possess a large perpendicular anisotropy, so the nucleation field is
greater than the effective pinning field of most pinning centers. Therefore the re-
versal process is described as nucleation followed by the viscous motion of the
domain wall.

3.2 Stability of the Perpendicular Anisotropy upon Mul-
tiple Reversals

Ni films on Cu(100) show a perpendicular magnetic anisotropy over a wide thick-
ness range [108, 204, 206, 207], which makes them interesting candidates for mag-
netic recording applications. It is well known that the magnetic stability upon mul-
tiple reversals is a prerequisite for storage media. The magnetic stability upon
multiple magnetization reversals has also recently been studied for several systems
[208, 221]. For spin-dependent tunneling devices, where a hard magnetic Co alloy
layer is coupled over an aluminum oxide film to a soft magnetic Co layer, a decay of
remanent magnetization is observed upon multiple magnetization reversals [208].
It has been suggested that the decay of the moment of the hard layer is caused by
the demagnetizing field at the hard layer associated with domain walls in the free
layer. Aging effects caused by structural alterations have also been observed in
Figure 3.13: Plots of saturation magnetization and coercive field as a function of temperature for (a) 18-ML Ni/Cu(100) and (b) 30-ML Ni/Cu(100).
Figure 3.14: Hysteresis loops at several typical temperature for (a) 18-ML Ni/Cu(100) and (b) 30-ML Ni/Cu(100).
metastable amorphous phases \[222\]. In this work, the stability of magnetic properties including the perpendicular anisotropy, the remanent magnetization, and the coercive field have been examined upon multiple magnetic reversals.

Ni films with four typical film thicknesses have been investigated. They are 8, 10, 20, and 30 monolayers. Once the film was fabricated, a hysteresis loop was recorded. Subsequently the film was subjected to continuous magnetization cycles in an alternating applied field, which is perpendicular to the film plane. For a typical field sweeping rate of 0.1 s per cycle, it usually takes about 30 h to perform \(10^6\) magnetization cycles. Hence we have first checked if the magnetic properties of Ni films change with time due to the absorption of residual gas. As soon as the Ni film was fabricated, a hysteresis loop was recorded. After 30 h a second hysteresis loop was recorded. Fig. 3.15 shows both hysteresis loops. The comparison reveals that the magnetic properties (Mr, Ms, Hc) are not affected by the 30 h exposure to residual gases. Having excluded the influence of the absorption of gases at the film surface, the magnetic stability with respect to magnetization reversal was examined. The amplitude of the alternating field is twice as large as the coercive field of the film studied. The changing rate of the applied field is 500 Oe/s. All experiments were carried out at room temperature, which is 31°C. A small increase of sample temperature by 1-2°C was observed after the film stayed in the alternating field for more than 2 h. Hysteresis loops were measured after certain numbers of magnetizing cycles (Fig. 3.16). One can see that the shape of the hysteresis re-

**Figure 3.15**: A comparison of the magnetic hysteresis measured immediately after film fabrication and 30 h later. The film is 10 ML thick.
Figure 3.16: Hysteresis loops recorded after various numbers of magnetization cycles for the films with a thickness of (a) 8 ML, (b) 10 ML, (c) 20 ML, and (d) 30 ML. The same symbols are used in (b), (c), and (d) as in (a).
mains unchanged even after $1 \times 10^6$ magnetization reversals. Basic parameters such as saturation magnetization, remanent magnetization, and coercive field are determined from the loops. They are presented in Fig. 3.17. The error bar for the remanent and saturation magnetization is 1%, while the error bar for the coercive field is 3%. As can be seen from Fig. 3.17, the data can be fitted by a constant value. The scatter in the data for the three quantities studied here lies well within the error bars. This implies that the remanence, the saturation magnetization, and the coercivity remain constant. We have also tried to fit the data with fit functions other than a constant behavior but could not get a significant improvement in the fit. Hence it is safe to say that the perpendicular magnetic anisotropy of Ni films on Cu(100) as well as the magnetic properties do not change even after a large number of magnetization reversals. This finding is crucial both for an application of magnetic thin films in storage media and for basic studies of ultrathin films. In such studies the magnetic signal is often averaged over a large number of loops to improve the signal-to-noise ratio. The present study shows that at least for Ni films on Cu(100), this approach is fully justified.

The high magnetic stability of Ni/Cu(100) films present above can be explained by a simple analysis. For Ni films on Cu(100), the magnetic anisotropy is governed by competition between the surface and interface magnetic anisotropy and two volume contributions, namely, the shape anisotropy and the magnetoelastic anisotropy. It is the interplay between the latter two quantities that determines the magnetic anisotropy. The shape anisotropy linearly increases with thickness, while the magneto-elastic contribution shows a somewhat more complicated behavior. It depends on the film thickness and the strain of the film, which itself is thickness dependent. The film strain is caused by the mismatch between the lattice parameters of the film and the substrate. For ultrathin films below the critical thickness pseudomorphic growth is expected. Above the critical thickness the strain energy will be reduced by dislocation formation. Both will contribute to the total energy of the film system. By minimizing the sum of the strain energy and the energy due to dislocations in the film the thickness dependence of both strain and interface dislocation density can be determined. For a small mismatch, a critical thickness exists, below which the film grows pseudomorphically. Above the critical thickness dislocations appear and their density increases with film thickness. Therefore the strain is uniquely decided by the film thickness and so is the perpendicular anisotropy. However, the energy of $\Delta E = 2\mu_0 M_s H_c$ released in the magnetization reversal process can perturb the system. Hence we have to compare to the elastic energy and the dislocation energy. The energy is given as an average per Ni atom. The values are listed in Table I. The energy release upon magnetization reversal has been derived from an estimated magnetic moment of 0.6 $\mu_B$ per Ni atom to obtain an upper limit of the energy release. Theoretical studies [223, 224]
Figure 3.17: Plots of (a) remanent magnetization, (b) saturation magnetization, and (c) coercive field against the number of magnetization cycles. The solid squares describe the 8 ML film, while solid circles, solid down triangles, and solid up triangles characterize the 10 ML film, 20 ML film, and 30 ML film, respectively. The dotted lines are generated assuming constant magnetic properties.
**Table 3.1:** Comparison between the energy released during magnetization reversal ($\Delta E$) and the elastic energy ($E_e$) or the dislocation energy ($E_d$) of the films. The energy is given as an average per atom.

<table>
<thead>
<tr>
<th>Thickness of film (ML)</th>
<th>8</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (meV)</td>
<td>$6.6 \times 10^{-6}$</td>
<td>$2 \times 10^{-5}$</td>
<td>$3.8 \times 10^{-5}$</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>$E_e$ (meV)</td>
<td>9.0</td>
<td>9.0</td>
<td>3.8</td>
<td>1.7</td>
</tr>
<tr>
<td>$E_d$</td>
<td>0</td>
<td>0</td>
<td>11.5</td>
<td>13.2</td>
</tr>
</tbody>
</table>

have predicted the magnetic moment of Ni on Cu(100) to be only reduced directly at the Ni/Cu interface but find otherwise bulk-like moments of around 0.6 $\mu_B$ in the Ni film. Experimental studies show a considerable scatter with some reports of reduced average moments in the Ni film [225, 226]. Recent reports indicate that there might be a strain effect on the magnetic moment of the Ni film, where relaxed films have larger moments [227]. Since we are mainly interested in an upper estimate we calculate the energy release using a high moment of 0.6 $\mu_B$ for the entire film. The data reported for the critical thickness of pseudomorphic growth show considerable scatter. The critical thickness was either determined by experiments or predicted theoretically. Here we use O’Briens data for which $h_c$ is 13 ML [228]. For film thicknesses $h$ larger than $h_c$, $\varepsilon$ is approximated by $\varepsilon = \eta h_c/h$ [229, 230], where $\eta$ is the mismatch between the substrate and the deposited film. The equation for $\varepsilon$ determines the remaining film strain and is used to calculate the dislocation density. The elastic constants are assumed to be the same as that for the bulk. In addition, a Poisson’s ratio of 1/3 is assumed. The Burgers vector is considered to be of $\frac{1}{2}(110)$ type, which is typical of fcc-structured films, yielding $b = (1/\sqrt{2})a_0$, where $b$ is the length of the Burgers vector and $a_0$ is the length of the cubic unit cell of Cu. A close look at Table 3.1 reveals that the energy per atom released in one hysteresis loop is significantly smaller than the energy of the dislocations ($E_d$) or the elastic energy of the strained film ($E_e$). Hence it is unfeasible that magnetization reversal will have a profound effect on the film strain and the perpendicular magnetic anisotropy. This conclusion should even remain valid if a large number of magnetization reversals have been performed. In this case there will be a considerably higher energy release, but only for very fast magnetization experiments will significant power be absorbed.

It is interesting to compare our experimental finding with a previous study that shows a decay of remanent magnetization upon multiple magnetization reversals [208]. In this case, however, the coupling between two magnetic layers leads to a new decay channel for the magnetization. Such a channel is not available in the present system. Aging effects have also been reported for metastable phases [222].
In such systems, the energy released during magnetization reversal accelerates the microstructural change. Metastable structures possibly also exist in Ni films on Cu(100), if, for example, the dislocation density would be lower than equilibrium density of dislocations. Under those circumstances, the energy released during magnetization reversal could be used to form dislocations and hence change the strain and the magnetic properties of the films. That we do not observe any change in magnetic properties indicates that the dislocation density is close to the equilibrium density. This is supported by the thickness dependence of film strain [216], which can be fairly well described by an equilibrium theory for the residual in-plane film strain.

In conclusion, Ni ultrathin films have been prepared with a perpendicular easy axis on a Cu(100) substrate using molecular beam epitaxy. The magnetic properties of the films were monitored during continuous magnetization reversals in an alternating magnetic field. The results show that the films keep the magnetic properties unchanged even after $10^6$ sweeps independent of the detailed strain state of the films. This finding can be understood based on the small energy released during each individual magnetization loop.
Chapter 4

Magnetic Properties of Fe, Ni bilayers on Cu(100)

In the last decade a number of new and exciting coupling phenomena and related effects such as oscillatory coupling, giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) have been discovered in ultrathin magnetic films [198, 199, 231]. This has led to very promising applications such as spin valves [232] and sensitive read heads [233]. On the other hand, in the last two decades a large number of metastable structures with novel and unusual magnetic properties has been stabilized by epitaxial growth [169, 234]. It is interesting to exploit such metastable structures to tailor the magnetic coupling between magnetic films. To determine the potential to tailor the magnetic coupling, the magnetic properties of Fe/Ni bilayers on Cu(100) have been studied. This system was chosen since both Fe and Ni grow epitaxially on Cu(100) and show interesting structural and magnetic properties as a function of temperature and film thickness.

Iron usually crystallizes in the bcc phase at room temperature, while the fcc \( \gamma \) phase only exists in the temperature range between 1184 K and 1665 K. However, microcrystalline particles of \( \gamma \) iron can precipitate from solid solution in copper and retain their structure at room temperature [235, 236]. Molecular beam epitaxy (MBE) provides another approach to stabilize fcc iron at room temperature. Ultrathin iron films grown on Cu(100) exhibit a rich variety of structural and magnetic phases as has been described in detail in 1.4. For the room temperature grown ultrathin films, two different fcc iron phases are stabilized on Cu(100) [169, 172, 173, 237]. The first one exists for iron layer thicknesses up to 5 monolayers (ML). This iron phase is characterized by a ferromagnetic coupling and an enlarged atomic volume of 12.1 Å\(^3\). For iron films on Cu(100) with thicknesses between 5 and 11 ML, only the first two layers couple ferromagnetically and show an atomic volume of 12.1 Å\(^3\). The rest of the film has an atomic volume of 11.4
Å$^3$ and is considered to be antiferromagnetic or paramagnetic [238, 239]. All films below 11 ML show a perpendicular anisotropy. The transition to the stable bcc ground state of iron is observed [179, 180, 240] above 11 ML and is accompanied by a switching of the magnetic anisotropy to in-plane orientation.

Ultrathin Ni films grown on Cu(100) also show a peculiar behavior regarding the magnetic anisotropy [108, 228]. For a film thickness between 7 ML and 9 ML, a sharp transition from in-plane to out-of-plane spin reorientation is observed. At much larger film thicknesses between 37 ML and 70 ML, the preferential magnetization direction gradually rotates back to the film plane. Hence in the range from 9 ML to 37 ML, the films show a perpendicular easy axis. This unusual perpendicular anisotropy has been discussed in Chapter 3.

Hence both systems are characterized by a number of different magnetic states with comparable energy. In such a situation the vicinity of a magnetic interface or simple temperature changes can already alter the magnetic ground state. This is an ideal situation to tailor or modify magnetic coupling phenomena. Therefore it is appealing to prepare Fe/Ni bilayers on Cu(100) to explore the interaction of the two magnetic layers through interfacial coupling.

In most of the published works, the main focus was the evolution of structure and magnetic phases of the Fe films with increasing film thickness. Less attention was devoted to other aspects, such as the evolution of the magnetic anisotropy of the bilayer upon changes of the thickness of both Fe and Ni layers. Furthermore, many previous measurements were carried out at room temperature only. Considerable insight into the coupling phenomena of metastable structures is expected from measurements of the temperature dependence of the magnetic properties. For example, an interesting temperature dependence of the magnetization was observed for 5.3-ML Fe/7-ML Ni/Cu(100) [242]. These data imply that the surface Fe live layer and the interface Fe live layer couple with each other and that the coupling strongly depends upon temperature. To obtain a deeper understanding of interface coupling in Fe/Ni bilayers, the magnetic properties of a series of Fe/Ni bilayers with different thicknesses and different deposition sequence for the two elements, have been investigated in this chapter. The results show a surprising variety of coupling phenomena that can be attributed to a number of competing contributions to the magnetic anisotropy.

### 4.1 A Comparison between 3-ML and 9-ML Fe/Cu(100) Films

In a conclusive study by OBrien and Tonner for Fe films on 15 ML Ni on Cu(100), a magnetic behavior of the Fe layer has been found that closely resembles the behav-
ior of Fe/Cu(100) in a number of aspects [241]. Fe films grown on Ni on Cu(100) show practically the same evolution of magnetic phases with Fe film thickness that was previously observed on Cu(100). Below 5 ML, the Fe film on Ni/Cu(100) is ferromagnetic. Between 5 and 11 ML, Fe films at room temperature show a ferromagnetic live Fe layer at the Fe/Ni interface. In contrast, magnetic live layers are only located at the surface in Fe/Cu(100) films and have a Curie temperature of about 273 K. Evidence for a magnetic live layer at the Fe film surface for Fe/Ni/Cu(100) comes from measurements at low temperature [242]. The temperature dependence of the saturation magnetization for 5.3 ML Fe on 7 ML Ni indicates that a live layer exists both at the surface as well as at the interface. Support for the surface live layer comes from the low-energy electron diffraction (LEED) observation of a (2 × 1) surface reconstruction [243], which is indicative for an enlarged interlayer spacing and hence ferromagnetic coupling. A similar behavior is also observed for Fe/Co bilayers where the same sequence of crystallographic phases is observed with increasing film thickness [185, 241].

To reveal the coupling properties of ultrathin Fe films at different magnetic phases with Ni films, two typical Fe layer thicknesses have been chosen in preparing Fe, Ni bilayers: 3 ML and 9 ML, which are located in regime I (uniform ferromagnetic) and regime II (ferromagnetic only at surface or interface) respectively, while the thickness of the Ni layers varies in a wider range. To clearly distinguish the new features resulting from the coupling of Fe and Ni layers, the magnetic properties of 3-ML and 9-ML Fe/Cu(100) have been first investigated and the results are separately present in this section.

The LEED pattern shows a (5 × 1) superstructure at low temperature for 3 ML Fe on Cu(100), while a (2 × 1) reconstruction is observed for 9 ML Fe/Cu(100) (Fig. 4.1). These LEED observations are consistent with previous studies [172, 184].

The key magnetic parameters such as remanent magnetization ($M_R$), saturation magnetization ($M_S$), and coercivity ($H_C$) are plotted in Fig. 4.2. The 3-ML-thick Fe film shows considerable $M_S$ even at 370 K. This is in agreement with a previous report that a 3-ML Fe film has a Curie temperature of 390 ± 30 K [244]. A rapid decrease in $M_S$ is observed around 270 K for the 9.2-ML Fe/Cu(100). Here a smaller overall magnetization as compared with the 3-ML film is observed. A vast number of studies confirms that for Fe films with a thickness between 6 and 11 ML, the film surface exhibits ferromagnetic ordering (magnetic live layer) below around 250–270 K [169, 173, 175]. The remaining inner part is believed to be paramagnetic at room temperature and antiferromagnetic at low temperature [171, 173, 238]. The existence of a surface magnetic live layer explains both the smaller magnetization and lower Curie temperature of the 9 ML Fe film compared with the 3 ML Fe film. Both 3- and 9-ML films show a perpendicular magnetic
anisotropy, but the coercive field of 9-ML Fe/Cu(100) is much larger than that of the 3-ML film. A close look at the hysteresis reveals subtle differences (see the insets in Fig. 4.2). For the 3 ML thick film, an ideal rectangular hysteresis loop is observed. The exact coincidence of remanent and saturation magnetization is indicative of a stable single-domain state. The magnetization reversal process is dominated either by a coherent rotation of all spins or by rapid motion of domain walls over long distances once a few areas with reversed magnetization have been nucleated [245]. The hysteresis loop of a 9-ML-thick Fe film, in contrast, is characterized by an inclined slope instead of a vertical slope. Similar loops have been observed for Au/Co/Au sandwiches. For this system it was found using Faraday-rotation microscopy [245] that the magnetization reversal is dominated by the formation of the nuclei. The process has been ascribed to the random appearance of nucleation centers in the sample and irregular domain growth of these nuclei over short length scales. Such a mechanism gives rise to a non-rectangular hysteresis because of the local variation of the nucleation and propagation fields, which provides a distribution of coercive fields throughout the sample. The proposed difference in reversal mechanism between these two films also explains the contrast in the coercivity.

For both films, a considerable difference between remanent and saturation magnetization is observed when the temperature approaches the Curie temperature. Above a certain temperature, which is considerably smaller than the corresponding Curie temperature, the hysteresis loop vanishes. The same phenomenon has also been observed in Ni/Cu(100) films, which also show a perpendicular easy axis.
Three different explanations have been put forward to account for the disappearance of the hysteresis loop. In the first model this was explained by a transition from a single-domain state to a multi-domain state with perpendicular magnetization component at a certain temperature below $T_c$ [210]. An alternative mechanism was proposed by Jensen and Bennemann [211]. They took the entropy of magnetization into account and deduced that above a temperature below the Curie temperature, the magnetization in the presence of a perpendicular anisotropy is aligned completely parallel to the surface plane. A third theoretical explanation for this reorientation of the magnetization was given by Pescia and Pokrovsky [246].

### 4.2 Ni/Fe Bilayers on Cu(100)

After the Fe/Cu(100) films with two typical thickness have been examined, the magnetic properties of Fe, Ni bilayers will be investigated. First, Ni/Fe bilayers
with a deposition sequence of Ni on Fe on Cu(100) substrate are considered and their results are present in this section, while films with opposite sequence i.e., Fe on Ni on Cu(100) will be investigated in the next section.

4.2.1 X-ML Ni/3-ML Fe/Cu(100)

The first case presented here consists of Ni films with different thickness on 3-ML Fe on Cu(100). A compilation of hysteresis loops at various temperatures can be found in Fig. 4.3. The 14-ML Ni/3-ML Fe/Cu(100) sample is characterized by well-defined rectangular hysteresis loops in the whole measured temperature range. This result reveals that this film possesses a perpendicular easy axis and a stable single domain state in the whole temperature range measured. The temperature dependence of the magnetization of the four films, which was measured in a field of 380 Oe perpendicular to the film plane, is displayed in Fig. 4.4. We denote this magnetization value as measured magnetization. For a perfect square-shaped hysteresis loop the measured magnetization is identical to both the saturation and remanent magnetization. For other hysteresis loops, like the ones characteristic for 4.7, 8, and 11 ML on 3-ML Fe on Cu(100), the magnetization measured at 380 Oe is much larger than the remanent magnetization, showing that the magnetization is only saturated at very high fields for these samples. The change of the magnetization with temperature measured at a field of 380 Oe for the 14-ML Ni/3-ML Fe bilayer on Cu(100) behaves as expected (Fig. 4.4). The magnetization increases with decreasing temperature.

The situation is more complex for the 11-ML Ni/3-ML Fe/Cu(100) sample. An interesting evolution of the hysteresis loop can be found with decreasing temperature (Fig. 4.3). Below the Curie temperature of 390 K for 3-ML Fe films on Cu(100) but above 300 K, no coercive behavior is observed. In this temperature range, the magnetization measured at 380 Oe increases dramatically with decreasing temperature. Discernible hysteresis loops begin to appear below 298 K. In this temperature regime, the difference between the remanent magnetization and the measured value at 380 Oe field is rather small. The magnetization shows a temperature dependence similar to the 14-ML Ni/3-ML Fe/Cu(100) sample. However, if the temperature is reduced below 170 K, the hysteresis loops become more and more canted. Hence, the ratio of the remanent to the measured magnetization gets smaller with decreasing temperature. In addition, the measured magnetization also drops with decreasing temperature. The drastic increase of the field necessary to reach saturation implies that the easy axis gradually deviates from the perpendicular direction with decreasing temperature. The disappearance of the hysteresis loop and the reduction of measured magnetization at high temperature for 11-ML Ni/3-ML Fe/ Cu(100) can be explained using the similarity with the high tem-
Figure 4.3: A compilation of hysteresis loops for a series of samples with different Ni film thickness on 3-ML Fe/Cu(100). For 4.7-ML Ni/3-ML Fe/Cu(100) and 8-ML Ni/3-ML Fe/Cu(100) inverted hysteresis loops are observed. The arrows indicate the field sweeping direction.
Figure 4.4: Temperature dependence of the measured magnetization at 380 Oe of a series of samples with different Ni film thickness on 3-ML Fe on Cu(100). The inset shows how the coercive field changes for the samples with 11- and 14-ML Ni on 3-ML Fe/Cu(100).

The rich variation in preferential magnetization shows that the anisotropies favoring perpendicular magnetization and those favoring in-plane magnetization are very similar in magnitude. Hence the anisotropy field is almost zero. This is quite surprising, considering the fact that the spin reorientation transition thickness to perpendicular is 7~9 ML for the Ni/Cu(100) system and that a 3-ML Fe film on Cu(100) shows a perpendicular easy axis as well. It indicates that the Fe/Ni interface has a considerable influence on the magnetic anisotropy and favors an in-plane alignment. We will discuss this issue again in § 4.4. Another conclusion can be
derived from the size of the magnetization for 14-ML Ni/3-ML Fe and 11-ML Ni/3-ML Fe bilayers. The magnetization values are higher than for the uncovered 3-ML Fe film on Cu(100), but the difference can be attributed to the contribution of the Ni film to the overall magnetization. The observed magnetization can be described as the sum of the contribution from the Ni film and the contribution from the 3-ML Fe film, which is of the order of 580 mrad. This implies also that the magnetic moment of the underlying Fe film cannot be dramatically altered by the presence of the Ni capping layers. Hence, we can conclude that the high-spin state of fcc iron is stable upon overcoating by Ni.

For the cases in which the Ni film thickness is 4.7 and 8 ML, respectively, the measured magnetization is much smaller. The reduction of total magnetic moment due to thinner Ni layers cannot produce such a dramatic decrease in the measured magnetization, because Ni has both a much smaller magnetic moment and a rather weak magneto-optic interaction compared to Fe. The small measured magnetization in these two samples unambiguously indicates that the easy axis is not aligned in the perpendicular direction. These two samples also show puzzling magnetization curves. Most of the M-T curves are characterized by an inclined line superimposed on an inverted hysteresis loop (Fig. 4.3). An inverted loop means that the coercivity and remanent magnetization are negative (see the loop of 4.7-ML Ni/3-ML Fe/Cu(100) in Fig. 4.3; the arrows denote the sweeping direction of the applied field). Identical loops have been measured in Cu/Co and Cu/Ni superlattices [248]. Negative remanent magnetization and coercivity have also been observed in Fe thin films [249, 250] and exchange-coupled systems [185, 251]. To our knowledge, negative remanence and coercivity only appear when the hysteresis loops are recorded in a direction almost perpendicular to the magnetic easy axis. A recent study [249] revealed that in a system with several competing anisotropies, negative remanence and coercivity can be observed if the magnetic field is not applied exactly perpendicular to the easy axis but rotated away from this direction by a small amount of less than 5°.

In conclusion, the Fe/Ni interface favors an in-plane alignment for the Ni/Fe bilayer with a 3-ML Fe underlayer, which leads to a higher Ni film thickness for the spin reorientation. The overlayer of Ni, however, does not destroy the ferromagnetic high spin state of the Fe underlayer.

4.2.2 X-ML Ni/9-ML Fe/Cu(100)

We now turn our attention to the Fe thickness regime where a ferromagnetic live layer exists on Cu(100). We want to see how this film is influenced by a Ni overlayer. In the following the Fe underlayer thickness is fixed at 9 ML but the thickness of the Ni top layer is varied. Seven samples have been studied with Ni film
thicknesses of 17.5, 16, 14, 12.5, 11.8, 10.4, and 8 ML, respectively.

LEED observations have been made for clean Cu(100) substrate, 9-ML Fe deposited on Cu(100) and at last 17.5-ML Ni deposited on 9-ML Fe on Cu(100) consecutively. The LEED spots become slightly dim after 9-ML Fe deposition but get rather blurred after the further deposition of 17.5-ML Ni. (see Fig. 4.5). Cooling the sample to 150 K partially recovers the distinctness of the spots. A collection of typical hysteresis loops is presented in Fig. 4.6. Data on the magnetization of these samples are plotted in Fig. 4.7 as a function of temperature. The coercive field of several samples is shown in Fig. 4.8. Depending on the thickness of the Ni layers, three different types of behavior are observed. For small Ni thicknesses, a positive anisotropy field $H_{an}$ is observed. This holds for 8-ML Ni/9-ML Fe/Cu(100) and 10.4-ML Ni/9-ML Fe/Cu(100). No hysteresis effect was measured and the measured magnetization is rather small. Therefore both samples are characterized by an in-plane anisotropy. However, this in-plane anisotropy decreases with increasing film thickness. Hence for the 10.4-ML Ni film there is already evidence for a rotation of the anisotropy. At 97 K, a very small but discernible hysteresis loop is detected, which implies that the easy axis has rotated out of the film plane. For the samples with thick Ni overlayers (14, 16, and 17.5 ML), rectangular-like hys-
Figure 4.6: A collection of hysteresis loops for a series of samples with different Ni film thicknesses on 9-ML Fe/Cu(100). The arrows indicate the starting points for the first loop.
Figure 4.7: Temperature dependence of the remanent magnetization for a series of samples with different Ni film thickness on 9-ML Fe on Cu(100).
Figure 4.8: Temperature dependence of the coercive field for a series of samples with different Ni film thickness on 9-ML Fe on Cu(100). For a comparison, the coercive behavior of Ni films on Cu(100) with different thickness is shown in the inset.
Hysteresis loops are recorded, indicating a negative anisotropy field. The temperature dependence of the measured magnetization can be described by a linear increase with decreasing temperature. Only in a limited temperature regime is a deviation from this linear behavior observed. The deviation is reduced with increasing Ni thickness. The linear temperature dependence is usually a distinctive phenomenon of two-dimensional systems [252, 253, 254]. A theoretical study [255] has predicted a linear temperature dependence of the magnetic moment of the Fe interface layer in the 11-ML Fe/Cu(100) system. So it is suggested that it is the Fe/Ni or Fe/Cu interface layer that contributes to this linear temperature dependence. The Ni film could not cause this effect since the dimensionality crossover from three-dimensional (3D) Heisenberg to 2D XY behavior occurs at 7 ML for Ni films [108], which is much lower than the thickness of our samples. For the two samples with a thickness of 11.8 and 12.5 ML, the magnetization curves present a deep dip around 175 K (Fig. 4.7). With temperature decreasing from room temperature, the magnetization at first increases slowly, but then starts to fall dramatically around 210 K. Between 160 and 170 K, a deep minimum appears until the magnetization starts to increase again with decreasing temperature. Traces of these dips are also visible for bilayers with larger Ni film thickness. This implies that the mechanism responsible for the decrease of magnetization is also present in the thicker Ni films but is compensated more efficiently by competing contributions to the total energy.

A close inspection of the evolution of the hysteresis loops with temperature for the 11.8-ML Ni/9-ML Fe bilayer is helpful for understanding this phenomenon. At room temperature, a narrow and corner-rounded hysteresis loop is measured. The sample shows almost 100% remanent magnetization, but the starting magnetization value, which was measured at the beginning when the applied field was swept from 0, is much lower than $M_R$ (see arrow in Fig. 4.6). These results suggest that the sample shows a small anisotropy field in the direction of the applied field, i.e., perpendicular to the film plane, but the single domain state is not the stable state, so the single domain in the field relaxes into multiple domains when the field is removed. This relaxation is much slower than the duration of one sweep of the applied field. This kind of relaxation procedure is easy to observe in magnetic films with a small anisotropy field [219]. With decreasing temperature, the remanent magnetization also decreases gradually and disappears at 220 K. Correspondingly, the loops become more and more inclined and gradually evolve into a sheared shape. However, the high field magnetizing curve after reversal remains a horizontal line until 220 K are reached. This shape evolution bears surprising resemblance to that reported in [219] but there the direction of change is reversed with respect to temperature. This implies that it is not the temperature itself but rather the different temperature dependence of the competing anisotropies that dominates the evolution. The shape change of the hysteresis loop mainly results from two factors: the anisotropy field
and the nucleation field of the reversal domain. When the temperature is reduced below 220 K, the shape of hysteresis evolves differently. The area of the hysteresis loop shrinks rapidly and degenerates into two almost overlapping inclined lines; the high-field part of the magnetizing curve now also becomes inclined. Hence the measured magnetization is no longer identical to the saturation magnetization. Reflected in the hysteresis loops is the steep drop in magnetization around 200 K. When the measured magnetization has reached the minimum value, the hysteresis effect is very small but still discernible. Therefore the magnetizing curve has the form of a straight line with two different slopes: a large slope for the center (low-field) segment and a small one for the high-field part. This magnetizing curve can be understood if the main mechanism involved in the magnetization reversal process is the reversible motion of the domain wall in low fields and the reversible rotation of magnetic moments in high field. The conclusion is that upon cooling below 210 K, the easy axis of magnetization rotates away from the perpendicular direction continuously. The angle with which the easy axis deviates from the film normal increases continuously when the temperature is reduced from 210 K to 160 K. With further reduction of temperature, the easy axis returns towards the normal direction, as is reflected in the increase of the measured magnetization and the hysteresis loop as well as the reduction in the slope of the high-field magnetizing curve.

The coercive field seems to be more pronouncedly affected by the interface coupling (Fig. 4.8). The coercive field of all the Ni/Fe bilayers, if they show measurable coercivity, present a more complicated behavior. With decreasing temperature, for the samples with a thick Ni top layer (17.5, 16, and 14 ML), the coercive field first increases, then gradually starts to decrease and at last rises sharply at low temperatures. Hence a minimum and a maximum are observed in the wave-shaped $H_C - T$ curves. The undulation amplitude becomes smaller when the Ni layer thickness increases. Even more complex is the behavior of bilayers with 11.2- and 12.5-ML Ni. Here a much wider dip is observed, with possibly two minima. Yet again, at low temperatures a rapid increase in coercivity is observed. It is noticed that 9-ML Fe/Cu(100) (see Fig. 4.2) shows a monotonically temperature-dependent coercivity. However 8-ML Ni/Cu(100) films (see the inset in Fig. 4.8) presents a shallow dip around 150 K but such dip does not appear for thicker Ni/Cu(100) films (10 and 20 ML). To exactly retrace the origin of the unusual behavior of $H_C$, further simulation or dynamic calculations are needed. Here the author just wants to associate them to the interfacial anisotropy and coupling.

In contrast to the Ni/3-ML Fe/Cu(100) films, two new features have been observed in Ni/9-ML Fe/Cu(100) bilayers. A magnetization drop was observed to start around 210 K for the samples that show a small perpendicular anisotropy field at room temperature. In addition the coercivity demonstrates a non-monotonic
temperature dependence.

4.3 Fe/Ni Bilayers on Cu(100)

The deposition sequence of the bilayer could have a pronounced impact on the magnetic phases and anisotropies in the bilayers. The slight difference in lattice constants of Cu (3.62 Å), Ni (3.52 Å), and γ-Fe (3.59 Å) [236] will introduce strain into the epitaxially grown bilayers. The strain will relax if the film thickness is beyond the pseudomorphic growth region [229]. The magnetic anisotropy is closely related to the film strain. In addition, the magnetic properties of the fcc Fe layer are very sensitive to the lattice spacing [256, 257, 258]. Theoretical calculations show that the nonmagnetic and antiferromagnetic solutions are almost degenerate for lattice constants around 3.5 Å. Hence the change of the deposition sequence could profoundly modify the magnetic properties of the bilayers. To confirm this, two typical samples with opposite deposition sequence to §4.2, i.e. 9-ML Fe/10-ML Ni/Cu(100) and 9-ML Fe/15-ML Ni/Cu(100) have been investigated in this section.

Figure 4.9: LEED patterns for (a) 10-ML Ni on Cu(100) and (b) 9 ML-Fe on 10-ML Ni on Cu(100). The observation were made at room temperature. The electron energies are 167.4 eV for (a) and 210.8 eV for (b) respectively.

At room temperature, the 9-ML Fe/10-ML Ni/Cu(100) sample shows no hysteresis loops but considerable measured magnetization (Fig. 4.10). This behavior indicates that the sample has a small positive anisotropy field. The magnetization prefers to lie in the film plane but is prone to follow the perpendicular applied field. No hysteresis effect is detected down to 222 K. At 204 K, however, a hysteresis loop appears. With decreasing temperature, the width of the hysteresis loop, i.e., the coercive field, increases rapidly. Fig. 4.11 shows how the measured
Figure 4.10: Magnetization curves at different temperatures for 9-ML Fe/10-ML Ni/Cu(100).
Figure 4.11: Magnetization $M_{MEAS}$ measured at 380 Oe (open circle) and remanent magnetization $M_R$ (open square) for 9-ML Fe/10-ML Ni/Cu(100). The sample is not yet saturated at 380 Oe. The coercivity is plotted in the inset.
magnetization and the remanent magnetization change with temperature. The temperature dependence of $H_C$ is plotted in the inset of this figure. Below 210 K, the difference between the magnetization measured at 380 Oe and the remanent magnetization is reduced rapidly. With a further decrease of temperature $M_R$ decreases again, presumably since now the in-plane anisotropy starts to prevail. It should be noted that both 10-ML Ni on Cu(100) and 9-ML Fe on Cu(100) show a perpendicular anisotropy. The fact that 9-ML Fe on 10-ML Ni on Cu(100) only show this anisotropy over a very limited temperature range implies again that the deposition of Fe on Ni enhances the in-plane anisotropy. The strong decrease of the magnetization measured at 380 Oe could be due to a ferromagnetic-paramagnetic phase transition around 250 K in parts of the film. Indeed, the Curie temperature for the surface live layer of 9-ML Fe on Cu(100) is about 270 K. Hence we suggest that the transition in the measured magnetization around 250 K could be related to the Curie temperature of the surface live layer of Fe on Ni/Cu(100). The situation is nevertheless not that clear cut since we cannot derive much further information from the magnitude of the measured magnetization. 10-ML Ni on Cu(100) has a Kerr signal at remanence of approximately 170 $\mu$rad at 250 K. 9-ML Fe on Cu(100) could add a Kerr signal of 225 $\mu$rad at 200 K (Fig. 4.2). However we also expect a contribution of similar size from the Fe/Ni interface, which should lead to a ferromagnetic live layer at the Fe/Ni interface. Then the measured magnetization above 250 K would be attributed to the Ni film and the magnetic live Fe layer at the Fe/Ni interface. A different behavior is found for the 9-ML Fe/15-ML Ni/Cu(100) sample. The hysteresis loops of two sweeping cycles at various temperature can be found in Fig. 4.12. At room temperature, a rectangular-like loop is observed. The remanent magnetization is identical with the magnetization measured at 380 Oe, which should correspond to the saturation magnetization $M_S$. Hence the sample possesses a perpendicular anisotropy field and a stable single-domain state. Below 220 K two changes are detected. The hysteresis loops become increasingly round. This leads to a reduction in remanent magnetization with decreasing temperature (see Fig. 4.13). In addition, the starting points of the hysteresis loops denoted by arrows in Fig. 4.12 are no longer located on the M-H curves recorded during the second sweeping cycle. The deviation of the starting magnetization $M_{START}$ from $M_R$ is first discernible at 207 K and increases with decreasing temperature. To understand this phenomenon it is necessary to describe the measuring procedure in more detail. The measurement was carried out with increasing temperature. Data were recorded for two sweeping cycles. The sweeping rate of the applied field is 0.015 s/Oe. The time interval between two subsequent measurements is about 5 min.

As is obvious from Fig. 4.12, the starting magnetization is smaller than the magnetization in the second loop once the sample temperature is less than 214 K.
Figure 4.12: Hysteresis loops for the first two sweeps at different temperatures for 9-ML Fe/15-ML Ni/Cu(100). The arrows indicate the starting points for the first loop.
Figure 4.13: Magnetization $M_{MEAS}$ measured at maximum field in Fig. 4.12 (○) and remanent magnetization (□) for 9-ML Fe/15-ML Ni/Cu(100). In inset (a), the difference between $M_{MEAS}$ and $M_R$ (▽) as well as between $M_{MEAS}$ and $M_{START}$ (△) is displayed. Inset (b) shows the temperature dependence of the coercivity.
CHAPTER 4. FE, NI BILAYERS ON Cu(100)

Fig. 4.13 shows in the top inset the differences between $M_{MEAS}$ and $M_R$ and between $M_{START}$ and $M_{MEAS}$ as a function of temperature. These plots strongly suggest that the magnetic anisotropy changes around 200 K. A non-monotonic temperature dependence has been observed for the coercive field, similar to what we see in Fig. 4.7. In Fig. 4.13 the remanent magnetization and the magnetization measured at 380 Oe are displayed as well. Within the whole temperature range studied no magnetization jump is observed. This implies that the Fe layer of this sample shows no magnetic live layer or it has a live layer but with a Curie temperature considerably above room temperature. A simple analysis can exclude the latter assumption. For 9-ML Fe/10-ML Ni/Cu(100) a measured magnetization of 290 $\mu$rad at 310 K is observed. For 9-ML Fe/15-ML Ni/Cu(100) a value of 380 $\mu$rad is found. The difference is attributed to the additional 5 ML of Ni [259]. Presumably the 9-ML Fe film on 10-ML Ni/Cu(100) has a live layer, but with an ordering temperature considerably below room temperature. Therefore it does not contribute to the magnetization. On the other hand, a magnetization of about 200 mrad was measured for 9-ML Fe on Cu(100) below 270 K, which is attributed exclusively to the magnetic live layer. Therefore if 9-ML Fe/15-ML Ni/Cu(100) had a live layer with a Curie temperature above room temperature, it should show a much higher magnetization at room temperature.

4.4 Discussion

4.4.1 Spin Reorientation Transition

The experimental results present in this chapter show unequivocally that in (Fe,Ni) bilayers the spin reorientation transition shifts to larger Ni film thicknesses compared with Ni/Cu(100). This conclusion is supported by the data presented in Figs. 4.6, 4.10, and 4.12. While 8-ML Ni on Cu(100) shows a rectangular hysteresis loop at room temperature neither 8-ML Ni/3-ML Fe/Cu(100) (Fig. 4.4) nor 8-ML Ni/9-ML Fe/Cu(100) (Fig. 4.7) shows a perpendicular anisotropy field. 9-ML Fe/10-ML Ni/Cu(100) also possesses a weak in-plane anisotropy field at room temperature. This demonstrates that the spin reorientation transition is shifted to larger Ni film thicknesses. Two effects caused by the Fe/Ni bilayer could explain the shift.

The demagnetization field of the bilayer is not the simple sum of the individual contribution of Ni and Fe films with the same thickness on Cu(100). The demagnetization field of the bilayer is usually larger than the sum of the individual contributions, since the magnetic moments of the Fe (Ni) layer also contribute to the local dipolar field exerted on the Ni (Fe) layer. Considering that Fe has a much larger magnetic moment (2.2 $\mu_B$) than Ni (0.62 $\mu_B$) implies a considerable
gain in shape anisotropy due to the bilayer. In addition, when Ni (Fe) is deposited on a Fe(Ni)/Cu(100) film, a Fe/Ni interface replaces a Fe/vacuum surface and a Ni/Cu interface. To our knowledge, no quantitative data on the Fe/Ni interface anisotropy are available. The interface anisotropy possibly contributes to the in-plane anisotropy [228]. This should lead to a thicker Ni layer necessary to achieve the spin reorientation transition in bilayers.

4.4.2 Magnetic Live Layers

It is well established that a magnetic live surface is located at the film surface in 5~11-ML-thick Fe/Cu(100) films [169, 175]. The magnetic live layer shows a Curie temperature around 270 K. The remaining fraction of the film couples antiferromagnetically at low temperature. The surface magnetism is related to the enlarged atomic volume, which favors a ferromagnetic ground state. The question arises whether the magnetic live layer only exists in the Fe/Cu(100) system or if it can also be stabilized in other systems. Measurements at room temperature did not find any evidence for a surface live layer in Fe/Co/Cu(100) and Fe/Ni/Cu(100) systems [185, 228, 241]. Instead in both cases magnetic Fe live layers at the interface were observed. For the different Fe/Ni bilayers studied here there is also ample evidence of magnetic Fe layers. This is mainly supported by the size of the Kerr rotation measured and the temperature dependence of the magnetization signal. Consider for example the 9-ML Fe overcoated by various Ni films. The resulting magnetization (Fig. 4.7) cannot be explained by the Ni film only. This becomes evident when films with different Ni thickness are compared. Subtracting the Ni magnetization, which has been determined in chapter 3 to be 18-24 µrad per Ni ML, which increases with increasing thickness, leads to a contribution of approximately 225 µrad from the Fe film. This is considerably lower than the magnetization of a homogeneously magnetized Fe film. Please note that the homogeneously magnetized Fe film with a thickness of 3 ML already has a magnetization of more than 600 mrad. On the other hand, the 9-ML Fe film on Cu(100) without a Ni overcoat has a remanent magnetization of approximately 225 mrad, in close agreement with the value attributed to the iron film in the Ni/Fe bilayer on Cu(100). Hence only a small fraction of the Fe film can be ferromagnetic. Since the film still shows a high magnetization above 320 K, i.e., much above the Curie temperature of 270 K for an 9-ML Fe film without Ni overlayer, this implies that the ferromagnetic fraction of the Fe film is located at the Fe/Ni interface. The bilayer hence shows a magnetic live Fe layer at the Fe/Ni interface. The most complex behavior is expected and observed for Fe/Ni bilayers on Cu(100), where the iron film grows on Ni. This deposition sequence should lead to a ferromagnetic live Fe layer at the Fe/Ni interface and possibly also a ferromagnetic surface
layer of the iron film. Indeed, evidence for two ferromagnetic live Fe layers with complex coupling phenomena has been observed in a recent study where the films were grown on a thinner Ni underlayer and hence showed an inplane anisotropy [242]. Again, the observed magnetization (Figs. 4.11 and 4.13) shows that only a fraction of the Fe film is ferromagnetic. However, the situation is more complex than that for the Ni/Fe bilayer on Cu(100), since we expect now a ferromagnetic contribution from both the Fe/Ni interface and the Fe film surface. The temperature dependence of the measured magnetization for 9-ML Fe/10-ML Ni/Cu(100) shown in Fig. 4.11 gives evidence that a fraction of the Fe film becomes paramagnetic above 250 K. This temperature is much below the Curie temperature of the Ni film and hence also presumably below the Curie temperature of the Fe magnetic layer at the Fe/Ni interface. Fe films on Cu(100) in this thickness range, however, have a Curie temperature of 270 K. Therefore we attribute the rapid reduction in magnetization observed for the 9-ML Fe/10-ML Ni/Cu(100) sample to the loss of ferromagnetic order of the film surface. No such temperature dependence is observed for the 9-ML Fe/15-ML Ni/Cu(100) sample. This would imply that in this case the Fe film surface has no magnetic live layer. Without further experimental data to support or contradict this assumption we can only speculate about the underlying cause of such a phenomenon.

A possible explanation is that the thickness of the underlying Ni layer has an influence on the lattice parameters of the top Fe layer. Ni can be grown on Cu(100) pseudomorphically up to a critical thickness. Beyond this thickness, dislocations form and the lattice constant starts to relax back to the bulk value. O’Brien et al. estimated the critical thickness to 13 ML [228]. Because bulk Ni has a smaller lattice constant (3.52 Å) than Cu (3.62 Å), a smaller atom spacing is expected at the surface of 15-ML Ni/Cu(100) compared with a 10-ML Ni film on Cu(100). Based on the close correlation between structure and magnetism found in the Fe/Cu(100) system where a ferromagnetic fcc Fe film is always associated with an enlarged atomic volume, we speculate now that the strain relaxation in the Ni layer reduces the atomic volume of the Fe surface layer, resulting in the loss of surface ferromagnetism. However, to confirm this assumption, further quantitative measurements such as a full dynamical LEED analysis would be necessary.

4.4.3 Anomalous Temperature Dependence of Magnetization and Coercive Field

For homogeneous bulk ferromagnetic systems, both magnetization and coercivity decrease with increasing temperature. For the bilayers studied here, we find several cases where deviations from this are observed, e.g., dips are present in the M-T curves for 11~13-ML Ni/9-ML Fe/ Cu(100) films. Traces of such dips can also be
distinguished for similar bilayers with larger Ni thickness (Fig. 4.7). All of these films show an S-shaped temperature dependence of the coercive field (Fig. 4.8). In addition, for 9-ML Fe/10-ML Ni/Cu(100) and 9-ML Fe/15-ML Ni/Cu(100), the magnetization was found to decrease at low temperature (Fig. 4.11 and Fig. 4.13). In all cases the deviation are observed to start upon cooling below 200 K. Since it is impossible for material to lose its magnetic order with decreasing temperature, one can speculate whether these anomalous phenomena are related to the reorientation of the film magnetization, which results from the different temperature dependence of competing anisotropies. This mechanism leads to the magnetization flip from the perpendicular to in-plane orientation upon decreasing temperature for the Ni/Cu(100) films [209, 213]. However the flip can only be observed within a very narrow Ni thickness interval around 7.4±0.3 ML. This implies that the in-plane and perpendicular anisotropies are very sensitive to thickness. They are of comparable magnitude only within this narrow thickness range. Since we observe the anomalous temperature dependence in a number of films whose Ni layer thickness differs considerably, the same mechanism in the Ni layer of the bilayers as in the Ni/Cu(100) system cannot be used to explain the observed anomalous behavior measured here. In addition, neither 3-ML nor 9-ML Fe films on Cu(100) shows such anomalous behavior (Fig. 4.2). Therefore it can be inferred that the anomalous phenomena arise from the coupling of the Ni and Fe films. There are several mechanisms which could account for the observed temperature dependence.

First of all, Li et al. have deduced a Néel temperature of 200 K from MOKE data for Fe film with a thickness of 5~11-ML Fe on Cu(100) [173]. In this study they observed a temperature-dependent oscillation of magnetization with thickness, which was explained by an antiferromagnetic coupling in the interior of the Fe film below 200 K. Such an onset of antiferromagnetic coupling in the interior of the Fe film could also explain why we observe anomalies in the temperature dependence of the magnetization for the Fe/Ni bilayer around 200 K. Unfortunately, up to now, no direct experimental evidence for a Néel temperature of 200 K for Fe films has been found. On the contrary, all experiments to measure the transition temperature of fcc Fe determine a Néel temperature around 70 K [171, 238, 260]. Hence, we have to exclude this explanation based upon the experimental data available.

Then one can wonder if interdiffusion at the Fe/Ni or Fe/Cu interface could substantially alter the magnetic coupling. Interdiffusion is a likely candidate for modified magnetic properties as can be inferred from data for various Fe-Ni bulk alloys, which show pronounced changes of magnetic coupling with composition. Even for Fe on Cu(100) interdiffusion has been reported at temperature as low as 300 K [261]. However, in this study it was found that interdiffusion is very pronounced for ultrathin Fe films (2 ML), while 6 ML of Fe could be heated to 420
K without Cu diffusion to the film surface. Since we do not anneal our samples above 300 K and find peculiarities in the temperature dependence always around 200 K irrespective of the thickness of the Fe film (3 or 9 ML) and for different Ni film thicknesses, we believe that interdiffusion is not very likely to explain the observed phenomena at least for the thicker films, even though we cannot completely exclude it.

The most attractive explanation could be combining the ferromagnetic order at both the Fe interface and the Fe film surface with a temperature dependent oscillatory coupling within the Fe film. In this scenario we would, for example, in the case of 11~13-ML Ni/9-ML Fe/Cu(100), propose that the Fe/Ni interface couples ferromagnetically, but a ferromagnetic contribution at temperatures below 200 K also comes from the Fe/Cu interface. These two ferromagnetic portions of the film are coupled. Since the coupling will oscillate with the thickness of the film between the two ferromagnetic films, we expect an oscillatory behavior of magnetization. This would nicely explain the data of Li for Fe on Cu(100), but with a somewhat modified interpretation: 200 K would now be the Curie temperature of the Fe/Cu(100) interface. This FM portion couples via an oscillatory exchange coupling with the ferromagnetic Fe film surface, leading to an oscillatory magnetization with Fe film thickness. Such an interpretation would resolve the present controversy between Mössbauer data and MOKE experiments. In this scenario the interior of the film should have a Néel temperature around 70 K, as determined by Mössbauer spectroscopy, a Curie temperature of 200 K for the Fe/Cu interface, and a Curie temperature around 270 K for the Fe film surface, both in line with the MOKE data. This sequence of transition temperature is very plausible and supported by theoretical calculations for Fe/Cu(100) [262], which show that the magnetic coupling of the Fe atoms is strongest at the film surface and weakest in the film interior. This scenario can hence resolve the above-mentioned controversy, furthermore it is confirmed by a recent study by Wu et al [263]. By analyzing element specific domain images using photoemission electron microscope, they have verified that the Fe layer at both the Fe/Ni and Fe/Co interface are ferromagnetically ordered in the 4-12 ML thickness range.

However, we have no reasons to exclude an alternative explanation. The S-shaped $H_C - T$ curve can also be understood by assuming that an in-plane magnetocrystalline anisotropy is introduced by the Fe/Ni interface and furthermore assuming that the interfacial anisotropy increases rapidly with decreasing temperature in the temperature range of 150~250 K, in which the anomalous behavior in $H_C$ appears, while it is a slowly-changing function of temperature in the remaining temperature range. This explanation is supported by the fact that similar anomalous phenomena have been observed neither in the Fe/Cu(100) system nor in the Ni/Cu(100) films.
Chapter 5

Exchange Anisotropy in Fe/Ni bilayers on Cu(100)

In the last chapter, the magnetic properties of (Fe, Ni) bilayers have been discussed where the thicknesses of Fe layer are fixed at 3-ML and 9-ML. In this chapter, the Fe/Ni bilayer is still concerned, but now the thickness of Ni layer is fixed while that of Fe layer is made to vary. Interesting phenomena have been found in this way. The most remarkable finding is the exchange biasing observed in ultrathin Fe/Ni bilayers on Cu(100).

Exchange biasing results from the exchange coupling at the interface of ferromagnetic (FM) and antiferromagnetic (AFM) layers, which leads to a shift of the hysteresis loop after cooling the system with an ordered FM layer below the Néel temperature of the AFM layer. The phenomenon of exchange biasing was first observed by Meiklejohn and Bean [157] in a Co/CoO granular system as early as 1957. Due to the extensive interest in the spin-dependent transport properties of magnetic systems, and due to the ability to lock the spin orientation of a ferromagnetic layer, renewed interest has been triggered in the exchanging bias phenomenon.

Though the exchange bias is successfully exploited in spin-valve magnetic-field-sensing devices, the microscopic origin of the exchange anisotropy has not yet been fully established [264]. The most important quantities in discussing exchange anisotropy are the size of the exchange bias and the magnetic orientation between the FM spins and the AFM spins. For the application of spin valves, tailoring of the exchange bias is of prime concern. Hence there are strong efforts to unravel the origin of the exchange anisotropy. Theoretical models have tried to establish the correlation between the exchange bias and the magnetic properties, including the coercive field and magnetic anisotropy, and the thickness of the FM

\[^{1}\text{The experimental data presented in this chapter were all measured by Dr. Bernd Schirmer.}\]
and AFM layer [160, 161, 167]. The first theoretical model to correctly reproduce
the magnitude of \( H_e \) was presented by Malozemoff and co-workers [161, 162]. He
described the anisotropy through a random exchange interaction between the FM
and AFM spins, which is caused by the roughness of the interface. Furthermore, he
considered a special micromagnetic structure in the AFM layer in which domains
were separated by domain walls. These walls include areas in the spin-flop state.
Subsequently, Mauri et al. proposed the domain-wall model [160]. They argued
that the effective exchange field is determined by the exchange stiffness and the
crystalline anisotropy of the antiferromagnet, e.g., the energy of the domain wall
that is located in the antiferromagnet for a frustrated FM/AFM interface. By mi-
cromagnetic calculations, Koon has recently shown that the interfacial energy can
be minimized for a perpendicular orientation between the FM and AFM axes for a
compensated interface [167].

One key assumption is common to the theoretical studies. They all assume that
the AFM layer has a certain minimum thickness for the occurrence of the exchange
bias. According to Jungblut et al. [265], this minimal AFM layer thickness is corre-
lated with the domain-wall thickness and hence depends on the order of magnitude
of the magnetic anisotropy and exchange in the AFM layer. Experimentally, this
has been confirmed for AFM layers like \( \text{Fe}_{50}\text{Mn}_{50} \) with an onset of \( H_e \) for a film
thickness of about 20 Å and NiO with an onset around 400 Å [266]. Nevertheless,
what will be present here are biased hysteresis loops in ultrathin Fe/Ni bilayers on
Cu(100) where the total thickness of the film is less than 20 Å. On the other hand,
up to now there is no evidence of an antiferromagnetic component existing at the
measurement temperature in the Fe/Ni bilayers. All of them are indicative of a new
mechanism which is responsible for the biased hysteresis loops in Fe/Ni/Cu(100)
bilayers. After the experimental results are present in the next section, a model will
be proposed in section 5.2 to explain the unusual biased hysteresis loops.

5.1 Experimental Results

In all measurements presented here, a Ni film thickness of 7 ML was chosen. Such
films still grow pseudomorphic, i.e., adopt the in-plane spacing of the Cu(100)
substrate [204]. A Ni/ Cu(100) film with a thickness above 9 ML has a perpendic-
ular magnetization, while films below 7 ML show an in-plane magnetic anisotropy.
That is to say, a spin reorientation transition occurs in the thickness range of 7–9
ML [108, 228]. All of our Ni films studied here show an in-plane magnetization.
In this case a Kerr ellipticity of less than 4 mrad is observed for the Ni film only.
Therefore this contribution to the Kerr ellipticity can be neglected in the follow-
ing discussion. The iron film thickness was varied between 1.5 and 10 ML, with
most measurements performed for Fe thicknesses below 5 ML. To investigate the magnetic properties, hysteresis loops were measured in longitudinal geometry at a temperature of 110 K. A selection of these curves is displayed in Fig. 5.1, that shows several striking features. The magnetization of the Fe films decreases with increasing thickness above 2.4 ML (Fig. 5.2), implying that the ferromagnetic portion of the film decreases with thickness. Furthermore, at intermediate film thicknesses of 2.7 ML and 3.8 ML, the films show a shift of the magnetization curves, i.e., evidence for exchange biasing loop. This implies that Fe films as thin as 3 ML are sufficient to provide exchange biasing. Films with a thicknesses of 2.4 ML and 4.4 ML, on the contrary, do not show this effect. Please note that the sample with 3.8-ML Fe, does not show a hysteresis loop. This implies that the coercivity of our sample is larger than the maximum magnetic field applied. A similar effect has been observed for Fe/Cu(100), where the region of co-existence of the $(4\times1)$ and $(2\times1)$ phases is related to a maximum in coercivity [267]. To unravel the origin and disappearance of exchange biasing with increasing film thickness, the thickness dependence of the magnetization and exchange bias was studied in more detail. Fig. 5.2 displays the saturation magnetization and the exchange bias field as a function of film thickness. Three regions with different magnetic proper-

**Figure 5.1:** Longitudinal MOKE hysteresis loops of the system Fe/ Ni/Cu(100) in the Fe thickness range between 1.4 and 4.4 (ML) measured at 110 K. The Ni thickness is kept constant at 7 ML. The loops for 2.7- and 3.8-ML Fe show a clear shift of the loop characteristic for exchange biased films.
Figure 5.2: Thickness dependence of the Kerr ellipticity at saturation ($M_s$), the bias field ($H_e$) and the superstructure LEED intensities of the (4×1) and the (2×1) spots for the system Fe/Ni/ Cu(100). All data have been measured at 110 K. The straight line identifies the transition thicknesses between the different regimes. These regimes are characterized by the magnetic behavior and the film structure. The different atomic arrangements present in the film are denoted in the figure at the bottom.
ties can be distinguished. For thicknesses below 2.2 ML (region I), the saturation magnetization increases linearly with thickness. This is the expected behavior for a homogeneously magnetized film. For film thicknesses above 5 ML (region III), on the other hand, the saturation magnetization is practically constant. This implies that in this thickness range only a small and constant number of iron layers contributes to the ferromagnetic signal. The most interesting magnetic behavior is observed in the transition regime between 2.2 and 4.6 ML (region II), where the magnetization initially drops rapidly and reaches a shallow minimum around 3.5 ML. In this thickness range, the largest exchange bias is found with approximately 70 Oe. Considerable scatter is seen in the data for the exchange bias in this region. We will come back to this observation later.

The three regions with different magnetic properties are also characterized by different structural properties. Up to 2.2-ML Fe (region I), a \((4\times1)\) superstructure is found for the Fe films. Fe films above 5 ML (region III) show a \((2\times1)\) superstructure, while in region II the coexistence of both superstructures is observed. This is displayed in Fig. 5.2(c) where the measured intensity of a half order spot of the \((2\times1)\) phase and a quarter order diffraction spot of the \((4\times1)\) phase is shown. The figure demonstrates that the coexistence range between the \((4\times1)\) and \((2\times1)\) structures is the thickness range, where a large exchange bias is found. Displayed in Fig. 3 are the temperature dependence of the magnetization, the coercive field, and the bias field \(H_e\) for an iron film thickness of 3.2 ML. The bias field decreases continuously with temperature until it vanishes at around 230 K. Above the same temperature, the saturation magnetization begins to decrease with temperature. However the coercivity does not show abnormal behavior around this temperature.

## 5.2 Model

The exchange bias, which has been observed in ultrathin Fe/Ni bilayers with a thickness where \((4\times1)\) and \((2\times1)\) structures coexist, is not easy to understand. The first question to answer is why the coexistence of the two different phases of Fe on Ni/Cu(100) should lead to an exchange bias that has never before been observed in such a thin bilayer system. To address this question we have to determine the structure and magnetic properties of the \((4\times1)\) and \((2\times1)\) phases. Both structures have been previously observed for iron films on Cu(100) without a Ni underlayer. The \((4\times1)\) phase of iron on Cu(100) is characterized by a ferromagnetic coupling in the entire film and a large atomic volume of 12.1 \(\text{Å}^3\), that is observed for an iron thickness of less than 4 ML [172, 268]. For the \((2\times1)\) phase on Cu(100) observed above 5 ML, only the film surface shows an enlarged atomic volume of 12.1 \(\text{Å}^3\) and a ferromagnetic coupling, while deeper layers in the interior of the Fe film have
an atomic volume of 11.4 Å³ and do not show ferromagnetic coupling [169, 269]. The film interior presumably undergoes a paramagnetic-antiferromagnetic phase transformation upon cooling below 200 K. Nevertheless, the transition temperature is still a point of dispute. A Néel temperature of around 200 K was proposed based on the temperature- and thickness-dependent magnetization measurements by magneto-optic Kerr effect (MOKE) [173], while direct measurements of the onset of magnetic order have never observed antiferromagnetic order above 70 K [238, 260]. Hence it is tempting to attribute the change of magnetization signal at 200 K to another magnetic transition [178].

There is considerable evidence that very similar structural and magnetic phases are also found for Fe films on Ni/Cu(100) [242, 241]. As can be seen from Fig. 5.2(a), the magnetization increases linearly with film thickness in region I, where the (4×1) phases is observed. This is indicative of ferromagnetic order in the entire film in this thickness range just as observed for Fe on Cu(100). On the other hand, for films with a (2×1) phase, only a small and constant magnetization is observed, which implies that only a small fraction of the film is ferromagnetic. This again

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**Figure 5.3:** Temperature dependence of the Kerr ellipticity at saturation, the coercive field ($H_C$) and the bias field ($H_e$) of the Fe/Ni/Cu(100) system for a 3.2-ML-thick Fe film. The straight line denotes the temperature where the bias field disappears.
closely resembles the behavior of Fe on Cu(100) \[172, 244\].

After having highlighted the correlation between the surface reconstruction and the magnetism, we will perform a close analysis of the 230 K blocking temperature at which the bias field vanishes. The blocking temperature of 230 K is not related to the Curie temperature of the Ni underlayer. This has been confirmed by measurements of Ni films on Cu(100), which show a Curie temperature of 380-420 K at 7 ML. The 3-ML Fe on Cu(100) shows a Curie temperature well above room temperature and the surface live layers of the thicker iron film exhibit ferromagnetic ordering around 270 K. All the temperatures differ significantly from the blocking temperature. Yet the blocking temperature is very close to the proposed 200 K Néel temperature for Fe/Cu(100) \[173\]. If we assume that the (2\times1) phase has a Néel temperature of 200 K while the (4\times1) phase shows ferromagnetic ordering at room temperature (see Fig. 5.2), the observed exchange bias can be explained in the same way as that for, e.g., Co/CoO granular FM/AFM film. In this case we would have an exchange bias caused by the phase separation of a single element film into two different structural and magnetic phases that posses FM and AFM properties, respectively. Unfortunately, up to now, no direct experimental evidence for a Néel temperature of 200 K has been found. On the contrary, all experiments to measure this quantity directly for the fcc phase of Fe determine a Néel temperature below 70 K \[238, 260\]. Hence, we have to exclude this mechanism at present based upon the experimental data available. This confronts us with the question that if the exchange bias does not result from the FM/AFM coupling, then which mechanism is responsible for the shifted magnetization curves?

To answer this question, we have checked the essential and indispensable conditions for the presence of shifted hysteresis loop for a ferromagnetic thin film (the pinned layer) in contact with another magnetic thin film (the pinning layer). First of all, an appropriate interface coupling between these two layers should exist. Then, the bulk spin configuration of the pinning layer must not change upon the reversal of the applied field. For the AFM/FM bilayer structure, the AFM spins are only weakly coupled to the external field through interfacial interactions since its net magnetization is zero. Therefore, their states that were frozen during cooling are stabilized by the AFM magnetocrystalline anisotropy. Finally, there must be some initial breaking of time-reversal symmetry. This is usually obtained by cooling the pinning layer through its ordering temperature while the pinned layer with a higher ordering temperature is in a single domain state introduced by an applied field. As we have seen, the involvement of an antiferromagnetic component is not an indispensable condition for an exchange anisotropy though exchange biasing always refers to the ferromagnetic/antiferromagnetic system. In fact, a hard FM layer can act as a pinning layer to shift the magnetization curve of a soft FM layer that is exchange-coupled with the harder layer. This is the case one has observed
in the exchange-spring magnet [270, 271]. In the following another mechanism is illustrated, which may result in an exchange biasing field in a Fe/Ni bilayer without an antiferromagnetic component.

Presumably the ferromagnetically ordered \((4 \times 1)\) Fe domains have a Curie temperature above room temperature just like the \((4 \times 1)\) structure in the Fe/Cu(100) system [172, 244]. For the \((2 \times 1)\) Fe domains only the surface layer is ferromagnetic while the internal part of the Fe film is paramagnetic within the whole temperature range employed in the present work [169, 269, 272]. For Fe/Cu(100) films, the Curie temperature of the surface layer has been determined to be around 270 K [169]. In the previous chapter, we have shown that the ordering temperature of the surface layer of 9-ML Fe decreases to 220-240 K when the Fe film is prepared on 10-ML Ni film on Cu(100). The decrease in the Curie temperature has been explained by the reduced in-plane lattice spacing of the Fe film on Ni/Cu(100). It is therefore reasonable to assume that the Curie temperature of the surface layer of the \((2 \times 1)\) domains here is slightly higher than that of 9-ML Fe on 10-ML Ni on Cu(100), but lower than 270 K, the ordering temperature of the \((2 \times 1)\) phase of Fe on Cu(100). Furthermore we believe that, the biquadratic coupling dominates the exchange interaction between the surface layer and the underlying Ni layer in the \((2 \times 1)\) domains. The biquadratic exchange coupling, which has been found in metallic multilayers a long time ago [273], favors a \(90^\circ\) orientation of the magnetization in the coupled layers. Several mechanisms are believed to create this non-Heisenberg coupling: thickness fluctuations, “loose” spins in the spacer, and the proximity magnetism of a spacer [155]. Keeping in mind that the internal part of the \((2 \times 1)\) Fe domains has an antiferromagnetic ground state, the loose-spin mechanism works well here. At the same time, it has been found that, in Fe/Si/Fe trilayers, the biquadratic coupling strength increases monotonically (exponentially) with a reduction in spacer thickness [274]. The biquadratic exchange in this system is believed to come also from the loose spins, i.e., the paramagnetic or superparamagnetic Fe clusters diffused into the Si spacer. In our case the spacer is only 1-2 ML thick, hence we envision that the biquadratic coupling resulting from loose spins could be very large. In contrast to the bilinear exchange coupling, the biquadratic exchange coupling shows a strong temperature dependence. It increases rapidly with decreasing temperature. Based on the above-mentioned facts, we believe it is possible that, below a certain temperature, the interaction between the surface layer and the bottom layer is dominated by a huge biquadratic exchange coupling. This temperature is the observed blocking temperature. Consequently, we believe that the magnetic moments in these two layers approximately keep an orthogonal orientation, even during the magnetization reversal procedure. By making such an assumption, we will now show that exchange biasing could be introduced into our special bilayer structure.
Figure 5.4: Scheme of the two-step asymmetric magnetization reversal of a 90° coupled two-phase system.

Let us first focus on the magnetization reversal of the (2×1) domains. Fig. 5.4(a) shows the initial state. $M_1$ and $M_2$ denote the magnetic moment of the surface layer and the bottom layer, respectively, which are coupled in an orthogonal orientation. Both $M_1$ and $M_2$ lie in the film plane. Each of them is aligned along one easy axis of the magnetocrystalline anisotropy that has a cubic symmetry. The external field is applied in the same direction as $M_2$. We assume that the magnetic domain rotation is the only reversal mechanism. This is true if the domain size is small. Then we switch the external field to the opposite direction. Now the magnetic moment tends to rotate following the reversal of the applied field to reduce the Zeeman energy. According to the symmetry of the cubic crystal structure, the in-plane magnetic anisotropy should present a fourfold symmetry. Therefore, we decompose the rotation into two steps: the first 90° rotation (step 1) and the second 90° rotation (step 2). In Figs. 5.4 (a) and (b), the Zeeman energy is reduced by $\mu_0(M_1 + M_2)H$ while the magnetic anisotropic energy remains constant. In Figs. 5.4 (b) and (c) the Zeeman energy is reduced by $\mu_0(M_1 - M_2)H$. We can consider the reduction in Zeeman energy as the driving force for the rotation of the magnetic moments. We can see that the driving force is smaller for step 2 than that for step 1 by $2\mu_0 M_1 H$. However, we notice that, without a magnetic anisotropy, we could not separate the rotation into step 1 and step 2. The second 90° rotation would follow the first one inevitably. Because of the existence of the fourfold magnetic anisotropy and the smaller driving force for the second 90 rotation, not only can the second step be separated from the first step but it is also more difficult to take place than the first step. For an extreme case of $M_1 = M_2$, the second step will never occur. Therefore, the magnetic-moment orientation is switched between (a) and (b) upon the multiple reversal of the applied field. This is to say, averaged over time, $M_2$ has a net component pointing to the left and $M_1$ shows a net com-
ponent pointing to the right. As we know, both $M_1$ and $M_2$ are coupled with the remainder of the bilayer. The (2 x 1) Fe domains are coupled with the (4 x 1) Fe domains at the surface and the magnetic domains under the (2 x 1) domains are coupled with those under the (4 x 1) domains in the underlying Ni film. The coupling strength depends on the structure of the domain boundary as well as the exchange stiffness. It is possible that one coupling dominates over the other even for $M_1 = M_2$. Therefore, this unbalanced coupling with the biased magnetic moment $M_1$ or $M_2$ will give rise to an exchange biasing. In a way, the 90° coupled (2 x 1) domains and underlying Ni layer play the same role as the pinning layer in FM/AFM system and provide a biased $M_1$ (or $M_2$). The bilinear coupling between $M_1$ (or $M_2$) and the remaining parts, for example, the (4 x 1) domains, is dominant over that between $M_2$ (or $M_1$) and the remaining part. Therefore, exchange biasing can be observed for the magnetization of the (4 x 1) domains. The time inversion symmetry is broken by magnetizing the Ni layer before the Fe (2 x 1) domains are ordered. It is obvious that the bias fields would be sensitive to the detailed domain structure and hence also the growth. Perhaps this is also the reason why our data for the coercive and bias field, respectively, show quite some scatter.

In conclusion, an exchange biasing in ultrathin Fe films on Ni/Cu(100) has been observed when the (2 x 1) and (4 x 1) phases coexist. This biasing could be attributed to the coexistence of AFM and FM domains as observed previously in granular systems. However, we believe that an alternative coupling mechanism provides a more plausible explanation. It results from an orthogonal coupling between the (2 x 1) surface layer and the Ni bottom layer. This finding could open up new avenues to tailor exchange biased devices. To clarify the details of this mechanism, further micro-magnetic calculations are desirable.
Chapter 6

Summary of Part I

To end the first part of this thesis, the main findings and conclusions on the magnetism of ultrathin Fe, Ni and their bilayers on Cu(100) with an emphasis on the later are summarized as follows.

1. By measuring and analyzing the hysteresis loops of Ni/Cu(100) films with several thicknesses at different temperatures, the magnetization reversal mechanisms have been investigated for Ni/Cu(100) films with perpendicular magnetic anisotropy. The magnetization reversal procedure consists of the nucleation of the reversed domains and the following motion of the domain wall. Which process is the dominant mechanism depends on the temperature and the film thickness. For thick films with large perpendicular anisotropy, the nucleation field, which is correlated to the anisotropy, is greater than the pinning field of most pinning centers. The magnetization reversal is dominated by the nucleation and the reversal procedure can be described by the nucleation followed by the viscous motion of the wall without obstacles, resulting in a high squareness in the shape of the hysteresis loops. With decreasing film thickness, the effective anisotropy field becomes comparable with the effective pinning field. Then the role of temperature becomes important. At high temperature, the motion of the domain wall is thermally assisted and thus easy, so the nucleation of the reversed domain is still the dominant process. However at low temperature the pinning effect of the wall motion is visible. Therefore the shape of the hysteresis loop changes from rectangular at high temperature to inclined and round at low temperature. In this case the adsorbed residual gases have a pronounced effect on the reversal procedure acting as pinning centers. The high stability of the magnetic properties of Ni/Cu(100) films with perpendicular anisotropy upon multiple magnetization reversals has been mea-
CHAPTER 6 SUMMARY OF PART I

sured and is confirmed by a theoretical analysis.

2. (Fe, Ni) bilayers with different individual thickness and different deposition sequences have been investigated experimentally with special attention to the temperature dependence of their magnetic parameters. It is unequivocally found that in (Fe, Ni) bilayers the spin reorientation transition shifts to larger Ni film thicknesses compared with Ni/Cu(100) films. This result is explained by an enhanced demagnetization field when the two magnetic layers with unequal magnetization are put together and possibly by a Fe/Ni in-plane interface anisotropy. The non-monotonic temperature dependence of the coercivity observed in the bilayers strongly suggests the existence of an in-plane anisotropy at the Fe/Ni interface. Magnetic live layers of Fe have been found at the Fe/Ni interface of the bilayers with 9 ML Fe. However the magnetic structure of the surface layer of 9-ML Fe on Ni on Cu(100) seems to be closely related to the thickness of the underlying Ni film. A magnetic live layer with Curie temperature around 230 K is observed when the thickness of Ni layer is chosen to be 10 ML, while it is absent when the Ni thickness increases to 15 ML. The structural relaxation of the Ni layers with thickness is thought to be responsible for the observations. These results provide a further evidence for a sensitive correlation between the structure and magnetism in fcc Fe.

The single domain state is not stable for the (Fe, Ni) bilayer with small perpendicular anisotropy. With the withdrawal of the external field, the single domain state gradually relaxes to a multi-domain state, resulting in a decay of remanent magnetization with time. The relaxation behavior disappears when the perpendicular anisotropy is large.

3. An exchange biasing in ultrathin Fe films on Ni/Cu(100) has been observed when the (2 x 1) and (4 x 1) phase coexist. This biasing could be attributed to the coexistence of AFM and FM domains as observed previously in granular systems. However, with all the direct experimental result objecting the existence of a AFM phase at the studied temperature, a new model is proposed to account for this unusual biased coupling phenomenon. It is based on the assumption that the strong biquadratic exchange coupling results in an orthogonal coupling between the (2 x 1) Fe domains and their underlying Ni layer.

Though the intensive research on the correlation between magnetism and structure of ultrathin films with Fe/Cu(100) as a prototype has lasted for more than 15 years, the understanding of this subject is far away from perfection. To the author's present comprehension, further interpretations are expected to set forth on a num-
The first issue concerns the magnetic structure of Fe films with a thickness of 5-11 ML. As a magnetic live layer at the surface is well established, the magnetic phase in the internal part is still a controversial issue. It had been a popular viewpoint that this part has an anti-ferromagnetic ground state with a Néel temperature around 200 K. However, up to now, all the direct measurements show the anti-ferromagnetic ordering temperature is below 70 K. On the other hand, around 200 K a series of anomalous phenomena have been reported [173, 174, 175, 242, 255] in the literature and also observed in this work (for example, see Fig. 4.13), so that very recently a spin density wave (SDW) antiferromagnetism model was proposed based on the thickness dependent anomalies in magnetization around 200 K [174]. Direct measurements of the wavelength, for example, by scattering experiments, are still needed to confirm this model. In addition, a nesting Fermi surface should be theoretically or experimentally elaborated for the SDW ground state. In conclusion, more work is needed to understand the anomalous behavior around 200 K and to establish a clear diagram for the magnetism of the Fe/Cu(100) system in regime II.

In Sec. 1.2.4 (interlayer exchange coupling), it is clearly demonstrated that the quantum size effect due to electron confinement becomes important and even plays a dominant role when the size of a physical system is reduced to the nanometer range. Then the question is if there also exist quantum well state for Fe/Cu(100) system, in which all the structure and magnetic phase transitions occur in monolayer range. What are the effects of electron confinement on the structure and magnetism if so? To the first question, a positive answer is implied by the recent observation that the Curie temperature of Fe/Cu(100) film oscillates with the thickness of its Cu cover layer [275].

The structure of Fe/Cu(100) films not only depends on the thickness but is also sensitive to the growth condition. For low-temperature grown Fe/Cu(100) film, the homogeneously magnetized fcc phase (regime I) can persist up to 10 ML. This result indicates that the growth kinetics play an important and sometimes a dominant role in determining the structure and magnetism. The details of the effect of growth kinetics are still waiting to be specified.
Part II

Growth of Perylene Crystals on Solid and Liquid Substrates
Chapter 7

Crystal Growth and Pattern Formation in Solution

Before the results of the growth of organic films are presented, the theoretical basis, which is necessary for analyzing the growth behavior of organic crystals, is introduced. Since the basic principles governing thin film growth have been already discussed in Chapter 1, only a brief introduction concerning crystal growth in solution and the interface shape accompanying the crystal growth is given in this chapter.

7.1 Nucleation

7.1.1 Driving Force for Phase Transformation

According to the laws of thermodynamics, the equilibrium state at given temperature and pressure is the state in which the Gibbs free energy has a global minimum. With the change of external conditions (temperature, pressure, concentration, etc.), the original equilibrium state would become instable and the system has a trend to transform into one or more new phases, in which the system has the minimum free energy again under the new conditions. The driving force for the transformation is the decrease in Gibbs free energy upon the phase transformation. During the transformation procedure, particles will flow from the parent phase(s) to the new phase(s) until a phase equilibrium is ultimately established. Under equilibrium conditions, the chemical potentials are identical in every phase for each species of particles.

In the following, we will limit our discussion to an important phase transformation, i.e., crystal growth from solution. For the reason of simplicity, we will concentrate on the two-component system. This is to say that the solution con-
tains only one kind of solute particle. To enable the continuous growth of crystals, certain supersaturation should be reached for the solution. The supersaturation is usually defined by the difference between the chemical potential of the substance in the solution phase and in the crystal phase. Therefore, supersaturation is also a measure of the driving force for crystal growth. Based on Henry’s law, which state that the equilibrium partial vapor pressure of solute \( p_{\text{solute}} \) is proportional to its mole fraction \( x_{\text{solute}} \) in the dilute limit, i.e., \( p_{\text{solute}} = x_{\text{solute}} K_{\text{solute}} \) with \( K_{\text{solute}} \) being a constant, the chemical potential of the solute in a dilute solution can be defined as

\[
\mu_{\text{solute}} = \mu_{\text{solute}}^0 + RT \ln (K_{\text{solute}}/p_{\text{solute}}^0) + RT \ln x_{\text{solute}}
\]

(7.1)

where \( \mu_{\text{solute}}^0 \) and \( p_{\text{solute}}^0 \) are the chemical potential and equilibrium of the solute in the pure state, respectively. Since both \( \mu_{\text{solute}}^0 \) and \( p_{\text{solute}}^0 \) are characteristic of the solute, the supersaturation for a two-component (one solute and one solvent) system can be written as

\[
\Delta \mu = \mu_S - \mu_C = kT \ln c_S/c_0,
\]

(7.2)

where \( c_0 \) is the saturation (equilibrium) concentration of the solute in the given solvent. \( c_S \) is the actual concentration which is larger than \( c_0 \). In more general case, \( c_0 \) and \( c_S \) must be replaced by the equilibrium activity \( a_0 \) and the actual activity of the solute \( a_s \), respectively, to account for deviation of the real solution from Henry’s law. For a real solution, the equilibrium vapor pressure is given by \( p_{\text{solute}} = a_{\text{solute}} K_{\text{solute}} \) instead of Henry’s law.

### 7.1.2 Critical Nucleus

When a solution becomes supersaturated, the driving force for crystallization is also presented. Crystal nuclei could be formed due to fluctuations. However, not all the nuclei can grow further. Only the nuclei, whose size is greater than a certain value, the critical size, are able to grow further. The others, who are smaller than the critical size, will decay and disappear at last.

From the viewpoint of thermodynamics, the small nuclei have a large surface to volume ratio and hence a positive free energy compared to the parent phase. Therefore, they are not stable. This can be clearly demonstrated by considering a spherical nucleus of radius \( r \) formed in solution. The total free energy change after the formation of such a nucleus is given by

\[
\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v
\]

(7.3)

where \( \Delta G_v \) is the change of Gibbs free energy for unit volume of solute crystallized from the solution, and \( \gamma \) is the surface free energy per unit area of the nucleus.
Figure 7.1: The change of Gibbs free energy as a function of the radius of a spherical nucleus in solution. The dash-dotted line represents the increase in surface free energy, while the dashed line describes the decrease in bulk free energy, respectively.

Equation 7.3 is plotted in Fig. 7.1. By setting the first derivative of $△G$ with respect to $r$ to zero, the critical radius $r_c$ is obtained as:

$$r_c = -\frac{2\gamma}{△G_v}$$  \hspace{1cm} (7.4)

and the critical Gibbs free energy as

$$△G_c = \frac{16\pi\gamma^3}{3(△G_v)^2}$$  \hspace{1cm} (7.5)

Actually, the crystal nucleus is more likely to show facets instead of being round. In this case, the free energy $△G(n)$ against the number of atoms (molecules) in the nuclei $n$ is given by Kern et al. [276]. For nuclei which can be described in terms of macroscopic surface energy terms, the form of $△G(n)$ for the three-dimensional case is given by

$$△G(n) = -n△\mu + n^{2/3}X,$$  \hspace{1cm} (7.6)

where $X$ is the surface free energy term and $△\mu$ is the gain of chemical potential upon crystallization. $X$ is given by

$$X = \sum_i c_i\gamma_i$$  \hspace{1cm} (7.7)
where the nucleus has a face $i$ of surface energy $\gamma_i$. The $c_i$ are geometrical constants describing the surface areas $s_i$ via $s_i = c_i n^{2/3}$. Clearly, the values of $c_i$ depend on the concrete shape of the nucleus.

In the same way as for a spherical nucleus, the critical size $N$ and the free energy barrier $\Delta G(N)$ are calculated as

$$N = \left(\frac{2X}{3\Delta \mu}\right)^3, \quad \Delta G(N) = \frac{4}{27} X^3 \Delta \mu^2. \quad (7.8)$$

### 7.1.3 Nucleation Rate

The nucleation rate is the product of the concentration of critical nuclei ($\sigma(N)$) and the probability (the capture rate $\alpha$) of the arrival of an additional particle to the critical nucleus per unit time:

$$J = \alpha \sigma(N). \quad (7.9)$$

The formation of the critical nucleus may result from fluctuation, where the number of particles joining the aggregate with $R < R_C$ for a certain period happens to exceed the number of monomers leaving it. This is the case of homogeneous nucleation and we will restrict our discussion to homogeneous nucleation. According to the fluctuation theory, the probability of the event for which the potential is higher than the average value by $\Delta G$ is proportional to $\exp(-\Delta G/kT)$. Therefore the
nucleation rate can be expressed as

\[ J \propto \alpha \exp\left(\frac{-\Delta G(N)}{kT}\right). \]  

(7.10)

The concentration of the solute particles \( \sigma_1 \) is usually much larger than the concentration of the critical nuclei. In this case, the number of critical nuclei can be calculated from the Maxwell-Boltzmann distribution law, which is given by

\[ J = \sigma_1 \alpha \exp\left(\frac{-\Delta G(N)}{kT}\right). \]  

(7.11)

In solution, the capture rate (\( \alpha \)) in the expression of the nucleation rate is proportional to the density of the dissolved substance, \( n(\text{cm}^{-3}) \), and to the particle flux towards the surface of the critical crystal nucleus, whose area is \( \sim 4\pi R_c^2 \). In solution this flux depends on the rates of diffusion and the probability of addition of particles to the nucleus. The addition of particles requires the breaking of several of their bonds with the solvent, i.e., overcoming a potential barrier. Thus the capture rate for the nucleation in solution is given by [277]

\[ \alpha \simeq 4\pi R_c^2 n^2 \nu a \exp\left(-E/kT\right), \]  

(7.12)

where \( a \) is the lattice parameter and \( \nu \) is a constant with the dimension of a frequency. Therefore the rate of nucleation can be written as

\[ R \simeq 4\pi R_c^2 n^2 \nu a \exp\left(-E/kT\right) \exp\left(-\Delta G(N)/kT\right). \]  

(7.13)

For the organic crystal growth from solution, another barrier exists associated with the rearrangement of the molecules, which becomes relevant when the particles come close to the nucleus since a complex molecule can not join the crystal in an arbitrary orientation. However, this process has been very poorly studied up to now, though it was pointed out by Chernov twenty years ago (see [277] page 106).

### 7.2 Crystal Growth in Solution

#### 7.2.1 Growth Mechanism

The growth of a crystal results from the addition of new atoms and molecules to the existing crystals. However, adsorption on a atomically smooth surface is not sufficient to be regarded as growth, because it may cease once a certain concentration of adatoms is achieved. This happens when the chemical potential of the adsorbed atoms or molecules becomes equal to that of identical atoms or molecules in the environment (vapor, solution). Atoms (molecules) adsorbed at steps may also have a chemical potential different from those in the crystal, because when such
Figure 7.3: A solute particle could be attached to a crystal at a position (a) at the kink, (b) in the step, and (c) on the facet. Only the particle at the kink has the same chemical potential identical to that of particles in the crystal. In this way, crystal growth means addition of particle to the kinks.

adsorbed particles are detached, the number of free bonds on the surface, and hence the surface energy, changes. On the other hand, removing an atom from or adding one to a kink does not affect the surface energy. Therefore the chemical potential of a particle in the kink can be identified with that of the crystal. Thus crystal growth means the addition of new particles to the kinks.

Two cases of growth can be distinguished, growth on atomically rough surfaces and growth on atomically smooth surfaces. An atomically rough surface means a high density of steps. It also means a high density of kinks, since thermal fluctuation always ensure a certain density of kinks on steps. Therefore the addition of new particles to atomically rough surfaces can occur anywhere on a macroscopic scale, so that in the course of growth the surface shifts along its normal at each of its points. Such growth is termed as normal growth. On the other hand, growth on atomically smooth surfaces requires a two-dimensional nucleation process to form steps and thus to start the growth. The growth is fulfilled by consecutive deposition of layers, i.e. by tangential motion of steps. This is called layerwise growth.

7.2.2 Normal Growth

The change in the average energy of a particle (atom, molecule, or ion) as it moves from the solution to the crystal is schematically depicted in Fig. 7.4. Under equilibrium conditions, the reduction in average energy is given by

$$\varepsilon_s - \varepsilon_C = \Delta H,$$

(7.14)

where $\Delta H$ is the crystallization enthalpy. The potential barrier $E$ depends on the configuration of the atom (molecule) in solution, and is closely connected to the
position and orientation of the nearest neighbors of the particle shifting from the liquid to the solid phase. Usually \( E \) is larger for low-symmetric particles. This potential barrier is specially important for the growth of organic crystals since the requirement of a specific orientation of the molecules when they are added to the crystal presents a large barrier.

Bearing Fig. 7.4 in mind, the growth rate can be deduced for crystal growth from solution. The arriving flux of particles per unit time can be written as

\[
J_+ = \nu c a^3 \exp(-E/kT).
\]  

(7.15)

The growth is actually a dynamic process including both particles going from solution to the crystal and the opposite flow \( J_- \) from the crystal to the solution with

\[
J_- = \nu (1 - ca^3) \exp[-(E + \Delta H)/kT].
\]  

(7.16)

In Eq. 7.15 and Eq. 7.16, the following symbols have been used: \( c \) (\( cm^{-3} \)) denotes the average concentration of the solution near the surface and at a kink and \( a^3 \) the volume per solute particle. \( \nu \) is the attempt frequency, which is associated with the vibration and the rotation of the particle. Considering that crystal growth means addition of particles to kinks, the growth rate is written as

\[
V = a (a/\lambda_0)^2 (J_+ - J_-),
\]  

(7.17)
with \( \lambda_0 \) being the average distance between kinks. For a system at equilibrium concentration \( c_0 \) at a given temperature, \( V = 0 \) means \( J_+ = J_- \), which gives

\[
c_0 a^3 = \frac{\exp(-\Delta H/kT)}{1 + \exp(-\Delta H/kT)}.
\]

Using Eq. 7.18, Eq. 7.17 can be rewritten as

\[
V = \beta a^3 c_0 \sigma
\]

with

\[
\beta = \alpha \nu (a/\lambda_0)^2 (a^3 c_0)^{-1} \exp[-(E + \Delta H)/kT] \cong \alpha \nu (a/\lambda_0)^2 \exp(-E/kT).
\]

and

\[
\sigma = (c - c_0)/c_0.
\]

\( \beta \) is called the kinetic coefficient and \( \sigma \) is sometimes also called the supersaturation. From Eq. 7.19 one can see that the growth rate shows a linear dependence on \( \sigma \) for normal growth.

### 7.2.3 Layerwise Growth

For the growth of an atomically smooth surface of a dislocation-free crystal, the sources of the growth are two-dimensional nuclei. Suppose that nucleation on the surface occurs at the rate of \( J \left[ cm^{-2}s^{-1} \right] \), \( L \) being the size of the face under consideration, and \( v \) the step propagation rate. The time needed for the propagation of a new layer from the nucleus over the entire surface with a linear dimension \( L \) is about \( L/v \). The number of nuclei formed on the surface within this time is \( J L^3/v \).

If this value is less than unity, i.e., \( L < (v/J)^{1/3} \), then each consecutive nucleus is created only after the layer initiated by the preceding nucleus has propagated over the whole face. In this case, the normal growth rate of the facet is

\[
V = J L^2 h,
\]

where \( h \) is the height of the nucleus.

If the supersaturation is high and/or the size of the facet is large enough, new nuclei may arise on the facet before the preceding layer completely covers the face and therefore Eq. 7.22 ceases to apply. Then the layer formed by the new nucleus at any point on the face has enough time to grow to a radius \( \lambda \cong (v/J \pi)^{1/3} \) before meeting the layers initiated by other nuclei. The reason for this is that during a time period of \( \lambda/v \) there should be about one nucleus formed within an area of \( \pi \lambda^2 \). That is to say, \( (\lambda/v) J(\pi \lambda^2) \cong 1 \). Therefore the growth rate is

\[
V \cong \pi \lambda^2 J h \cong h(v^2 J)^{1/3}.
\]
The step propagation rate $v$ is determined jointly by the diffusion field which determines the solution concentration around the facet and the kinetic coefficient.

# 7.3 Growth Shape and Pattern Formation

The evolution of the crystal shape is another important aspect of crystal growth. When the crystals are grown near equilibrium, either a convex round or faceted crystal shape is observed depending on the anisotropy of surface energy. The crystals remain similar in shape to themselves in the course of growth. Otherwise, if the crystals are grown under a condition far from equilibrium, a morphological instability arises which renders the planar or circular shapes unstable. The interplay of the macroscopic growth environment and the microscopic crystal anisotropy results in interesting crystal shapes. For example, the various wonderful snow flakes always catch ones eyes, though we have not up to now reached a complete understanding of their formation.

## 7.3.1 Equilibrium Shape and Growth Shape

The equilibrium crystal shape—sometimes called crystal habitus—results from the minimization of the surface free energy and is purely thermodynamically determined. However crystal growth always proceeds under a non-equilibrium condition and thus the shape we usually observe is the growth shape, which arises from the growth kinetics. The growth shape can approach the equilibrium shape if the crystal is grown slowly at a temperature near the melting point [278], where the thermodynamic equilibrium is easy to reach and the kinetic effect on the shape is minimized.

When the polar plot of the surface free energy is known, the equilibrium crystal shape can be obtained through a geometrical construction, the Wulff construction [279].

**Wulff’s construction:** *the equilibrium shape of a crystal is found by taking, for each direction $n$, the point $H$ defined by $OH = \sigma(n)$, lying on the polar plot $\Sigma$ of the surface free energy, and the plane $\Pi$ orthogonal to $OH$ and cutting $\Sigma$ in $H$. The crystal surface $S$ is then the inner envelope of the planes such as $\Pi$. (Fig. 7.5).*

The Wulff’s construction can be mathematically proven to yield the unique solution to the problem of finding the convex crystal shape minimizing the surface free energy [280]. It is also valid for the crystal with singular surface orientation, at which orientation the surface has a discontinuous second derivative with respect to its orientation and thus a facet arises (Fig7.5-(b)). For a faceted crystal, minimizing the surface energy at a given volume gives rise to another important relation.
Chapter 7. Crystal Growth and Pattern Formation

Figure 7.5: (a) The Wulff construction for a rounded crystal. (b) for a crystal with singular facet. [41].

\[
\mu = \frac{2v\sigma_f}{h_f},
\]  

where \(\sigma_f\) is the surface tension of facet \(f\), \(h_f\) the distance that facet \(f\) grows away from the origin, and \(v\) the atomic volume. \(\mu\) is the chemical potential and it is a constant for all facets at equilibrium.

The physics of crystal growth and thus the growth shape are in contrast to the equilibrium shape complex subjects. It is tempting to treat the problem of the growth shape with a simple model—the Frank model [281].

Frank’s model: Take a crystal bounded by a surface \(S\), and let \(n\) be the normal to \(S\) at a point \(M\) on the surface, then, the velocity of the propagation of the surface at \(M\) is \(v(n) = n v(n)\), where \(v(n)\) is a given function of the local orientation of the surface.

Frank’s model neglects the effect of the diffusion field on crystal growth thus it is a geometric growth model only valid for interface controlled crystal growth. Within this framework, the crystal growth is self-similar, and a variant of Wulff’s construction exists, which allows to find the crystal growth shape [282, 283].

Kinematic Wulff’s construction: A self-similar crystal growth shape is obtained by considering for each vector \(n\) the point \(H\) defined by \(O H = n v(n)\) and the plane \((\Pi)\) perpendicular to \(O H\). The crystal surface is the interior envelope of \((\Pi)\). Refer to Fig. 7.5(a) for an explanation of the symbols.

However, in actual crystal growth, especially at high supersaturation, the diffusion near the surface has a significant and even dominant effect on the crystal
growth. As one of the most spectacular effects of diffusion, an instability appears for planar and spherical growth interfaces and forces the growth front to adopt complicated shapes. This is the topic that we will discuss in the coming subsections.

### 7.3.2 Mullins-Sekerka Instability

Crystal growth always involves certain diffusion processes, for example, solute diffusion for crystals grown in solution and heat diffusion for the solidification from the melt. If the growth interface is rough enough at the molecular level, then the crystal growth is diffusion controlled. Mullins and Sekerka first pointed out through linear-stability analysis that, for diffusion controlled crystal growth, an interfacial instability exists for the simple form of the growth front [284, 285]. Roughly speaking, this instability occurs because the diffusion kinetics favors configurations in which the growing solid has as large a surface area as possible. In the following we will give a simple mathematical description of this instability, taking the planar interface in crystal-solution systems as an example [286, 287].

For the diffusion controlled growth of a planar interface, which moves at a velocity $v$, the diffusion equation reads

$$D_c \nabla^2 c(x, t) = \frac{\partial c(x, t)}{\partial t}, \tag{7.25}$$

and the continuity equation is

$$-D_c \nabla c(x) = \Delta c u. \tag{7.26}$$

Here $c(x)$ is the solute concentration, $D_c$ the diffusion coefficient, and $\Delta c$ the difference in solute concentration between the crystal and the solution at equilibrium.
In the frame of reference moving in $x$ direction at the same velocity as the crystal growth front, as a result of coordinate conversion $x' = x - vt$, the diffusion equation has a form of

$$D_c \nabla^2 c(x', t) + v \frac{\partial c(x', t)}{\partial x'} = \frac{\partial c(x', t)}{\partial t}$$

(7.27)

Thus under the circumstance of steady-state growth, the diffusion equation in the moving reference is written as

$$D_c \nabla^2 c(x', t) + v \frac{\partial c(x', t)}{\partial x'} = 0.$$  (7.28)

The associated boundary conditions are

$$c(x'=0) = c_0(x), \quad c(x'=\infty) = c_\infty,$$  (7.29)

where $c_0(x)$ is the interface-curvature dependent equilibrium concentration. For the sake of convenience, the concentration $c(x)$ is usually replaced by a dimensionless chemical potential $u$. $u$ is related to $c(x)$ by

$$u = \frac{\tilde{\mu}}{\Delta c(\frac{\partial \mu}{\partial c})}; \quad \tilde{\mu} = (c(x) - c_0)(\frac{\partial \mu}{\partial c})_{c=c_0},$$  (7.30)

where $\mu$ is the chemical potential of the solute molecule and $c_0$ its equilibrium concentration. After such a transfer, the steady-state diffusion equation has the form of

$$\nabla^2 u + \frac{1}{l} \frac{\partial u}{\partial x} = 0.$$  (7.31)

with $l$ being the diffusion length defined by $l = D/v$. Now using the Gibbs-Thomson relation, the boundary condition at the interface can be conveniently written as

$$u_{\text{interface}} = -d_0K$$  (7.32)

with $d_0$ being the capillary length defined by

$$d_0 = \frac{\gamma}{(\Delta c)^2 \frac{\partial \mu}{\partial c}}.$$  (7.33)

$K$ is the interface curvature and $\gamma$ the surface energy. Another boundary condition is given by the supersaturation in place infinitely far from the crystal, i.e. $u(\infty) = u_\infty$ (see through Eq. 7.30). At the same time, the continuity condition become

$$v \mathbf{n} = -D(\nabla u)_{\text{interface}} \cdot \mathbf{n},$$  (7.34)

where $D$ denotes the chemical diffusivity. One has

$$D = M \frac{\partial \mu}{\partial c}.$$  (7.35)
where $M$ is proportional to a mobility. Eq. 7.31 and 7.32 are the general forms for diffusion controlled crystal growth. For example, they are also valid for crystal growth from the melt, where the growth is controlled by the diffusion of the latent heat, in case that $u$ and $d_0$ are defined in another way:

$$u = \frac{T - T_m}{L/c_p}; \quad d_0 = \frac{\gamma T_m c_p}{L^2}. \quad (7.36)$$

Here $T_m$, $L$, and $c_p$ are the melting temperature, solidification latent heat and the heat capacity of the melt, respectively.

Eq. 7.31 has a steady-state solution under the boundary conditions $u(x=0) = 0$ and $u(x=\infty) = -1$:

$$u = e^{x/p} - 1. \quad (7.37)$$

Such boundary conditions characterize a small supersaturation and a planar growth front.

Now we turn to discuss under what conditions the planarly growing interface becomes unstable. This goal can be reached through the so-called linear-stability analysis. To do it, a small perturbation of the steady-state interface is considered (see Fig. 7.7(a)):

$$x(y,t) = \delta(y,t) = \delta_k e^{i ky + \alpha_k t}. \quad (7.38)$$

It is easy to see that $\alpha_k$ is the relative increasing rate of the perturbing amplitude by

$$\alpha_k = \frac{1}{\delta_k} \frac{\partial \delta(t)}{\partial t}; \quad (7.39)$$

where $k$ is the wave vector of the perturbation wave. The next step is to find the expression of $\alpha_k$ using the diffusion equation and the continuity condition. If $\alpha_k > 0$, the amplitude of the perturbation will increase with time. That is to say.
that the planar growth front is unstable. On the contrary, if $a_k < 0$, the planar growth interface is stable and the perturbation will disappear with time. Under quasi-stationary approximation, $a_k$ has an expression of

$$a_k \cong kv(1 - d_0lk^2). \tag{7.40}$$

Meaningful conclusions can be drawn from Eq. 7.40. The first term on the right side, which is proportional to the growth speed, contributes a positive value to $a_k$, destabilizing the planar front. The second term, proportional to the surface capillary length, has a negative contribution, which stabilizes the planar interface. Thus one see two competing factors, the diffusion kinetics induced instability and the limitation to this instability by the surface energy.

$a_k$ depends on the wave length of the perturbation in the way as shown in Fig. 7.7(b). There exists a critical wavelength $\lambda_c$. The planar interface is unstable against perturbation with a wavelength larger than $\lambda_c$, which is

$$\lambda_c = 2\pi \sqrt{\frac{1 + d_0D}{v}}. \tag{7.41}$$

### 7.3.3 Dendrite Growth

As the Mullins-Sekerka instability described, when a sinusoidal rippling perturbation appears at the interface, the "hills" on this interface landscape are exposed to more supersaturated solution than the "valleys", and consequently they will grow even faster into the supersaturated solution, increasing hereby the amplitude of the interface deformation. After this instability has developed, individual spikes will peak out from the rest of the wavy structure. These individual spikes are called "dendrites". During dendrite growth the growth pattern evolving from a nucleus acquires a star-shaped envelope surrounding a well-defined backbone. The distance between the corners of the envelope increases with time. Dendrite growth usually requires crystalline anisotropy in either surface tension or growth kinetics. Otherwise the dense-branching morphology (or called seaweed structure) is developed [289]. Fig. 7.8 shows a simulated dendrite structure.

The dendrite growth can be inspected from two aspect, the stationary growth of the backbone and the random launching of the side-branches. Early in 1947, Ivantsov deduced a formula on the growth of a parabolic needle crystal at the absence of surface tension [290]. The Ivantsov’s solution is known as

$$\triangle u_0 = p\exp(p)E_1(p), \tag{7.42}$$

with

$$E_1(x) = \int_x^\infty \frac{\exp(-x')}{x'} dx'. \tag{7.43}$$
Figure 7.8: Dendrite structure (from ref. [288]).

Here $u_0$ is the normalized supersaturation (see eq. 7.30 and 7.36). $p$ is known as the Péclet number, which is

$$p = \frac{\rho v}{2D}.$$  \hspace{1cm} (7.44)

However, Ivanstov’s solution only fixes the Péclet number, i.e., the product of the curvature radius of the tip and the growth velocity, rather than the individual value of them. Though Ivanstov’s solution has been modified, for example, taking the surface tension into account, it is still incapable to give individual value for $\rho$ and $v$ [291]. Therefore, a hypothesis is proposed that takes the point with maximum velocity on the modified Ivanstov curve as the actual working point, but this hypothesis was refuted by experiments [292, 293]. The first successful theory is proposed by Langer and Müller-Krumbhaar, known as the marginal-stability hypothesis [294]. The main-point of this theory is that the growth front is just at the margin of the stability. This is to say, the radius of curvature of the growth front has the same length-scale as the critical perturbation wavelength, i.e.,

$$\rho \simeq \lambda_c.$$  \hspace{1cm} (7.45)

$\lambda_c$ is determined by stability analysis (see the previous subsection). With Eq. 7.45, now the growth velocity can be decided separately for a given supersaturation.

The launching of the side-branch can be explained within the framework of the marginal-stability theory. Since the radius of curvature at the location behind the growth tip is larger than that of the tip, if the tip is at the margin of the stability, the area behind the tip is in the unstable zone. Fig. 7.9 shows a series of consecutive geometric shape of growth tips calculated according to the marginal-stability theory.
Figure 7.9: Geometric shape of growth tips calculated according to the marginal-stability theory (from [286]).
Chapter 8

Growth of Thin Perylene Films

In this chapter, a systematic study on the growth of perylene films on an Au-substrate and on an Au-substrate coated additionally with a self-assembled monolayer (SAM) of 1-Octadecanethiol is presented. The effects of the SAM on the growth of the perylene film have been identified by comparing the growth behavior and film morphology on these two substrates. Possible mechanisms for these effects are discussed.

8.1 Introduction

Recently, molecular films have emerged as candidates for electronic and optoelectronic applications. Organic semiconductors have been successfully employed to fabricate field effect transistors, light emitting diodes and photovoltaic devices [295, 296, 297, 298]. Furthermore, molecular materials are expected to play a prominent role in next generation electronic technology due to their versatility in modifying the physical properties by molecular design. For example, single-molecule transistors have been demonstrated [299] and many efforts are directed towards exploring organic magnets [300]. It is therefore not surprising that more and more attention has been focused on organic film deposition, since films are a prerequisite to exploit the full potential of molecular materials. In organic devices, carrier transport and luminescent behavior are governed by the orientation and packing of molecules. For organic field effect transistors, one always aims at achieving the utmost perfection of molecular order and particular molecule orientations to obtain large carrier mobilities. For light emitting devices, on the contrary, one hopes that the active organic material exists in amorphous form to avoid concentration quenching [301]. Thus reaching a complete understanding of the nucleation and growth of molecular films and exploring new methods to tailor the structure of molecular films for a given application are of paramount importance.
In contrast to the strong atomic binding forces in inorganic crystals, in organic, molecular crystals and films the building blocks of the crystal - organic molecules - are bound to each other by the relatively weak van der Waals forces. Furthermore, the organic molecules possess extended, generally anisotropic shapes, which introduce specific steric requirements with respect to molecular orientation and order for the crystal and thin film nucleation and growth. Therefore, the knowledge accumulated during the last several decades on the deposition and growth of inorganic thin films cannot be directly applied to the growth and nucleation of organic films. Compared with what is known about conventional inorganic systems, there is up to now only a limited understanding of the microscopic growth mechanisms of organic systems [302, 303, 304]. Even the dependence of the film structure and morphology upon growth conditions is still missing for many organic films. Nevertheless, it has been realized that the molecule-substrate interaction plays a crucial role in determining the molecular orientation [304], growth mode [302], film morphology [304], and even the crystal structure [305], though the mechanisms by which the molecule-substrate interaction affects the film properties still remain unclear.

Self-assembled monolayers (SAMs) have already been successfully explored to modify surface properties, for example, to control the surface wetting behavior [306], to modify the electrochemical potential of metal electrodes [307], and to develop novel lithographic methods [308]. Recently, SAMs have also been used as growth templates to define size, morphology, structure and orientation of growing crystal grains in thin films through modifying the interfacial structure. A number of reports have been published but most of them are concerned with the growth of inorganic films predominantly prepared by chemical solution or chemical vapor deposition [309, 310, 311, 312, 313, 314]. In the following section, it will be shown how a SAM can modify the evolution and properties of a vacuum evaporated perylene film on a polycrystalline Au substrate. Before the experimental results are presented, a compact introduction to self-assembled monolayer follows in the next section.

8.2 Self-assembled Monolayers

Self-assembled monolayers (SAMs) consist of densely packed long-chain organic molecules which are chemisorbed on inorganic substrates through a head group which has a specific affinity to the substrate [315]. Three SAMs are popularly investigated. They are organic acids on mica or sapphire, alkyltrichlorosilanes on $SiO_2$, and alkanethiols on Au. Here we will focus on the alkanethiols SAM on a Au(111) substrate. An alkanethiol molecule consists of a alkane group and a
thiol group with a formula of $\text{CH}_3(\text{CH}_2)_n\text{S}$, just as suggested by its name. The thiol group is chemisorbed on the gold substrate. The S-Au bonding energy is estimated to be greater than 1 eV [317]. While the monolayer/substrate interaction is determined by the type of bond between the head group and the substrate, the intralayer, i.e., the inter-molecular cohesive energy comes from Van der Waals (VDW) interactions and is directly proportional to the hydrocarbon chain length. Although the VDW interaction is only 0.07 eV per CH$_2$ unit and thus is much weaker than the S-Au chemisorption bond, the sum of the interactions between a hydrocarbon chain and its neighbors is also considerable. The structure of the SAM is mainly determined by these two interactions. While an epitaxial registry of the SAM on the substrate is strongly preferred by the S-Au bonding, the SAM has a trend to form close-packing structures to minimize the inter-molecule interactions. The actual structure of the SAM results from the energetic equilibrium between these two interactions. Thus it is easy to understand why the tilt angle of the molecule chains changes with the coverage and depends on the length of the alkyl chain (see Fig. 8.1). The structure for full coverage of alkanethiol on Au(111) has been determined by He atom diffraction [318] and confirmed by grazing incidence X-ray
diffraction [319], which reveals an orthorhombic primitive unit cell with a dimensions of $3a \times 2\sqrt{3}a$ ($a = 2.884$ Å, the Au lattice constant) (see Fig. 8.2).

### 8.3 Experimental

The films were prepared by sublimation in a vacuum system with a base pressure in the low $10^{-7}$ mbar range. Perylene evaporation for thin film growth causes typically a pressure rise to $1-2 \times 10^{-6}$ mbar. The deposition rate was measured by a quartz crystal microbalance. Two kinds of commercial substrates [321] were used. One is a 10 nm Au/2 nm Ti/glass substrate, subsequently denoted as Au-substrate. The Au film has a (111)-texture. The second type of substrate has additionally a monolayer of self-assembled 1-Octadecanethiol molecules adsorbed on the Au layer (SAM-substrate). To enable a direct comparison for each growth experiment, these two kind of substrates were installed side-by-side in the deposition chamber. Perylene was deposited upon evaporation at room temperature. Afterwards, the films were characterized using scanning force microscopy (AFM) and x-ray diffraction.


8.4 Effect on the Nucleation Rate

To obtain a coherent picture of perylene growth on the Au- and the SAM-substrate, we have examined perylene films of different thickness on both substrate types. To unravel the initial growth stage, discrete thin films, in which islands do not coalesce, have also been prepared. The evaporation rate constant is kept at 0.11 nm/s and the deposition time is varied. By analyzing the island density as a function of deposition time, the nucleation behavior of the perylene films on the two kinds of substrates was investigated. Fig. 8.3 shows AFM pictures of discrete perylene films with deposition times between 10 s and 40 s. Several features can be deduced from the pictures: 1) For all pairs of samples installed side-by-side in the chamber with exactly the same amount deposited (arranged in the same row in Fig. 8.3), the films prepared on the SAM-substrate present a larger island density and hence smaller island size compared to the Au-substrates. Please take notice that the scanning size is 5 µm for the films on the SAM-substrate (left column in Fig. 8.3) and 15 µm for the films on the Au-substrate (right column in Fig. 8.3), respectively. 2) With increasing deposition time, the island density rises until coalescence occurs for the films on the SAM-substrates. For films on the Au-substrates the island density stays almost constant (see Fig. 8.4), whereas the grain size increases with deposition time. The obvious difference in perylene island density and its deposition time dependence between growth on the Au-substrate and on the SAM-substrate indicates that the adsorbed SAM considerably alters the surface properties of the Au-substrate. We envision two different scenarios. First, if the adsorption energies of perylene on both substrates are large enough, nucleation and growth occur in the complete condensation regime. The single molecule density increases initially until they turn to decrease at time \( \tau_c = \frac{1}{\sigma DN} \) [67], where \( D \) is the molecule diffusion coefficient, \( N \) is the island density, and \( \sigma \) is the capture number, which is a slowly varying quantity with values between 5 and 10. As nucleation is essentially terminated on the Au-substrate already for the smallest deposition time of 10 s, \( \tau_c \) must be considerably smaller than the measurement time scale. Contrary, \( \tau_c \) must be comparable to the measurement scale on the SAM-substrate. As the island density on the Au-substrate is much smaller, it follows that \( D_{Au}/D_{SAM} \gg N_{SAM}/N_{Au} \), i.e. the surface diffusion coefficient on the Au substrate must be much larger than on the SAM substrate. Second, we are unable to rule out incomplete condensation. In this case the observed continuing nucleation on the SAM-substrate would imply a much larger adsorption time \( \tau_a \) (longer increase of single molecule density) and thus a much larger adsorption energy of the molecules on the SAM-substrate. In this scenario, a large molecule diffusion coefficient on the Au-substrate is still needed to explain the much lower island density. We consider this last scenario as less likely, but in order to unambiguously identify the mechanisms of how the
Figure 8.3: AFM topographs of discontinuous films. Each row represents a pair of simultaneously deposited samples. The deposition time is specified for each row. The left column shows perylene films deposited on SAM-substrates, the right column depicts films deposited on Au-substrates. The image size for each column is indicated.
8.5 Effects on the Film Roughness and Texture

As we saw, the introduction of a 1-Octadecanethiol monolayer at the perylene-Au interface strongly modifies the nucleation behavior of perylene films. The change in nucleation behavior might further result in a modification of the film microstructure such as grain size, roughness, etc. Hence we have also examined to what extent the microstructure of a thick film is modified by the SAM. We prepared several pairs of thick films at various evaporation rates. For all samples, the product of evaporation rate and evaporation time was kept constant, i.e. the same amount of material was deposited. The resulting film thickness is calculated to be 100 nm, using the single crystal density and assuming that the accommodation and sticking coefficients do not vary significantly between the gold covered quartz of the quartz crystal microbalance and the substrates used in the present work. The AFM topographs are presented in Fig. 8.5, all in the same scale. The left column displays the samples prepared on the SAM-substrates and the right column those deposited on the Au-substrates. The two samples of each row were installed in the chamber side-by-side and deposited at the same time. The evaporation rates labelled on each

\[\text{Figure 8.4: Deposition time dependence of island density. The island density increases with deposition time on the SAM-substrate, while it stays nearly constant on the Au-substrate. Lines to guide the eye.}\]

SAM modifies nucleation, additional measurements would be needed.
Figure 8.5: AFM topographs comparing the effect of evaporation rate on film microstructure for SAM-substrates (left column) and Au-substrates (right column). Evaporation rates and the deposition time for each row are indicated. The nominal thickness of all films is about 100 nm.
The film roughness calculated on the basis of the AFM is plotted in Fig. 8.6 versus the deposition rate. In agreement with our finding discussed above that on a SAM-substrate compared to an Au-substrate a larger maximum island density is reached during the initial deposition stage, all films on the SAM-substrates shown in Fig. 8.5 exhibit a smaller grain size and accordingly also a smaller roughness than their counterparts on the Au-substrates. The evaporation rate itself greatly affects the film morphology for both types of substrates. With increasing evaporation rate, the grain size decreases and the film becomes smoother. However, at a deposition rate above about 1 nm/s, the dependence of film roughness on deposition rate as well as substrate type becomes weak.

Another important feature seen from Fig. 8.5 is that most crystal grains in the film deposited on the SAM-substrate show a flat top facet, in contrast to the films directly grown on gold films. This feature is seen more clearly when the scanning sizes are smaller (see Fig. 8.7) This observation implies that the perylene films deposited on the SAM possess a better ordering of grain orientation. X-ray diffraction measurements confirm this conclusion. Fig. 8.8 shows the $\theta - 2\theta$ diffraction pattern of a pair of samples, which both were 100 nm thick and which both were prepared with an evaporation rate of 0.11 nm/s. Only three peaks are observed, the (001) and (002) peaks of $\alpha$-perylene and the (111) peak of Au. To obtain a clear comparison, we normalize all peak intensities to the Au(111) peak.

![Figure 8.6: Dependence of film roughness on the deposition rate. Typical morphologies of the associated samples are shown in Fig. 8.5](image-url)
thickness of the perylene films and the underlaying Au films are the same for both samples, the higher intensities of the perylene (001) peaks suggest a better c-axis texture. The corresponding rocking curves of the perylene (001) peaks are shown in the inset of Fig. 5. As is expected, the full width at half maximum (FWHM) is much smaller for the perylene films grown on the SAM-substrate. The introduction of the 1-Octadecanethiol monolayer thus introduces a stronger c-axis orientation. A c-axis orientation means that the perylene molecules prefer to stand upright on the molecular monolayer [324]. The formation of c-axis texture in perylene thin films can be understood on the basis of our observations in single crystal growth of perylene by the temperature-gradient sublimation method. Single crystals of perylene fabricated in this way are always thin platelets, with the c-axis perpendicular to the platelet surface. It can thus be assumed that the dense packed (001) surface is the surface of lowest surface free energy. This argument is supported by a recent theoretical study [325]. Thus in thin film growth, there is an energetic driving force, which tends to push the average grain orientation towards a c-axis texture.

The different degrees of perfection of the c-axis texture in the thin films grown on the Au- and the SAM-substrate point to a second factor, which determines texture formation. Evidently, this second factor must be related to the substrate. It is the interaction of the deposited molecules with the substrate in the nucleation phase. Let us assume two different scenarios. First, a situation of weak molecule-substrate interaction (which is equivalent to a high interface energy), imposing no specific constraints on molecule orientation during nucleation. In such a case the nucleating crystal grains will right from the beginning possess the molecule orientation minimizing their surface energy and thus develop a perfect texture. Second, let us consider a situation of strong molecule-substrate interaction (corresponding to a small interface energy). This strong interaction may easily imply a specific orientation of the molecules with respect to the substrate in the nucleation
8.6 Summary

In summary, AFM and x-ray diffraction were used to show that an additional self-assembled monolayer of 1-Octadecanethiol molecules on an Au-substrate greatly
modifies the properties of the subsequently vacuum deposited perylene films. The grain size becomes smaller and a strong c-axis texture is introduced. Both factors tend to reduce the roughness of the perylene films. These effects are attributed to the changes in the perylene molecule-substrate interaction by the additional self-assembled monolayer. It appears very desirable to extend this investigation to other SAMs and organic molecules. Such a systematic study might reveal general trends that would enable a structure and hence also property tailoring for organic films.
Chapter 9

Asymmetric Growth of perylene Crystal on Oil Films

In contrast to the metal atoms, an organic molecule can no longer be considered as a rigid ball or even as a zero-dimensional object. Additional parameters such as the molecular orientation are needed to completely define the structure of an organic crystal. Additionally, the van de Waals nature of the intermolecular interaction and thus the requirement of close packing usually results in a low-symmetry crystal structure. This complicates the description of the nucleation and growth processes in organic films. In this chapter, it is illustrated that an asymmetric growth behavior arises from the unidirectional growth kinetics along the crystallographic $<100>$ axis which has a steric origin.

9.1 Crystal Structure of $\alpha$-perylene

Perylene is chosen to be the study object for two reasons. First perylene and its numerous derivatives are important organic semiconductors with extensive applications. Secondly perylene can be taken as a prototype of polycyclic aromatic hydrocarbons due to its relatively regular molecular shape.

Perylene is a planar, aromatic hydrocarbon ($C_{20}H_{12}$) consisting of five benzo rings. Fig. 9.1 (a) shows the molecular structure.

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<th>a</th>
<th>b</th>
<th>c</th>
<th>$\beta$</th>
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<td>10.31</td>
<td>100.8°</td>
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<tr>
<td>Camerman</td>
<td>11.27</td>
<td>10.82</td>
<td>10.26</td>
<td>100.55°</td>
</tr>
</tbody>
</table>
Chapter 9. Asymmetric Growth of Perylene Crystal on Oil Films

Figure 9.1: (a) The molecular structure of perylene. The long axis of the molecule is indicated. (b) Crystal structure of $\alpha$-perylene: end view of perylene molecules projected onto (001). (c)-(e) Crystal structure of $\alpha$-perylene: side view along [010] direction, [100] direction, and [110] direction respectively.
Table 9.2: Molecular orientation in α-perylene. This table gives the angles in degree between two axes. L, M, N are the long axis, the short axis, and the normal of the molecule respectively. a, b, c’ are the crystallographical axes. Note that c’ is taken perpendicular both to a and to b.

<table>
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<tr>
<th></th>
<th>a</th>
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<td>89.2</td>
<td>6.8</td>
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<td></td>
<td>55.4</td>
<td>35.0</td>
<td>94.5</td>
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<tr>
<td></td>
<td>144.5</td>
<td>55.0</td>
<td>84.9</td>
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<tr>
<td>Camerman</td>
<td>82.9</td>
<td>89.6</td>
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<td>55.9</td>
<td>34.5</td>
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<tr>
<td></td>
<td>144.8</td>
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Perylene presents two forms of crystal structure, the α phase and the β phase. Both phases have a monoclinic structure, but α-perylene shows a dimeric structure while β-perylene is monomeric. Since under the preparation condition in the present work, perylene always crystallizes as α-perylene, here only the crystal structure of α-perylene is specified in details. The crystal structure of α-perylene was first measured by Donaldson et.al. [324] and refined later by Camerman and Trotter [327]. α-perylene is a centrosymmetric crystal and shows a P2_1/a (or C_{2h}) symmetry. That means that the crystal has a screw axis (2_1) parallel to b and a glide plane (/a) parallel (010). The glide plane intersects the b axis at (0,1/4, 0). There are four perylene molecules in one unit cell. The four molecules in the unit are grouped into two pairs and in each pair, the two molecules are centrosymmetrically related. A projection of the structure on (001), showing an end-on view of the molecules, is depicted schematically in Fig. 9.1(c). The unit parameters are listed in Tab. 9.1 in the unit of Å.

For organic crystals built by molecules with non-zero dimension, besides the unit parameters, additional information about the molecular location and orientation in the unit cell is necessary to give a complete description of the structure. This is distinctively different from metal crystals, where the metal atom may be considered as a zero-dimensional dot. Tab. 9.2 gives the angles defining the molecular orientation in α-perylene. The orientation of the molecules long axis and the crystallographic c-axis with respect to the crystallographic axes [100]/[T00], [010]/[0T0], and [1T0]/[1T0] are calculated based on ref. [324] and schematically depicted in Fig. 9.1(c)-(e). Both axes are taken as vectors pointing from the oil-vacuum interface to the interior of the oil film for the reason I will explain later. A conspicuous feature is that, both axes are accordingly inclined close to [100]-, [1T0]-, and [110]-directions and correspondingly tilted away from their opposite
directions. On the contrary, these two vectors are almost unbiased between the [010]- and [001]-directions. One will see that this feature is the structural origin of asymmetric growth along $a$-axis described in Sec. 9.4.

9.2 Experimental Methods

The growth behavior of perylene crystals on a liquid film is investigated using an elaborately designed set-up, which is schematically depicted in Fig. 9.2 [328]. A small vacuum system with a base pressure of $1 \times 10^{-7}$ mbar is equipped with a shutter controlled evaporator and a packaged transparent polycarbonate window. A silicone oil (pentaphenyltrimethyltrisiloxane) film with a vapor pressure below $10^{-10}$ mbar was spin-coated onto the polycarbonate window and serves as the substrate. The average thickness of the oil film was determined by weighting with a microbal-
Evolution of the Growth Shape with Supersaturation

Evolution of the Growth Shape with Supersaturation

In contrast to the usual crystal growth method by cooling the saturated solution, in this work the required supersaturation is obtained by evaporating perylene molecules onto the oil films in vacuum. One advantage of the present method is that the supersaturation can be tuned over a wide range by changing the evaporation rate and deposition time. This allows us to investigate the evolution of the crystals interface with supersaturation in detail. Fig. 9.3 shows a panorama of growth shapes of perylene crystals with increasing supersaturation. For all pictures, the evaporation rate is kept constant at 68 ± 5 Å per second, and the oil film thickness is 20 µm. The shutter opening time varies from 5 seconds to 40 seconds. The solubility limit \( c_0 \) of perylene in silicon oil was measured to be 0.5 ± 0.05% in volume. The normalized perylene concentration in the oil film \( \sigma = c/c_0 \) is calculated on the basis of the deposited amount of perylene and the known \( c_0 \) and is specified for subsequently discussed experiments. At low supersaturation, thin square crystals are observed (Fig. 9.3(a)). With increasing supersaturation, the straight growth front becomes unstable, and skeleton and needle-like crystals develop subsequently. The transition mechanism will be discussed below. When a large supersaturation is reached by further increasing the shutter opening time, nucleation becomes an easy event and is not limited at the corners any more. At this time, the growth behavior is closer to normal growth. The growth is dominated by diffusion. In this case, dendrites are formed due to the interplay of the diffusion
Figure 9.3: Growth shapes resulting after a short deposition interval (5s to 30s) with the deposition rate of 68 Å/s. The normalized perylene concentration in the 20 µ thick oil films is (a) $\sigma = 0.34$, (b) $\sigma = 0.54$, (c) $\sigma = 0.82$ (d) $\sigma = 1.16$, (e) $\sigma = 2.04$, and (f) $\sigma = 2.72$
field and the crystal anisotropy, as is discussed in Section 7.3.

It has been noticed that the nucleation of perylene crystal actually occurs at under-saturation, i.e., $\sigma < 1$. Crystal nucleation and growth were even observed at $\sigma = 0.34$ (Fig. 9.3(a)). Hereby the diffusion of perylene molecule in silicon oil is deduced to be difficult and thus the molecule concentration at the oil surface considerably exceeds the average one. This is consistent with the microscopic observation that nucleation takes invariably place at or near the oil-vacuum interface.

The transformation from square crystal to skeleton can be understood in the following way. At low supersaturation, the nucleation rate is low. The nuclei are preferentially formed at the corners of a square crystal for two reasons: 1) the nucleation barrier is lower at the corner than that on the flat face [330]. 2) the gradient of concentration is larger around the corners. Therefore, the crystals proceed a layerwise growth (see Section 7.2.3). Under the condition that crystal size is small and/or supersaturation is low so that the nucleation rate at crystal corners is smaller than $L/2V$, a new nucleus is not formed at the corners before the previous layerwise growth launched there is completed. Here $L$ denotes the crystal size and $V$ the layerwise growth speed. In this case the crystals keep the square shape. If the nucleation rate is greater than $L/2V$, one will see an opposite situation. A new layer will start to grow before the previous layer is completed. In this case, the crystal shape gradually changes into skeleton, as is schematically illustrated in Fig. 9.4. From this simplified model, one can see that there exists a crystal size at a given supersaturation above which the square crystal changes into a skeleton.
The critical size is dependent upon supersaturation. The smaller the supersaturation is, the larger the size of crystal which can remain the square shape. Fig. 9.4(b) and (c) show several square crystal, whose sizes are much larger than those of the skeletons in Fig. 9.3(b). These crystals result from two depositions with a time interval of three hours. For both depositions, the evaporation rate was about 2.3 Å/s. The deposition times are 240s for the first deposition and 120s for the second deposition. Using such a low deposition rate allows more molecules to diffuse into the oil bulk and thus decreases the vertical concentration gradient. Therefore, the concentration at the oil surface, where the nucleation and growth take place, is low. This observation indicates that the nucleation rate increases faster with the supersaturation than the step growth velocity.

With a further increase in supersaturation, the destabilized faceted crystals will at last evolve into dendrites (Fig. 9.3 (e) and (f)). However between skeleton and dendrite, there exists another crystal shape, i.e., needle crystal (Fig. 9.3 (d)). These needles grow at a constant velocity (steady-state growth) without launching of side-branches. That is to say, there are different critical supersaturations for the formation of needle crystals and dendrites.

Fig. 9.3 (c) describes an intermediate situation between needle crystal and skeleton. A striking finding is that the short needles are all formed by growth along only one of the four corners. In other words, the growth is asymmetric. This is the topic of the coming section.

9.4 Asymmetric Growth along [100] Direction

The asymmetric growth of perylene crystals on the oil film can also be derived from other observations. As is addressed above, within a proper range of supersaturation, the crystal growth is governed by the steady-state needle-shaped growth (Fig. 9.3(d)). The growth velocity is a well-defined parameter. Measuring the distribution of the growth velocity provides a useful method to investigate the growth anisotropy. Fig. 9.5(b) shows a typical result of such a measurement. The optical microscope image of the measured needles is presented in Fig. 9.5(a). These needle-crystals result from 20 seconds of deposition at an evaporation rate of 68 Å/s on a 20 µm oil film (σ = 1.36).

Important conclusions can be drawn from the measurements. In the first place, according to their growth speeds, the needles fall into three groups: a) needles A, B, C, D, and E, which have a common fast growth velocity around 3.90 µm/s; b) needles F, G, H, and I, whose growth speeds (1.67 µm/s in average) are notably smaller than the first group but discernably larger than that of needles J and K; c) the slowest growing needles J and K, which show a velocity of 1.45 µm/s.
Figure 9.5: (a) Optical microscopic image ($800\mu m \times 600\mu m$) of needles which grow in steady-state. (b) The growth velocity of the needles specified in (a).
Chapter 9. Asymmetric Growth of Perylene Crystal on Oil Films

Table 9.3: Growth speeds of needle-crystals

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Fast growth speed ($\mu m/s$)</th>
<th>Slow growth speed ($\mu m/s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.09 ± 0.01</td>
<td>0.75 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1.904 ± 0.008</td>
<td>0.84 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2.059 ± 0.005</td>
<td>0.7 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>2.059 ± 0.007</td>
<td>0.691 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>1.883 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.56 ± 0.01</td>
<td>1.14 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2.52 ± 0.01</td>
<td>1.11 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2.58 ± 0.01</td>
<td>1.18 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2.58 ± 0.02</td>
<td>1.18 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.164 ± 0.004</td>
</tr>
<tr>
<td>C</td>
<td>2.67 ± 0.03</td>
<td>1.23 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2.67 ± 0.03</td>
<td>1.19 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2.71 ± 0.03</td>
<td>0.93 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>2.69 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>3.95 ± 0.03</td>
<td>1.73 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>3.97 ± 0.01</td>
<td>1.65 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>3.91 ± 0.03</td>
<td>1.62 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>3.83 ± 0.03</td>
<td>1.66 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>3.83 ± 0.01</td>
<td>1.45 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.44 ± 0.02</td>
</tr>
</tbody>
</table>

Secondly, the needles originating from the same crystal and growing towards the same direction (A and C, E and B) show the same growth speed, while the needles belonging to the same crystal but growing towards the opposite direction (A and C versus K) demonstrate the largest and smallest growth speed respectively. These observations are quite reproducible and point directly to an unidirectional anisotropy in growth. The velocity ratios of the fastest growing needle to both the slowest growing needle and those with mediate growth speed are found insensitive to the deposition time, i.e., the supersaturation. These ratios are summarized in Tab. 9.3 and Fig. 9.8.

After the fact has been solidly established that two kind of needle-crystal growth speeds coexist at a given supersaturation, now the question is what we can learn from this finding. As has been addressed in Sec. 7.3.3, the diffusion equation and the continuity condition can only give the product of the growth velocity and the curvature radius, even if the crystal anisotropy and the surface tension are taken into account. The principle of velocity selection for needle crystal had been a perplex-
ASYMMETRIC GROWTH ALONG [100] DIRECTION

ing problem until the marginal-stability hypothesis was proposed [294]. However the marginal-stability hypothesis is a hypothesis without proof, so it still leave us room to ask if the observed coexisting multiple growth velocities is an exception to it. On the other hand, the crystal structure is actually rather complicated as we have seen in Sec. 9.1. Therefore, the multiple growth velocity is likely to have an origin associated with the crystal anisotropy. To confirm or refuse the crystal anisotropy mechanism, the crystal growth behavior of perylene has been investigated in a different way. In this experiment, the evaporation rate is reduced to a quite small value (1.8 ± 0.2 Å/s), and the shutter is always open. Therefore, the supersaturation increases slowly and steadily with time. Imaging during deposition allows us to follow the shape evolution of a single perylene crystal as function of supersaturation, and the large crystal size enables us to label the images with crystallographic indices using x-ray micro-diffraction technology. An example for such a growth sequence gives Fig. 9.6. Shortly after nucleation a nearly square shaped crystal starts to develop concave sides (σ = 0.56, Fig. 9.6(a)). The shape quickly destabilizes by preferential growth into the [100]-direction [329] (σ = 0.79, Fig. 9.6(b)) and rampant needle growth follows (Figs. 9.6(c) and (d)). After a significant increase of σ the primary needle destabilizes and the formation of secondary dendrite tips growing into the [010]- and [0¯10]-directions is initiated (Fig. 9.6(e), σ = 1.23). Soon after the onset of secondary dendrite tip growth, tertiary dendrite tips shoot out from these secondary dendrites (Fig. 9.6(f)). The tertiary dendrites emerging into the [100]-direction - growing back to the initial nuclei - grow much faster than the primary dendrite and the tertiary ones growing into the [100]-direction (compare Fig. 9.6(f), (g), (h) and (i)). The growth speeds into the specified directions have been measured simultaneously for a time interval of 60s. Within such a short time, the perylene concentration is nearly constant (σ ≈ 1.3) and thus the grown length should be a linear function of time, as indeed observed in Fig. 9.7(b). Again we obtain three different velocities: 3.5 ± 0.01 μm/s for the first [T00] tertiary-dendrite, 2.39 ± 0.02 μm/s and 2.37 ± 0.01 μm/s for the two first secondary-dendrites growing into [010] and [0T0] respectively, and 2.15 ± 0.01 μm/s for the [100] primary dendrite. However the velocity ratios of $v_{[T00]}/v_{[100]} = 1.63$ and $v_{[T00]}/v_{[010]} = 1.47$ are small compared to what we got for the needle crystals in the first type of experiments.

Similar experiments have been repeated several times with slightly changed evaporation rates. We have always observed the same asymmetric growth with velocity ratios around 1.7. X-ray micro-diffraction measurements reveal that the split of growth velocity takes place along the <100> direction. Here we define the direction along which the backbones grow as the [100] direction, then [T00] denotes the growth direction of the fast 2nd-order side-branch. We will use this definition in the remaining part of this chapter and in the next chapter.
Figure 9.6: Evolution of perylene crystal growth shapes under continuous deposition with a rate of $1.8 \pm 0.2 \AA/s$. The normalized perylene concentrations in the oil film of 28 $\mu m$ thickness are (a) $\sigma = 0.56$, (b) $\sigma = 0.79$, (c) $\sigma = 1.04$ (d) $\sigma = 1.10$, (e) $\sigma = 1.23$, (f) $\sigma = 1.27$, (g) $\sigma = 1.30$, (h) $\sigma = 1.34$ and (i) $\sigma = 1.39$. The [100]-orientation is indicated in (e). The image sizes are $85\mu m \times 65\mu m$ for (a) and (b), $340\mu m \times 260\mu m$ for (c) and (d), and $680\mu m \times 520\mu m$ for the others.
**Figure 9.7:** Measurement of the lengths as a function of time of (a) the backbone within the whole growth duration. (b) the backbone and the side-branches in a short time interval.

**Figure 9.8:** The ratio of the growth velocity for the coexisting needle-crystals. The open data are measured from experiments with small deposition rate and long deposition time such as that shown in Fig. 9.6, while the solid data points are obtained from experiments with large deposition rate and short deposition time as shown in Fig. 9.5.
It is reasonable to assume that the velocity split along \(<100>\) crystallographic axis observed at slow continuous deposition and the coexistence of multiple needle growth velocities observed after short-time exposure to large flux actually reflect the same physical phenomenon: asymmetric growth properties along \(<100>\) direction. The difference in the velocity ratio can be explained by the difference in the diffusion field between these two cases. In the later case, the concentrations at the growth fronts are the same for all the needle since the nuclei are almost simultaneously formed shortly after the exposure and the needles are sufficiently far apart enough away during growth. However, in the former case, the situation is different. Before the fast growing side-branch is launched, the crystal has existed for long time (around 1000s) and thus an equilibrium diffusion field has been established. That is to say, the concentration in the area surrounding the backbone (the primary dendrite) is lower than that far away from it. The situation we have observed is that the fast growing tertiary dendrites grow into the area near the backbone, while the backbone and the secondary dendrites all grow into the "fresh" area. Thus it is easy to understand why the velocity ratio is lower in the former case. The growth envelope also contributes to lowering the velocity ratio in the case of continuous deposition. Langer discussed this effect in his review article [286]. Therefore, it is more appropriate to take the ratios of the growth speed of the needles to characterize the growth anisotropy (Fig. 9.8).

It is unusual that the growth velocities are distinctively different between the two opposite directions of the same crystallographic axis of a crystal with centrosymmetry. The most plausible mechanism will be discussed in the next section.

9.5 Discussion

In a homogeneous environment for a crystal with an inversion center – like \(\alpha\)-perylene – facets with normal vectors in opposing directions should be equivalent with identical growth speeds. Therefore, the observed unidirectional growth behaviors should result from the anisotropic growth environment. In our experiment, the existence of the oil surface, which acts as a confining boundary for the growth, breaks the center-inversion symmetry of the growth environment and thus the crystal growth itself. This point can be more clearly seen by analyzing the steric properties of the steps and kinks with different orientations (see Fig. 9.9). As mentioned above, nucleations always take place at the oil surface due to the existence of the concentration gradient along the oil film normal. On the other hand, crystal growth only progresses at one side of the oil surface (in the oil film). These two factors determine that only appear the steps and kinks depicted in Fig. 9.9). Their reverse counterparts can not exist. This is the reason why we draw the crystallographic
**Figure 9.9:** Schematic illustration of the different steric situation between the steps and kinks moving towards the two opposing directions of ⟨100⟩.

The c-axis and the molecular long axis as vectors. As a result, the steps propagating towards [010](α) show different steric properties, for example, different angles of the c-axis and molecular long axis with respect to the terraces and the propagation direction, from those propagating towards [100](α). Similar situation is found for the kinks moving towards these opposing direction (B and B'). These differences in the steric properties of the steps and kinks result in an asymmetric kinetic coefficient along ⟨100⟩ direction.

In the experiment employing continuous deposition, the initial square crystal are always destabilized at the [100] corner by preferential growth into [100] direction—the slowest growing direction. This finding indicates that the steric properties have a different effect on growth and nucleation. As we know, the stable growth of the faceted square crystal is dominated by the nucleation of steps. The preferred nucleation sites are the corners because of the smaller nucleation barrier [330] and the larger concentration gradient. Let \( \tau_N \) being the average time interval for nucleation events at a corner and \( v_S \) being the step propagation velocity. The destabilization condition is given by \( \tau_N < l/v_S \), where \( l \) is the size of the facet. For the reason of simplicity, here we assume nucleation only happens at the corner in consideration. Therefore, we can deduced from the destabilization behavior that, the step propagation velocities towards [110] and [100] are larger than the others, but the nucleation rate at the [100] corner is even much larger than that at other corners, resulting in the smallest \( \tau_N v_S / l \) for the [100] corner.

At last, I would like to point out that, all the conditions leading to the asymmetric kinetic coefficient persist when α-perylene is deposited on a solid substrate.
The only difference is that the substrate surface replaces the oil surface as confining growth boundary. Therefore, it can be predicted that the mechanisms leading to the asymmetric growth behavior discussed in this thesis also apply to organic film deposition on solid substrates. To confirm it, a dynamic scanning probe microscopic study is favored.
Chapter 10

Deformation of Perylene Crystals on Oil Film upon Growth

During the investigation of the growth behavior of perylene crystals on oil film, interesting regular deformations have been observed upon growth under particular conditions. In this chapter, I will illustrate these deformations and explore the underlying mechanisms responsible for their formation.

10.1 In-plane Deformation in Dendritic Growth

In the last chapter, the asymmetric growth behavior has been discussed. The author ascribes the asymmetry to the confinement of the crystal growth to the oil surface and the resultant discrepancy in steric situation between the steps and kinks propagating towards the opposing directions. Associated with this growth asymmetry, a special crystal deformation was observed, as is shown in Fig. 10.1(a). The image was recorded 6 minutes after the shutter was opened in a continuous deposition experiment. The deposition rate was chosen to be 4.4 Å/s. One finds that, the secondary dendrites, from both side of whom the tertiary dendrites are initiated and grow in the opposing directions ([100] and [T00]), are curved with a deviation for the [100] direction. However for the primary dendrite and the tertiary dendrites, trajectories of the growth tips are straight lines throughout the whole growth procedure.

To explore the mechanisms leading to the curved dendrite shape, at first one needs to know whether the curved shape is a growth shape resulting from the inhomogeneous diffusion field or if it is stress-induced deformation. In the first case, the molecule orientation and the crystal orientation should be identical for any part of the dendrite. However if a stress-induced deformation happens, the above orientation will change with the deformation. Thus a polarizing microscope image
Figure 10.1: (a) The [010] and [0\overline{1}0] secondary dendrites are symmetrically curved and deflected to the primary dendrite growth direction. (b) The polarizing microscopic image of the curved dendrite shows a brightness contrast with the deflection, indicating that the deflection results from deformation. To clearly demonstrate the contrast, the negative of the original image is shown here.
IN-PLANE DEFORMATION IN DENDRITIC GROWTH

will easily distinguish these two cases. Indeed, a clear color contrast was observed along the curved secondary dendrite. Fig. 10.1(b) shows a typical picture of a curved perylene dendrite under polarized microscope. The picture was recorded after 15 minutes of continuous deposition at a rate of 1.8 Å/s. Based on this polarizing microscope image, it can be concluded that the curved shape has an stress associated origin.

Now the question is, where does the stress come from? Obviously the stress arises from the asymmetric growth between the [100] and [\overline{1}00] directions. Therefore the first picture which came across the author’s mind is that the impulses exerted on the crystal by the impingement of the molecules do not counteract and result in a net force on the secondary dendrites and thus the deformation. The asymmetric growth means a difference in the amount of molecules impinged from the two sides of the secondary dendrites. Consequently a difference in pressure appears between the two opposite sides of the secondary dendrites and forces the secondary dendrite to deflect towards slow-growth direction as we really observed. However a simple estimation to the order of the magnitude of this pressure can rule out this mechanism. For the reason of simplicity, we just take a cuboid perylene crystal for the calculation. The growth rate of a couple of opposite faces are taken to be 4 and 1.4μm/s, the typical values in our experiments. We treat this problem as a inelastic collision between the moving molecule and the immobile crystal. The kinetic energy of the molecules before the engagement is estimated from the data of the enthalpy of sublimation of α-perylene, which is $\Delta H = 139$ kJ/mol [331].

Therefore the pressure difference induced by the asymmetric growth is given by $P = \frac{\Delta R \sqrt{2M \Delta H}}{\Omega}$, where $\Delta R$ is the difference in growth rates between the opposingly growing dendrites, and $M$ and $\Omega$ are the mass and average volume in crystal of one perylene molecule respectively. In this way the net pressure is estimated to be around 3.5 Pa.

In the next step, we will assess whether this pressure can explain the observed deformation. As a starting point, we assume that the deformation is an elastic one though we actually do not know whether it is elastic or plastic. To estimate the Young’s modulus $E$, we directly apply the elastic curve formula of a beam shown in Fig.10.2 to the deflection of the secondary dendrites [332]. The elastic curve of the beam is given by

$$v = \frac{P_0}{24EI} (x^4 - 4L^3x + 3L^4) + \frac{h^2 P_0}{10EI} (x^2 - 2Lx + L^2),$$  \hspace{1cm} (10.1)

where $I$ is the moment of inertia of the section of the beam and $EI$ is called flexural rigidity. The deflection of the free end is

$$\delta = \frac{P_0 L^4}{8EI} \left[1 + \frac{4}{5} \left(\frac{h}{L}\right)^2\right].$$  \hspace{1cm} (10.2)
Let’s take the first appearing secondary dendrite shown in Fig. 10.1(a) as an example to calculate $E$. The section of the dendrite is approximately treated as a rectangle with a dimension of $10 \mu m \times 20 \mu m$. The later is the width of the dendrite. Additionally we have $L = 350 \mu m$, $\delta = 115 \mu m$, and $P_0 = 3.5 Pa \times 10^{-6} Pa \times 10^{-6} m = 35 Pa \mu m$. The moment of inertia of the section $I$ is calculated to be $2.7 \times 10^{-20} m^4$. Using Eq. 10.2, $E$ is hereby calculated to be $2.1 \times 10^4 Pa$. This is an unrealistic small value. The elastic constants of molecular crystals usually have an order of magnitude of GPa [333, 334]. In other words, the effect of unbalanced molecular impingements is too small to produce the deflection.

After excluding the unbalanced impingement mechanism, it is tempting to examine the role the oil film can play. While the tertiary dendrites grow into the perylene-oil solution, the crystal occupies the volume which was originally occupied by the solution. Therefore during the growth the solution is extruded out by the crystal. The growth induced motion of the oil is actually observed in our recorded videos. Considering the used silicone oil is rather viscous, the internal friction will result in a counteracting force on the growing crystal. Theoretical calculation of this effect is quite complicated. I have not found any published results in fluid dynamics which can be applied to the present problem. Therefore here I just give a qualitative analysis to show this effect should be much larger than the impingement effect, which has been discussed above. As we have observed in the experiments, the tertiary dendrites are initiated within a short time interval. Since their birth on, they grow steadily with constant rate. Because of the incompressibility and the large viscosity of the oil film, accompanied with the forward motion of the growth tips of the tertiary dendrites, a velocity field is established in the oil film in front of the growth front. The size of the oil film showing a velocity vector with a component parallel to the dendrites growing direction is dramatically larger compared with that of the crystal. Therefore it can be deduced that, upon the launch of the tertiary dendrites, the secondary dendrites experience a large pressure. In this scenario the deflection is produced by such a short-time pressure. Similar to the discussed impingement mechanism, the pressure increases with the growth rates.
of the tertiary dendrites. The instantaneous pressure is also unbalanced because of the difference in growth rates between the opposingly growing dendrites. The resultant deformation is stabilized subsequently by the formation of dislocations. That is to say, in this picture the deflection is a plastic deformation.

At last, I like to point out that there could be an interaction between the parallel-aligned tertiary dendrites, which has a van der Waals origin. However according to the theoretical results given by Isroaelachvili [335], the van der Waals interaction between two identical surface across any medium is always attractive. The attractive force between the tertiary dendrites will result in an opposite deflection to the observed. Therefore this mechanism can be excluded from our considerations.

10.2 Buckling Morphology in Faceted Crystal Growth

Besides the in-plane deflection for the dendrite growth, another kind of deformation— a buckling pattern— has been observed for square crystals grown at low supersaturation. In this section, all the experimental observations associated with the buckling pattern will be first illustrated, followed by a brief discussion on the mechanisms of the pattern formation.

10.2.1 Observations

As is discussed in Chap. 9, the perylene crystal usually presents a flat square shape with smooth edges at low supersaturation. At very low supersaturation such square crystals can be classified into two groups, the big one and the small one (Fig. 10.3). The big crystals look brighter under the optical microscopy and they grow much faster than the small ones. The small square crystals show dark edges, which indicates that the small crystals are much thicker than the big crystals. The thicknesses of the crystals are determined during nucleation and keep constant in the subsequent growth stage. We do not understand why there exist two types of crystals. However here we will put aside the small crystals and focus on the big, thin, bright crystals. Only for the latter, buckling patterns have been observed under several circumstances.

As the first example, the buckling patterns is developed upon the consecutive growth of a ready-grown square crystal when the supersaturation is increased promptly by a subsequent evaporation. Fig. 10.4 illustrates a typical observation. In this experiment, perylene was first evaporated at a rate of 1.7 Å/s onto a 30 µm thick silicone oil film for 330 s. A thin square crystal gradually grew after the evaporation. 3 hours later, the growth of the crystals was found finished, then the second evaporation was made at the same rate for 120 s. From this time on, the crystal started to grow into a buckling patterns. The buckling amplitude at
the growth front diminished with time and finally a flat and smooth growth front was restored (Fig. 10.4(e)). The formed buckling patterns also relaxed with time. At last no trace of the buckling growth is left (Fig. 10.4(g)). The buckling growth patterns recurred after a new evaporation (the third) was added 2 hours after the second evaporation (Fig. 10.4(h)). In the third evaporation, the same evaporation rate and time are employed as in the second evaporation.

In order to characterize the geometry of the patterns, observations were also made upon shifting the crystal around the focal plane of the microscopy. When the crystal was moved slightly away from the focal plane, a stamp-like image was observed (Fig. 10.4(a)). The position of the bright round teeth of the ”stamp” changed with respect to the initial indentation position when the crystal was moved from one side of the focal plane to the other side. When the crystal was just at the focal plane, smooth edges were observed (Fig. 10.4(b)). Crystals with such buckling patterns have also been taken out of the chamber so that the other side of the crystal can also be observed. Buckling patterns have been observed for both sides of the crystal. By comparing the pictures for different sides of the same buckled crystal, we can conclude that the pattern does not come from thickness fluctuations, since the protruding area of the pattern on one side happens to be the depressed area on the other side. We can thus conclude that the thickness of the thin crystal keeps almost constant.
Figure 10.4: The development and relaxation of the buckling pattern. The times counted from the second deposition are labelled on the right top of the picture. See text for details. All pictures have a size of $420 \mu m \times 420 \mu m$. 
It is important to point out that only the part of the crystal grown after a new evaporation is buckled. The part of crystal grown before remains flat all the time so that a clear boundary exists, which separates the before-grown part from the after-grown part (see, for example, Fig. 10.4(d)). This observation reveals that the formation of the buckling patterns is tightly correlated with the growth procedure. This is to say, they are growth-mediated patterns rather than shear stress-induced elastic or plastic deformations.

As mentioned above, the buckling part can be relaxed into a flat plane by plastic deformation. However, if the crystal is big and the buckling amplitude is large, the relaxation is a very slow process. In this case we have the chance to observe the metastability of the buckling patterns. Fig. 10.5 shows how the buckled part of the crystal redissolved. Obviously the redissolved molecules ultimately crystallized into other crystals. One find that the before-grown unbuckled part was not involved in the re-dissolution so that its straight edge kept intact during the re-dissolution process. This means the chemical potential of the molecules in the buckled region is higher than that in unbuckled region.

The buckling patterns can be formed by very small continuous deposition. The sequential images in Fig. 10.6 show how the crystal shape evolves from a small square to a corrugated four-corner star and how the buckling pattern appears accompanying this evolution. Here a very small deposition rate (0.18 Å/s) is used and the deposition is always on during the observation period. The buckling pattern is observed when the initial straight edges are inwardly curved upon growth. Furthermore, the buckling pattern is only located at the middle of the edges. This finding is quite important because it allows us to derive an argument about the formation mechanism of the buckling patterns. The buckling pattern at last either evolves into a big corrugation or vanish by plastic relaxation.

There is another observed phenomenon, which is considered to be related to the buckling patterns described above. In the previous chapter, we have discussed that under certain supersaturation, perylene crystals growth on the silicone oil film is governed by a steady-state growth with a needle shape. The needles fall into two groups according to their growth rates. The ratio of the growth rate of the fast to the slow is around 2.2. The difference in growth rate has been explained to arise from an anisotropic kinetic coefficient, which has a steric origin. Associated with the different growth rate, a morphological difference of the growth tip between the slow-growing needle and the fast-growing needle has also been observed, which is shown in Fig. 10.7(a) and (b) respectively. The growth tip of the fast-growing needle presents regular corrugations, while that of the slow-growing needle is relatively flat. That is to say, the corrugated tip morphology is related to a fast growth speed. Recalling that the buckling patterns are formed soon after a new evaporation for square crystals and considering that a new evaporation means a sudden increase
Figure 10.5: The metastability of the buckled crystal is shown by the transfer of the molecules from the buckled part to the unbuckled crystals, which results in the redissolution of the buckled part.
Figure 10.6: Buckling pattern appears only at the middle of the crystal edges when the crystal shape is changed from square into four-corner star under continuous small deposition.
in supersaturation and thus a rapid increase in growth rate, it is reasonable to think the corrugation present by the fast-growing tip of the needle crystals has the same origin as the buckling patterns shown by the square crystals.

To precisely explore the forming mechanism of the buckling pattern is difficult only with optical microscopy observation. However I will discuss several possibilities in the coming subsection.

10.2.2 Discussions

It is helpful to take an inspect of the formation mechanisms of buckling patterns reported on the literatures before any argument is made to explain our buckling pattern.

Complex buckling patterns of thin metal films have been observed on compliant substrates. As an example, for gold films deposited from the vapor phase on a thermally expanded polymer, the subsequent cooling of the polymer creates compressive stress in the metal film. The stress is ultimately relieved by buckling the film, resulting in regular patterns, which are shown in Fig. 10.8 [336]. During the buckling process, the metal films always remain attached to the polymer layer. The ordered patterns can be regulated by patterning the polymer surface with ordered structures. The buckling kinetics of this compressed thin films on viscous substrates have been investigated in detail by Sridhar et al. [337]. In this problem, the stress distribution and viscosity of the compliant substrate play critical roles. The patterns actually arise as stress-induced deformation cooperated by the creeping of the underlying substrate.

Even though our buckled thin perylene crystals are also grown on a viscous soft substrate, the above discussed mechanism does not apply to our case. As we remember, in our case only the newly emerging part of the crystal is buck-

**Figure 10.7**: The microscopic images of the growth tips of needle crystals with (a) fast growth rate and (b) slow growth rate.
CHAPTER 10. DEFORMATION OF PERYLENE CRYSTALS

Figure 10.8: Optical micrographs showing representative patterns that formed when the metals were evaporated onto warm (110°C) polydimethylsiloxane (PDMS), and the sample then cooled to room temperature. (a) Disordered regions covered flat PDMS far from any steps or edges. (b) Micrograph showing the transition from disordered waves to waves ordered by rectangular ridges (100µm wide and 1020µm high; separated by 300µm). (c) A flat, waveless region of gold near an edge in the PDMS gradually became a system of waves ordered by the rectangular ridges (100µm wide and 1020µm high; separated by 800µm). (d) and (e) Flat squares (300µm on each side) and circles (150µm in radius) elevated by 1020µm relative to the surface showed no buckling on the plateaux, but ordered patterns of waves on the recessed regions between them. (f) Rectangular ridges (100µm wide and 1020µm high; separated by 100µm) aligned the waves parallel to the direction of the raised portions of the PDMS. These pictures are representative of the patterns that form over the whole surface area for each sample (up to 25cm²). The PDMS was coated with 5nm of titanium or chromium and 50nm of gold [336].
Figure 10.9: Wrinkle pattern at the surface of single crystal films of polymerized polydiacetylene in epitaxy with their monomer substrate. Polymerization induces a uniaxial stress. The wrinkle pattern serves as experimental evidence for the Grinfeld instability [338].

led (Fig. 10.4), while the old part which has grown before the buckling portion is formed keeps intact. Therefore the buckling pattern can not be explained only as stress-induced elastic or plastic deformation. Its formation is coupled with the crystal growth process. It is likely that this pattern results from a certain kind of growth instability, though it may have a stress origin. In this way, our patterns more resemble wrinkle surface morphology resulted from the Grinfeld instability [339](see Fig. 10.9). The Grinfeld instability arises for stressed heteroepitaxial growth, where the surface is modulated so that the elastic energy is partially relaxed.

It is tempting to seek a similar mechanism to the Grinfeld instability for our buckling patterns shown by the perylene crystals. In the Grinfeld instability, the stress comes from the lattice mismatch between the film and the substrate. Now the question is, where does the stress come from for the perylene crystals growing on the liquid substrate? The experimental observations under small continuous deposition (Fig. 10.6) provides us with an important clue to the answer of this question.

From these observations, at least two facts are well established: 1) the pattern does not appear until the straight edge becomes unstable; 2) the pattern only appears in a very limited zone at the middle of the edge. These two facts strongly imply that the formation of the pattern is associated with the increase in step density. As we have discussed in Sec.9.3, the growth of the square crystals is dominated by the nucleation of the steps. The preferred nucleation sites are the four corners.
When the time interval between two consecutive nucleation events is larger than the time required for the completion of the layer growth, the straight edge becomes unstable. Since the concentration gradient is large around the corner and small at the middle of the edge, the step propagation velocity decreases with its departure from the corners. Therefore once the straight edges destabilize, the steps will accumulate at the middle of the edges. The larger step density at the middle of the crystal edges is reflected by the corresponding larger curvature.

Based on the above discussion, I prefer to think the buckling patterns result from a stress-induced growth instability, similar to the Grinfeld instability, but the stress comes from the step interaction. This step-interaction mechanism seems to explain all the experimental observations. A sudden increase in supersaturation means a prompt increase in step density through two-dimensional nucleation. This explain why the buckling patterns present after the consecutive deposition is added. As a conclusion drawn in the last chapter, a steric condition favorable for step growth is even more favorable for step nucleation. This explains why the growth tip of the fast-growing needles are corrugated. The step-interaction induced growth instability only exist at the growth front, where the steps are located. This explain the metastability of the buckled crystals.

It is well known that the crystal surface layer is naturally in a state of stress. The stress arises from the fact that the equilibrium atomic spacings at, or near the crystal surface are different from what they are in the interior. This phenomenon is referred as “surface misfit”. In the direction normal to the crystal surface, this manifests itself as multilayer relaxation. The relaxed separation of atomic layers often oscillates, but always converges rapidly with the depth to the bulk value. In the direction parallel to the crystal surface the atomic spacings are constrained to the bulk values by the underlying crystal. Consequently no significant lateral relaxation takes place except perhaps in some form of surface reconstruction. The near-surface atomic planes are accordingly in a state of lateral stress.

To illustrate more clearly the surface relaxation and surface stress, I will assume a two-dimensional triangular Bravais lattice with pair interactions between nearest and next nearest neighbors, following Pimpinelli and Villain [41] (Fig. 10.10). The interaction potential is assumed to be the same for the nearest and the next nearest neighbors. If there were no surface, the distance between nearest neighbors should minimize the energy, which is $3N[V'(r)+V(\sqrt{3}r)]$. Therefore, $V'(r)+\sqrt{3}V'(\sqrt{3}r) = 0$. Noticing $V'(r)$ is the force between two atoms at a distance $r$, each atom is subject to a force $f_1$ exerted by each nearest neighbor, and $f_2 = \frac{f_1}{\sqrt{3}}$ exerted by each next neighbor. Clearly, the force $f_1$ is repulsive while $f_2$ is attractive. Now we turn to consider a planar surface. Each surface atom has lost two nearest neighbors and three next nearest neighbors so that it is subject to a force directed towards the outer side, normal to the surface and equal to $\sqrt{3}f_1-2f_2 = -f_2$. 
Figure 10.10: Forces responsible for surface relaxation and surface stress in a twodimensional triangular lattice with pair interaction only between nearest ($f_1$) and next nearest neighbors ($f_2$). The forces equilibrium on a bulk atom A gives $f_1 = \sqrt{3} f_2$. For atoms at a planar surface like atom B, a net force directed toward the outer side and normal to the surface exists, leading to the surface relaxation. At the same time, the net force exerted on a surface atom (like C) by the atoms on the right side of this surface atom is nonzero, indicating the existence of surface stress.

Therefore the surface atoms move out until the force exerting on them vanishes. This is the surface relaxation. On the other hand, there is also a force acting on the two parts of the surface atomic layer on both sides of the plane $x = 0$ (see Fig. 10.10(b)). If the relaxation is neglected, the in-plane component is easily seen to be $(3f_1 - \sqrt{3}f_2)/2$. This means the existence of surface stress.

It should be pointed out that with interactions between nearest neighbor only, there would be no surface relaxation and the surface stress would vanish\(^2\). This means that the long-range interactions play particularly important roles for the occurrence of surface relaxation and surface stress. In molecular crystals, the long-range property of van der Waals force, which binds the molecules together, implies the existence of considerable surface relaxation and surface stress for molecular crystals. To give a convincing explanation for the buckling pattern observed in the growth of perylene crystals, it is crucially important to know the stress field at the growth interface and around a growth step. Only after the stress field is determined, one can analyze the effects of the density of growth step on the crystal growth shape. Therefore a theoretical calculation of these stress field is desirable. However such a calculation is beyond the scope of this dissertation. Therefore the author has to stop the discussion here without a definite conclusion.

\(^2\)Actually, more long-range interactions should be taken into account to give a precise description of surface stress. Only considering the interactions between the nearest and the next nearest neighbors results in a wrong conclusion that stress also exists in the interior part even for free crystals.
Chapter 11

Summary of Part II

In this chapter, the main experimental results and the conclusions drawn from these results are summarized.

1. AFM and x-ray diffraction have been used to investigate the growth behavior of perylene films on a (111)-oriented polycrystalline Au substrate, as well as on the same substrate but additionally coated with a self-assembled monolayer (SAM) of 1-Octadecanethiol molecules. On a bare Au substrate, the density of perylene islands quickly reaches its maximum and then keeps constant until coalescence happens. In contrast, on the SAM-coated substrate, the films show a much larger density of islands, and the density of islands increases monotonically within a much larger time window. An argument is derived from these observations that the perylene molecules have a smaller diffusion coefficient on the SAM than on the Au surface. Our results also show that an additional self-assembled monolayer of 1-Octadecanethiol molecules on an Au-substrate greatly modifies the properties of the subsequently vacuum deposited perylene films. The grain size becomes smaller and a strong c-axis texture is introduced. Both factors tend to reduce the roughness of the perylene films. These effects are attributed to the changes in the perylene molecule-substrate interaction by the additional self-assembled monolayer. It appears very desirable to extend this investigation to other SAMs and organic molecules. Such a systematic study might reveal general trends that would enable a structure and hence also property tailoring for organic films.

2. A break of symmetry has been observed for the growth of perylene crystals on an oil film. The growth speed along the crystallographic [100] axis is found to be dramatically different from that along its opposite [T00]. The
ratio of two growth speed is around 2.3, and does not show an obvious dependence on supersaturation. This asymmetric growth has a steric origin, which is special for organic crystals. An organic molecule, which is the unit building block of an organic crystal, consists of a number of atoms and shows a finite size and specific shape. These features complicate the growth behavior of organic crystals. To give a precise description of organic crystal growth, steric factors, such as molecular size, molecular shape, and mutual orientation in the crystal should be taken into consideration, though these factors are usually neglected for inorganic crystals. For the growth of perylene crystals on an oil film, the steric environment for a perylene molecule to be incorporated into a crystal is different for [100] and [001], resulting in a difference in the growth speed.

3. Interesting growth patterns have also been observed for perylene crystals grown on an oil film. Though it is preliminary, our study indicates that the stress field at the growth interface and especially around a step has significant effects on the growth behavior.
Bibliography


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[329] For the convenience of narration, we assume this direction to be [100]. Actually, our measurements do not distinguish [100] from [T00].


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