Organo-metallic structures for spintronic applications

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Organo-metallic structures for spintronic applications

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Chapter 1

Introduction

1.1 General introduction

Widely known as “plastics”, polymers became popular as structural materials after the second World War, and can be found in almost all products in present society: clothes, furniture, cars, electronics, etc. In electronics, polymers have been utilized mostly for their insulating properties or as passive media for photolithographic patterning processes. The idea of using polymers as active media in electronic devices was proposed already in the 1960s [1] but this idea was mostly ignored until 1977 [2], when it was discovered that upon doping of a polymer called trans-polyacetylene its conductivity increased up to nine orders of magnitude. Interest in the field of polymers has grown dramatically since then. Early on, most of the research effort was concentrated on the conducting properties of doped polymers and they were referred to “conducting polymers”. Gradually interest also has increased in the semiconducting (generally undoped) forms of polymers and organic materials including their photophysics.

Reports of light-emitting devices (OLED’s) fabricated from organic constituents, registered already in 1960 [3, 4], subsequently in the mid-1980s [5] and from polymeric constituents in 1990 [6], stimulated interest in this area. The structural flexibility due to weak intermolecular bonds and the endless possibilities for chemical synthesis of new molecules give molecular systems a unique advantage over inorganic semiconductors for relatively simple and cheap fabrication of flexible applications. Nowadays, organic light emitting diodes have been successfully implemented into displays by industrial companies such as Pioneer (automotive), Kodak/Sanyo (color display in digital camera) and Philips (monochrome displays in shaver and mobile phone). Universal Display has even demonstrated the possibility of realizing transparent displays. Currently, a wide range of other applications such as transistors, solar cells, sensors and solid state lasers, are under investigation.

Although intensively studied both in industrial and academic environments, there is little control over the structural and electronic properties of conjugated\(^1\) polymers

\(^1\)We introduce the term of conjugation in Sec. 1.1.1
and oligomers\textsuperscript{2} in bulk and at interfaces with metallic contacts. These are decisive parameters for achieving molecular electronics with high carrier mobility. Fundamental research aiming at understanding the structural and electronic properties of molecular films and interfaces involved in molecular devices, is a requirement for further development of molecular applications.

As one of the entirely new routes, the idea has been launched recently to incorporate organic films in so-called “spintronic” devices, which derive a magnetic functionality from explicitly exploiting the spin degree of freedom of the electrons. Also in spintronics an intimate relation is witnessed between fundamental scientific activities and technological breakthroughs, such as hard-disk read heads and field sensors based on the giant magnetoresistance (GMR) effect. For a complete overview on the advances of this field we refer to early published work \cite{7, 8}. As to the integration of molecular electronics with spintronics\textsuperscript{3}, it has recently been suggested that ordered molecular films are ideal candidates to replace insulating layers in magnetic tunnel junctions (MTJ’s)\textsuperscript{3}, new spintronic devices for high density magnetic random access memories. Also, organic materials have specific properties that make them appealing for implementation in spin injection applications, such as the intrinsically low spin-orbit coupling that provides long spin relaxation times. Finally, it has been argued that the efficiency of existing organic light emitting diodes (OLED’s) would profit from controlling the spin state of the two injectors, by increasing the formation rate of radiative singlet excitons.

Despite these promising opportunities, little is known about the fundamentals of spin-polarized transport through molecular media. Moreover, severe practical complications such as the apparent incompatibility of reactive ferromagnetic interfaces with organic molecules that often hinders ordering of a molecular film or even causes decomposition of the molecules, are being faced. This thesis is aiming at investigating the possibility of implementing molecular systems into spintronic devices. Before we present a complete description of the contents of this thesis, we first introduce the concept of organic (semi)conductors and describe different approaches used by several groups for the development of molecular devices that exploit the spin degree of freedom of the electron. We will refer to this field of research as molecular spintronics.

\subsection*{1.1.1 Organic semiconductors}

In this section we introduce conjugated molecular systems and discuss the basic differences between the organic and inorganic semiconductors.

Conjugated polymers and oligomers

It has been recognized that a key feature of semiconducting polymers and oligomers is a backbone consisting of alternating single/double bonds, resulting in a so called “\textpi conjugated system”. The electronic properties of these systems follow from the way the constituent carbon atoms hybridize.

\textsuperscript{2}An oligomer is a polymer with a short chain length

\textsuperscript{3}A more detailed description will be given in Sec. 1.1.2
Carbon has four electrons in its outer shell, two in the 2s orbital and two in the 2p orbital (Fig. 1.1 (a)). It is well known that carbon can show different hybridization configurations, among which the sp\(^2\) hybridization is the case of the semiconducting polymers and oligomers. In this type of hybridization, two p orbitals of the carbon atom combine with an s orbital resulting into sp\(^2\) orbitals that are directed toward the corners of an equilateral triangle. The p\(_z\) orbital remains unhybridized. This is illustrated in Fig. 1.1 (b). Each of these orbitals is occupied by an electron (half-filling). A σ bond between two neighboring carbons can then be formed by the overlap of two sp\(^2\) orbitals. The energy difference between the occupied orbitals and the unoccupied orbitals is quite large. Correspondingly, longer chains of bound carbon atoms would have a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), leading to insulating properties. However, the p\(_z\) orbitals form additionally π bonds. These bonds have much smaller energetic difference between the bonding and anti-bonding levels.

![Figure 1.1: Scheme of the orbitals and bonds for (a) single carbon atom; (b) two sp\(^2\)-hybridized carbon atoms; for the latter situation, we plotted a scheme of the energy level diagram, showing the formation of occupied (−) and unoccupied (+) π and σ levels; π− and π+ represent the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO)](image)

In a polymer with a long chain of alternating single/double bonds, the π electrons become delocalized along the chain, and, because of this, the polymer is called π conjugated. In benzene, π electrons delocalize around the ring. If carbon atoms form molecules, typically with benzene rings as the basic unit, the π orbitals delocalize around the benzene consisting unit and form a π system. The gap between occupied (HOMO) and empty (LUMO) states in these π systems becomes smaller with increasing delocalization.
Organic versus inorganic semiconductors

In the solid-phase there is a weak Van der Waals interaction between molecules, with bonding energy considerably lower than that of covalent bonding in inorganic semiconductors. Because of the weak interaction, organic semiconductors differ considerably in their optical, electronic and mechanical properties from conventional inorganic semiconductors. The main differences in the electrical and optical behavior of the two types of semiconductors are further discussed.

Generally, the dynamics of charge carrier motion in solids depends on two competing trends: delocalization of the carrier in the form of Bloch waves and localization as a result of interaction with the local surroundings [9] (and in some cases as a result of electron-electron interaction). The localization or delocalization of a charge carrier in a solid is determined by the transfer integral $t$ and the electron-phonon coupling. The value of $t$ actually determines the effective width of permitted energy bands for charge carriers in a solid.

In many common inorganic semiconductors, the strong interaction between the constituting atoms has as effect a large transfer integral $t$, leading to the formation of broad bands. The charge carriers are completely delocalized and move almost coherently in the form of Bloch waves with a definite wave vector $\vec{k}$. The effective mass of the electrons ($m_{eff}$) is close to the free electron mass ($m_e$), or even smaller than that. The transport gap ($E_t$), is defined as the energy necessary for the formation of a free electron-hole pair. An electron-hole pair is loosely bound (the so called Wannier exciton), with a binding energy in order of a few meV. Thus, $E_t$ equals basically the optical gap ($E_{opt}$), which is the lowest absorption energy. This is schematically shown in Fig. 1.2.

Electronic transport in inorganic semiconductors is strongly influenced by doping. Generally, chemical defects in a crystal introduce states in the forbidden energy gap, spatially localized at the defect. In this case carriers may tunnel from one localized state to another when the wave functions of the defect states have sufficient overlap. The carriers may overcome the energy differences between the defect states by absorbing or emitting phonons. This mechanism of phonon-assisted tunneling or “hopping” is extremely sensitive to structural as well as energetic disorder. Reviews on hopping transport in disordered media can be found in [10, 11].

In organic solids the situation is different. In passing by, we note that there are two types of organic materials used in the organic semiconductor industry: oligomers and polymers. Polymers form disordered phases. Transport occurs via a sequence of charge transfer steps from one molecule to another, similar to the hopping between defect states in inorganic semiconductors [13]. The microscopic origin of the trapping effects in polymers has been attributed to structural defects and disorder.

Oligomers can crystallize in the so-called “molecular crystals”. Typically, in a molecular crystal there is a weak interaction between the molecules. A weak intermolecular interaction has as a consequence a small intermolecular transfer integral. As a result, the transport bands are narrower than those of inorganic semiconductors, corresponding to a large effective mass of the carriers. In organic semiconductors there is a strong
1.1. General introduction

Figure 1.2: (a) Energy diagram of a covalently bonded inorganic semiconductor. \( E_t \) is the transport gap, \( E_{opt} \) the optical gap. (b) Energy diagram for organic semiconductors, taken after [12]. The electron affinity (\( EA \)) and ionization potential (\( IP \)) are determined from the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. In a solid-phase the energies of HOMO relaxed polaron levels, including polarizations \( P_+ \) and \( P_- \) of the molecules in condensed phase; The optical gap is smaller than the transport gap in the soft condensed matter.

The single electron approach is no longer valid for molecular solids and one must consider both the electronic as well as the molecular (vibronic) and lattice polarization within the framework of the extended polaron theory approach [9]. The charge carriers are surrounded by self-consistent polarization clouds. So, the position of the levels in a molecular solid are correlated with the polarizability of the direct environment [12]. To emphasize this correlation, we have drawn in Fig. 1.2 (b) the electron affinity and ionization potential in the case of isolated molecules and that of a condensed phase. Formation of polarization clouds is associated with stabilization energy \( P_+ \) for cations (the “holes”) and \( P_- \) for anions (the “electrons”). The polarization energy \( E_P = P_+ + P_- \) reduces the transport gap of the molecules, \( E_t = IP - EA - E_P \), where \( IP \) and \( EA \) are the ionization potential and electron affinity, respectively, in the gas-phase. Since Coulomb interactions are long-ranged, polarization clouds extend over many lattice constants and \( E_P \) depends on the proximity to surfaces and interfaces.

Also the nature of the optical spectrum is different in organic semiconductors. In the case of organic semiconductors the excitons are more strongly bound (Frenkel excitons), which is in contrast to the inorganic semiconductors. This can be simply understood if we consider a simple (hydrogenic) model to evaluate the binding energy of an exciton.

It is well known that an exciton results from the binding of the electron with its hole; as a result, the exciton has slightly less energy than the unbound electron and hole. The wavefunction of the bound state is hydrogenic. However, the binding energy is much smaller and the size much bigger than a hydrogen atom because of the effects of screening and the effective mass of the constituents in the material. By replacing the
atom reduced mass by the reduced effective mass \( m^* \) \((1/m^* = 1/m_c + 1/m_v, \) with \( m_c \)
and \( m_v \) the hole and electron effective masses, respectively) and the electronic charge by \( e^2/\varepsilon \) (with \( \varepsilon \) the dielectric constant of the material), we derive the following expression for the binding energy of the exciton:

\[
E_b = -(13.6) \frac{m^*}{m} \frac{1}{\varepsilon^2} \text{ (eV)} \tag{1.1}
\]

where \( m \) is the free electron mass (taken from [14]).

Since the dielectric constants in organic semiconductors are lower than in inorganic materials, the excitonic binding energy is larger in the case of organic semiconductors. The charge separation energy, \( E_t - E_{opt} \), equivalent to the binding energy of the exciton, is far larger than in inorganic semiconductors (see Fig. 1.2). In organic molecular crystals, it was found that the transport gap (\( E_t \)) to create separate electrons and holes has a substantial polarization energy contribution, and exceeds the optical gap by, e.g. 1.4 eV in Alq3 [12].

There has been a great deal of theoretical work on conduction mechanisms in molecular crystals. Descriptions within a band model, tunneling model, hopping model and polaron model have been used to explain the experimental observation of charge carrier transport in these systems. It is outside the scope of this thesis to describe these models. The reader who wishes to know more details on this subject is referred to the reviews of Kao and Hwang and the references therein [15].

At the moment, it is not clear what type of mechanism determines the electrical conduction in these class of molecular systems. Often, molecular materials are (unintentionally) doped and such impurities are not taken into account in these models. It is believed that a band-like transport could exist in the very pure crystals, in the case of a substantial overlap of the \( \pi \) orbitals [16].

### 1.1.2 Molecular spintronics

Several groups worldwide have started pilot projects aiming at challenging studies related to the spin transport in molecular media. First experimental reports have been published. In this section we introduce some basic notions on spintronics and present the state of the art of the molecular spintronics field.

Spintronics (derived from spin electronics) exploits the fact that an electron does not only carry a charge but also a small magnetic moment, its “spin”. The spin degree of freedom offers an additional handle to electronic devices. It allows manipulating the electrical transport by magnetic fields. The field of spintronics has attracted past years a lot of attention because of the application in future magnetic sensor and memory technology.

An important development of spintronics has been the discovery, in 1988, and the subsequent technological development of devices showing the giant magnetoresistance (GMR) effect [17, 18]. A typical GMR structure consists of two ferromagnetic separated by a nonmetallic layer. The GMR effect is the increase in the resistance when magne-
1.1. General introduction

tizations of the magnetic layers are switched from parallel to antiparallel orientations. Examples of (“conventional”) GMR structures are Fe/Cr/Fe and Co/Cu/Co.

A second major breakthrough has been the discovery and reliable fabrication processes of magnetic tunnel junctions (MTJ’s). Although the functioning of the structure is similar to that of a GMR element, the underlying physics is completely different. In a MTJ the two ferromagnetic layers are separated by a very thin insulating layer. When a bias voltage is applied between the two ferromagnetic electrodes, a current starts to flow by tunneling across the classically forbidden region of the insulator. We note that the thickness of the spacing layer should be only a few nanometers in MTJ’s, in order to allow the tunneling of electrons from one electrode to the other. The tunneling process is spin dependent, i.e. the tunneling current depends on the relative orientation of the magnetization of the two metal electrodes. Such an effect is called tunnel magnetoresistance (TMR). To date, AlOx has proven to be the most suitable insulator. With optimized processing and the proper choice of material for the ferromagnetic layers, AlOx-based junctions have a TMR effect of 70% at room temperature [19].

Other experiments in the field of spintronics lead to intense focus on realizing spin injection in semiconductor structures. With respect to the issues of how to realize in practice spin injection and detection, approaches such as all-optical experiments or electrical spin injection, were taken [8]. With respect to the physics underlying spin injection, it has been shown that the difference in conductivities between a metal and a semiconductor gives a basic obstacle to spin injection [20].

Spin-injection devices can be divided into lateral and perpendicular devices. Examples of these two different layouts are represented in Figs. 1.3 and 1.4. Typically, the experiments of spin injection from a ferromagnetic contact are performed using a device with a simple injector-detector geometry, where two ferromagnetic electrodes are separated by a non-ferromagnetic (semi)conductor medium. One ferromagnetic metal contact can be used to inject spin polarized carriers into the (semi)conductor material. If the spacing between both contacts is shorter than the spin flip length, the interface to the second ferromagnet should act as a spin detector by exhibiting either low resis-

![Figure 1.3](image_url)

**Figure 1.3:** Lateral spin injection structure, using magnetic electrodes of different widths to achieve separate switching fields.
1. Introduction

Figure 1.4: Schematic diagram of an organic light emitting diode (OLED). The molecular film can consist of two layers for the transport of electrons and holes, respectively. A spin-OLED is created when the two metallic electrodes are ferromagnetic materials. A similar structure can be used to study spin injection into organic films. In the latter case only one type of organic transport layer is used.

It has been recognized that molecular systems will be particularly advantageous for spin polarized injection. The spin relaxation times in organic semiconductors is in the $10^{-5} - 10^{-7}$ s range [21, 22]. Such long times provide efficient devices, and once spin is injected into the semiconducting organic layer, its optical and electronic functionality can be fully exploited.

One of the most exciting experimental developments has been the observation of spin-polarized transport through (single) carbon nanotubes over more than 100 nm, with a magnetoresistance up to 9% at 4 K [23]. Theoretical work has addressed the fundamentals of spin-polarized currents through a (single) molecular constriction, where effects of tens of percents have been predicted [24].

Besides the spin polarized transport through single molecular entities, first steps have been taken for the study of spin injection and transport through molecular films. In lateral devices, a MR up to 30% has been reported by Dediu et al [25]. The authors study the spin injection in sexiphenyl, making use of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) electrodes. A fast decrease of the magnetoresistance with the transport channel length has been attributed to the low mobilities of the carriers in this material. However, the magnetic orientation of the electrodes was ill-defined and because electrodes of the same dimensions were used, a clear hysteretic magnetoresistance (MR) curve could not be measured. Since the applied field was perpendicular to the current plane, it is still unclear to which extend the observed MR is due to spin injection. In particular, the effect of increased carrier mobilities of semiconductors in external applied magnetic fields is not taken into account by the authors [26]. In order to investigate spin injection...
1.1. General introduction

into organic semiconductors, a better defined magnetic orientation of the electrodes is required.

First experimental reports on organic barriers in MTJ's date back to 1998 [27]. The authors studied the spin-dependent tunneling through three different organic films, which were deposited by a Langmuir-Blodgett technique. In this deposition method, molecules are dissolved in a solvent, compressed until reaching a high molecular packing, and transferred onto a substrate placed in the solvent, by slowly lifting up the substrate out of the solution. The junctions had electrodes made out of Ni$_{80}$Fe$_{20}$ and Co. The organic materials used were tris(bipyridine) ruthenium complex (Ru), poly-N-dodecyl-acrylamide and its copolymer with a ferrocene derivative (Fc). A magnetoresistance effects (MR) of 0.5% at room temperature, was reported. Layers were found to be rather inhomogeneous and suffered from interdiffusion of the top electrode. Moreover, the bottom electrodes were oxidizing during the deposition of the organic film via the Langmuir-Blodgett technique.

Also, first preliminary steps towards the realization of spin-organic light emitting diodes (spin-OLED) have been taken [22, 28]. Such a device is a stacked multilayer of the type shown in Fig. 1.4, in which two electrodes are separated by an organic light-emitting active layer. The active layer may consist of a bilayer for the hole and electron transport, respectively. After the injection of carriers in the two layers, light is generated by the decay of excitons. Excitons form as either a singlet ($S = 0, m_s = 0$) or one of the triplet states ($S = 1, m_s = -1, 0,$ or $1$), depending on the correlation of the spins of the electronhole pair. Because of the electric dipole selection rules, only singlet excitons decay radiatively.

It is expected that the population of the singlet and triplet states can be influenced by the use of spin polarized electrodes. Thus, the electroluminescence (EL) yield of OLED’s can be tuned when ferromagnetic electrodes are used (spin-OLED’s). Currently, no evidence for an increased efficiency of spin-OLED’s has been found.

The first clear indication of a MR effect in hybrid organo-metallic devices has been recently demonstrated by Xiong et al. The authors used structures similar to OLED’s, to study the spin transport in Alq$_3$ [29]. LSMO and Co, were used as bottom and top electrodes, respectively. A MR of 40% at 11 K, decreasing exponential with temperature and thickness of the Alq$_3$, was reported. The resistance of the device varied only slightly with temperature. Moreover, strong interdiffusion of the top electrode into the Alq$_3$ film is reported. The authors attributed their experimental observations to a low spin diffusion length in the organic film. At the moment, it is not clear what mechanism causes this MR effect.

In conclusion to this section, we presented concepts of molecular spintronic devices developed up to now. Despite the experimental observations, little is understood about the spin transport into molecular media. Some of the experiments clearly indicated the necessity of preparing well-defined interfaces between the ferromagnetic materials and molecular films.
1.2 This thesis

The main subject for the research described in this thesis is to investigate spin polarized transport in molecular systems. To be able to do so, we concentrate on two major aspects related to the fabrication of molecular spintronic devices.

Deposition of metallic contacts on molecular films is one of the major concerns in the physics of molecular devices. Surface spectroscopy techniques such as photoelectron spectroscopy, vibrational spectroscopies, and near edge X-ray absorption fine structure (NEXAFS), were used to gain insight into diffusion of metals in soft condensed matter [30]. In contrast to the noble metals like gold and palladium, it was found that metals of high reactivity, including ferromagnetic metals, form sharper interfaces with polymer films [30]. Contrasting results were found by Hirose et al. in the case of several metals and perylene - tetracarboxylic - dianhydride (PTCDA) compounds, for which strongly interacting metals such as indium, magnesium and titanium were found to interdiffuse strongly into the PTCDA film [31]. Thus, the interdiffusion of metals is found to be dependent on the chemistry at the interface with molecular systems. At the moment it is not clear whether diffusion occurs via defects in the organic layer or because the high energetic atoms brake the weak bonds in the molecular matrix. Obviously, to minimize such effects, we need to find out ways for the preparation of (ordered) smooth molecular films on metallic substrates.

Not only the structural properties of the organic-ferromagnetic metal interfaces are of importance for the engineering of devices. For a specific application one would require a specific energy level diagram at the involved interfaces. For example, to be able to inject spin polarized carriers, we need a small barrier for the carrier injection, i.e the Fermi level of the metallic contact should be aligned close to the LUMO or HOMO of the molecular film, depending on whether electrons or holes should be injected. Experimental studies performed on interfaces between metals and molecular systems have shown that the prediction the energy level diagram at the interface between these systems and metals is difficult [32].

1.2.1 Our approach

Having discussed some of the key issues related to the development of molecular devices, we now present our approach for the realization of the molecular spintronic devices.

One of the demands for spin injection devices is to use organic materials that show a high charge carrier mobility. Up to now, the highest carrier mobilities in organic semiconductors were achieved for molecular crystals [9, 15]. Such crystals are mostly obtained by physical vapor deposition under a stream of an inert gas [16, 33]. Also, large crystalline domains of molecules can be obtained by evaporation in vacuum [32].

As to the spin dependent tunneling process, it has been recognized that it is an interface sensitive process [34]. Investigation on the inorganic MTJ's revealed a decrease in TMR when the ferromagnetic electrodes were oxidized. Thus, wet processes
such as Langmuir-Blodgett or self-assembly \(^4\) are not suitable for the deposition of the organic barriers, because of the oxidation of the ferromagnetic electrodes. Le Clair et al. demonstrated that, in the case of inorganic MTJ’s, the TMR decreased drastically when thin nonmagnetic metallic layers were inserted between the ferromagnetic electrodes and the insulating layers [34, 35]. This means that using a nonreactive metallic layer as a protective layer against oxidation, such as Au, is not a feasible option. Therefore, the fabrication of organic MTJ’s in an ultrahigh vacuum environment (UHV) is a requirement.

Up to now, only a limited number of studies on structural properties of organic molecules on ferromagnetic transition metals have been reported. It was found that often ferromagnetic metallic substrates hinder ordering of a molecular film or even cause decomposition of the molecules [36–41]. For a detailed overview, we refer the reader to the introductory part of the chapter 3.

To conclude, we have seen that besides the challenging opportunities that organic materials offer for spintronic applications, several fundamental issues related to the engineering of these devices have to be answered. Three main questions will be addressed in this thesis:

- Is it possible to prepare (ordered) smooth layers of organic molecules onto ferromagnetic substrates?
- Can we gain more insight into the electronic properties of organic materials at interfaces with (ferromagnetic) metallic contacts?
- What is the impact of the interdiffusion of metallic top contacts onto the magnetic and electric properties of MTJ’s?

1.2.2 Thesis outline

Having discussed the goal of this work, we now proceed with a detailed description of the separate chapters of this thesis.

Chapter 2: This chapter discusses the experimental approach of this thesis. We start with a description of the deposition method of molecules and the setup which we used in our laboratory for these purposes. An ellipsometry-like technique is used to determine the thickness of the film during growth. The basic physics and the implementation of this technique is discussed. Structural analyses are performed using standard techniques such as Low Electron Energy Diffraction (LEED), Atomic Force Microscopy (AFM), and Scanning Tunneling Microscopy (STM). The basics of these techniques, together with their specific use for the case of molecular systems are briefly presented. Also magnetic characterization techniques, used to characterize the magnetic properties of metallic electrodes are described. Finally, we describe on a more tutorial level photoemission experiments, which we use to determine the electronic properties of molecules in films and at the interfaces with ferromagnetic substrates.

\(^4\) these techniques are widely used for the cheap fabrication of molecular devices
Chapter 3: This chapter is dedicated to the structural properties of molecular systems deposited on ferromagnetic substrates. Before presenting results on several new organic-ferromagnetic interfaces, we introduce the reader into new terminologies used for describing the ordering and growth of organic molecules onto inorganic substrates. The experiments are dedicated to the growth of two large aromatic molecules, perylene-tetracarboxylic-dianhydride (PTCDA) and pentacene, on 3d ferromagnetic Ni(111) and Co. Single- and poly-crystalline substrates are used. PTCDA is widely used as a model system for the growth of organic semiconductors in vacuum. Pentacene is one of the organic semiconductors with a high carrier mobility. The effects of substrate pretreatment and growth conditions, on the ordering and morphology of PTCDA and pentacene films are analyzed. Despite the high reactivity of the ferromagnetic metallic substrates, we demonstrate that, under certain conditions, large range ordering of these molecules can be obtained.

Chapter 4: Here we address aspects related to the energy level diagram of interfaces between pentacene and ferromagnetic substrates. First, we present a study on the electronic structure modification as going from the gas-phase to the solid state. Such a study could help us in a latter stage to relate the electronic structure of pentacene with the transport properties in this medium. We then investigate the alignment of the energy levels of pentacene with the metallic states of Co and Ni(111). We show that at these interfaces charge redistribution occurs, but with molecular levels that keep intact. As a consequence, an increased barrier for the hole injection is registered.

Chapter 5: This chapter is dedicated to the fabrication of organic MTJ’s. We fabricated junctions using different spacers and different deposition methods for the ferromagnetic electrodes. We have been able to produce a promising TMR of 7% at 5 K for junctions based on “TERPY” deposited in a UHV environment, although still hampered by a poor reproducibility, severe interdiffusion, and a full quenching of TMR above 30 K. Furthermore, we investigate the magnetic properties of Co thin films onto different organic films, for which we found different characteristics, when compared with similar films deposited on inorganic substrates.
Chapter 2

Experimental

Abstract: In this chapter we describe the techniques and the deposition methods which we specifically used for the study of molecular systems. Rather than a full in-depth discussion we concentrate on specific properties when used for studying thin molecular films. We will provide examples for some of the techniques as references for further inquiring.

2.1 Deposition facility

In the introductory chapter of this thesis, we outlined the importance of the deposition of molecules in an UHV environment. In this section we describe the deposition set up used in our laboratory and present some aspects related to the deposition of molecules in vacuum. The deposition system is a part of the Eindhoven University nano-Film deposition Research and Analysis Center (EUFORAC).

2.1.1 Evaporation of organic molecules in UHV

The growth of organic thin films under UHV conditions is similar in many respects to conventional beam epitaxial growth and is sometimes also referred to organic molecular beam epitaxy - OMBE. The evaporation cells used for organic materials are similar to the normal evaporation cells used for the deposition of inorganic materials. Such a cell consists of a crucible, which is surrounded by a wire for resistive heating. Normally, the organic material in powder form is inserted in crucibles and heated at temperatures well below the decomposition temperature, such that sublimation occurs. The crucibles are preferably made out of glass or quartz, in order to avoid reactions with the organic material.

Only molecules that show crystallization can be evaporated. Polymers with long chains can not be sublimated, since breakage of the molecular bonds occurs before any evaporation rate is registered.

The material, purchased from the Aldrich company, has mostly a purity of 98% which is not satisfactory for the vacuum sublimation. Purification of the source mate-
rials is essential to assure that the grown film is reasonably free of impurities. Additionally, it has been shown that impurities act as charge traps, causing low charge mobilities in molecular media [16]. Furthermore, purification is required to prevent contaminants from entering the vacuum chamber which might result in high background pressures [42].

The purification method we use in our lab is gradient sublimation. A schematic of this method is shown in Fig. 2.1. Typically, several grams of powdered source material is loaded into the end of a glass tube. Glass sleeves are then inserted into the tube, followed by a wad of glass wool placed at the open end of the tube, to minimize the contamination of the pumping chamber with the source material. The tube is evacuated to $10^{-6}$ mbar and inserted in a furnace with a gradient temperature. The temperature of the furnace is then increased until the sublimation point of the material. The most volatile impurities are pumped down while the nonvolatile ones are left at the hottest end of the glass tube. The molecules condense in a well-defined temperature range (or zone of the gradient oven). So, the purified material can be collected from one of the inserted glass sleeves.

Organic compounds are often purified in multiple cycles using this method. One should be aware of the fact that gradient sublimation does not always lead to very pure compounds, since in some cases the impurities can co-crystallize with the material itself. The sublimation temperatures used in our purification setup were 640 K for PTCDA and 490 K for pentacene.

Methods for checking the purity of organic molecules

In this section we describe briefly the most common methods used for the purity analysis in organic compounds.

A very fast method is measurement of the melting point transition. The method itself requires only heating up a small amount of molecules inserted in a capillary, and observe the transition to the melt phase. The degree of impurity will show up in the

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1 The structural formulas of PTCDA and pentacene are schematically shown in Fig. 3.5 and 3.19
temperature range at which the transition takes place: the more impurities, the broader the range. There are commercially available instruments for this method, although the standard ones can only reach temperatures up to 573 K.

Another method to study the purity of the molecules is infrared (IR) spectroscopy, which measures the vibrational modes of the molecules. The IR spectra of large molecules are very rich but for most molecules the IR spectra can be found in chemical data bases. Generally speaking, quantification using this method is not straightforward. To determine the type of impurities in a material, one should combine this method with other techniques. In specific cases, the type of impurities can be found in literature [16]. For example, a most prominent impurity in pentacene (C_{22}H_{14}) has been found to be 9,13- pentacenequinone (C_{22}H_{12}O_{2}). This impurity is a derivative molecule of pentacene, for which two hydrogen atoms from the middle benzene ring of pentacene are substituted by two oxygen atoms. The presence of the quinone in pentacene is seen in the additional features located in the region around 1760 cm^{-1} in the IR spectra.

Also mass spectrometry (MS) is often used for the identification of impurities in a certain compound. MS is an analytical spectroscopic tool primarily concerned with the separation of molecular (and atomic) species according to their mass. A substance is bombarded with an electron beam having sufficient energy to ionize the molecule. The ions which are produced are accelerated in vacuum through a magnetic field and are sorted on the basis of mass-to-charge ratio.

Another method for the determination of purity of organic compounds is chromatography. This method can also be used for the purification of organic materials although only small amounts of material can be purified. In chromatography the components to be separated are distributed between two phases: a stationary phase (bed) and a mobile phase, which percolates through the stationary bed. The different components of the analyzed compound are flushed through the system at different rates, which basically provides the required separation. There are different varieties of chromatography techniques. In principle chromatography can be performed in the gas-phase or in liquid, depending on the type of stationary and the mobile phase. Gas chromatography makes use of a pressurized gas cylinder and a carrier gas, such as helium, to carry the solute through the column. For the liquid phase solvents instead of gas carriers are used. The stationary bed can be, for example, a "dry" absorbent (zeolite, silica gel, activated alumina), an inert porous solid coated with a viscous liquid, or a glass or fused silica capillary with walls that are coated with an absorbent. Chromatography can separate complex mixtures with great precision.

In our lab we used IR spectroscopy and melting point measurements to determine the purity of the used organic materials.

### 2.1.2 Deposition setup

Having outlined the procedure of evaporating organic compounds in vacuum, we now proceed with a description of the vacuum setup used in our laboratory. We will refer to it, from now on, as the OMBE chamber.

A photograph of the OMBE setup is shown in Fig. 2.2. At the lower part of the
chamber, there are six 45 CF ports (see 1 in the figure), four of which can be used for evaporation cells. The other two ports are dedicated to optical access to the sample for in-situ differential ellipsometry measurements (see Sec. 2.1.3). The ports are oriented under an angle of 45 degrees. Two flanges of 150 CF size (indicated by 2 in the figure) are free to use for additional options such as view ports, leak valves and shutters. The substrates are attached to a manipulator (3) which has four degrees of freedom ($x$, $y$ and $z$ movement and rotation around the $z$ axis).

The samples can be resistively heated up to 800 K and cooled down to liquid nitrogen temperatures. The temperature of the sample is measured with a K type thermocouple, and controlled using a WENST PID controller. The as-received controllers have a linear output, with an on/off type of switching of the output current. In order to avoid stresses in the heating filament by the sudden interrupt of the current, the controller has been modified such as to allow a graduate variation of the output current.

The vacuum in the chamber is achieved using a turbo pomp (4), backed by a rotary pump, for pressures down to $10^{-8}$ mbar range and an ion pomp (5) for pressures below $10^{-8}$ mbar. The base pressure in the system can be brought in the low $10^{-10}$ mbar regime only after backing the system at temperatures around 410 K, heating in the same time the evaporation cells. Only in doing so the outgassing of the organic material is properly done. Moreover, it shortens the time to reach a good vacuum during the evaporation of molecules.

The OMBE system is fully compatible with the rest of the EUFORAC system, assuring full access of the grown molecular films to the deposition and characterization facilities.
2.1.3 In-situ layer thickness determination using differential ellipsometry

Differential ellipsometry is an optical polarization-modulation technique, which we use to determine the thickness of the organic films during the deposition process. In normal MBE systems the thickness of a layer can be determined using a quartz crystal oscillator. As some material is deposited on the thickness monitor, the frequency of the oscillations changes, and by this, the deposition rate can be determined. However, for a substrate of a different nature, the sticking coefficient of a certain type of material can differ substantially from the one of the quartz. In this case, significant errors can be made in the determination of the real thickness of the film grown. The main advantage of using the differential ellipsometry technique is that the actual thickness of a layer can be determined. Moreover, it is possible to determine optical constants of the grown film.

![Figure 2.3: Schematic of the experimental setup used for in-situ differential ellipsometry.](image)

The technique makes use of the fact that the reflection coefficients of the light incident on a multilayer structure are different for different polarization of the light (p or s). Experimentally, we use a He-Ne laser ($\lambda = 632.8$ nm) as a light source (see Fig. 2.3). The light passes through a polarizer with a direction of polarization that is described by an angle $\alpha$ and arrives under an angle of incidence of $45^\circ$ on the sample. After reflection on the sample the laser light passes through a photoelastic modulator (PEM), an analyzer, and a photodetector. The direction of polarization of the analyzer is $45^\circ$ with respect to the $x'$ direction indicated in Fig. 2.3. The PEM is placed under an angle of $45^\circ$ with respect to the $x'$ axis. The PEM modulates the polarization of light between the right and left-circularly polarization with a frequency $f$ of 50 kHz.

Using the Jones formalism we can demonstrate that the intensity of the light measured at the detector consists of harmonics of the oscillation frequency of the PEM ($dc$, ...
Experimental

The relation between these components and the reflection coefficients is given by the following equations:

\[
V_{dc} = \frac{1}{2} \cos^2(\alpha) \left[ |r_p|^2 - |r_s|^2 + J_0(A_0) \left( |r_p|^2 + |r_s|^2 \right) \right] + \frac{1}{2} |r_s|^2 (1 - J_0(A_0)),
\]

\[
V_{1f} = J_1(A_0) \cos(\alpha) \sin(\alpha) \left( r_{pi} r_{sr} - r_{si} r_{pe} \right),
\]

\[
V_{2f} = \frac{1}{2} J_2(A_0) \cos^2(\alpha) \left( |r_p|^2 + |r_s|^2 - |r_s|^2 \right),
\]

(2.1)

where \(A_0\) is the amplitude of oscillatory retardation of the PEM. \(J_i(A_0)\), with \(i = 0, 1, 2\), are Bessel functions. \(r_s\) and \(r_p\) are the reflection coefficients of s- and p- polarized light, respectively. Indices \(r\) and \(i\) indicate the real and imaginary part of the coefficient. We assume normal incidence on the view ports and neglect strain-induced birefringence. Thereby the polarization state of the light is conserved while transmitting through the optical ports of the vacuum chamber.

The reflection coefficients are determined using the transfer matrix description [43, 44]. For a given multilayer stack, \(r_s\) and \(r_p\) depend on the thickness and optical constants of the individual layers. Thus, thickness changes in one of the layers in the multilayer film, determines modification of \(r_{s,p}\) and by this, the \(dc, 1f\) and \(2f\) signals are also modified.

For a simple stack of layers consisting of a single molecular film and a silicon substrate with a 2 nm thick oxide, the expected dependence of the \(dc, 1f\) and \(2f\) signals on the thickness of the molecular layer are shown in Fig. 2.4. We assume that the layers have uniform thicknesses. The value for the index of refraction of molecular film is in this case 1.85 at \(\lambda = 632.8\) nm. We can see that all these components show an oscillatory dependence on the thickness of the molecular films. We note that in the case of materials with an refractive index containing a small extinction coefficient, the oscillations in the \(1f, 2f,\) and \(dc\) signals are damped.

To be able to compare the simulations with the measurements, the \(1f\) and \(2f\) components were divided by the the \(dc\) component. From these plots, it is clear that, in this particular case, the normalized \(1f\) signal is the most sensitive to changes in the thickness of the organic layer. Notice that for very small thicknesses (up to \(\sim 50\) nm), which is the region of interest for the preparation of MTJ’s, \(V_{1f}/V_{dc}\) varies linearly with the thickness of the molecular film.

When metal substrates are used, the \(1f, 2f\) and \(dc\) components vary differently, because of the different contrast in the optical constants. It turns out, however, that the \(V_{1f}/V_{dc}\) still shows the most significant changes with the thickness of the organic layer. This is illustrated in Fig. 2.5 for three different substrates: Au, Co and Si with a 2nm oxide layer. In this figure we plot the normalized \(1f\) and \(2f\) components as a function of the thickness of the molecular film. We can see that for thicknesses up to about 20 nm the normalized \(1f\) signals for the three systems show linear dependencies of about same slopes. Thus, it is expected that the sensitivity of this technique should not depend on the type of substrate.
2.1. Deposition facility

Experimentally, the $1f$, $2f$ and $dc$ components of the signal can be separately measured, using a lock-in amplifier with a reference signal coming from the photoelastic modulator. In practice $A_0$ can be arbitrary chosen. We can chose therefore such a value that the Bessel functions reach maximum, and by this the corresponding measured signal becomes larger\(^2\). In order to be more sensitive to changes in the layer thicknesses, the angle of the polarizer $\alpha$ can be chosen such that the $2f$-signal vanishes at the start of an experiment. It can be demonstrated that this leads to an improved signal-to-noise ratio.

As an example, we represent in Fig. 2.6 (a) and (b) plots of the measured $1f$ and $dc$ signals, respectively, as a function of deposition time, for a PTCDA film. The normalized $1f$ signal ($V_{1f}/V_{dc}$) is displayed in Fig. 2.6 (c). We can see that these signals vary according to the expected behavior.

The value for the index of refraction was determined assuming an uniform thickness of the PTCDA film. We compared the damping of the oscillations in the $dc$ signal with the simulated $dc$ value using a trial and error method. A value of $1.85 + 0.1i$  

---

\(^2\) $J_1$ is maximal at $A_0=1.94$, $J_2$ is maximal at $A_0=3.05$. 

**Figure 2.4:** Simulated $dc$, $1f$ and $2f$ signals as a function of thickness for a molecular layer on Si/SiOx(2 nm).
was found for the index of refraction of PTCDA. This value was compared with the pseudo-refractive index reported in literature for PTCDA [45]. For the real part of it we could find an excellent agreement to the values found in literature (1.85). We can not verify the value for the extinction coefficient at the moment. For the index of refraction for TERPY molecules (structural formula is shown in Fig. 5.3) we found a value of 1.59 ± 0.2.

With the known value for the refractive index, we can now determine from the simulations the thickness of the film. AFM measurements were used to check if the thicknesses determined with ellipsometry were correct. A tantalum ribbon of 0.25 µm thickness attached to the SiOx substrate was used as a mask for the deposition of the molecular film. After deposition, the ribbon was removed and the profile at the edge between the covered and uncovered region was measured with an atomic force microscope (AFM).

In Figs. 2.6 (d) and (e) we illustrate the two independent measurements, performed on the same sample. The results of the differential ellipsometry measurements performed on a PTCDA thin film, are shown in Fig. 2.6(d). In this plot we represented the $V_{1f}/V_{dc}$ signal versus deposition time. We can see that the slope of the normalized $1f$ signal changes in time, probably due to the variations in the molecular flux. The total change of $V_{1f}/V_{dc}$ is 0.18, which corresponds to a change in the PTCDA thickness of 33 nm (as determined from the simulations). We note that the energy of the radiation we used for these experiments is smaller than the optical gap of PTCDA (2.2 eV) [42].

The AFM results are shown Fig. 2.6 (e). The inset represents the AFM image performed at the step edge of the PTCDA sample. The graph represents the profile of the line shown in the AFM image. The height of the step corresponds to an average height of 33 nm. Thus, a very good agreement is found with the two independent measure-
2.1. Deposition facility

Figure 2.6: (a) Plot of the normalized \(1f\) signal as a function of thickness for a PTCDA layer, as measured with differential ellipsometry technique. (b) top panel: AFM height channel profile of the layer.

Also for TERPY we found a good agreement between the AFM measurements and ellipsometry.
2.2 Structural characterization techniques

In this section we give an overview of the characterization techniques used for the determination of the structure of the vacuum-deposited molecular films.

Low electron energy diffraction (LEED) is a technique performed in-situ, to study the symmetry, periodicity and atomic arrangement of solid crystal surfaces and thin films. The principle of this technique is based on electron diffraction. For LEED low energy electrons (1-500 eV) are used. In a sample showing lateral order, the diffraction pattern gives information on the 2D reciprocal space of the sample. Thus, the LEED pattern symmetry, peak position and intensities give direct information on surface lattice parameters and the position of atoms in the surface unit cell. Information obtained about the surface always originates from an area with a diameter smaller than the coherence width of the electron beam, i.e. for conventional LEED systems smaller than $\sim 100 \text{ Å}$ [46].

In the case of molecular thin films one needs to use low energies electrons (up to about 50 eV), because of the large lattice constants. This also means that one has to keep in mind that decomposition of the molecules can be induced by charging effects due to exposure of the sample to the low energy electrons. Such effect can be identified by deterioration of the LEED pattern in time, i.e. broadening of the diffraction spots.

In order to gain more insight in the structural properties on a more local area, scanning probe techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are often used. Additionally, it is possible to image individual molecules\(^3\), which makes it possible to identify the orientation of the molecules within an unit cell. We will now briefly describe the working principles of the STM and AFM techniques.

In STM one makes use of a sharp metallic tip, which is placed few angstroms above the studied sample. When a bias voltage is applied between the tip and sample, a tunneling current occurs. This current can be used to identify the topography of a sample, by scanning the tip along the surface. The most common method used for STM imaging is the constant current mode, in which the topography of the surface is measured by keeping constant the tunneling current. Since the tunneling current is exponentially dependent on the tip-surface distance, a one to one correlation can be made to identify the topography of the sample. A schematic of this mode is shown in Fig. 2.7. For a detailed description of the STM technique, we refer to dedicated books [49–51].

STM can be applied to study conductive surfaces or thin nonconductive films and small objects deposited on conductive substrates. Usually, high resolution images of molecular systems are obtained for low tunnel currents (few pA) and high bias voltages (from few hundreds mV up to few V) [42, 52–57].

The operation of an AFM is based on the measurement of the force between the sample surface and a sharp probe (Fig. 2.8 (a)). A probe used in AFM is in fact a sharp

\(^3\)Nowadays it is possible to obtain molecular resolution even with AFM, but under UHV conditions [47, 48]
2.2. Structural characterization techniques

Figure 2.7: Basic principle of the STM working in constant current mode

tip located at the free end of a flexible cantilever plate. The probe tip interacting with
the sample surface is scanned over the surface and the interaction force between the
tip and the sample surface causes the cantilever plate to deflect. The deflection of the
cantilever is measured by means of a laser beam, which is focused on the cantilever.

Depending on the distance between the tip and surface, i.e. on the interaction
strength between the two, AFM can be divided in three main operation modes: (1)
contact (2) non-contact and (3) semi-contact, which is a transition mode between the
contact and non-contact modes (see Fig. 2.8 (b)). Details on the AFM technique can
be found for example in [49–51].

The big advantage of AFM is that any type of sample can be scanned, although
the resolution that one can achieve with AFM is under normal operating conditions
lower than in STM. However, scanning soft samples (like oligomers, polymers, biological
samples) in contact mode may cause damage of the sample. It is desirable in this case to
use the tapping mode, which is a semi-contact mode. The cantilever oscillates vertically
at its resonance frequency or close to it (typically values are found in the range of 50
kHz to 500 kHz). Mechanical oscillations of the cantilever are excited by the piezodriver
that has a direct contact with the cantilever substrate. The particular feature of this
mode is that the oscillating tip slightly knocks the sample surface during the scanning
only in the lowest point of its amplitude. In the same time, during the most of its
oscillation period the cantilever does not touch the surface and their interaction level
is relatively low.

In tapping AFM mode it is still possible to damage soft samples when high ampli-
tudes for the oscillating cantilever are used. High amplitudes means stronger interaction
forces. Thus the interaction forces should be kept as low as possible. In this case, The
AFM mode is also referred as to soft tapping AFM.
2.3 Magnetic characterization techniques

The most common methods for measuring magnetic thin films are SQUID (Superconducting Quantum Interference Device) magnetometry and MOKE (Magneto-Optic Kerr Effect) magnetometry. We have used these techniques to measure the magnetic behavior of thin ferromagnetic layers deposited onto organic films (chapter 5).

The principle of SQUID technique is based on the detection of magnetic flux originating from a sample. The sample is placed in a magnetic field created by a superconducting magnet. The SQUID sensor, shielded from the applied and external magnetic fields, is comprised of a superconducting ring interrupted by one or two Josephson junctions. The sample is moved slowly through a detection coil coupled to the SQUID via superconducting wires. The SQUID sensor then measures variations in the persistent current within the superconducting ring and outputs a voltage that is proportional to the magnetic moment of the sample. The SQUID output voltage, when properly calibrated using a sample of known magnetic moment, can be used to provide accurate values for the magnetization of the sample. For the SQUID-magnetometer in our laboratory, a r.f.-type MPMS-55 SQUID from Quantum Design, a sensitivity of $10^{-7}$ emu (= $10^{-10}$ Am$^2$) is specified by the manufacturer. The temperature can be varied between $T = 1.7$ K and 400 K. The maximum attainable magnetic field amounts to 5 T.

MOKE (Magneto-Optic Kerr Effect) magnetometry measures changes in the polarization state of light caused by reflection on a magnetic surface. In contrast to SQUID magnetometry, MOKE gives only a qualitative measure for the magnetic moment, unless detailed modelling is performed. Furthermore, due to the limited penetration depth of the light ($\sim 15$ nm in the experiments described in this thesis), MOKE can provide information only from a limited amount of material. However, MOKE represents a
series of advantages when compared with SQUID. MOKE is a local probe measuring over an area covered by the laser beam (of few tens of micrometers diameter), whereas a SQUID magnetometer measures the overall magnetic moment of a sample. This local sensitivity enables the use of wedge-shaped samples, in which properties depending on the layer thickness can be measured in a single sample. In that case, the effects of variations of other growth parameters are eliminated. A second advantage of MOKE is that the time needed to measure a magnetization curve at room temperature is typically two orders of magnitude less than for our SQUID magnetometer.

2.4 Electronic structure analysis using photoelectron spectroscopy

In this section we give an overview on the application of photoelectron spectroscopy (PES) on molecular films. Photoemission is widely used to study the electronic structure of solids. The principle of this technique is based on the photoelectric effect. PES consists of bombarding a sample with monochromatic photons and measuring the kinetic energy distribution of the emitted electrons (also called photoelectrons) as shown in Fig. 2.9. The total energy of the electrons, which can be written as a sum of its energy above the vacuum level – its kinetic energy ($E_{\text{kin}}$) – and the amount of energy it took to remove the electron from its host atom to the vacuum level – its binding energy ($E_b$) – must be equal to the energy of the incident X-rays ($h\nu$):

$$E_{\text{kin}} + E_b = h\nu, \quad (2.2)$$

Note that the binding energies of metals are usually measured with respect to the Fermi level of the solid rather than the vacuum level, which requires a correction for the work function $\Phi$ of the analyzed sample [58]. By measuring the the photoelectron intensity as a function of kinetic energy, a set of peaks will be observed, at energies which are determined by the photon energy and the orbital’s binding energy. Equation 2.2 shows that only the electrons of high enough kinetic energy can escape in the vacuum. Thus, one needs a minimum photon energy to excite the electrons into the vacuum.

It must be noted that the photoemission spectrum does not directly reflect the density of states of the material. As in any optical transition, a PES spectrum depends on the photon energy used and the symmetry of the involved levels. Also some other effects such as lifetime broadening, finite source width, instrumental resolution, phonon or vibrational-rotational broadening, many electron effects can cause line broadening. Additionally, the photoelectrons in their way out to the vacuum can suffer inelastic collisions, loosing some of their energy. The scattered electrons are called secondary electrons and give rise to an additional background in the PES spectra (see also Sec. 2.4.1). As we will demonstrate later in this section, this secondary electron background plays an important role into the determination of the work function of materials.

In a photoemission experiment, one can use X-ray sources to probe deep-lying lev-
Figure 2.9: Simplified representation of photoemission experiment. A monochromatic incoming light interacts with the solid and photoelectrons with enough kinetic energy are excited into the vacuum. A one to one relation between the density of states of the material and the PES spectrum is given. In this particular example, the binding energy of electrons in the solid state \( E_b \) is measured with respect to the Fermi level of the sample. VL is the vacuum level. \( \Phi \) is the work function of the material, i.e. the minimum energy required to extract an electron out of the solid. \( E_{\text{kin}} \) is the kinetic energy of the photoelectrons.

els of the analyzed system; in this case the technique is called X-Ray Photoelectron Spectroscopy (XPS). For XPS, Al K\( \alpha \) (1486.6 eV) or Mg K\( \alpha \) (1253.6 eV) are often the photon energies of choice. Ultra-violet photon sources with energies in the range of 10 to 40 eV can be also used. In the latter case, the PES technique is called Ultra-violet Photoemission Spectroscopy (UPS). UPS is advantageous when requiring a better sensitivity and resolution to the valence band. For UPS the most common sources are He lamps emitting at 21.2 eV or 40.8 eV, which are sometimes referred as He I and He II radiation, respectively. To cover a very broad energy range, synchrotron radiation can be used.

The photoelectrons excited in vacuum are analyzed with a spectrometer (or analyzer). Such a spectrometer selects the photoelectrons by their kinetic energy and measures them by means of a detection system (normally a channeltron). The best resolution in PES can be obtained by using hemispherical analyzers. Such an analyzer consists of an electron lens system, two concentric hemispheres and an electron detection system. Usually the system is operating with the so-called constant analysis energy (CAE) mode. The electron lenses focus the photoelectrons onto the entrance slit of the
hemispheres. The hemispherical analyzer acts as narrow pass filter, letting through only electrons with a pass energy $E_{\text{pass}} = HV$, where $H$ is a constant determined by the physical characteristics of the analyzer and $V$ is the potential between the inner and outer hemispheres. This voltage is directly related to the voltage applied on the lens. Electrons with a kinetic energy higher than $E_{\text{pass}}$ meet the exit plane closer to the outer hemisphere. Electrons with kinetic energy lower than $E_{\text{pass}}$ meet the exit plane close to the inner hemisphere. A high resolution of the spectrometer can be therefore achieved when low pass energies are chosen.

When deriving Eq. 2.2, we assumed that the spectrometer has the same work function as the measured sample. Often this is not the case. Assuming that the work function of the detector is higher than that of the sample, the electrons loose kinetic energy between the sample surface and the entrance of the detector, by the amount equal to the difference between the work function of the sample and that of the detector. Measuring, for example the work function of metals by just determining the position of the Fermi cutoff is wrong. The value should thus be corrected for the spectrometer work function. We will describe in a Sec. 2.4.1 a method to determine the real work functions of the materials.

2.4.1 Ultra-violet Photoemission Spectroscopy

UPS was used in this work to study the electronic structure of molecular films and at interfaces with ferromagnetic metallic substrates. With this technique, direct information about changes in the electronic structure of molecular films in the proximity of metal surfaces, as well as values for the ionization potential and hole injection barriers can be extracted. Furthermore, one can learn about the way the molecular environment influences the local electronic structure of the molecules, by comparing the solid state phase UPS spectra with the gas-phase UPS spectra. In what follows we describe the most important aspects of photoemission experiments on molecular systems, both in gas and solid state phases.

Gas-phase versus solid state photoemission spectra

The photoemission process is often interpreted using a sequence of three steps, as it was defined by Berglund and Spicer [58, 59]: after the photoexcitation, an electron has to travel through the solid to the surface (transport), and escape from the surface into vacuum.

The photoexcitation step is similar for photoemission from the gas-phase and solid films, only the relaxation effects differ. The time scale of the photoemission process is in the order of $10^{-16} - 10^{-15}$ s. Although the nuclei may not be able to move in this time, the electrons in the ion left behind may have time enough to readjust to the perturbed electrostatic potential. In this way the hole that is left behind in the molecule is partly screened, which reduces the energy necessary to withdraw an electron from the molecule (intra-molecular relaxation, $E_{iR}$). When the molecule is placed in a polarizable medium (solid state), the electronic relaxation during the photoemission
event has an additional contribution due to inter-molecular electronic relaxation (also called polarization energy, \(E_P\)). Thus, in the solid state, the kinetic energy of the photoelectrons increases with the amount \(E_{iR} + E_P\). In other words, the ionization potential of the molecules in solid state, i.e. the minimum energy required to extract an electron in vacuum, decreases due to solid state electronic polarization of the surrounding medium (see also the example shown in Fig. 2.10). The polarization contribution (or the inter-molecular relaxation energy) is in the order of 1 to 3 eV for the valence electrons in molecular solids [9, 60, 61].

The transport step is absent in the gas-phase, at least if we disregard the travel of the photoelectron within the molecule itself. In solids, the photoelectron has a certain probability that it is inelastically scattered when it travels over a certain distance (i.e. it loses some kinetic energy by electron-electron or electron-phonon interaction). The photoelectrons contributing to the photoemission spectrum in solids are therefore divided in two groups: primary electrons, that did not undergo an inelastic scattering event and secondary electrons, which have lost some of their kinetic energy during their travel to the vacuum. The secondary electrons contribute to a tail in the PES spectrum at the low kinetic energy side of the spectrum (see Fig. 2.9). In PES on isolated molecules at low pressure, the mean free path of an electron is many orders of magnitude larger, and the contribution of the secondary electrons is generally small, if not negligible.

For the escape step, in order to cross the solid/vacuum interface, the kinetic energy of the photoelectrons must be infinitesimally higher than the energy of the vacuum level. This requirement results in a cut-off at the low kinetic side of the spectrum. In a PES spectrum recorded on a solid film, this part of the spectrum is dominated by the secondary electrons, and the cut-off is easily identified as a sudden drop in intensity (see Fig. 2.9). As we will see latter in this section, this cut-off plays an important role for the determination of the binding energies of the solids.

The resolution of PES spectrum in gas-phase is determined by effects such as lifetime broadening, source width and the instrumental resolution. For most molecular systems, the lifetime of the final state is in the order picoseconds or larger, and it has therefore only a negligible contribution to the line width [62]. For the source, there are several effects influencing its shape and width. The intrinsic linewidth of He-I radiation is of the order of 1 meV. Since this width is determined by the atomic lifetime of the excited state, the lineshape is expected to be Lorentzian. In a real gas discharge the linewidth is further increased by inelastic collisions and Doppler shifts due to the relative motion of the gas atoms. The collisional broadening is also Lorentzian, while the Doppler broadening is more likely to be Gaussian (depending on the velocity distribution in the gas). Another source of broadening in the source is self-absorption (in the He gas itself), which leads to saturation, “cutting out” the high-intensity center of the peak. The lineshape of this broadening is much more difficult to predict, but is neither Lorentzian nor Gaussian. The instrumental resolution is determined by the analyzer. As explained above, the best resolution in hemispherical analyzers can be obtained for low pass energies.
In the PES spectra of thin molecular films, some additional effects can lead to line broadening. Salaneck et al. [60] identified a temperature dependent and a temperature independent contribution to the line width. The temperature dependent contribution is attributed to a coupling of the photo-generated molecular ion with low lying vibrational modes. The temperature independent contribution is explained by differences in the relaxation in the final state by the surrounding molecules due to local polarizability variations. For example molecules at the surface of a condensed film have a lower coordination number when compared to molecules in the bulk. This leads to a less complete screening of the cation at the surface of a condensed molecular film. Further, local variations of the ion-state energies due site to site differences in the environment (homogeneous and inhomogeneous effects) lead to broadening of the spectral features as well [32, 60, 63, 64].

Experimentally, the photoemission experiments performed on isolated molecules are very similar to the ones performed on thin solid films. To measure the UPS spectrum in gas-phase, one uses a beam of molecules. The molecular beam is obtained by heating the desired material from an evaporation cell, placed horizontally, such that a high enough vapor pressure is obtained. The total number of photoelectrons, related to the vapor pressure of the molecular beam, is relatively low when compared with UPS experiments on thin films, because the density of molecules in a solid is much higher than that of a gas-phase. One should keep in mind that the vapor pressure should not be increased too much in order to improve the count rate. This is to avoid the formation of molecular clusters but also to prevent inelastic collisions of the photoelectron or building up of space charge fields, since such effects will shift and broaden the features in the UPS spectrum.

An aspect that should be kept in mind when performing photoemission experiments on molecular crystals is charging at the sample surface. For this reason only thin organic layers, deposited on good conductors, can be measured. Charging of the sample can easily be checked by changing the illumination intensity. Charging effects lead to broadening of the spectral features and a shift of the spectrum to lower kinetic energy upon higher illumination intensities.

Charging phenomena can also result in damaging the organic materials since bond breaking or cross-linking within the organic material might occur [65]. Radiation-induced damages has been mostly observed when high intensity He lamps or electron beams were used. To make sure this is not the case, one should therefore compare photoemission spectra measured at different exposure times. The spectra measured in a very short while after exposure should be the same with the spectra after a long exposure. Damaging would result in broadening of the features and an increased background of the secondary electron tail.

To illustrate the influence of the environment on the electronic structure of the molecule, we represent in Fig. 2.10 the UPS spectra of oligo(para-phenylene) or OPV5, measured both in gas and condensed phases.

In Fig. 2.10 we can clearly observe the decrease in ionization potential in the condensed phase with respect to that of the isolated molecules. As explained above, this is
Figure 2.10: UPS spectra of OPV5 measured in the gas-phase (grey) and in the solid state (black); the experimental resolution in both experiments is approximately 0.15 eV. \( IP \) abbreviates the ionization potential, \( E_P \) gives the intermolecular polarization energy. The intermolecular relaxation energy is mainly caused by screening effects. These effects stabilize the final state and therefore lower the energy necessary to remove an electron from the solid to the vacuum level, and thus the \( IP \)

predominantly caused by the difference in the polarizability of the medium surrounding the photoionized molecule. This also means that the electronic structure of the molecules in the proximity of metal surfaces can differ from the bulk ones. One specific effect is the band-gap narrowing at the interface between the molecular layer and metal, as it was observed in the case of the C\(_{60}\)/Ag system [66, 67].

Note that the spectrum of the film retains its molecular identity. We can still recognize features in the spectrum that are derived from delocalized (intramolecular) \( \pi \)-orbitals. We can also observe that the features in solid state are broadened. The full width at half maximum (FWHM) of the highest molecular orbital (HOMO) increases from 0.4 eV in the gas-phase UPS spectra to 0.5 eV in the solid-state UPS spectra. The persistence of the molecular orbital structure is a signature of weak intermolecular interaction.
How to extract an energy level diagram from UPS measurements

In this section we describe how the true work function of a metal should be determined and how to build an energy level diagram based on photoemission spectra. Since UPS is a surface sensitive technique, one way to study the interfaces between the organic layers and substrates is to record UPS spectra for each subsequently deposited organic layer.

The method we describe below is based on the measurement of the secondary electron cutoff of the UPS spectra. These electrons have very low energies and because of the stray fields in the detector some of the electrons will be lost. To overcome this problem, a sample bias with a negative polarity should be applied. Due to this, all the electrons are accelerated to the detector, leading therefore to a true measurement of the secondary electron cut off. The bias can be applied using a regular power supply. We mention that the ground of the power supply should be connected with general ground of the setup and the applied bias should not be current limited.

Typical spectra measured at the pentacene-Co interface, with sample bias of $-4 \, \text{V}$ is shown in Fig. 2.11. The left panel represents the photoemission spectrum of a pure Co substrate. In the right panel we plotted the photoemission spectrum of a thick pentacene film deposited on the Co substrate. The highest kinetic energy (lowest binding energy) are attributed to emission of electrons from the Fermi level of the metal ($E_{k,max}(\text{Co})$) or from the HOMO of the oligomer ($E_{k,max}(\text{pentacene})$). The low-kinetic-energy cut-off ($E_{k,min}(\text{Co})$, $E_{k,min}(\text{pentacene})$) corresponds to electrons having suffered energy loss processes and ended up at the minimum kinetic energy in the solid to escape into the vacuum. The low-energy edge of the secondary electron peak corresponds to the vacuum level of the sample. Thus, the position of the vacuum level of a material in the diagram is determined by adding 21.2 eV (energy of the incoming photons) to the cut-off energy to give $E_{\text{vac}}(\text{Co})$ and $E_{\text{vac}}(\text{pentacene})$. The work function of the metallic substrate is determined by subtracting the width of the spectrum, measured from the low-energy onset to the the position of the Fermi level, from the photon energy width:

$$\Phi_{\text{Co}} = h\nu - (E_{k,max}(\text{Co}) - E_{k,min}(\text{Co})) \quad (2.3)$$

Since all the photoelectrons are accelerated by the an equal amount, which includes the work function of the detector, the value extracted from Eq. 2.3 represents the true work function of the Co sample.

In a similar way, the position of the (onset of the) HOMO level (or ionization potential $IP$) is calculated as the photon energy minus the total width of the UPS spectrum, measured from the low-energy onset to the high kinetic energy edge of the HOMO molecular level, as illustrated in Fig. 2.11.

$$IP = h\nu - (E_{k,max}(\text{pentacene}) - E_{k,min}(\text{pentacene})) \quad (2.4)$$

Note that the energy of the HOMO thus obtained corresponds to the ionization potential of the molecule. By comparing the two UPS spectra, the energy diagram can be constructed as shown in the middle panel of Fig. 2.11 and determine the positions of
Figure 2.11: Method for determining the energy diagram of the metal/oligomer interface using the ultraviolet photoelectron spectra of the metal and the oligomer. The spectra were recorded with a bias of -4 V between sample and analyzer. The y-axis represents the kinetic energy of the photoelectrons at the entrance slit of the analyzer. Left panel: Photoemission spectra of the Co substrate; Middle panel: energy diagram of the pentacene-Co interface; right panel: photoemission of 20 nm of pentacene on the Co substrate.

- $E_{k,max}(Co)$: maximum kinetic energy (KE) of a photoelectron (PE) excited from Co with photon energy $h\nu = 21.22$ eV;
- $E_{k,max}(pentacene)$: maximum KE of the PE excited from pentacene;
- $E_{k,min}(Co)$: minimum KE of the scattered PE excited from Co;
- $E_{k,min}(pentacene)$: minimum KE of a scattered PE from pentacene;
- $E_{vac}(Co)$: vacuum level of Co;
- $E_{vac}(pentacene)$: vacuum level of pentacene;
- $\Phi_{Co}$: work function of Co;
- $E_{HOMO}$: energy level of HOMO of pentacene;
- $\varepsilon_{v-F}$: hole barrier or the energy difference between the Fermi level of Co and the HOMO level;
- $\Delta$: vacuum level shift. With the definition given in Ref. [32] the vacuum level shift in this particular case has a negative value.

The energy levels at both sides of the interface. The difference ($\Delta$) between the vacuum levels of the metal and the oligomer layer is given by:

$$\Delta = E_{k,min}(pentacene) - E_{k,min}(Co)$$  \hspace{1cm} (2.5)

Since the vacuum level of the oligomer is lower than the vacuum level of Co, the electric field points from the oligomer ($\delta^+$) to the metal ($\delta^-$), making $\Delta < 0$ (as defined in
2.4. Electronic structure analysis using photoelectron spectroscopy

Ref. [32]). In this case, the vacuum level shift leads to an increase of the barrier for holes ($\varepsilon_{v-F}$) according to:

$$\varepsilon_{v-F} = IP - \Phi(Co) - \Delta \quad (2.6)$$

In analogy, with invers photoemission electron spectroscopy (IPES) the energy of the lowest unoccupied molecular orbital (LUMO) can be determined (the IPES process is the invers process of the photoemission). The values given for the HOMO and LUMO in the energy diagrams correspond to the ionization potential ($I_E$) and electron affinity ($E_A$), respectively. The combination UPS/IPES yields directly the transport gap.

2.4.2 X-ray photoemission spectroscopy

XPS is generally used to gain information about the deeper levels in a solid. XPS can also be used to check the chemical composition and to determine the stoichiometry of materials consisting of several compounds. For standard XPS sources, the sensitivity of this technique is 1%. The existence of a core hole after ionization affects the energy distribution of the emitted electrons in different ways. Besides the screening of the hole, due to the local environment, there can be reorganization of the electronic structure. Such processes give rise to additional peaks in the PES spectra, called satellites. In addition Auger processes can occur. For a description of these processes, we refer to the dedicated books [46, 58, 68–71].

![XPS spectrum of Polyethylene terephthalate (PET) recorded with monochromatic AlK-α source. The structural formula of this polymer is also shown and the carbon atoms are identified to show their contribution to the spectrum. Taken from [72].](image)

**Figure 2.12:** XPS spectrum of Polyethylene terephthalate (PET) recorded with monochromatic AlK-α source. The structural formula of this polymer is also shown and the carbon atoms are identified to show their contribution to the spectrum. Taken from [72].
XPS can also be used to study polymeric materials. As all organic polymers contain substantial quantities of carbon, it is the chemical shift of the C1s electrons that predominates the interpretation of XPS. In many organic compounds the C1s spectrum is extremely complex and in order to resolve all the components in the chemical structure it is necessary to carry out XPS at the highest possible resolution. By careful analysis it is possible to identify peaks corresponding to carbon atoms bound to different atoms and even to differentiate between aliphatic and aromatic carbons.

As an illustration we show in Fig. 2.12 an example of the XPS spectrum of polyethy-

![XPS spectra](image)

**Figure 2.13:** (a) XPS spectra of Co and Ni(111) taken with an Al K-\(\alpha\) source. The peaks originating from the different levels in the two films were labelled according to the description found in literature [68]. The rest of the peaks are satellites or peaks caused by Auger transitions. (b) XPS spectra of a pentacene film
2.4. Electronic structure analysis using photoelectron spectroscopy

Pristine terephthalate (PET) - taken from [72]. The structure of this polymer is also shown in this figure. The different peaks correspond to aromatic carbon (1) at a binding energy around 284.70 eV, aliphatic carbon (2) at 286.24 eV and a carboxyl carbon (3) at 288.66 eV. The peak at the binding energy around 293 eV corresponds to a shake-up satellite, which is attributed to a $\pi \rightarrow \pi^*$ transition in the aromatic ring [72].

For the work described in this thesis, XPS was used to study the composition of the substrates and of the grown pentacene films. The quality of the Ni(111) and Co substrates used for this work is illustrated by the XPS spectra shown in Fig. 2.13 (a). The spectra consist of peaks originating from the different levels of the two studied materials, some additional satellites and Auger peaks. The different peaks are assigned in this figure. We note that the spectra of Co and Ni(111) resemble those reported in literature [68]. The presence of oxygen in the sample is normally marked by a peak around 531 eV, corresponding to O 1s level. The absence of this peak in the two spectra indicates the high degree of purity of the two films.

In Fig. 2.13 (b) we show an example of a pentacene XPS spectrum, measured on a film of 200 Å thickness, which was grown on a Co substrate. The spectrum consists mainly of a carbon peak at a binding energy of 284.6 eV. The high background at high binding energies (> 750 eV) is due to the secondary electrons. Besides the C 1s peak, at binding energies around 750 eV traces of some of the Co peaks are also seen. The presence of the quinone impurities would lead to an additional oxygen peak or even an extra peak related to the C=O bond. The absence of an oxygen peak in the spectra of pentacene shown in Fig. 2.13 (b) is therefore an indication of the good quality of the pentacene films used in this work. Notice that the valence band of the pentacene appears as a broad feature in the XPS spectrum of pentacene. This is due to the low ionization cross-section of X-rays for these levels. For the information of the density of states at the valence band in these materials UPS is therefore recommended.
Chapter 3

Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

Abstract: In this chapter we investigate the structural properties of novel molecular-ferromagnetic metal systems. First we introduce some concepts related to the growth of organic molecules in vacuum. Then we study the growth of two large aromatic molecules, Perylene- tetracarboxylic- dianhydride (PTCDA) and pentacene, on 3d ferromagnetic Ni(111) and Co. Well-oriented substrates as well as polycrystalline substrates are used. Effects of the deposition parameters on the ordering and morphology of the films is studied by means of STM and AFM. Despite the high reactivity of the ferromagnetic substrates, we demonstrate that molecular ordering is possible when the substrate is passivated, or when the proper molecule-substrate combination is chosen.

3.1 Introduction

The growth of large aromatic molecules on the 3d ferromagnetic transition metals is studied, in view of application into hybrid organo-metallic electronic devices in which the spin degree of freedom is exploited. It has been reported up to now that deposition of large aromatic molecules on such reactive substrates lead mostly to disordered structures [36, 41]. In the case of molecules containing sulphur, such as thiols and thiophenes, the high reactivity of the substrate determined even decomposition of the molecules, at temperatures below room temperature [36–39].

Koller et al. showed that the interaction between bithiophene and Ni(100) was reduced when the substrate was exposed to small amounts of sulfur, inducing the formation of ordered rows of bithiophenes, at low coverages [40]. No ordered structures have been observed in this system at higher coverages. Ordered overlayers of large
aromatic molecules were registered in the case of naphthalene dicarboxylic anhydride (NDCA)/Ni(111) system, only for the monolayer structure. In this case NDCA molecules lie flat\(^1\) on the substrate and align in rows that are not densely packed [41]. Alternatively, it has been suggested that a change to a perpendicular orientation\(^2\) of the molecules is possible when the Ni(111) substrate is exposed prior to NDCA deposition to small amounts of oxygen.

Up to now, C\(_{60}\) is the only stable molecular system at the interface with an ferromagnetic substrate that shows densely ordered multilayer structures [73, 74]. On a Ni(110) substrate, several ordered overlayers were obtained at different substrate temperatures. The lattice parameters of these ordered structures are distorted. This effect was attributed to a strong interaction of C\(_{60}\) with the Ni(110) substrate. Additionally, Murray et al. showed that absorption of C\(_{60}\) leads to roughening of the Ni(110) substrate [75]. The decomposition temperature of C\(_{60}\) at this interface is well above room temperature (around 690 K). However, the growth mode is of the Stransky - Kras-tanov type (island growth), which we consider inappropriate for the implementation into spintronic devices.

In this work we report on the structural properties of two new systems: pentacene and PTCDA. The structure of these molecules will be introduced in Sec. 3.2 and 3.3. The ordering and morphology of the thin organic films as a function of coverage, deposition rate and substrate temperature is addressed. First, we introduce the reader with basic notions related to the growth of molecular systems in UHV environment.

### Organic molecular beam epitaxy

The oriented growth of a crystalline material on substrates is called epitaxy. As in the case of inorganic materials, epitaxy refers to systems where a one-to-one commensurate relationship between the molecular positions in the deposited layer and the substrate is formed. In the case of growth of inorganic films, epitaxy is determined by the lattice mismatch between the the lattice parameter of the substrate \(a_s\) and that of the grown film \(a_{film}\). The lattice mismatch is defined as \(|a_{film} - a_s|/a_s\) and should be in the order of few percents, in order to allow formation of well-oriented films.

At the organic-inorganic interface, two systems with different dimensions, different size of the unit cell, and often a different symmetry group interact with each other. The lattice parameters of an organic film are much larger than the ones of the inorganic substrates. The weak van der Waals interaction between neighboring molecules in molecular crystals offers these systems an inherent flexibility to adjust to the lattice parameters of the underlying substrates. Rotation, stretching or twisting of bonds within a molecule can occur, and even the relative position of two molecules within a cell can be changed [42, 53]. It is believed that for a weak molecule-substrate interaction long range ordering can be obtained without having fulfilled any epitaxial relationship. In some cases, long range ordering has been reported even on amorphous substrates,

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\(^1\)Flat orientation: the molecular plane is parallel to the surface of the substrate

\(^2\)Perpendicular orientation: the molecular plane is perpendicular to the surface of the substrate
such as glass or SiOx [42, 76]. Due to the large number of degrees of freedom in these systems, prediction of epitaxy on the basis of energy considerations is difficult [42].

For organic layers, new epitaxial terms have been introduced [77]. The lattice vectors $b_1, b_2$ of the overlayer are expressed in vector form as function of the lattice vectors $a_1, a_2$ of the substrate surface:

$$b_1 = p a_1 + q a_2; \quad b_2 = r a_1 + s a_2,$$

(3.1)

With the definitions of the unit cells given in Fig. 3.1, $p, q, r$ and $s$ have the following expressions:

$$p = \frac{b_1 \sin(\alpha - \theta)}{a_1 \sin(\alpha)}, \quad q = \frac{b_1 \sin(\theta)}{a_2 \sin(\alpha)}$$
$$r = \frac{b_2 \sin(\alpha - \theta - \beta)}{a_1 \sin(\alpha)}, \quad s = \frac{b_2 \sin(\theta + \beta)}{a_2 \sin(\alpha)}$$

(3.2)

Depending on the values of $p, q, r, s$ parameters, epitaxy for molecular films has been defined in terms of comensurism, point-on-line coincidence and incommensurism. These terms are described bellow. In Fig. 3.2 we represent examples for each type of epitaxy.

- **Comensurism or point-on-point coincidence**: Each primitive overlayer lattice vector is an integer multiple of an identically oriented (primitive or non-primitive) substrate lattice vector; $p, q, r$, and $s$ are all integers. All lattice points of the overlayer coincide with lattice points of the substrate. In the example shown in Fig. 3.2 (a) $p = 3, q = 3, r = -3, s = 3$.

- **Coincidence**: It is sufficient if the adsorbate lattice points coincide only partially with substrate lattice points. The coinciding points form a supercell.
Figure 3.2: Different types of epitaxial relationships between the two-dimensional lattices of the substrate surface (lattice vectors $a_1$ and $a_2$) and an adsorbate layer (lattice vectors $b_1$ and $b_2$). The overlayer lattice points are drawn in light gray. (a) Commensurate structure: all the lattice points of the overlayer coincide with the lattice points of the substrates; (b), (c) Point-on-line coincidence: only few points of the overlayer coincides with the lattice points of the substrates. The squares indicate the supercells for which the lattice points of the overlayer coincide with the lattice points of the substrate. (b) Coincidence I; (c) Coincidence II; (d) Incommensurate structure.

the coinciding points lie on a line parallel to one of the crystalline directions of the underlying substrate, this type of epitaxy is called point-on-line coincidence. This type of epitaxy has been divided in two classes. Coincidence I: among $p$, $q$, $r$, and $s$, there are at least two integers. In the example shown in Fig. 3.2 (b), $p = 3$, $q = 0$, $r = -1/5$, $s = 3$. The supercell is indicated in figure. In this case, every point lies on a line parallel to the [100] direction of the underlying
lattice. In the case of hexagonal substrates, if the lattice parameters are defined by a lattice angle of 60° for integer values of the sum \( p + q \) and \( r + s \) will produce coincidence. If the lattice angle of 120° is chosen, coincidence will be given in the case for which \( p - q \) and \( r - s \) are integer numbers. Coincidence II forms when \( p, q, r, \) and \( s \) are rational, but none of them is integer. Consequently, only some of the overlayer lattice points lie on substrate lattice points. In the example shown in Fig. 3.2 (c) \( p = 1/2, q = -5/2, r = 5/2, s = -1/2 \). In this case, the overlayer lattice points lie on a line parallel to the \([1\bar{5}0]\) direction of the underlying lattice.

- **Incommensurism** exists when at least one of the elements \( p, q, r, \) and \( s \) are irrational numbers. Under this condition, no distinctive registry between the substrate lattice and the deposit lattice exists. Such growth appeared to occur for a weak molecule-substrate interaction [42].

**Thermodynamics versus kinetics**

Next, we describe the process of growth and the underlying principles that determine the structure and morphology of a particular film. Studies of several organic-inorganic thin film systems implied that many of the fundamental concepts of inorganic MBE can be transferred to the growth of organic films [78–81].

Similar to the inorganic films, nucleation and growth processes are responsible for the structure and morphology of thin films grown on surfaces. It is generally accepted that the growth of molecules occurs via one of three modes: layer-plus-island (Stranski-Krastonov), layer-by-layer (Frank-van der Merwe) or island growth (Volmer-Weber), as illustrated in Fig. 3.3.

A simple formal distinction between the conditions for the occurrence of the various growth modes is very often made in terms of specific free surface energies of the substrate-vacuum \( \gamma_S \), film-vacuum \( \gamma_F \) and substrate-film interface \( \gamma_{S/F} \). Depending on the relation between these surface energies, the two limiting growth modes, layer-by-layer and island, can be distinguished by the following relations:

layer-by-layer growth: \( \gamma_S \geq \gamma_F + \gamma_{S/F} \)

island growth: \( \gamma_S < \gamma_F + \gamma_{S/F} \)

![Figure 3.3: Various modes of epitaxial growth: (a) layer-by-layer (Frank-van der Merwe); (b) layer-plus-island (Stranski-Krastonov); (c) island (Vollmer-Weber). The horizontal lines on the epitaxial layers schematically represents individual atomic or molecular layers](image)
If the grown film is strained, an additional energy term is implemented in the specific surface-film free energy. The lattice of the film tries to adjust to the substrate lattice, at the expense of elastic deformation energy. The transformation from the layer to island growth occurs when the spatial extent of the elastic strain field exceeds the range of the adhesion forces within the deposited material. When strain is present, after a certain thickness (also called critical thickness) the strain relaxes. If the lattice mismatch is too great, misfit dislocations will form, but even if misfit dislocations do not form, the strain can influence the crystal growth [82].

The above-mentioned criterium holds under the condition that the particle is transferred from the gas-phase into the solid at the equilibrium vapor pressure $p_\infty$. If the particle changes over from vapor to solid at a pressure $p_v$, one has to take into account a contribution $n\Delta\mu = nkT\ln \frac{p_v}{p_\infty}$, which is the change in Gibbs free energy when a particle is transferred from the gas-phase into the condensed phase. Here, $n$ is the particle number within a nucleus. $\Delta\mu^3$ is the difference between the chemical potential of the vapor phase and the infinitely large crystal. $\Delta\mu$ appears as one of the thermodynamic driving forces for the crystallization process. In most of the growth processes in vacuum, the vapor phase is supersaturated ($\Delta\mu > 0$). In this case $\Delta\mu$ is called supersaturation. Markov defined the condition for a 2D or 3D growth of inorganic materials, in supersaturation conditions, by the following relations [83]:

**layer-by-layer growth:**

$$\gamma_S \geq \gamma_F + \gamma_{S/F} - \Delta\mu/2s_c$$

**island growth:**

$$\gamma_S < \gamma_F + \gamma_{S/F} - \Delta\mu/2s_c$$

with $s_c$ surface of the unit mesh of the grown material. We can see that under supersaturation conditions, a film will have the tendency to grow in a layer-by-layer fashion. This classification is worked out within a thermodynamic model [83].

Recently, Verlaak et al. adapted the microscopic theory of nucleation to explain the growth of pentacene, tetracene and perylene onto weakly interacting substrates [76]. This theory predicts the type of growth on thermodynamic considerations. The different surface free energies were calculated in terms of energy required to form different edges of a surface. With other words, from the strength of interaction along different edges into the crystal one can estimate the Gibbs free energy required to form a nucleus, i.e. energy of formation [83]. In the energy of formation, the supersaturation term is also taken into account.

The different interaction energies were calculated by Verlaak et al. using a so-called MM3 van der Waals potential [84]. In such calculations, the interaction between two molecules accounts for the total number of atoms that contribute to the interaction, i.e. an atom-atom interaction. The MM3 force field takes into account stretching, torsion and bending of the different bonds. From the minimization condition of energy of formation, the authors calculate the transition supersaturation, i.e. supersaturation at which the transition from 2D to 3D growth occurs. The supersaturation was expressed by the authors in terms of measurable quantities such as flux and substrate temperature. Furthermore, the authors predicted that molecules with long interaction length for

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3The chemical potential $\mu$, expresses the work that has to be done in order to change the number of particles in the phase by 1
3.1. Introduction

Intralayer interaction and short interaction length for interlayer interactions, have a larger region for 2D growth\(^4\). In this case, there is a high energy of nucleus formation due to higher intralayer interactions. Higher activation energy of nucleus formation, means higher barrier against nucleation and thus contributes to a lower nucleation rate, favoring larger grain size when the growth is diffusion mediated. In contrast, a molecule showing a low aspect ratio, i.e. short intralayer interaction length and long interlayer interaction width, would have a bigger chance to adopt a 3D growth.

Other approaches developed for the understanding of film growth are based on kinetic models. Such models take into account diffusion processes. First steps have been taken to test the applicability of diffusion models to organic films prepared by OMBD [81, 85]. Below, we describe some basic aspects related to the kinetic theory, as developed for the growth of inorganic materials.

The final microscopic state of the system depends on the route taken through the various processes, as depicted in Fig. 3.4. There are three essential irreversible microscopic processes taken into account: condensation, adsorption and diffusion. Other processes such as capture at an already existent island and diffusion on and from an island are in some cases also important [82].

\[ E_i \quad \text{critical nucleus} \]

\[ \text{Arrival rate (R)} \quad \text{diffusion (E_d)} \quad \text{desorption (E_a)} \]

\[ \text{substrate (T)} \]

**Figure 3.4:** Schematic illustration of the processes occurring during growth. The independent variables are arrival rate (R) and substrate temperature (T). The activation energy for adsorption (or desorption) and diffusion are \( E_a \) and \( E_d \), respectively. The binding energy of the critical cluster, which contains \( i \) atoms (or molecules) is \( E_i \). Capture at an already existent island and diffusion on and from an island are also represented.

Condensation is the process in which an atom from the vapor arrives at random position on the interfaces, forms bonds with the surface atoms and sticks. Condensation of the film from the gas-phase (molecular beam) is described by an incoming flux (number of particles per cm\(^2\) per second)

\[ R = p(2\pi M k T_o)^{-1/2} \]

where \( p \) is the vapor pressure, \( M \) the molecular weight of the particles, \( k \) Boltzmann’s constant, and \( T_o \) the source temperature.

Secondly, an atom can desorb from the surface, with a desorption energy \( E_a \). The desorption process depends on how strong the atom is bonded with the crystal surface.

\[^4\text{interaction length is defined by the number of atoms within a molecule that participate at the intra- or inter-layer interaction}\]
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

The strength of bond depends on the type of the atom and the local geometry of the surface where the atom sticks. This process is characterized by the adatom lifetime \( \tau_a \), which is the time spent by an adatom form the arrival on the substrate until it leaves the surface. \( \tau_a \) follows the Arrhenius law, i.e \( \tau_a = \tau_{a_0} \cdot \exp \left( \frac{E_a}{kT} \right) \), \( T \) being the substrate temperature. In order to estimate the relevance of desorption process, one must compare \( \tau \) with the time scale set by the condensation process.

The most interesting process is probably surface diffusion. After an atom or a molecule arrive on the surface, it performs a random walk and searches for the energetically most favorable position. Surface diffusion is an activated process that relies on the temperature and the binding energies. For a particle on the surface to diffuse to the next lattice, it must overcome potential barrier \( E_d \) that exist between the particle and its neighbors. The magnitude of the potential barrier varies from system to system. The adatom diffusion over a surface is characterized by the \( E_d \). The adatom diffusion coefficient is \( D = D_0 \cdot \exp \left( -\frac{E_d}{kT} \right) \).

Generally speaking, the process of growth is microscopically described as follows: an adatom (molecule), or monomer, impinges on a substrate, then undergoes a random walk and has two alternatives that determine its fate: (i) the monomer may find an existing island and become incorporated leading to growth, or (ii) it may find one or more other diffusing atoms and nucleate a new island. This new island may be stable or unstable against dissociation depending on the binding energy of the cluster and the surface temperature. The size \( i \) at which an island consisting of \( i \) or less atoms is unstable, but \( i + 1 \) atoms is stable, is labelled the critical size. In general the critical nucleus size \( i \) will depend on temperature.

From the evaluation of rate equations applied for different condensation regimes, Venables determined a general equation for the island density [82]:

\[
N \sim R^\kappa \cdot \exp \left( \frac{E_N}{kT} \right)
\]  

(3.3)

with \( R \) the deposition rate, \( E_N \) activation energy, \( k \) Boltzman constant and \( T \) substrate temperature. This equation indicates that the island density shows a power dependence law on the deposition rate, with an exponent \( \kappa \) and an thermally activated behavior. \( E_N \) and \( \kappa \) depend on the type of condensation regime. Generally, two main regimes of condensations exists: complete and incomplete, depending whether the process of re-evaporation is significant or not. Obviously, in the former the process of re-evaporation is negligible. The latter regime was further classified into extreme incomplete and initially incomplete regimes. In the extreme incomplete regime the diffusion distance on the surface is so short that only atoms which impinge directly on the islands condense. In the initially incomplete regime, both diffusion and direct impingement contribute to the formation of clusters.

Tab. 3.1 summarizes the results of the kinetic theory, for the three condensation regimes, which we have just mentioned. We can see that exponent \( \kappa \) depends on the critical nucleus size \( (i) \). Because the minimum size of a critical nucleus is \( i = 1 \), we can deduce that the complete condensation regime is characterized by a power law with an exponent \( \kappa \) always smaller than 1, whereas for the two incomplete regimes of condensation it could be that \( \kappa > 1 \) when the critical nucleus size reaches large values.
Table 3.1: Parameters dependencies of the maximum cluster density in various regimes of condensation. Taken from [82]. $E_a$ and $E_d$ are adsorption and diffusion energies and $E_i$ is the binding energy of the critical nucleus of a size $i$

<table>
<thead>
<tr>
<th>Regime</th>
<th>3D islands</th>
<th>2D islands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete</td>
<td>$\kappa = i/(i + 2.5)$</td>
<td>$\kappa = i/(i + 2)$</td>
</tr>
<tr>
<td></td>
<td>$E_N = (1/(i + 2.5))[E_i + iE_d]$</td>
<td>$E_N = (1/(i + 2))[E_i + iE_d]$</td>
</tr>
<tr>
<td>Initially incomplete</td>
<td>$\kappa = 2i/5$</td>
<td>$\kappa = i/2$</td>
</tr>
<tr>
<td></td>
<td>$E_N = (2/5)[E_i + iE_a]$</td>
<td>$E_N = (1/2)[E_i + iE_a]$</td>
</tr>
<tr>
<td>Extreme incomplete</td>
<td>$\kappa = 2i/3$</td>
<td>$\kappa = i$</td>
</tr>
<tr>
<td></td>
<td>$E_N = (2/3)[E_i + (i + 1)E_a - E_d]$</td>
<td>$E_N = [E_i + (i + 1)E_a - E_d]$</td>
</tr>
</tbody>
</table>

Notice also in Tab. 3.1 that the expression for the activation energy $E_N$ for each of the three condensation regimes depends as well on the critical nucleus size ($i$) as on the adsorption energy ($E_a$), diffusion energy ($E_d$) and the binding energy of the critical nucleus size ($E_i$). It must be noted that the equations displayed in Tab. 3.1 are valid for substrate coverages smaller than 100%.
3.2 Growth of PTCDA on ferromagnetic metals

PTCDA is widely used for the study of the epitaxial growth of organic molecules. The structural formula of PTCDA is represented in Fig. 3.5. PTCDA consists of a perylene core with a delocalized $\pi$-electron system and two anhydride endgroups. The endgroups give rise to a permanent quadrupole moment with the positive charge situated around the center of the molecule, and the negative charge around the endgroups. The dimensions of PTCDA, calculated from the van der Waals radii of the constituents, corresponds to 14 Å in length and 9.2 Å in width. The crystal structure of PTCDA is monoclinic. Two polymorphic phases ($\alpha$ and $\beta$) of very similar lattice constants, but different inclination of the $a$ axis, were observed [86]. In both structures, the two molecules of the unit cell are coplanar and order in a herringbone-like pattern in the (102) plane, which is the cleavage plane of the crystal. These molecular sheets are stacked and the distance between these two planes is different for the two different polymorphs. A schematic drawing of the crystal structure of PTCDA is shown in Fig. 3.5. Table 3.2 summarizes the crystal parameters of the structure.

STM studies performed on PTCDA films deposited on inert substrates such as Au, Ag, SiOx, MoS$_2$ and highly oriented pyrolytic graphite (HOPG), revealed that PTCDA forms well ordered layers [41, 42, 53, 86, 87] with the (102) plane parallel to the substrate plane. So far, on the ferromagnetic substrates, Umbach et al. showed in a study performed on PTCDA/ Ni(111), that ordering of PTCDA is not possible, due to the high reactivity of the substrate [41].

In this work we study the structural properties of PTCDA films deposited on ferromagnetic substrates. The choice of this particular molecular system was motivated by
the interesting properties of the strongly similar naphthalene-dicarboxylic-anhydride (NDCA), which shows a change to a perpendicular orientation when the Ni(111) is exposed to small amounts of oxygen. The aim of this study is to investigate whether well ordered overlayers, preferentially with a perpendicular orientation, can be achieved when providing the proper molecule-substrate combination. First we investigate the growth on single crystalline substrates. As a prototype system of a fully reactive ferromagnetic substrate we study ordering on Co(001). As a prototype system with reduced reactivity we analyze the growth of PTCDA on Ni(111) substrates covered with an ordered p(2 × 2) oxygen overlayer. In addition to the single crystalline substrates we analyze the effect of polycrystalline substrates on the ordering and morphology of PTCDA. The role of deposition parameters on the structural properties of PTCDA is addressed as well. The morphology of the PTCDA films was studied by means of local probe techniques such as STM and AFM.

3.2.1 Experimental

For this part of the work, experiments were performed in two different UHV systems. The STM measurements on PTCDA films deposited at room temperature on Ni(111) were performed in a STM/AFM combined system, equipped also with cleaning facilities and LEED. The rest of the experiments were performed in the EUFORAC system (Sec. 2.1).

The Ni(111) single crystal was cleaned by repeated cycles of argon ion bombardment and heating to 1150 K. The O−p(2×2) − Ni(111) structure was prepared following one of the following procedures: (i) substrate exposure to 3 L of oxygen, and subsequent heating to 673 K and (ii) substrate exposure to 2 L oxygen at a temperature of 100 K. LEED patterns showed in both cases a characteristic p(2×2) structure, as indicated by the Fig. 3.6. We will refer to the O−p(2×2) − Ni(111) structure, from now on, as the passivated Ni(111).

Monocrystalline Co(001) films were grown by molecular beam epitaxy (MBE) on a Cu(001) single crystal. The polycrystalline Co films were grown by magnetron sputtering.

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Table 3.2: Parameters of the monoclinic unit cell of PTCDA. a, b, c, and β are the parameters of the three-dimensional bulk unit cell, and d102 is the inter-planar spacing for the (102)-plane. Taken from [86, 88, 89]

<table>
<thead>
<tr>
<th>form</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>d102 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α phase</td>
<td>3.74</td>
<td>11.96</td>
<td>17.34</td>
<td>98.8</td>
<td>3.22</td>
</tr>
<tr>
<td>β phase</td>
<td>3.87</td>
<td>10.77</td>
<td>19.3</td>
<td>83.5</td>
<td>3.25</td>
</tr>
</tbody>
</table>
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

Figure 3.6: LEED patterns of Ni(111) before (a) and after (b) oxygen exposure, measured at an energy of 79 eV. Fig (b) is an indication of the O p(2x2) reconstruction.

tering on silicon substrates with a natural oxide. Tantalum buffer layers were used to provide growth of smooth Co films. The silicon substrates were carefully cleaned by sonication in ammonia, acetone and ethanol and outgassed in UHV for several hours. PTCDA was purified by gradient sublimation and evaporated according to the description given in Sec. 2.1.1. The crucible of the evaporation cell was made out of molybdenum. The evaporation rate was determined in the EUFORAC system by differential ellipsometry or by AFM measurements, as explained in Sec. 2.1.3 of this thesis. For the experiments performed in the STM/AFM combined system, the coverage was determined by STM.

The STM measurements were carried out with a commercial UHV STM system (Omicron). The tips used in this study were prepared by electrochemically etching tungsten wires. The STM images were taken in constant current mode. In order to achieve images with molecular contrast, we varied the scanning parameters. In the STM images shown in this chapter we used settings that provided the best molecular contrast. Although molecular resolution could be obtained at relatively high biases (above 1V) only, the images were stable for hours, which indicates that no tip induced effects were present. STM images could mostly be achieved for low tunneling currents (few pA). We could not find systematic values for the bias voltage. The AFM measurements were performed ex situ in the soft tapping mode (see Sec. 2.2).

3.2.2 Results and discussion: Monocrystalline substrates

In this section we present the morphology of PTCDA films deposited on different ferromagnetic monocrystalline substrates. First we describe ordering at low substrate temperatures (100 K). Secondly we address ordering at enhanced temperatures (RT). In both cases we investigate the role of deposition rates on the structural properties of PTCDA.
3.2. Growth of PTCDA on ferromagnetic metals

PTCDA deposition at low substrate temperatures

First, we address the initial stages of growth, by depositing a sub-monolayer coverage of PTCDA. Generally, when substrate temperatures of 100 K were used, PTCDA molecules were randomly oriented and spread relatively uniformly over the substrate. This is illustrated in Fig. 3.7.

The STM images shown in Fig. 3.7 (a, b) correspond to a passivated Ni(111) substrate, before and after the deposition of PTCDA, respectively. The PTCDA film has a nominal thickness of 1.5 Å (∼ 0.5 ML) and it was deposited with a deposition rate of 3 Å/min. The images were measured at room temperature. The two STM images are very similar but the roughness of the covered substrate is bigger than for the clean Ni(111) substrates. For the clean substrate the corrugation corresponds to about 3 Å, whereas the PTCDA film shows features with an apparent height of 4 Å. The latter value is the closest to the interlayer spacing of PTCDA crystal structure (see Tab. 3.2), indicating that the molecules lie flat or almost flat onto the substrate. A closer look

![Figure 3.7](image)

**Figure 3.7**: STM images of: (a) the passivated substrate (O−p(2×2) − Ni(111)) - before deposition; Scanning parameters: \(V_{\text{sample}} = 0.1 \text{ V}; I = 1000 \text{ pA}\); (b) PTCDA layer, deposited at a substrate temperature of 100 K; Scanning parameters: \(V_{\text{sample}} = 0.7 \text{ V}; I = 20 \text{ pA}\); (c) Small area scan showing the morphology of the PTCDA layer on a terrace; (d) STM image showing (sub)molecular resolution; The image represents the derivative of the height channel.
into one of the terraces in the PTCDA covered sample is shown in Fig. 3.7 (c). The bright spots visible in Fig. 3.7 (c), correspond to single molecules or molecular clusters of flat orientation. Since the PTCDA film is disordered, the steps visible in Fig. 3.7 (b) should be attributed to the Ni(111) substrate. To better illustrate the different features on the substrate, we plotted in Fig. 3.7 (d), the derivative \( dz/dx + dz/dy \), with \( z \) the height signal and \( x, y \) - scanning directions, for a smaller area scan. The features which we indicated in Fig. 3.7 (d) by “1” and “2” have lateral sizes of about 16 Å in length and 12 Å in width. Within the experimental resolution these values correspond to the expected sizes for a PTCDA molecule. Within a cluster (see Fig. 3.7 (d)), features of smaller size can be distinguished. We conjecture that these features indicate the

Figure 3.8: STM images of: (a) Co(001) film with a nominal thickness of about 10 ML. Scanning conditions: \( V_{\text{sample}} = 0.04 \) V; \( I = 500 \) pA; (b) PTCDA layer deposited on Co thin film with a (001) orientation. Scanning conditions \( V_{\text{sample}} = 0.04 \) V; \( I = 500 \) pA; (c) Smaller area scan indicating the disordered structure of PTCDA.
internal structure of the spatial distribution of the electrons within such a cluster. Due to the random orientation of molecules, it is difficult to assign single molecules within such a cluster.

Next, we increased the coverage to above a monolayer, to verify whether ordering occurred at a later stage of growth. We investigated layers with nominal thicknesses up to 20 Å (≈7 ML of flat oriented molecules). Also different deposition rates in the range 3 to 10 Å/min were tried out. Altogether, we verified that ordering of PTCDA at low substrate temperatures is not possible on the passivated Ni(111). Results were identical, independent on the coverage and deposition rate. A comparative study on the Co(001) lead to similar results.

We illustrate the disordered character of the morphology of the PTCDA layer at higher coverage for a film deposited on a Co(100) substrate. Figure 3.8 (a) represents a STM micrograph for a Co film with a thickness of about 10 ML. This image shows 3 different height levels with terraces of a rectangular shape, which is the equilibrium shape of a (001) surface. Figure 3.8 (b) indicates the morphology of a PTCDA film with a nominal coverage of 8 Å (2.7 ML). The PTCDA layer was deposited at a rate of ≈3 Å/min and a substrate temperature of 100 K. Figure 3.8 (c) shows features identified with single PTCDA molecules. We can see that the molecules are uniformly distributed over the substrate and form disordered structures. Also in this case we can identify terraces in the PTCDA covered substrate, corresponding to the underlying Co film. This means that the PTCDA film follows the morphology of the substrate.

In conclusion, deposition of PTCDA at low temperature substrates lead to disordered structures, even on the passivated Ni(111). We attribute these observations to a low mobility of the deposited molecules.

**PTCDA deposition at room temperature substrate**

After having verified that ordering of PTCDA on clean and passivated substrates is not possible at low temperatures, due to a too low mobility of molecules, we proceed with deposition of molecules at room temperature substrates. We present further the results of experiments performed on the passivated Ni(111) substrates.

We observed different ordered structures of PTCDA for different coverages and evaporation rates. At these substrate temperatures, the PTCDA molecules adopted an island growth. We could obtain molecular resolution only for islands with thickness up to 50 Å.

As a typical example of ordering at low coverage (few ML), we show in Fig. 3.9 (a) an STM image of a PTCDA layer with a nominal coverage of 4 ML. The film was deposited at a rate of ≈1.2 Å/min. Islands with irregular hexagonal shape that have heights up to 24 Å and lateral size of typically 100 nm, can be seen. The corrugation within the PTCDA layer was in the order of few Å, which leads us to conclude that the deposition of PTCDA on O−p(2×2) − Ni(111) does not induce large surface reorganizations, as it has been observed in the case of C_60/Ni(110) [75] and PTCDA/Cu(110) systems.

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8 These results have been published in [91], with a slightly different interpretation.
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

Figure 3.9: (a) STM image of PTCDA islands; Scanning parameters: $V_{\text{sample}} = -2.693$ V; $I = 25$ pA and (b) Structure of PTCDA within an island; Scanning parameters: $V_{\text{sample}} = -3.26$ V; $I = 18$ pA.

[52]. The structure within such an island is displayed in Fig. 3.9 (b). The image reveals individual molecules of flat orientation that arrange in the herringbone-like (HB) structure. The unit vectors $b_1$ and $b_2$ of the PTCDA lattice is shown in figure.

A schematic real space model of the HB structure is shown in Fig. 3.10. Next to the arrangement of the molecules within the HB structure, we indicate the $p(2 \times 2)$ structure of the oxygen. The lattice dimensions and the angles between the unit-lattice vectors measured from images of different samples are reproducible within the limits displayed in Tab. 3.3, but do not allow us to clearly classify the lattice as either $\alpha$- or $\beta$- PTCDA. For the the angle between the unit-vector $b$ of the PTCDA film and

Figure 3.10: Real space model of the absorption geometry of PTCDA on O$-p(2 \times 2)$ – Ni(111). The herringbone angle $\tau$ and the unit vectors are drawn as well. The points indicate the sites of O atoms on (111) surface.
3.2. Growth of PTCDA on ferromagnetic metals

Table 3.3: Comparison of the structural data of PTCDA thin films deposited on O−p(2×2) − Ni(111) with those existent in literature

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$b_1$ (Å)</th>
<th>$b_2$ (Å)</th>
<th>$A = b_1 b_2 \sin \gamma$ (Å$^2$)</th>
<th>$\gamma(0)$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)− p(2×2)O</td>
<td>11.5 ± 1.0</td>
<td>19.5 ± 1.0</td>
<td>225 ± 30</td>
<td>91 ± 2</td>
<td>this work</td>
</tr>
<tr>
<td>Au(111)</td>
<td>11.96</td>
<td>19.912</td>
<td>238.15</td>
<td>90</td>
<td>[57]</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>12.6</td>
<td>18.95</td>
<td>238.7</td>
<td>89</td>
<td>[92]</td>
</tr>
<tr>
<td>HOPG</td>
<td>12.69</td>
<td>19.22</td>
<td>243.9</td>
<td>89.5</td>
<td>[54]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>12.4</td>
<td>19.7</td>
<td>244.2</td>
<td>88.8</td>
<td>[55]</td>
</tr>
<tr>
<td>GeS(010)</td>
<td>13.1</td>
<td>19.6</td>
<td>257</td>
<td>90</td>
<td>[56]</td>
</tr>
<tr>
<td>Cu(110)</td>
<td>12.5 ± 0.7</td>
<td>19.5 ± 0.7</td>
<td></td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>(102) plane α phase</td>
<td>11.96</td>
<td>19.91</td>
<td>238.1</td>
<td>90</td>
<td>[89]</td>
</tr>
<tr>
<td>(102) plane β phase</td>
<td>12.45</td>
<td>19.3</td>
<td>240.3</td>
<td>90</td>
<td>[86]</td>
</tr>
</tbody>
</table>

the direction [110] of the substrate (or the symmetrical equivalent [010] or [011]), we found values of 13° ± 2° and 28° ± 2°. The [110] direction is determined from atomic resolution STM images of the Ni(111) substrate. The herringbone angle ($\tau$), defined in Fig. 3.10, is in this case 85° ± 2°.

Remarkably, the observed structure is very similar to those obtained on Au(111), Ag(111), Cu(110), HOPG, MoS$_2$ and GeS(101) [52, 54–57, 86, 89, 92]. For comparison, the lattice parameters of PTCDA on these substrates are included in Tab. 3.3, as well as the data on the (102) crystal stacking planes of the $\alpha$- and $\beta$- phases. In all cases, herringbone-like structures consisting of flat lying molecules with very similar lattice constants and expansion of the unit-cell area up to 8% were observed. We note that in the case of PTCDA on O−p(2×2) − Ni(111) a compression of the unit-cell area of about 5% with respect to that of the (102) plane of the $\alpha$ phase, is found.

It is interesting to note that the symmetry of the herringbone like structure is square, which at first sight is not compatible with the irregular hexagonal shape of the PTCDA islands. A similar shape of islands has been observed in the case of PTCDA layers deposited on the Cu(110) [52] but also for different molecular systems, such as pentacene [76]. In the particular case of the pentacene/SiO$_x$ system, it has been shown that the surface energies for different faces of the crystal that bind to a nucleus (island) have similar values, meaning that they can not be excluded from the equilibrium shape of a pentacene crystallite. This should also be the case for PTCDA.

In order to explain the different angles between the lattice vector $b_1$ and the [110] direction of the substrate in the herringbone-like structure, we looked at the geometric considerations, developed within epitaxy concept for molecular systems (see Sec. 3.1, Eqs. 3.1 and 3.2). We note that $p$, $q$, $r$, and $s$ were deduced considering a value of 2.49 Å for the lattice constant of Ni, which we measured separately from atomically resolved STM images taken on a clean Ni(111) substrate. No atomic resolution could be obtained for the O passivated Ni(111) substrates. Generally, we found for the $p$, $q$, $r$, and $s$...
and \( s \) noninteger values, indicating that the observed PTCDA structures were incommensurate to the substrate. However, because the binding strength of the molecules with the substrate is unknown, we have to be aware of the fact that the O and Ni atoms on the substrate can reconstruct upon the absorption of the molecules, in a case of a strong interaction with the substrate. We did not observe big surface roughening, as it was reported in the case of C\(_{60}\) [75], but we can not exclude small displacements of the Ni and O atoms. Thus, an unambiguous explanation of the observed orientations is not only complicated by the uncertainty in the measured angles and distances, but also by the unknown relative binding strength of PTCDA to Ni and O sites.

Next, we discuss the morphology of the PTCDA films at larger thicknesses. At nominal coverages above 6 ML we observed different structures within islands. The lateral size of the islands is about 100 nm, similarly to the lower coverage films. Within islands, STM revealed domains of typically 10 nm diameter, where two distinct stripe like phases could be distinguished. Similar results were obtained with increased evaporation rates. The lateral size of the islands decreases by increasing the evaporation rate. For example, an increase in the evaporation rate to 4 Å/min leads to a decrease in the lateral size to about 40 nm. Below we present the structure of the film within islands.

One of the stripe-like phases (labelled “S–A”) is represented in Fig. 3.11. The width of the stripes is approximately 14 Å, a value that corresponds to the length of a PTCDA molecule. The size of the single features identified in this figure correspond to a flat lying molecule. Based on the STM observations, we draw in Fig. 3.11 an
3.2. Growth of PTCDA on ferromagnetic metals

Figure 3.12: (a) STM image (10.4×8.2 nm²) of the “S−B” phase. Scanning parameters: \( V_{\text{sample}} = -1.304 \text{ V} \); \( I = 19 \text{ pA} \); The insert defines the unit cell; (b) Schematic diagram of the PTCDA molecular arrangement in the “S−B”; The unit vectors of the PTCDA film are represented by the arrows; Lattice parameters \( b = 15.0 \pm 1\text{ Å} \); \( a = 14.5 \pm 1\text{ Å} \); \( \gamma = 34^0 \pm 1^0 \)

approximate model for the “S−A” phase. The unit cell parameters corresponding to the domain shown in Fig. 3.11 are: \( a = b = 15.5 \pm 1.0\text{ Å} \); \( \gamma = 34^0 \pm 1^0 \). However, we could not find any evidence for preferred orientation of the lattice unit vector \( a \) with respect to the \([110]\) direction of the substrate. Moreover, slight spatial variations of \( a \), \( b \), and \( \gamma \) within a single island were found.

In addition to this phase, a contrasting stripe like phase (“S−B” phase) with different molecular orientation could be imaged, although it was less frequently observed. Figure 3.12 (a) shows a typical example of the “S−B” structure. In this image, single entities with lateral sizes of 14 Å in length and 4 Å in width can be seen. Within the same stripe, these entities are not parallel one to another, like in the “S−A” phase, but form a zigzag structure, with an angle between molecules of \( 18^0 \pm 1^0 \) degrees. These observations leads us to conclude that the molecules are oriented with the molecular plane approximately perpendicular to the substrate. A schematic real space model for the “S−B” phase is shown in Fig. 3.12 (b). The unit cell of this phase consists of 2 molecules and the lattice parameters, derived from the STM data, are: \( a = 15.0 \pm 1.0\text{ Å} \); \( b = 14.5 \pm 1.0\text{ Å} \), \( \gamma = 34^0 \pm 1^0 \). To the best of our knowledge, both of the stripe like phase structures have not been observed on any other substrate, neither do they correspond to the bulk-like \( \alpha \)- or \( \beta \)- phase.

We address next the structure of the film upon annealing a thick (polycrystalline) film at 470 K. Islands of about 20 nm in lateral size that show the HB structure were observed. The lattice parameters agree, within error limits, with the ones presented previously. However, Auger spectra measured after heating the film showed a decreasing C/O ratio. This suggests that local decomposition of the PTCDA molecules occurs. Therefore, we have to conclude that the procedure to obtain an ordered film by annealing a thicker polycrystalline film is not proper.

To explain the growth mode of PTCDA on the passivated substrates, we refer to the
work of Verlaak et al. [76]. Within the HB structure PTCDA adopts a flat orientation. With this configuration, within an atomistic approach, the interaction of the molecules with the substrate is stronger then the intralayer interaction because there are more atoms within a PTCDA molecule participating at the interaction with the substrate that between the molecules. According to the prediction of Verlaak et al. [76], this should lead to a 3D growth, which agrees with our experimental observations. Because of the stronger molecule-substrate interaction, the supersaturation transition is moved towards deposition at low substrate temperatures. At these low temperatures, the molecules do not have the chance to diffuse on the substrate and form amorphous films. At room temperature, diffusion is high enough and ordered domains are formed. When higher rates are used, the molecules do not have time to diffuse on the substrate and due to this, the ordering is reduced to a short range.

The oxygen acts indeed as a passivation layer for Ni(111). Yet, we consider that the interaction with the substrate is strong, because of the 5% lattice compression of PTCDA in thin film with respect to the bulk one, as can be deduced from Tab. 3.2. With a strong molecule - substrate interaction, the substrate will determine the lattice parameters of the overlayer [42]. The film grows strained and after a critical thickness the built-in strain relaxes progressively, giving rise to to short range ordering.

Summarizing this section, we presented a STM study on the growth of PTCDA on monocrystalline Co(100) and passivated Ni(111) substrates. Deposition of PTCDA at low substrate temperatures indicate the formation of uniform covered areas but with no evidence for molecular ordering. PTCDA films follow the substrate morphology and the molecules adopt mostly a flat orientation onto the substrate. Deposition of molecules on a oxygen passivated Ni(111) surface, at room substrate temperatures, lead to formation of oriented islands, up to nominal coverages of about 4 ML. The PTCDA grows in this case with the (102) plane of the crystal structure parallel to the substrate, which is indicated by the herringbone like structure observed with STM. Also in this case the molecules orient flat onto the substrate. So, the substrate passivation did not have in this case an effect on the orientation of the molecules, as it was in the case of NDCA. At higher coverages PTCDA films showed formation of short range ordered domains. Two novel, short range ordered structures, have been observed. We attribute the latter observations to a strong interaction between the PTCDA molecules and passivated Ni(111).

3.2.3 Results and discussion: Polycrystalline substrates

In this section we present the morphology of PTCDA films deposited on polycrystalline substrates. Co thin films have been used in this case as substrates because we expect that interaction with PTCDA is weaker than in the case of Ni(111). We performed a systematic study of the structure of PTCDA as a function of coverage, substrate temperatures and evaporation rates, exploiting soft tapping mode AFM. To avoid any confusion, we note that in this section the results of the experiments performed on the PTCDA/Co system will be discussed only after the complete overview of the different morphologies is given.
3.2. Growth of PTCDA on ferromagnetic metals

Morphology at low substrate temperatures

We first address the morphology of the films grown at low substrate temperatures. Figure 3.13 shows the effect of coverage on the morphology of the films, grown at a temperature of 100 K and an evaporation of $\sim 2\ \text{Å/minute}$. Nominal thickness: (a) 5 Å; (b) 20 Å; (c) 70 Å; (d) 150 Å; (e) Plot of the island density (no islands/$\mu\text{m}^2$) as versus coverage; (f), (g) Histograms of the maximum height of the islands and area of the islands, respectively, for a PTCDA film with a nominal coverage of 20 Å (image (b)); (h) Histogram of the maximum height of the islands for a PTCDA film with a nominal coverage of 70 Å.
substrate temperature of 100 K and a deposition rate of about 2 Å/min. The AFM images were recorded at room temperature. All micrographs clearly indicate that at this evaporation rate PTCDA adopts an island growth.

It is remarkable that at a nominal thickness around 10 Å (∼ 3 ML) only 15 % of the substrate is covered (see Fig. 3.13 (b)). Even at nominal coverages of 200 Å the film is disrupted, as we measured height variations as large as 240 Å. Notice in Fig. 3.13 that the islands have different sizes and heights. This is a clear indication that nucleation during growth occurs, i.e. new nucleation centers form while other existing islands grow.

In Fig. 3.13 (e) we plotted the island density (number of islands in 1 µm²) for different coverages. The values represented in this plot were extracted from AFM images measured in different points of the sample and different samples. We can see that up to a nominal thickness of 20 Å, the island density increases fast. At higher thicknesses the island density increases further but with a much smaller slope and it reaches a saturation value around 166 ± 8 µm⁻² at coverages around 250 Å.

We note that the main difference in the morphology of the 20 and 70 Å thick films is to be seen in the distribution of the heights and areas of the islands. In Figs. 3.13

![Figure 3.14](image_url)

**Figure 3.14:** (a) AFM micrograph (height channel) indicating the morphology of PTCDA films grown at substrate temperatures of 100 K and evaporation rate 30 Å/min; (b) Plot of the root mean square roughness versus thickness for three different evaporation rates. The different evaporation rates are indicated by different symbols. When not specified, the error bars were smaller than the symbols; (c) AFM micrograph indicating the morphology of the Co substrate.
(f, g) we represent the histograms of the maximum height and area of the islands, for the PTCDA films with 20 Å nominal thickness (the corresponding image is shown in Fig. 3.13 (a)). The two distributions are broad. For the 70 Å thick films, we measured a more uniform distribution in area of the islands ($\sim 15000 \text{ nm}^2$). The islands still show thicknesses at different height levels, as indicated by the height histogram from Fig. 3.13 (g).

The morphology of PTCDA films at higher rates is illustrated in Fig. 3.14. The AFM micrograph shown in Fig. 3.14 (a) corresponds to PTCDA layers of 2 Å thickness, deposited at evaporation rates of 8 Å/min. Similar to the films grown at 2 Å/min, PTCDA films consist of grains. However, the grains have smaller lateral size ($\sim 150 \text{ Å}$) and higher density ($1300 \pm 200 \mu \text{m}^{-2}$) than for the films grown at lower rates. The RMS roughness of these layers is $6.5 \pm 0.5 \text{ Å}$. At higher coverages, no changes were observed anymore in the grain density and size. Instead, the films were rougher, as indicated by the square symbols in Fig. 3.14 (b). At even higher rates the AFM images were similar with the ones shown in Fig. 3.14 (a). Interestingly, we measured a smaller roughness for the films grown at higher rate. The open circles from Fig. 3.14 (b) represent the RMS roughnesses of films grown at 30 Å/min at different coverages. An increased roughness with coverage is registered for these evaporation rates as well.

We note that the average grain size for the PTCDA films grown at 30 Å/min is higher than that of the Co films. The morphology of the substrate is illustrated in the AFM micrograph shown in Fig. 3.14 (c). Grains of lateral sizes up to 100 Å are formed. The RMS roughness of the substrate is $3 \pm 2 \text{ Å}$.

**Dependence on growth temperature and flux**

Next, we address the change in the morphology of PTCDA films with substrate temperature. Figure 3.15 shows examples of AFM micrographs corresponding to PTCDA layers grown at four different substrate temperatures, as specified in the figure caption. All layers have a nominal coverage of 200 Å and the deposition rate is 8.6 Å/min. Up to a temperature of 333 K the layers consist of uniformly distributed grains. We can see that the films grown at a substrate temperature of 100 K the grain size is smaller than for the films grown at room temperature. As the temperature is increased, the roughness of the layers and the size of the grains increases, as indicated by the line scans in the top panel of each micrograph.

A change in morphology is registered at a temperature of 383 K (see Fig. 3.15 (d)). In this figure we can identify PTCDA islands with dendritic shapes. Within a dendritic island we measured differences in height as large as 150 Å. We can identify smaller domains of various sizes and well-defined edges, which is a clear evidence for crystallinity.

Dendritic islands have been observed at various elevated temperatures, depending on the combination of substrate temperature and deposition rate. To illustrate how the dendritic islands develop, we show in Fig. 3.16 AFM micrographs for different coverages. In this example the PTCDA films were grown at a substrate temperature of 360 K and an evaporation rate of 2 Å/min. In all images we can identify 3D islands of different
sizes and heights, which indicates that also under these deposition conditions nucleation during growth occurs. At a nominal coverage of 15 Å, the islands are compact and are distributed at a density of $6 \pm 2 \, \mu m^{-2}$. A close inspection of the image reveals that the islands are relative flat. The height of the different islands is distributed over a broad range, as indicated in Fig. 3.16 (b). At thicknesses above 40 Å (images c, e, and f) the islands have larger sizes and the difference in the height of the various islands becomes higher. As an example, we represent in Fig. 3.16 (d) the histogram of the maximum height of the islands for the films of 50 Å thickness.

Within some of the islands observed in Fig. 3.16 (c) we can clearly distinguish separate smaller domains. Because for the films with a nominal thickness smaller than 50 Å the islands are compact, we can conclude that the dendritic islands are formed by coalescence of of the close-lying islands. The variety in the shape of the islands can be explained by the hypothesis that unification of neighboring islands depends on
the crystalline phase and (or) orientation. Due to the polycrystalline nature of the substrate, it is easy to imagine that PTCDA forms islands of different orientation. The observation that the area over which crystalline order is achieved is much larger than the size of the grains may be considered remarkable. We conjecture that a PTCDA grain with a well-defined orientation nucleates at a single Co grain, but during successive ripening of the island the interaction between PTCDA and Co is weakened enough to let additional molecules to attach to an existent island.
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

Discussion

As discussed previously in Sec. 3.1, the rate equation theory predicts for the island density \( N \) a power dependence on the deposition rate \( R \) and an exponential dependence on \( 1/T \), with \( T \) the substrate temperature (see Eq. 3.3). The coefficient \( \kappa \) allows us to determine the critical nucleus size.

The island density vs. \( 1/T \) for nominal thicknesses of 50 Å and 200 Å are shown in Fig. 3.17 (a). From the experimental data it is seen that there is a linear regime for temperatures down to about 360 K \((1/T \text{ in the } 2.42 \text{ to } 2.83 \text{ range}) \) followed by a downward

**Figure 3.17:** Plot of the island density versus (a) \( 1/T \), with \( T \) substrate temperature (b) deposition rate \( (R) \).
bending of the island densities measured for lower temperatures. The change in slope in the island density versus $1/T$ plot is due to the fact that for lower temperatures, diffusion becomes slow with respect to the incoming flux of admolecules. This behavior can be seen as a decrease of the critical island size ($i$). From the dependence shown in figure for the 200 Å nominal thickness, we divided the $N$ versus $1/T$ dependence into two main regions of increasing critical nucleus size.

It has been previously pointed out by Brune et al. that the rate equation theory can only be used to analyse films that cover the substrates for less than 50% [93]. Because of these considerations, from our data we can only determine the critical nucleus size and the activation energy for layers grown at elevated temperatures. From the $N$ versus $1/T$ dependence above 360 K, an exponential decay emerges, with an activation energy of $0.37 \pm 0.05$ eV.

A plot of the island density versus rate for films of 50 Å nominal thickness, grown at substrate temperatures of 380 K is shown in Fig. 3.17 (b). The error bars were smaller than the symbols, unless specified. The figure clearly shows a power dependence of the island density on the evaporation rate, with an exponent $\kappa > 1$. Due to the limited amount of experimental data, an exact power dependence can not be extracted from this plot, but we can certainly deduce that the power coefficient $\kappa$ has a value of at least 4. As a guide to the eye, we show in figure two curves corresponding to power-dependencies with exponents $\kappa = 2$ (solid line) and $\kappa = 4$ (dashed line).

As discussed in Sec. 3.1, the power-law dependence of $N$ versus $R$ with an exponent $\kappa > 1$ corresponds to a incomplete condensation, i.e. the re-evaporation rate can not be neglected. It is well known that when polycrystalline substrates are used, the diffusion coefficient is smaller than in the case of monocrystalline substrates, because of the high density of defects [82]. Cumulated with the fact that the islands have a very small density, it is very unlikely that the PTCDA has a large diffusion constant on the polycrystalline Co. Thus, we consider that the extreme incomplete condensation regime should apply to the case of PTCDA/Co, which yields a critical island size $i$ of 6 molecules. Such a large number for the critical nucleus size has also been found in the case of Alq$_3$ molecules, grown on H-passivated Si(100) surfaces [81]. A large size of critical nucleus means a higher barrier against nucleation, thus a lower nucleation rate and obviously a small island density.

Figure 3.18 gives an overview of the conditions under which different morphologies have been observed. Solid squares show the experimentally determined growth conditions at which the film consists of dendritic islands, open circles are compact islands and triangles indicate the points at which the films appear to be continuous at 200 Å nominal thickness. As a guide to the eye we plotted two lines of the same slope that could be used to descend the three growth regimes.

Notice that continuous films have been obtained at low temperatures and high evaporation rates. The growth under these conditions most probably occurs by direct impingement. As a consequence, it is possible that different phases of PTCDA form. As the temperature is increased, or the rate is decreased, islands are formed. As a reminder, we note that the island density decreases and their height increases when
higher temperatures and (or) lower rates are used. The most remarkable observation is that at elevated temperatures the islands have well-defined shape, which is a sign of ordering. We note that the shape of the islands varied with temperature, which can be explained if we consider that indeed different phases of PTCDA form. At elevated temperatures re-evaporation and diffusion become important. Thus, the less energetically favorable phases disappear and only the most stable phases form.

According to the approach of Verlaak et al. the 3D type of growth, which we observed for PTCDA on Co substrates, is expected when a large interaction length for interlayer interaction and short interaction length for intralayer interaction exists. This would mean a flat orientation of the molecules. The low limit for the transition supersaturation is explained by a strong molecule-substrate interaction.

To summarize this section, we investigated the morphology of PTCDA films deposited at different deposition parameters. Deposition at low temperature and high rates lead to formation of relatively smooth layers. At elevated temperatures we demonstrated that ordering of PTCDA is possible. However, the molecules follow an island growth mode, with a remarkably low density of islands. The latter observation was explained by a small diffusion length of PTCDA on the Co and a large size of the critical nucleus. Most probably PTCDA adopts a flat orientation on the polycrystalline Co substrate.
3.3 Growth of pentacene on ferromagnetic metals

Pentacene is an aromatic molecule consisting of five benzene rings and is one of the molecular systems showing a high charge carrier mobility in molecular devices [16, 94]. There has been in literature a controversy on features related to the crystalline structure of pentacene. Recently, Mattheus et al. showed the existence of four different polymorphs in pentacene [95]. Up to now only the crystalline structure of one of the polymorphs has been completely determined. A scheme of the generic crystal structure of pentacene is shown in Fig. 3.19. Pentacene has a monoclinic crystal structure, in which molecules orient in a herringbone like structure within the (001) plane. The four polymorphs are distinguished by the different intralayer distance \( d_{001} \), for which values of: 14.1 Å, 14.5 Å, 15.0 Å and 15.4 Å have been reported.

Growth investigations of pentacene refer mostly to weakly interacting substrates such as Au and SiOx or surface treated silicon substrates [76, 79, 94, 96]. In the thin film form, it has been shown that pentacene grows with the (100) plane parallel to the substrate, therefore the molecules adopt an almost perpendicular orientation. The growth of the four polymorphs in thin film form was shown to depend strongly on the evaporation conditions, substrates used and film thickness [95]. Alternatively, it has been suggested that on flat surfaces pentacene adopts in the initial stage of growth a flat orientation [97]. Tilting of pentacene starts only after completion of the first monolayer of flat molecules.

In this work we report on the structural properties of pentacene films grown on Ni(111) and polycrystalline Co substrates. We study the morphology of the films by means of AFM. The choice of this molecular system was based on its promising electric properties, but also because of its ability to orient perpendicularly onto substrates. We demonstrate that pentacene forms on the studied ferromagnetic substrates large

![Figure 3.19: Scheme of the generic crystal structure of pentacene. Within the (001) plane the molecules arrange within a herringbone like structure. The interplanar distance \( d_{001} \) is used to identify the different polymorphs.](image-url)
oriented domains, even on the polycrystalline substrates. In all cases the molecules adopt an almost perpendicular orientation. The morphology of the films showed to depend on the evaporation conditions but also on the substrate roughness.

3.3.1 Experimental

Pentacene films were purchased at Aldrich company and purified by vacuum sublimation, as described in chapter 2 of this thesis. The films were evaporated in UHV conditions at temperatures around 500 K. The evaporation rates were estimated by means of ellipsometry or a microbalance quartz monitor, and verified by AFM and profilometer measurements, as explained in chapter 2 of this thesis. For example, a temperature of the evaporation cell of 500 K lead to fluxes of 3.5 Å/min. The substrates were prepared in the same way as described in Sec. 3.2.1. Additionally, we prepared polycrystalline Co surfaces by thermal evaporation. This lead to formation of rough films. For example a film of 100 Å thickness showed a value of 8 Å for the route mean square of the roughness (RMS). The AFM measurements were performed ex-situ in the soft tapping mode.

3.3.2 Results and discussion: polycrystalline substrates

In this section we present the structural properties of pentacene films deposited on polycrystalline Co thin films. The morphology of the films is analyzed as a function of coverage, substrate temperature and evaporation rate. Selected AFM micrographs of pentacene films at several coverages, are shown in Fig. 3.20. The films were grown on a substrate temperature of 360 K and an evaporation rate of 3.5 Å/min. Figure 3.20 (a) corresponds to a pentacene film with a nominal coverage of 7 Å. Large islands with a lateral size of 10 µm can be observed. The density of these islands is $\sim 2.5 \times 10^{-3} \mu m^{-2}$.

A beter resolved scan is represented in Fig. 3.20 (b). This image reveals the existence of a few gaps within the large island but also formation of smaller clusters. The fine structure within a big island resembles the morphology of the substrate, i.e a granular structure, with domains of 10 nm in lateral dimension and a peak to peak roughness of 7 Å. Against our expectations, the large area scans show sharp edges of the big islands, indicating that the pentacene film is ordered.

The average height of a terrace such as displayed in Fig. 3.20 (a), corresponds to about 15 Å. This is indicated by the height profile from Fig. 3.20 (c). The value for the terrace height is close to the interlayer spacing $d(001)$ of one of the pentacene crystal phases [94, 95]. Because we can not resolve the step height with a beter accuracy than 2 Å, we can not precisely determine which of the polymorphs appears in these pentacene layers. Nevertheless, this is a clear indication that the molecules grow almost perpendicularly to the substrate. Thus, the (001) plane of the pentacene crystal is parallel to the substrate surface. As indicated previously, pentacene molecules form a herringbone like structure within this plane.

The smaller clusters have a height of 15 to 90 Å and a lateral size around 300 Å. This is indicated by the height profile of a line taken through these clusters (black line),
Figure 3.20: Coverage dependent morphology of pentacene films grown on a polycrystalline substrate. Growth conditions: substrate temperature: 360 K; evaporation rate: 3.5 Å/min; nominal coverage: (a) and (b) 7 Å, (c) 15 Å, (f) 27 Å; In the plots (c) and (d) we represent the height profiles of the white and black lines, respectively, indicated in image (b).
which is shown in Fig. 3.20 (d). For nominal coverages of about 4Å only such clusters were observed.

In Figs. 3.20 (e, f) AFM micrographs of pentacene films with coverages of 15 Å (1ML) and 27 Å (1.7 ML), respectively, are displayed. Heights at different levels can be distinguished, meaning that sequent layers nucleate in the same time with the first monolayer. We found different orientation of the ordered domains, in different points on the sample. We could not find a correlation between the relative orientation of different domains. This could be due to the fact that growth of pentacene occurs along different crystalline directions.

The size of the terraces showed to depend on the evaporation rate and the temperature of the substrate during the growth. The higher the deposition temperature, the larger the size of the terraces. The temperature effect on the morphology of the films is illustrated in Fig. 3.21. The nominal coverage of these films corresponds to ∼ 60 Å. The evaporation rate is 3.5 Å/min in both cases. Figure 3.21 (a) shows the AFM micrograph of a pentacene layer grown at 320 K. We can see that large oriented terraces, with heights at 6 different levels, are formed. Figure 3.21 (b) corresponds to a layer grown at 340 K. The terraces have an average height of 15 Å in both cases, but the size and the density of the terraces are different. We note that increased temperatures had similar effects on the morphology of the films with decreased evaporation rates.

To identify the temperature effect on the size of the monocrystalline domains, we performed also annealing experiments on samples that were grown at 340 K. Figure 3.22 (a) shows the AFM image of a film with a nominal coverage of about 2.3 ML. The film was grown with a molecular flux of 5 Å/min. The image reflects formation of terraces at 5 different height levels. We then annealed gradually the films in vacuum,
3.3. Growth of pentacene on ferromagnetic metals

Figure 3.22: (a) Morphology of pentacene films grown at a temperature of 340 K and an evaporation rate of 5 Å/min; the nominal thickness of the film is \( \sim 30 \) Å. (b) Height profile of the line indicated in image (a); (c) Morphology of pentacene films after annealing at 380 K; (d) Height profile of the line indicated in image (c).

with 10 degrees steps and 30 minutes each time. Up to a temperature of 370 K, no significant changes in the morphology of the films were observed. At a temperature of 380 K, we observed disruptions within the film. This is indicated in Fig. 3.22 (b). The height profiles of the line shown in the AFM micrograph indicates the increase in roughness within a pentacene terrace, with formation of gaps of about 10 Å in height.

At substrate temperatures below room temperature a strongly contrasting morphology of the films is observed. AFM images shows the formation of circular shaped clusters. The clusters are ill connected, even for nominal coverages corresponding to 200 Å. This is indicated by the Fig. 3.23. The substrate temperature was in this case 100 K and the evaporation rate 5 Å/min. The clusters have a lateral size of 100 to 200 nm and heights up to 400 Å, as shown by the height profile from Fig. 3.23 (b). We note that the pentacene films grown at low temperature substrates are much rougher
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

Figure 3.23: (a) Morphology of a pentacene film growth at 100 K substrate temperature; The nominal thickness of the film is 450 Å; The evaporation rate is 5 Å/min; (b) Height profile for the line shown in figure (a)

than the PTCDA films grown at about the same (low T) conditions.

Finally, we found that the morphology of the pentacene films depended on the substrate roughness. All the images shown up to now correspond to a substrate RMS roughness around 3 Å. As an illustration, we show in Fig. 3.24 (a) and (b) the morphology of pentacene films, grown on substrates with a RMS roughness of 8 Å and 3 Å, respectively. The nominal thickness of the films is about 27 Å. The two films were grown in the same conditions. The evaporation rate was 5 Å/min and the substrate temperature 340 K. In both images, domains of well-defined orientation is seen, indicating that the films are ordered. Also the perpendicular orientation of the molecules was not altered, as we can see in the height profiles of the lines indicated in each AFM image. However, the lateral size of the ordered domains decreases by one order of magnitude for the substrates with a RMS roughness of 8 Å.

Qualitatively, several features can be extracted from the AFM measurements we have just presented. The growth of pentacene appears to be diffusion mediated. We also have evidence for ripening, which we explain in the following. Initially, single molecules diffuse on the substrate and when a critical number of them meet, a stable nucleus is formed. In a second (intermediate) step, adsorbates still nucleate new islands but also start aggregating into existing ones. This explains the different size and height of the clusters observed in the AFM images at submonolayer coverages (Fig. 3.20). When islands reach a critical size, they become unstable and the diffusion and/or dissociation of smaller islands occurs. Hence, the small islands disappear to the expense of larger ones (ripening).

The increased size of the crystalline domains with temperature can be explained by an increased diffusion with temperature. The dependence on the evaporation rate can be understood if we consider that at higher rates more nucleation centers are formed, thus the density of the terraces is higher.

At low temperatures, the films are much rougher than the PTCDA films grown in
3.3. Growth of pentacene on ferromagnetic metals

Figure 3.24: Morphology of pentacene films for different substrate roughnesses. The growth conditions were the same for the two films. Substrate temperature: 360 K; evaporation rate: 3.5 Å/min; nominal coverage: 27 Å. Substrate roughness (RMS): (a) 8 Å (b) 3 Å

similar conditions. We attribute this observation to a much smaller activation energy for the diffusion of pentacene.

The decrease in the lateral size of the ordered domains for higher substrate roughnesses, can be explained if we consider the rougher substrate as a surface with higher density of defects then for smoother layers. If the nucleation starts at defects or impurities, as it was shown to be the case for pentacene films grown on SiOx substrates [98], the number of nucleation centers also increases. Such defects can influence strongly not only the nucleation behavior but also diffusion of the molecules [82]. Because a molecule that attaches to such a defect is stronger bound than on a smooth terrace, the diffusion is decreased, therefore smaller domains are formed.

Within the perpendicular orientation, pentacene has a smaller number of interaction sites (atoms) with the substrate than within the plane. Thus, according to the predictions of Verlaak et al. [76], a 2D growth should be promoted for pentacene. This is consistent with our observations.

In summary, we presented an AFM study on the morphology of pentacene films grown on polycrystalline Co substrates, at different coverages and deposition parameters. Despite the high reactivity of the substrate, large oriented domains of pentacene could be obtained at elevated temperatures. In contrast to the case of PTCDA, pentacene showed a 2D growth on the polycrystalline Co.
3. Growth of molecular systems on ferromagnetic metals: PTCDA and pentacene on Co and Ni

3.3.3 Results and discussions: monocrystalline substrates

In this section we present morphology studies of pentacene films on Ni(111) substrates. Selected AFM micrographs of this system are shown in Fig. 3.25. The growth parameters of these films are specified in the figure caption. Large terraces of a square symmetry, with heights at 7 different levels can be distinguished.

![AFM micrographs](image)

Figure 3.25: Morphology of a pentacene films grown on a Ni(111) substrate at different coverages. Growth conditions: substrate temperature: 325 K; evaporation rate: 5 Å/min; nominal coverage: 40 Å; (c) Height profile of the grey line indicated in image (a).

A height profile taken through the different terraces is indicated in Fig. 3.25 (c). Similarly to the polycrystalline Co substrates, we found an interlayer distance around 15 Å. We can conclude that also on the Ni(111) substrate pentacene molecules adopt a perpendicular orientation. Apparently the (001) crystal face of pentacene is the most energetically stable.

In addition to the terraces corresponding to the pentacene, several steps, corresponding to the underlying substrate, can be identified. As a guide to the eye we
indicated a line that follows the direction of the steps, i.e. the [110] direction of the substrate.

Unlike in the case of Co substrates, the pentacene films grown on the Ni(111) seem to show more local order. However, the different terraces of pentacene are defined by directions of different orientation. This makes it difficult to determine the exact orientation of the pentacene domains relative to the [110] crystalline direction of the substrate.

As a final remark to this section we note that the crystalline domains of pentacene grown on the Ni(111) substrate were smaller in size than those of the films grown on the polycrystalline Co substrate in similar conditions. This indicates that pentacene has to overcome a higher diffusion barrier in the case of Ni(111) substrates than on Co.

In summary to this section, our observations demonstrate that also monocrystalline Ni(111) surfaces with (111) orientation are excellent templates for an oriented growth of pentacene. Similarly to the polycrystalline Co substrates, pentacene adopts a 2D growth, with an almost perpendicular orientation.

3.4 Conclusions

We have presented an STM/AFM study on ordering and morphology of molecular structures deposited both on ferromagnetic single-crystalline and polycrystalline substrates. In spite of the high reactivity of the 3d- ferromagnetic metals, we have been able to demonstrate that ordering of PTCDA and pentacene can be achieved on these substrates if the proper molecule-substrate combination is chosen. In the case of PTCDA on passivated Ni(111) we have shown that thin ordered films with coverages up to several monolayers can be formed, wherein the molecules adopt a flat orientation. Crystallites with a lateral size of about 500 nm could be obtained on polycrystalline Co substrates for deposition at elevated temperatures. PTCDA follows a Vollmer-Weber growth mode (island growth) with molecules lying flat on the substrate. Most interestingly, deposition of pentacene on a polycrystalline Co film at elevated temperatures lead to formation of uniform single crystalline areas of several microns size with molecules arranging almost perpendicular to the substrate.
3. Growth of molecular systems on ferromagnetic metals:

PTCDA and pentacene on Co and Ni
Chapter 4

Electronic structure of organic -
ferromagnetic metal interfaces

Abstract: In this chapter we study the electronic structure of pentacene at the interfaces with ferromagnetic Ni and Co, exploiting ultraviolet photoemission spectroscopy (UPS). For the interface with Co, we make use of polycrystalline films, whereas in the case of Ni we use single crystalline substrates with a (111) orientation. To understand the electronic structure of solid state pentacene, we first look at the electronic properties of solid films of pentacene. In this study we compare the UPS spectra of the gas-phase with those of the vacuum evaporated films. In the solid state we found significant redistribution of spectral weight, as a result of the overlap of the molecular orbitals between neighboring pentacene molecules. At the interface with the studied metals, we found in both cases evidence for hybridization of the molecular orbitals with the metallic states of the substrates. The vacuum levels do not align at these interfaces and the barriers for the hole injection are larger than expected.

4.1 Electronic structure of pentacene thin films:
gas-phase versus solid state UPS spectra

4.1.1 Introduction

Despite the recent technological success of polymer and molecular-based electronics, charge injection and transport processes in these devices are still intensively being debated. For the study of the electrical conduction mechanism in these materials field-effect transistor-like structures have been used. Organic conductors are conjugated materials where the delocalized $\pi$-electrons are responsible for the intermolecular conduction. Molecular crystals are formed by relatively weak van der Waals interaction between molecules, where the molecular packing determines the electronic behavior. Thus the charge carrier transport must be described using completely different models than for covalently bonded inorganic semiconductors.

As already outlined in chapter 1 of this thesis, the nature of the conduction mecha-
nism of charges in organic semiconductors is at the moment not completely understood. For the charge transport in these systems several models, such as the band model, tunneling model, hopping model and polaron model, have been used [15]. Moreover it has been emphasized that in (unintentional doped) organic semiconductors, the charge carriers can be localized at single sites. In pentacene, Jurchescu et al. emphasize the importance of the control of defects and impurity traps in the crystals, for achieving high electronic mobilities [16]. The authors report a band-like transport in pentacene single crystals of a good purity.

We consider it of relevance to correlate the electric behavior of organic materials in devices with the electronic properties measured by means of photoelectron spectroscopy. From PES experiments, information about the bandwidth of the molecular levels responsible for conduction can be extracted. Moreover, as we have seen in the example shown in Sec. 2.4.1, by a comparison of the UPS spectra of molecules in the gas-phase and the solid-phase, one can extract the polarization energies in the solid state. Additionally it is possible to gain insight into the type of interaction in the system. As an example, a weak interaction would manifest itself in a rigid shift of the solid state spectrum with respect to the gas-phase spectrum. In this section we present such an analysis for pentacene. We show that in the pentacene films grown, redistribution of the topmost energy levels occurs. This indicates that significant overlap between the molecular orbitals of neighboring pentacene molecules exists.

4.1.2 Experimental

The experiments were carried out in an UHV system with a base pressure of $2 \times 10^{-10}$ mbar. The system was equipped with UPS, XPS and a preparation chamber with deposition facilities. As substrates for our organic layers, we used clean polycrystalline Co films (100 Å thick), which were deposited by thermal evaporation on silicon substrates with a natural oxide. The silicon substrates were carefully cleaned by sonication in ammonia, acetone and ethanol and outgassed in UHV for several hours.

Pentacene was purchased at Aldrich company and further purified by gradient sublimation in $10^{-6}$ mbar (see Sec. 2.1.1). The purified material was then deposited in ultra-high vacuum using an evaporation cell. The crucible of the evaporation cell was made out of glass. The material was resistively heated at temperatures around 480 K, leading to growth rates of about 5 Å/min. Before evaporation, the material was carefully outgassed for several days at temperatures that were 50 degrees lower than the evaporation temperature. The pressure during evaporation of pentacene never exceeded $8 \times 10^{-10}$ mbar. The evaporation rate was determined using a quartz crystal microbalance and verified by AFM and profilometer measurements, as explained in chapter 2 of this thesis. The thickness of the pentacene films used for this work was 20 nm.

For the UPS studies in the solid state, we used a He I gas discharge lamp. The radiation emitted by this lamp has a main line of 21.22 eV and a satellite of 1.86 eV higher in energy. The intensity of the satellite was lower than 2% of the main line. In this study we used XPS with a non-monochromatic Al K$_\alpha$ x-ray source (1486.6 eV) to
4.1. Electronic structure of pentacene thin films: gas-phase versus solid state UPS spectra

check the purity of the samples. The photoelectrons were analyzed with a hemispherical analyzer from Vacuum Generators. The angle of incoming light was 35° from the surface normal; the outgoing electrons were collected under an angle of 35° with respect to the surface normal. The experimental resolution, determined from the width of the Ag Fermi edge at room temperature (80% - 20%), was 1.5 eV for XPS and 0.15 eV for UPS. All the UPS spectra presented in this work were satellite-corrected. The spectra were analyzed using the Winspec program developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. We mention also that no change in time was registered in the spectra, meaning that the pentacene layers were not degraded by the UV source used for the UPS experiments.

The gas-phase spectra were measured in a separate vacuum chamber with a base pressure of $2 \times 10^{-7}$ mbar. The excitation source for the gas-phase photoemission experiments was a high-intensity source from Omicron (HIS 13), also with a photon energy of 21.22 eV energy. The photoelectrons were analyzed with a home-made hemispherical analyzer equipped with 3 channeltrons. The cell we have used for the gas-phase photoemission spectrum contains a conical nozzle, which is normally used in supersonic cells. The flux of the molecular beam was measured with a microbalance quartz monitor facing the evaporation cell. For these experiments, typical evaporation rates of 1 to 2 Å/s were used, which were obtained at cell temperatures around 550 K.

4.1.3 Results and discussion

The gas-phase (thick line) and the solid-phase spectra (thin line) of pentacene are plotted in the top panel of Fig. 4.1. The solid state UPS spectrum corresponds to a 200 Å pentacene thick film, which was grown on a polycrystalline Co substrate. The two spectra are plotted as a function of binding energy of the molecular orbitals with respect to the vacuum level. The gas-phase spectrum was corrected for the spectrometer work function by simultaneous measuring the spectra of Xe, for which the emission lines are well known (see also chapter 2 of this thesis). The shift registered for the Xe lines was then added to the measured spectra of pentacene. The solid state UPS spectrum was corrected for the spectrometer work function in a different way. We measured the spectrum with a sample bias of $-4$ V, which allows the measurement of the secondary electron cutoff. The secondary electron cutoff defines the vacuum level, as explained in Sec. 2.4.1. The binding energy was then determined with respect to the measured secondary electron cutoff.

In the gas-phase spectrum, the feature identified at the lowest binding energy corresponds to the highest occupied molecular orbital (HOMO). The rest of the peaks correspond to the deeper lying levels (HOMO−1, HOMO−2, etc.). We determined the character of the orbitals from electronic structure calculations, using the semi-empirical AM1 method [99]. Pentacene belongs to the D$_{2h}$ symmetry group, therefore the energy levels are non-degenerated. By the symmetry of the molecular orbitals, we divided the gas-phase UPS spectra in 3 regions:
Figure 4.1: (a) UPS spectrum of pentacene, measured in the gas-phase (thick line) and in the solid state (thin line); \( IP \) abbreviates the ionization potential; (b) contour plots of the electron density for different occupied levels in pentacene, together with the symmetry of each orbital; note that the plotted orbitals have all a \( \pi \) character

(i) a region indicated by \( \pi \), from 6.5 eV to about 10.5 eV, where only orbitals with \( \pi \) character exist (HOMO to HOMO-6). The spatial distribution of the electron density for these 7 orbitals is represented in the bottom panel of Fig. 4.1. The type of symmetry for each orbital is also specified;

(ii) \( \pi + \sigma \), from 11 eV to 14 eV, is a mixed region consisting mostly of orbitals with a \( \sigma \) character but also \( \pi \) orbitals;

(iii) region \( \sigma \) above 14 eV corresponds to \( \sigma \) orbitals.

We note that our results are in agreement with the ones found in literature (see for
The solid state spectrum shows an overall shift of 1.5 eV with respect to the gas-phase spectrum. For the ionization potential of pentacene in the gas-phase ($IP_{\text{gas}}$) we found a value of 6.45 eV. This value was determined by the high kinetic energy cutoff of the HOMO. The ionization potential in the solid state ($IP_{\text{solid}}$) corresponds to a value of 5.0 eV, which was determined according to Eq. 2.4. The difference in the two ionization potentials is obviously a consequence of the change in the local environment of pentacene molecules in the two phases.

![Graph](image)

**Figure 4.2:** UPS spectra of pentacene as depicted in Fig. 4.1 after shifting such that the "a" and "b" peaks have the same positions; grey: fitted curves using Gaussian peaks

Besides the shift between the two spectra, we can observe that the features in solid state broaden significantly. The full width at half maximum (FWHM) of the HOMO peak increases from 0.2 eV in the gas-phase UPS spectrum to 0.8 eV in the solid-state. To see whether the relative positions of the molecular levels in the two phases correspond, in Fig. 4.2 we aligned the spectra such that the contribution from the deep-lying levels coincides. The two spectra were aligned with respect to the peaks indicated by “a” and “b”. The only peak that can be clearly separated in the solid state spectrum is the HOMO peak. In order to derive the exact positions of the other molecular orbitals we had to rely on a fit of the UPS spectra. We used peaks of a gaussian shape. In the gas-phase spectrum, only the positions of the HOMO to HOMO–6 peaks can be clearly distinguished. We have therefore limited the fitting procedure to the region from
5 to 10 eV. In the solid state spectrum we fitted the HOMO peak with an asymmetric shape. In the fitting procedure of the solid state spectra we tried to keep the same intensity ratio of the peaks as for the gas-phase spectrum. However, in doing so, the solid state spectrum could not be reasonably fitted. We then fitted the spectrum such as to keep the same integral intensity of the HOMO−1 and HOMO−2 peaks on the one hand, and of the HOMO−4 and HOMO−5 peaks on the other hand. This resulted in a strongly deviating intensity of the HOMO−3 peak for the different spectra. Although the procedure gives a relatively accurate estimate of HOMO−1 and HOMO−2, the lower lying orbitals are so poorly resolved, that an accurate position could not be derived. Therefore, for the rest of the discussion, we limit the analysis only to the modifications of HOMO, HOMO−1 and HOMO−2.

The vertical lines in Fig. 4.2 clearly show that the HOMO, HOMO−1 and HOMO−2 peaks in the solid-phase are shifted towards higher binding energies with respect to the gas-phase. The HOMO and HOMO−2 levels are shifted by 0.2 eV, whereas HOMO−1 shifts only by 0.1 eV. Moreover, the relative intensity of the peaks does not correspond to the gas-phase. Our observations are in contrast to the example shown in Sec. 2.4.1, which is illustrative for disordered organic semiconductors. Usually, these materials only show a rigid shift of the solid state spectrum and a slight broadening of the features. The non rigid shifts and the broadening observed in pentacene should be attributed to the interaction between pentacene molecules themselves. Overlap of the molecular orbitals of neighboring pentacene molecules leads to shifts and broadening of the topmost orbitals. This is indicative for band formation rather than localized states at single pentacene sites. Thus, the difference in the two ionization potentials is not only due to the polarization energy ($E_P$) in pentacene, but also to the interaction between molecules themselves.

4.1.4 Conclusions

To summarize, we have compared the UPS spectra of pentacene in the gas-phase and solid state. We demonstrated that in pentacene thin films a significant overlap of the topmost $\pi$ orbitals exists, i.e. hybridization of the individual molecular orbitals. Our observations are consistent with pentacene being one of the organic systems with a high carrier mobility.

4.2 Electronic structure at the interface between pentacene and ferromagnetic metals

4.2.1 Introduction

Up to now we discussed the electronic structure of bulk pentacene films, which is considered relevant for the engineering of molecular devices. Another important aspect is the electronic structure at molecular-metallic interfaces. The alignment of the electronic levels of the organic layer with respect to the Fermi level of the metal electrodes
controls the injection of electrons and is expected to have a crucial effect on the device properties [32]. To improve the characteristics of these devices, one needs to understand the electronic properties of the interfaces between organic semiconductors and metals.

Investigations on a variety of organo-metallic interfaces revealed that their electronic properties differ considerably from the ones of inorganic semiconductor-metal interfaces [32]. One of the issues, generally recognized for the hybrid organo-metallic systems, is the vacuum level misalignment. Up to now, vacuum level shifts as large as 1.5 eV have been found. Lowering as well as raising of the organic vacuum level with respect to that of the metal substrate have been observed. This has been attributed to an abrupt change in electrostatic potential energy at the interface, i.e. formation of an electrical dipole layer. Such shifts have been observed not only for molecules with a permanent dipole moment, but also for nonpolar molecules. The dipole formation in the latter case has been related to molecular polarization induced by the electronic image force, formation of interfacial states, and charge transfer across the metal-organic interface. Besides the vacuum level misalignment, it has been shown that the barrier for the hole (electron) injection varied considerable from one molecular-metal system to the other.

The electronic properties of molecular-metal interfaces are currently not completely understood. Prediction of an energy level diagram for a given interface, based on individually determined material properties such as metal work function, ionization potential and electron affinity, is impossible. It has been pointed out by Seki et al. that for a generalization of the existing data, the energetics of organic-metal interfaces should be correlated to the chemistry of the systems.

Generally, techniques such as Kelvin probe [102–104], internal photoemission, electroabsorbtion [105] and photoelectron spectroscopy [32, 104] have been used to characterize the electronic properties of the organic-metal systems. Out of these techniques, photoelectron spectroscopy has proven to be a very powerful method for the analysis of interfaces involved in hybrid devices. This technique can provide work functions of the metals and the ionization potential of molecules, which are ingredients necessary to build an energy level diagram. Moreover, making use of the UPS technique, information about the interaction at a certain interface can be extracted.

As already pointed out in chapter 1, there is only a limited amount of information on the properties of interfaces involved in molecular spintronics. In chapter 3.3 of this thesis we investigated the interesting structural properties of the pentacene-polycrystalline Co and pentacene-Ni(111) interfaces. In this chapter we investigate the electronic properties of these two particular systems by means of UPS. The specific interaction and the energy level alignment at each of these interfaces is addressed.

### 4.2.2 Pentacene-Co interface

In this section we present the electronic properties of the interface between pentacene and polycrystalline Co. Besides the motivations we have just pointed out, pentacene-Co is an interesting system for the study of the band alignment. The reported work function of Co is 5 eV. For the ionization potential of pentacene values from 4.9 to 5.2 eV have been reported [101, 106–108]. If no chemical interaction takes place and the
vacuum levels align at the pentacene-Co interface, one would expect a very small hole injection barrier in this system. Contrary to this expectation, we show that the vacuum level is significantly misaligned. As a consequence, the barrier for the hole injection is higher than naively expected. In addition, we find that the values of the vacuum level shift and the barrier for the hole injection are lowered when the Co substrates are exposed to small amounts of oxygen. The charge redistribution at the pentacene-Co interface, will be discussed.

Experimental

The UPS experiments were performed in the same system described in Sec. 4.1.2. In order to address the electronic structure at the pentacene-Co interface, we measured the photoemission spectra for different thicknesses of pentacene. To avoid differences in the work function from one sample to the other, we deposited the pentacene films in small subsequent steps on the same Co substrate. After each step of deposition, the UPS spectrum was recorded. During deposition, the substrate was kept at a temperature of 345 K. The Co and pentacene films were deposited as described in section 4.1.2. The reference Co films that were slightly oxidized were obtained by shortly exposing the pure Co films to a vacuum of $10^{-7}$ mbar.

Results

Figure 4.3 shows the UPS spectra at the interface between pentacene and pure Co polycrystalline substrates. The spectra are plotted as a function of the kinetic energy of the photoelectrons. No corrections to the applied bias voltage or the spectrometer work function have been applied, as we wanted to keep the diagrams as close as possible to the raw data. The only correction made in these spectra is subtraction of the contribution coming from the secondary line of He lamp (satellite correction).

The photoemission spectrum of Co is denoted by “0 Å” in Fig. 4.3. This spectrum consists only of a peak around kinetic energy of 20.5 eV, characteristic to the occupied 3d and 4s bands, which dominate the region near the Fermi level. For the work function of Co, we found a value of 5.1 eV. This value was determined according to the description given in Sec. 2.4.1, Eq. 2.3. Within the experimental resolution the work function found is in good agreement with published values [109].

We next turn to the UPS spectra corresponding to pentacene films of different thicknesses. The corresponding pentacene coverage is indicated in Fig. 4.3 for each spectrum. For small amounts of pentacene, both Co and pentacene contribute to the measured spectrum. Spectral features originating from the density of states at the Fermi level of Co are observed up to a thickness of 45 Å (~3 ML of molecules arranging perpendicularly on the substrate). In order to clearly distinguish the modification in the valence band UPS spectra, we have normalized the measured spectra with respect to the intensity at 20.3 eV. This value corresponds to the maximum intensity of the Co 3d band. The molecular orbitals of pentacene are visible at kinetic energies below 20 eV. The signal originating from the HOMO level is found at kinetic energies around
4.2. Electronic structure at the interface between pentacene and ferromagnetic metals

Figure 4.3: (a) Valence band photoemission spectra at the pentacene-Co interface; (b) Low kinetic energy side of the spectra; (c) A close up into the spectral region around HOMO, in the submonolayer regime; (d) UPS spectra of small amounts of pentacene, from which Co spectrum was subtracted - only the region around the HOMO is shown.

19.3 eV. The signature of molecular orbitals of pentacene appears already at very low coverages.

The spectral region around the secondary electron cutoff (SEC) for different amounts of pentacene is represented in Fig. 4.3 (b). For the clean Co layer the SEC corresponds to 4.6 eV. A sudden drop of $-1.0$ eV in the SEC occurs at the very first layer of pentacene with a thickness of 2 Å. This shift corresponds to the formation of an interfacial dipole with the positive charge at the pentacene side. To assess the origin of the dipole, we have to analyze more closely the valence band spectra.

The most obvious modification in the spectra occurs in the region around the HOMO of the pentacene. A plot of the UPS spectra at the high kinetic energy side is represented in Fig. 4.3 (c). For clarity, we show in this figure only the spectra corresponding to pentacene thicknesses up to 15 Å, since most of the modification in the spectra happens...
in the submonolayer regime. In this figure we can clearly see that the HOMO peak shifts towards higher kinetic energies (smaller binding energies), as the amount of pentacene is increased. A shift of the HOMO by almost 0.3 eV is registered, and completes upon deposition of about 7 Å of pentacene. The position of the HOMO for thick layers corresponds to an energy that is about 1 eV below the Fermi edge of Co. This distance represents in fact the barrier for the hole injection.

For those spectra that show a contribution from the density of states of Co, there is a discrepancy in the region located between the HOMO of pentacene and the Fermi level of Co. In this region the spectra do not completely overlap with the spectrum of pure Co. This can be seen more clearly in the spectra from which the Co spectrum is subtracted. Figure 4.3 (d) represents such subtracted spectra, which were further normalized in such a way that the baseline and the maximum intensity at the HOMO is the same for each spectrum. We observe two features:

(i) enhancement of spectral weight at 20 eV, i.e in the band gap of the pentacene. When doing the normalization of the subtracted spectra, it appears that the intensity of this “additional” feature, diminishes for higher coverages of pentacene.

(ii) a broadening of the HOMO for the 6.5 Å spectrum of pentacene. This broadening could be seen as an overlap of the thick and thin layer spectra. As soon as the amount of pentacene is increased, the contribution from small amounts of pentacene decreases.

Note that the relative spectral weight of the other peaks in the spectra changes for the different coverages, so we have to be careful with interpretation of the spectra. If the normalization would not be performed, the difference in the two sets of spectra were the same.

Besides the modification in the spectra around the HOMO of pentacene, other levels are found to be shifted. We indicate in Fig. 4.4 the shifts registered for HOMO, HOMO−1 and HOMO−2 and the peaks labelled as “a” and “b” in Fig. 4.3 (a). We note that the contribution to the “a” and “b” peaks comes from σ orbitals. The position of the HOMO, HOMO−1 and HOMO−2 peaks were determined from fitting procedures of the subtracted spectra, as explained in Sec. 4.1. The position of the deeper lying “a” and “b” peaks are determined at the maximum intensity of these peaks. The fitting procedure indicates that for the 2 Å coverage, the HOMO−1 and HOMO−2 peaks are about 0.2 eV broader than in the multilayer case.

In Fig. 4.4 we can see that for the 2 Å and 3 Å spectra, the discussed peaks shift in the same direction, but by different amounts. However, in the 4 Å spectrum we can see that different levels shift differently. Beyond a thickness of 4 Å, the −0.1 eV shift gradually decreases and at a thickness of about 15 Å it becomes zero. A drastic change in the “a” and “b”, HOMO-1 and HOMO-2 peaks occurs therefore at thicknesses around 4 Å. We mention that we also monitored the C 1s peak for each layer of pentacene, by means of XPS measurements. However, within the experimental resolution, we did not observe any change in the shape or position of this peak.
4.2. Electronic structure at the interface between pentacene and ferromagnetic metals

Figure 4.4: Shifts of the molecular levels for different layers of pentacene, with respect to the ones of a thick pentacene layer. The levels labelled “a” and “b” are defined in Fig. 4.3 (a).

Another experimental observation to mention in the case of the pentacene-Co interface is that the barrier for the hole injection is very sensitive to small amounts of adsorbates on the Co layer. This is illustrated in Fig. 4.5 in which we plotted the UPS spectra of pentacene films of the same thickness (∼20 Å), deposited on Co films containing different amounts of oxygen.

The UPS spectra of the bare substrates exposed to different dose of oxygen are plotted in Fig. 4.5 (a). The presence of the oxygen in the layer is indicated by the feature present between 14 and 17 eV, assigned to the O 2p level and is commonly found with oxygen atoms adsorbed on transitional metal surfaces [110]. The spectra after deposition of pentacene films are plotted in Fig. 4.5 (b). The spectra were normalized to the spectral weight at the Fermi level of Co. The plots for the secondary electron cutoff of Co and pentacene layers are represented in the small inserts of each panel.

For the bare Co films we measured shifts up to 0.25 eV in the SEC, as the amount of oxygen was increased. These shifts correspond to an increased work function of Co when the amount of oxygen is increased. These observations are consistent with previous reports [111, 112].

As to the pentacene spectra, we can see that the distance between the HOMO and Fermi edge decreases as much as 0.25 eV for substrates that were mostly oxidized. For the substrates with increased oxygen content, the modification in the spectra for different amounts of pentacene is similar to the pure Co substrates. However, the total shift of the HOMO in the submonolayer regime with respect to the multilayer films.
Figure 4.5: (a) UPS spectra of recorded on Co substrates containing different amounts of oxygen. Samples Ox1 and Ox2 correspond to Co films that were exposed in $10^{-7}$ mbar for 2h and 15h, respectively. (b) UPS spectra corresponding to pentacene films of similar thicknesses (30 Å) deposited on the different Co substrates. The inserts represent the secondary electron cutoff part of the spectra.

is 0.2 eV. The intensity of the HOMO of pentacene is found to be slightly dependent on the degree of oxidation of the substrate. This could be due to a different sticking coefficient of pentacene for the three substrates, or because the pentacene films form a closed layer at different nominal thickness.

Discussion

We first address the modifications seen at the spectral region around the Fermi level of Co. Similar changes in the spectra have been previously reported in the case of ferromagnetic metals such as Co and Ni, upon exposure to small amounts of oxygen (see for example [113–115] and refs. therein). In the case of the O–c(2×2) – Ni(100) system, such changes were related to hybridization of the 3d and 4sp bands of Ni with the 2p level of oxygen. Because of hybridization, $(2p4sp)$ and $(2p3d)^1$ hybrid states are

\[1\] This notation is reproduced from reference [114]. The notation specifies which states are mixing. The underline indicates which states give the main character of these hybrid states.
formed well below the Fermi level. Additionally there are partially filled interface states with a 2p character, located around the Fermi level. UPS experiments performed on the O-Ni system do not clearly indicate the existence of these latter interfacial states. Additional supporting experiments such as inverse photoemission spectroscopy and X-ray emission spectroscopy but also first-principles density functional theories have been used to clarify the electronic structure of this particular system.

Returning to the pentacene-Co interface, from the modification in the high kinetic energy side of the UPS spectra, in the case of small amounts of pentacene, we can conclude that the 3d bands of Co hybridize with the molecular levels of pentacene. We conjecture that the increased spectral weight at the high kinetic energy side of the HOMO of pentacene, should be attributed to formation of interface states. However, we can not indicate the exact nature of these states at the pentacene-Co interface. Additional experiments such as high resolution electron energy loss spectrometry (EELS) as well as theoretical support, are needed to elucidate the nature of the interaction between pentacene and Co.

The decrease of the barrier for the hole injection for the films exposed to oxygen is consistent with the idea of passivation that we have mentioned in chapter 4 of this thesis. More oxygen on the surface means weaker interaction and because the ionization potential of the pentacene has a value close to the work function of the substrate, the barrier for the hole injection gets smaller.

The sudden change in the spectra around 4 Å can originate from two effects. One possibility is that the molecules adopt a different orientational conformation in the very beginning stage of growth. The other possibility is that pentacene starts to nucleate at step edges, defect sites or grain boundaries of the Co film. For the first hypothesis, we refer to the case of the pentacene-Au(111) interface for which it has been shown that the molecules adopt a flat orientation on the substrate in the beginning stage of growth [97]. The pentacene starts tilting out of the plane only after completion of the first monolayer of flat-lying molecules. This coverage would correspond to a thickness around 3 Å. In the case of flat orientation there is much bigger overlap between the π orbitals and the substrate then in case the molecules would adopt a perpendicular orientation. This would result in different features in the electronic structure than for the perpendicular orientation. In the other hypothesis, we assume that the molecules gather first in nucleation points at defects, and only after 4 Å coverage start diffusing. At these defects, a stronger interaction of pentacene is expected. In fact we can not exclude the possibility that within such a cluster the molecules adopt an orientation mostly with the molecular plane parallel to the substrate at the very early stage of nucleation.

Our AFM images for low pentacene coverages (see chapter 5) indicate that the molecules cluster in small nucleation points of heights up to 90 Å, rather than distribute uniformly on the substrate. This would exclude in fact the formation of the flat-lying monolayer of pentacene. We have to realize, however, that it is not possible to identify with AFM a flat layer of pentacene. An indirect way to verify which of these hypotheses is valid, is to analyze the electronic structure of pentacene films on single crystalline
surfaces. If we assume that in an initial stage pentacene grows flat on smooth surfaces, as it was suggested by Casalis et al. [116], indeed a similar trend should be observed on a single crystalline ferromagnetic substrate.

Conclusions

In conclusion, the UPS measurements performed at pentacene-Co interfaces show that the vacuum level of pentacene does not align to that of Co, leading to an increased barrier for the hole injection. Exposure of Co substrates to oxygen resulted in a decrease in the hole injection barrier, indicating a lower interaction of the pentacene with these substrates. We explain the formation of the interfacial dipole by hybridization effects. The hybridization has been related to the interaction with the step edges or to a change in the orientation of the molecules when going from low to high coverages. In the XPS measurements performed on the different layers, within the experimental resolution, we did not see any modification of the C1s peak.

4.2.3 Pentacene-Ni(111) interface

Introduction

So far, we addressed the electronic structure of pentacene on polycrystalline Co, which is certainly of relevance from a technological point of view. We have to realize that a real interpretation of the electronic structure in the case of polycrystalline substrates is hard to make since molecules can interact differently with different faces of a crystal. For a better understanding of the electronic structure of organic molecules in the proximity of metal surfaces, photoemission experiments on better defined interfaces are therefore needed.

In this section we investigate the electronic properties of the pentacene-Ni(111) interface, making use of UPS. Just like the case of pentacene-Co interface, we found a misalignment of the vacuum level. A larger shift of the SEC is found for the pentacene-Ni(111) interface. Also at the pentacene-Ni(111) interface evidence for significant charge redistribution is found. However, the modification of the electronic structure of pentacene with coverage is different when Ni instead of Co substrates is used.

Experimental

The experiments were performed in the same way as described in Sec. 6.2.2. For the experiments described in this section, we used a Ni single crystal with a (111) orientation. The substrate was cleaned by repeated cycles of argon ion bombardment and heating to 1100 K until no contamination was registered by XPS. During the pentacene deposition, the substrate was held at a temperature of 320 K.
4.2. Electronic structure at the interface between pentacene and ferromagnetic metals

Results

Figure 4.6 shows the results of UPS measurements at the interface between pentacene and Ni(111). The spectra are plotted as a function of the kinetic energy of the photoelectrons. The photoemission spectrum of the Ni substrate is denoted by “0 Å”. In the region around 20 eV spectral weight coming from the spin split density of the 3d states is distinguished. Notice that the spectral weight of the 3d states of Ni is different than that of Co (compare Fig. 4.6 (b) with Fig. 4.3 (c)). For the work function of Ni we found a value of 5.45 eV, which is within experimental resolution in good agreement with published values [109].

The following spectra correspond to pentacene films deposited in subsequent step...
in small amounts on Ni. The signature of the molecular orbitals of pentacene at kinetic energies below 20 eV appear in this case also at very small amounts of pentacene. The spectra for coverages up to 7 Å were normalized with respect to the intensity at 20.35 eV. It is interesting to note that for the 30 Å UPS spectrum there are no spectral features associated to the density of states of Ni anymore. Disappearance of Ni features occurs at a lower coverage than in the case of Co substrates, indicating that the first pentacene monolayer is completed earlier in the case of Ni substrates.

The most obvious changes in the spectra appear at the high kinetic energy side. A plot of this region is represented in Fig. 4.6 (b). Only the spectra corresponding to pentacene thicknesses up to 7 Å are displayed in this figure. For the low coverage pentacene spectra, the Fermi edge shifts by 0.05 eV to high kinetic energy. The position of the Fermi edge in the case of pentacene spectrum was reproduced within 0.01 eV range. However a shift of 0.05 eV falls within the experimental resolution. Therefore, an interpretation of this shift is inappropriate at the moment. To figure out whether this shift is true, measurements at higher resolutions should be performed. Nevertheless, we can clearly see that the pure Ni spectrum does not overlap with the features of Ni in the spectra corresponding to small amounts of pentacene.

The position of HOMO peaks for the spectra corresponding to small amounts of pentacene can not be distinguished as clear as in the case of Co substrates. By subtraction of the Ni spectrum, the modification in this region of the spectra were resolved more clearly. To avoid negative signals, we had to normalize the spectra to the intensity at 19.8 eV. Furthermore, we normalized the subtracted spectra in such a way that the base line and the maximum intensity of the HOMO feature coincides for each spectrum. The results of these operations are displayed in Fig. 4.6 (d).

At the high kinetic energy side of the HOMO peak (region 19.2 to 19.8 eV), we observe a shift of about 0.15 eV to lower kinetic energies, when the pentacene coverage is increased. This is opposite to the trend observed in the case of Co. It also appears that additional spectral weight is present at the low kinetic energy site of the HOMO. The intensity of this feature decreases for increased pentacene coverages. Also in the region 19.8 eV - 21 eV, additional peaks are observed. The intensity of these peaks seems to decrease with increasing pentacene coverage as well. However, the spectral weight of the features originating from molecular orbitals of pentacene also changes. Care should be taken with the interpretation of these features.

The secondary electron cutoff part of the spectra is plotted in Fig. 4.6 (c) for different pentacene thickness. The SEC shifts about 1.5 eV to the lower kinetic energy. Thus, the vacuum level is lowered, similarly to the pentacene-Co interface. Notice that the vacuum level shift in the case of Ni is about 0.5 eV larger than in the case of Co.

Further analysis of the UPS spectra indicate that the deep-lying levels also shift to low kinetic energies when going from low to high coverages. A shift of about 0.15 eV in the 2 Å spectrum gradually decreases until a coverage of approximately 30 Å (∼ 2 ML). We can conclude therefore that also a rigid shift of 0.15 eV of the spectra appears.

We compared the UPS spectra for different pentacene thicknesses and shifted the spectra such to align the deep-lying levels in the position. For the spectra corresponding
to thicknesses above 15 Å the position of the peaks coincide with the ones of 150 Å. For coverages below 15 Å some differences can be seen. Figure 4.7 shows the comparison between the 150 Å spectrum and the 3 Å spectrum, which was shifted rigidly 0.15 eV. The spectrum of Ni was subtracted from the 3 Å spectrum, such as to avoid negative signals. For reference we also plotted the gas-phase spectrum. The gas-phase spectrum and the solid-phase spectrum have been fitted using gaussian peaks, as described in Sec. 4.1. The high intensity of the HOMO in the 3 Å spectrum makes a separation of the HOMO−1 difficult. Therefore, a fitting procedure for this spectrum would be unreliable. It is nevertheless clear that the two solid-phase spectra are different in the region 17 eV - 21 eV. This is a region where HOMO−1 and HOMO−2 contribute to the spectra. If we attribute the peaks at 18.0 eV and 17.4 eV to HOMO−1 and HOMO−2 respectively, a shift of 0.1 eV to lower kinetic energies of HOMO−2 occurs, whereas HOMO−1 remains unshifted.

![Figure 4.7](image)

**Figure 4.7:** UPS spectra corresponding to: top - gas-phase; middle - 200 Å pentacene and bottom - 3 Å pentacene from which the spectra of Ni was subtracted. The spectra were shifted such that the deep-lying levels coincide. The fits of the UPS spectra are plotted in grey.
Discussion

We first address the origin of the interfacial dipole. From Fig. 4.6 (d), some relevant features can be extracted. First of all, the shape of the HOMO peak for the thinner layers is different than for the multilayer spectra. Secondly, there is a shift of the HOMO to low kinetic energies with increased coverage. Notice that this trend is opposite to the case of pentacene-Co interface. Finally, additional spectral weight in the region 20 to 21 eV is present, indicating the formation of interface states. We can conclude that also in the case of Ni substrates, hybridization of the pentacene HOMO with the 3d band of Ni occurs.

We consider the UPS spectra at the pentacene-Ni(111) interface as a sum of a rigid shift and some additional modifications around the top of the valence band spectra (high kinetic energy side). Rigid shifts have commonly been observed for several organic-metal interfaces [32]. They have been attributed to image charge effects. Because of the motion of the electrons in the molecule, instantaneous dipole moments in the molecules exists, thus dynamic long-range fields are generated. The electrons in the metal respond to the fields and screen them. The interaction of the fluctuating dipole moment with the screening charge can lead to a net displacement of the electron distribution in the adsorbate. In a simple physical picture, an electron closer to the metal substrate is attracted more strongly by its positive image charge than an electron far from the substrate. Thus, the distribution of the electron cloud is shifted toward the metal surface. In this case the adsorption-induced polarization should lead to the formation of a dipole layer with its vacuum side positively polarized, i.e. lowering of the vacuum level. This is consistent with our observations.

Next, we address the striking difference between the multilayer spectra of pentacene at the interface with Ni(111) and Co. The two spectra are plotted in Fig. 4.8 in the binding energy representation. The spectra are corrected for the spectrometer work function and the bias voltage applied on the samples. The energy of the molecular orbitals of pentacene deposited on the two different substrates correspond very wel. However, the features at 7.25 eV (HOMO−2), 8.6 eV (HOMO−4,5), 9.7 eV and 10.9 eV have significant higher intensities in the case of Ni substrates. Remarkably, in the case of Ni substrates the HOMO peak is more asymmetric than for pentacene-Co system.

We fitted the two spectra using gaussian peaks, in order to explain the observed differences. We limited the fits only to the 5 eV - 8 eV range (HOMO, HOMO−1 and HOMO−2 peaks). The aspect ratio of the two peaks was kept as much as possible the same as for the gas-phase spectrum. The results of the fits are displayed in table Tab. 4.1. The position, full width at half maximum (FWHM) and integral area of each peak is represented.

Several features can be extracted from this table. We can see that the position of the levels is basically the same, but the width of the peaks for the two layers are different. The HOMO−1 and HOMO−2 for the layer grown on Co are broader then for Ni substrates. In contrast, the HOMO of the pentacene layers grown on Co is narrower that for the films grown on Ni. As a consequence, the relative intensity of the three
peaks differ for the two systems.

We think that the difference in the two spectra should be attributed to differences in the structural properties of the two layers. One possible explanation is that the two pentacene films have different lattice parameters. This would cause a different overlap of the molecular orbitals, which implies different positions and widths of the different molecular levels in the solid-phase. Another explanation is related to the different ratios of the polymorphs in the two pentacene films. It has been demonstrated that separation in the thin film form of the $\alpha$ and $\beta$ phases of pentacene is difficult. Our AFM measurements on the two layers can not provide such information. X-ray diffraction measurements on these substrates could clarify which of the supposition is feasible. We have to realize, though, that for the low-weight materials XRD measurements for thicknesses of a few nanometers are difficult, because of the increased intensity of the zero-order reflection coming from the substrate.
Table 4.1: Representation of the position, full width at half maximum (FWHM) and integral intensity of HOMO, HOMO−1 and HOMO−2 peaks for the multilayer spectra of pentacene, grown on Ni(111) and polycrystalline Co substrates. These parameters were determined from fitting the curves with gaussian shapes. The two different numbers for the width of the HOMO represent the high and low binding energy width, respectively of the asymmetric (see Sec. 4.1 for details of the fitting procedure).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>parameter</th>
<th>HOMO</th>
<th>HOMO−1</th>
<th>HOMO−2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>position</td>
<td>5.41</td>
<td>6.65</td>
<td>7.14</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td>0.87 - 0.49</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>integral intensity</td>
<td>160.6</td>
<td>150.2</td>
<td>209</td>
</tr>
<tr>
<td>Co</td>
<td>position</td>
<td>5.44</td>
<td>6.67</td>
<td>7.14</td>
</tr>
<tr>
<td></td>
<td>width</td>
<td>0.73 - 0.51</td>
<td>0.51</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>integral intensity</td>
<td>158.2</td>
<td>161.2</td>
<td>225.6</td>
</tr>
</tbody>
</table>

Conclusions

In conclusion, similar to the Co substrates, the electronic structure of pentacene at the interface with Ni also showed some modifications. The vacuum level of pentacene does not align to the one of Ni. Hybridization effects have been observed for this system as well. The molecular orbitals of pentacene, however, were differently affected by the hybridization with the 3d band of Ni. Moreover, the spectra of pentacene multilayers grown on the Ni substrates were found to be dissimilar from the ones grown on Co substrates. This has been related to different crystal structures of the two pentacene layers. A real interpretation of our UPS measurements is difficult at the moment. For the pentacene-Ni(111) interface the vacuum level shift is bigger than the shift at the pentacene-Co interface. We can conclude therefore that the interaction between pentacene and Ni is stronger than pentacene-Co.

4.3 Energy level diagrams

As a summary to the photoemission experiments, we draw in Fig. 4.9, the energy level diagrams at the interfaces between pentacene and the two studied ferromagnetic substrates. In such a diagram, the values for the work function of the metal, vacuum level shift and position of the HOMO for different pentacene thicknesses, are plotted. The work functions were measured as described in section 2.4.1 of this thesis. The values for the work function are 5.45 eV for Ni and 5.10 eV for Co. The position of the HOMO is given for the maximum of the HOMO peak. We indicate in this figure a gaussian envelope, representing the width of the HOMO.

For both substrates the vacuum level is shifted in the same direction. The vacuum level shift is about 1 eV for pentacene-Co and 1.4 eV for pentacene-Ni(111). Also the barrier for the hole injection is different in the two cases. We found values of 1.0 eV...
Figure 4.9: Energy level diagrams of (a) pentacene-polycrystalline Co interface; (b) pentacene-Ni(111) interface

and 1.1 eV for the hole injection barrier at the pentacene-Co and pentacene-Ni(111) interfaces, respectively. Note that these values were measured from the Fermi edge to the high kinetic energy side of the HOMO peak. For increasing pentacene coverage, shifts in opposite directions of the HOMO for the two interfaces were registered. This indicates that hybridization of the molecular orbitals with the 3d bands of the substrates is different.

To complete the energy level alignment scheme, we also plotted the position of the lowest unoccupied level (LUMO). This was determined by adding a constant value,
equal to the band gap of pentacene reported in literature. Values for the band gap in the range 2.2 eV to 2.7 eV have been found [105, 108, 117]. In figure Fig. 4.9 we represent the low limit of this value.

The increase in the carrier injection barrier due to a vacuum level shift is in fact a very well-known effect for interfaces between organic semiconductors and metals. In a recent report, Watkins et al. studied the band alignment of pentacene at different metal interfaces by means of UPS [107]. Their work refers to calcium, silver and gold substrates. The electronic structure of pentacene films deposited on the three metals, but also of the reversed interface (metals deposited on pentacene films) were presented. Although the interaction of pentacene with the metals have shown to depend on the deposition sequence, the authors report a linear dependence of the hole injection barrier on the metal work function. Since that time, new data on gold and samarium has been published [97, 108].

We summarize in Fig. 4.10 (a) and (b) all the existent data related to pentacene - metal interfaces, which we could find in literature. In these plots we represent the dependence of the vacuum level shift (Δ) and barrier for the hole injection (ε_v−F) on the work function of the metals (Φ). Additionally, we plotted our results. For reference we plot in Fig. 4.10 (c) an energy level diagram at the interface between an organic film and a metal. As already introduced in chapter 2 of this thesis (Eq. 2.6), the relation between Δ and ε_v−F is given by:

\[ ε_v−F = IP − Φ − Δ \]  \hspace{1cm} (4.1)

In the plot Δ versus Φ (Fig. 4.10 (a)), a line with a slope of \( S = -0.564 \), reported by Watkins et al., is also represented. According to the Eq. 4.1, ε_v−F should show an linear dependence with the slope \(-1 − S\), assuming that the ionization potential of the organic material is independent on the metal substrate. We can see however, that the different points represented in Fig. 4.10 deviate from these linear dependencies.

Besides the photoemission studies, Campbell et al. have used a different approach to study the band alignment of pentacene at different metal systems [105]. In this contribution, the authors make use of internal photoemission and electroabsorbtion experiments. Remarkably, the data published by Campbell et al. in Fig. 4.10 (b), do not correspond to the photoemission experiments of Watkins et al. In addition, we can see that for the pentacene-gold interface, different research groups reported results that are consistently different one from another.

We think that these discrepancies can be related to the degree of impurities in the substrates or to a different morphology of the films. The first hypothesis is supported by our observations, which clearly show that the barrier for the hole injection is very sensitive to small amounts of adsorbates on the substrate surface. We can not completely verify this supposition, since in the other reported pentacene-metal interfaces the pressures during the deposition of the pentacene are not clearly specified.

As to the structure of the pentacene layers deposited on the substrates discussed above, the films grown by Campbell et al. were amorphous or polycrystalline, with small crystalline grains (5 to 20 nm) [105]. Koch et al. report pentacene films grown
4.3. Energy level diagrams

![Energy level diagrams](image)

**Figure 4.10:** (a) Plot of the vacuum level shift ($\Delta$) versus work function ($\Phi$) of metals; A negative value for the $\Delta$ means lowering of the vacuum level (b) Plot of the hole injection barrier ($\epsilon_v - \Phi$) versus work function of metals. The literature data is taken from [101, 105–108]. The parameters $\Delta$, $\epsilon_v - \Phi$ and $\Phi$ are defined figure (c)

on polycrystalline gold substrates, with needle-like crystallites of 100 nm wide [118]. Schroeder et al. [101] report randomly spaced pentacene domains on the gold surface,
ranging in size from 500 nm to about 1.5 µm. The type of the structure in pentacene films is not indicated by Watkins et al. Thus, neither this hypothesis can be entirely verified.

We note that in the case of bithiophenes, Ramsey et al. reported also a deviation from the linear dependence of the vacuum level shift [119]. It has been suggested by Ishi et al. that the dependence of the vacuum level shift on the work function of metals should be related to the type of interaction with the systems [32].

Our work demonstrates that summarizing the existing data is difficult at the moment. We think that experiments should be performed such as to relate the electronic properties not only to the chemistry of the system but also to the structural properties of organic films. Also care should be taken with the vacuum conditions. As demonstrated by the case of pentacene, significant error can be made in the prediction of the electronic structure of an unknown interface, only on the basis of the existent literature.
Chapter 5

Organo-metallic magnetic tunnel junctions

Abstract: We present results on hybrid organo-metallic magnetic tunnel junctions aimed at developing a novel class of spintronic devices, in which the spin-polarized electron tunneling through an organic layer is being exploited. We have been able to produce a promising TMR of 7% at 5 K, with junctions based on "terpyridines" deposited in ultra high vacuum conditions, although still hampered by a poor reproducibility, severe interdiffusion and a full quenching of TMR above 30 K. Experiments aiming at gaining insight into the process of interdiffusion of metals into molecular systems will be further addressed.

5.1 Introduction

The field of organic semiconductors has been one of the highlights in physics in the past decade. Organic based electronics applications such as light emitting diodes for flat-panels displays, transistors, solar cells, sensors and even solid state lasers have been widely investigated [13, 15]. Recently, the idea has been generated to incorporate molecular layers in the so-called spintronic devices [7, 22, 25, 27, 29]. An overview on the advances of this field was given in chapter 1 of this thesis.

In this chapter we describe experiments aiming at investigating spin dependent tunneling through molecular films. The magnetic and electrical properties of hybrid organo-metallic magnetic tunnel junctions (OMTJ’s) are discussed.

Background

A tunnel junction consists of two metal layers separated by a thin (typically a few nanometer) insulator. When a voltage is applied over the insulator a current starts to flow by tunneling of electrons. For the description of transport of electrons in a tunnel junction various types of models are available. The models differ mainly in the way the electron states in the metal electrodes are described, but also in the way the barrier is
described. Because of the ease of use and the clarity, the so-called free-electron model is used here to describe the electron states in the electrodes. The description of the insulating layer is poorly known, because it has a very complex structure. Simple model assumptions, such as trapezoidal barriers or vacuum gaps, have been used.

In the free-electron model of a metal, the electrons are assumed to be free particles, having neither interaction with each other nor with the ion cores of the lattice. The electrons in the metals can thus be described by one-electron wave functions with a wave vector $\mathbf{k}$ and energy

$$E = \frac{\hbar^2}{2m_e} |\mathbf{k}|^2,$$

(5.1)

where $m_e$ is the electron mass and $\hbar$ is Planck’s constant. The wave vector $\mathbf{k}$ has components in the $\hat{x}$, $\hat{y}$ and $\hat{z}$ direction. Since the interaction of the electrons with the positive ion cores in the lattice is not considered in this model, there is just one continuous energy band without gaps. This parabolic energy band is filled with electrons up to the Fermi level. The density of states $\varrho$ is equal to [26]:

$$\varrho(E) = \frac{1}{2\pi} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \frac{E^{1/2}}{2},$$

(5.2)

In order to get more realistic results with this model, the bare electron mass can be replaced by an effective electron mass $m_e^*$. The tunneling between two free-electron metals is regarded from an independent-particle point of view. To describe the electron states in a tunnel junction, a free-electron with a certain energy is considered, moving in a potential. The tunnel junction is assumed to be infinitely large in two dimensions and therefore the potential energy depends only on one spatial coordinate, e.g. $z$. For convenience, we consider in figure 5.1 the potential energy $V(z)$ only in one dimension. This potential is divided in three regions: the left electrode, the barrier and the right electrode. The potentials of both electrodes are flat, whereas the potential of the barrier depends on $z$. The electron-wave function $\psi$ is obtained from the time-independent Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m_e^*} \nabla^2 + V(z) \right] \psi = E \psi.$$

(5.3)

In both electrode regions the wave functions are free-electron like, with real wave vectors. These waves are matched in amplitude and derivative at the interfaces with the wave function in the barrier region, as can be seen in Fig. 5.1. From this, the transmission probability (also called tunnel probability) through the barrier follows, which is used in calculating the tunnel current.

In a normal steady state, electrons will tunnel from the left to the right electrode as well as in the inverse direction in equal amount. There is no preferred direction for the tunneling electrons if the barrier height is the same for the left and the right electrode. When a bias voltage $V_b$ is applied across the junction, the Fermi level at one side will shift by $eV_b$ with respect to the other and the barrier is tilted with the same energy.
5.1. Introduction

Figure 5.1: The potential of a tunnel junction. Over the insulating barrier, with thickness $d$, a bias voltage $V_b$ is applied. The potential energy of the barrier is given by $V(z)$. The Fermi energy $E_F$ is also shown. An incoming electron wave is partially reflected and partially transmitted through the barrier.

eV_b$ (see Fig. 5.1), where $e$ is the electron charge. Now there are empty electron states available above $E_F$ in the right electrode, by which a net current will flow through the barrier from left to right. The tunnel current density $J$ is given by:

$$J(V_b) \propto \int_{-\infty}^{+\infty} dE \, g_l(E)g_r(E - eV_b) \, |M|^2 [f(E) - f(E - eV_b)], \quad (5.4)$$

where $g_l(r)$ is the density of states for the left (right) electrode. The $f(E)$ is the usual Fermi-Dirac distribution function and $|M|^2$ is the square of a matrix element, which is essentially the probability of transmission through the barrier. The term including $f(E)$ and $f(E - eV_b)$ expresses the requirement that electrons on one side of the barrier must have empty states to tunnel into the other side of the barrier.

The transmission probability $|M|^2$ can only be determined exactly for artificial and simplistic barriers, like square barriers (see e.g. [120]). In order to calculate it for more realistic barrier potentials, approximations have to be applied. Suppose that the barrier potential $V(z)$ varies rather slowly in comparison to the wavelengths of the tunneling electrons. Then the so-called WKB approximation [120] can be applied to calculate the tunnel probability. According to the WKB approximation the matrix element $|M|^2$ is given by

$$|M|^2 \propto \exp \left( -\frac{2}{\hbar} \int_0^d \sqrt{2m^*} \left[ V(z, V_b) - E \right] dz \right), \quad (5.5)$$

where $d$ is the barrier thickness and $V(z, V_b)$ is the barrier height at the bias voltage $V_b$ and the position $z$ in the barrier.

Simmons [121] used the WKB approximation to obtain the matrix elements $|M|^2$ for an arbitrary barrier of average height $\bar{\varphi}$ above the common Fermi level $E_F$. The tunnel current density is calculated from Eq. (5.4), assuming the Fermi-Dirac distributions as
step functions (i.e. \( T = 0 \)) and using equation (5.2) for \( \sigma_{l,r} \). For voltages lower than the barrier height, the result is:

\[
J = \frac{J_0}{d^2} \left( \frac{\varphi}{e} - \frac{V_b}{2} \right) \exp \left[ \alpha d \left( \frac{\varphi}{e} - \frac{V_b}{2} \right)^{\frac{1}{2}} \right] - \frac{J_0}{d^2} \left( \frac{\varphi}{e} + \frac{V_b}{2} \right) \exp \left[ \alpha d \left( \frac{\varphi}{e} + \frac{V_b}{2} \right)^{\frac{1}{2}} \right],
\]

(5.6)

with \( J_0 = e^2/2\pi h = 6.166 \cdot 10^{10} \text{ Acm}^{-2} \text{Å}^2 \text{V}^{-1} \) and \( \alpha = -4\pi \sqrt{2m_e e / h} = -1.025 \text{ e V}^{-1/2} \text{Å}^{-1} \). The resulting current density \( J \) is in Acm\(^{-2}\). The expected exponential dependence of the tunnel current on barrier thickness and the square root of the barrier height are correctly recovered. For \( V_b \ll \varphi/e \), it is easily seen that the \( J(V_b) \) is linear, while for larger voltages it becomes rapidly nonlinear. At moderate voltages, Simmons showed that \( J \sim \beta(V_b + \gamma V_b^3) \), which leads to one of the key-characteristics of tunneling: a parabolic dependence of conductance \( (G \equiv dI/dV) \) on voltage, which is frequently observed for tunnel junctions with non-magnetic electrodes. This formula (5.6) is often used to fit experimental \( J(V_b) \) characteristics to obtain effective barrier heights and thicknesses.

For a tunnel junction with different electrode materials, the difference in barrier height at both metal-insulator interfaces makes the barrier oblique, resulting in an asymmetric current voltage behavior. Upon closer examination of Simmons’ equation (5.6), however, it becomes clear that the predicted transport characteristics are always symmetric in voltage. The Simmons model fails to capture this fundamental asymmetry. Brinkman et al. [122] have addressed this problem by assuming a trapezoidal barrier, introducing an additional, asymmetry parameter \( \Delta \varphi = \varphi_l - \varphi_r \) to account for the tilted barrier. It is found that:

\[
J(V) = G(0) \left[ V - \left( \frac{\sqrt{2me}}{24h} \frac{d\Delta \varphi}{\varphi^{3/2}} \right) V^2 + \left( \frac{2me^2}{24h^2 \varphi} \frac{d^2}{d \varphi} \right) V^3 \right]
\]

(5.7)

where \( G(0) \) is the conductance at zero bias voltage, which has the value equal to \( 7.9 \times 10^9 \left( \frac{e^{1/2}}{d} \right) \exp(-\alpha d \sqrt{\varphi}) \)

In the approaches of both Simmons [121] and Brinkman [122], the transport characteristics are independent of the electronic density of states of the electrodes, a direct result of the oversimplified model used. An overview of the subtle role of the density of states in solid state tunneling is given in [123].

**Julliere’s Model for Tunneling Between Ferromagnets**

Consider a junction with two equal ferromagnetic electrodes separated by an insulating barrier. Julliere proposed a simple model to understand the TMR-effect in such a junction. In this model it is assumed that the spin of an electron is conserved during
Figure 5.2: Schematic spin split density of states vs. energy for two identical ferromagnetic electrodes with (a) parallel magnetizations and (b) anti-parallel magnetizations. The tunnel conductance $G$, through an insulating layer, that separates the two electrodes, is proportional to the product of the density of states at the Fermi level of both electrodes.

tunneling, so spin-flip processes are neglected. This implies that spin up electrons only tunnel to and from spin up states, and vice versa. Further it is assumed that the tunnel conductance $G$ is proportional to the product of the density of states of the different spin states of the electrodes. Figure 5.2 (a) shows that the conductance for parallel magnetizations $G_p$ is then given by:

$$G_p = G_\uparrow + G_\downarrow \propto \varrho_{\text{maj}}^2 + \varrho_{\text{min}}^2,$$  \hspace{1cm} (5.8)

where $G_\uparrow(\downarrow)$ is the conductance in the up- (down-) spin channel and $\varrho_{\text{maj(min)}}$ is the majority (minority) density of states at the Fermi level. In a similar manner, the conductance for the antiparallel magnetizations $G_{ap}$ of the two electrodes can be determined (Fig. 5.2 (b)). Tunneling between equal spin orientations states implies tunneling from a majority to a minority band, and vice versa. The conductance for anti-parallel alignment is then given by:

$$G_{ap} = G_\uparrow + G_\downarrow \propto \varrho_{\text{maj}} \varrho_{\text{min}} + \varrho_{\text{min}} \varrho_{\text{maj}} = 2\varrho_{\text{maj}}\varrho_{\text{min}}.$$  \hspace{1cm} (5.9)

It can be easily verified that $G_{ap} \leq G_p$, giving rise to a magnetoresistance. The tunnel magnetoresistance at zero bias is then defined as:

$$\text{TMR} = \frac{G_p - G_{ap}}{G_{ap}} = \frac{R_{ap} - R_p}{R_p} = \frac{2P^2}{1 - P^2},$$  \hspace{1cm} (5.10)

where $R_{p,ap}$ are the junction resistance in the parallel and anti-parallel configuration, respectively. $P$ is the polarization of the density of states at the Fermi level:

$$P = \frac{\varrho_{\text{maj}} - \varrho_{\text{min}}}{\varrho_{\text{maj}} + \varrho_{\text{min}}}. \hspace{1cm} (5.11)$$

In general, for a MTJ with non-identical electrodes,

$$\text{TMR} = \frac{2P_pP_t}{1 - P_pP_t}, \hspace{1cm} (5.12)$$
where $P_{b(t)}$ is the spin polarization of the bottom (top) electrode. It should be noted that the formula (5.10) is only a first-order approach for the spin polarization. Though, the Eq. (5.12) gives a good estimate for the TMR effect, when experimental values for the spin polarizations are used.

**Temperature Dependence of the Junction Resistance**

At zero temperature and in the limit of zero bias voltage, only elastic tunnel processes contribute to the conduction in MTJ’s. This implies that both the energy and the spin of the conduction electrons are conserved. Under these conditions, each incoming electron state has a single corresponding transmitted electron state to tunnel into. Also only the electrons with energies at the Fermi level will contribute to the tunnel current, since only for those electrons empty states are available in the counter electrode to tunnel into.

At elevated temperatures (or at non-zero bias voltages), these assumptions may not be completely valid. The obvious effect of the increase of the temperature will be thermal smearing of the electron states in the energy range of a few $k_B T$ ($k_B$ is Boltzmann’s constant) around the Fermi level, and a decrease of the magnetization of the electrodes [124]. Further, at finite temperatures, inelastic tunneling processes become possible, for which the initial and final energy of the tunneling electrons are not equal. The energy difference is released by excitation of phonons (lattice vibrations) and/or magnons (spin-waves), or gained by their absorption. As phonon excitations conserve spin, the resulting additional conductance will not have a large influence on the TMR. Magnon excitation, on the other hand, leads to spin flip and thereby reduces the TMR. An additional transport mechanism, for both non-magnetic and magnetic tunnel junctions, is hopping conduction. Hopping conduction is spin-independent indirect (inelastic) tunneling via localized impurity and/or defect states inside the barrier.

The temperature dependence of the TMR and the conductivity for tunnel junctions was explained within a simple model by Shang et al. [124]. The conductance $G$ of a tunnel junction is assumed to consist of two independent conduction channels: a contribution $G_e$ due to elastic tunneling and a contribution $G_i$ due to inelastic tunneling. The latter contribution, caused by hopping electrons through localized states in the barrier, depends strongly on the temperature and increases like $G_i \sim T^n$ [125]. For example, in the case of AlOx barriers, Shang et al. reported for the inelastic tunnel conductance versus temperature an exponent $n$ of 1.33 [125]. It is assumed that only the elastic contribution depends on the angle $\theta$ between the magnetic moments of the two electrodes. Thus the conductance is written as:

\[ G(\theta) = G_e(\theta) + G_i, \]  
\[ (5.13) \]

with

\[ G_e(\theta) = G_T [1 + P_b P_t \cos(\theta)], \]  
\[ (5.14) \]

where $P_{b(t)}$ denote the effective tunneling electron spin polarizations of the bottom (top) ferromagnet, while $G_T$ is the prefactor for direct elastic tunneling. Notice that all the variables in Eqs. (5.13) and (5.14) depend on temperature.
Simmons [126] derived a model for the temperature dependence of the direct elastic tunneling conductance $G_T$ at small bias voltages. Using Fermi-Dirac statistics, a free-electron model and the WKB-approximation for the tunnel probability it was derived that:

$$\frac{G_T(T)}{G_T(0)} = \frac{R_J(0)}{R_J(T)} = \frac{cT}{\sin(cT)},$$

(5.15)

where $R_J(T)$ is the elastic junction resistance as a function of temperature (in K) and the constant $c$ is given by $c = 0.1387 \cdot 10^{-3} d/\bar{\phi}^{1/2}$, with the barrier width $d$ in Å and the average barrier height $\bar{\phi}$ in eV. At sufficiently low temperatures, the inelastic tunnel contributions are small and only the elastic contributions prevail. Thus the barrier parameters obtained from fits of Eq. (5.6) to $J - V_b$ measurements at low temperatures can be used to predict the elastic contribution to the junction resistance $R_J$ at elevated temperatures.

5.2 Experimental

The OMTJ’s were grown in a UHV environment. The importance of this route has been emphasized in the introductory part of this thesis (see Sec. 1.2).

In this work we prepared junction having as barrier three different materials: PTCDA (Sec. 3.2), pentacene (Sec. 3.3), and [2,2'; 6',2"] terpyridine-4-ylxy-hexanoic acid (TERPY). The latter type of molecules were synthesized in the Macromolecular Chemistry and Nanoscience group at the Eindhoven University of Technology. We will refer from now on to these molecules as TERPY.

The Lewis structure of TERPY is shown in Fig. 5.3. Such a molecule contains a terpyridine core and a hexanoic acid tail, which is bound to the terpyridine entity through an oxygen atom. The terpyridine group is known to adopt a perpendicular orientation on a gold substrate when deposited via a self-assembly process [127]. The hexanoic acid consists of a pentane chain, in which the carbon atoms form unsaturated bonds, and a COOH group. One would expect therefore that in the case of a perpendicular orientation of the molecules, tunneling electrons would encounter a higher energetic barrier. An additional reason to use the hexanoic acid group, was to increase the melting point.

![Lewis structure of the [2,2'; 6',2"] terpyridine-4-ylxy-hexanoic acid (TERPY)](image-url)
of terpyridine (373 K) such as to allow evaporation in a UHV environment (the melting point of TERPY is 453 K). The crystal and electronic structures of TERPY have not been determined yet.

Prior to the deposition of the MTJ, the substrate was carefully cleaned, loaded in the UHV system and plasma oxidized. The bottom electrode is required to be extremely flat such that a closed and pinhole-free organic barrier can be deposited on it. From growth mode and surface energy considerations [123], it follows that most metals (including Al and Co) do not grow very well on oxidic surfaces. Thus simply growing them on the substrate would result in an extremely rough surface unsuitable for MTJ’s. However, metals such as Ru and Ta, have exhibited relatively smooth growth on SiO$_2$ substrates. Therefore a thin (35 Å) Ru layer was used as a buffer to promote flat growth of the bottom electrode. The ferromagnetic metals were deposited using magnetron sputtering or evaporation.

The MTJ’s were patterned using shadow masks (see Fig. 5.4). The junction mask is a flat, thin plate, with lines of $\sim$ 0.25 mm width (see Fig. 5.4 (a)), forming junctions with areas of about $\sim 6 \cdot 10^{-4}$ cm$^2$. The basic junction structure is displayed in Fig. 5.4 (b, c).

First, the mask is positioned on the sample, such that the six stripes are directly above the substrate, nearly in contact with it. The bottom magnetic subsystem is now

**Figure 5.4:** (a) Schematic illustration (top view) of a shadow mask used for the patterning of the MTJ’s. (b) Schematic of the resulting MTJ structure. (c) Layout of a typical OMTJ.
deposited through these lines. In the current experiments we used an antiferromagnetic coupled Co/Ru/Co system as bottom electrode, as discussed in Sec. 5.3. When the bottom magnetic subsystem is finished, the sample is transported to the OMBE chamber, where the organic barrier is grown. The organic materials were deposited as explained previously. After the deposition of the organic barrier the sample is transported back to the sputter system for the deposition of the top electrode. The top electrode has to be protected from oxidation in air, which is achieved by capping it with a thin Al layer.

The transport measurements were performed with a home-built setup, which is equipped with a 4-400 K variable temperature helium flow cryostat and a 1.35 T magnet. Several custom probes are available for insertion into the cryostat, allowing the measurement of six junctions per run with a magnetic field parallel to the plane of the layers.

The magnetic characterization was performed using MOKE and SQUID measurements. A schematic representation of the MOKE geometry is displayed in Fig. 5.5. The magnetizations of the Co layers are in the xy-plane and the laser light is incident in a plane parallel to the yz-plane on this sample. The magnetic field $H$ is applied in the y-direction.

\[ \text{Figure 5.5: Schematic illustration of the longitudinal MOKE technique. The arrows indicate the magnetization directions of the two Co layers. The laser light is incident in the yz-plane.} \]

5.3 Results and discussion: Magnetic characterization

Julliere’s simple model for the TMR effect was discussed previously (see section 5.1), with the result that the conductance (resistance) of a MTJ is lower (higher) when the magnetizations of the two ferromagnetic electrodes are anti-parallel. Experimentally, one must realize both a parallel and an anti-parallel magnetization alignment. This can be achieved in several ways. One possibility is to use two ferromagnets with different coercive fields [128, 129]. Another route is the use of an exchange biased electrode, i.e. an antiferromagnetic/ferromagnetic double layer [130, 131]. Also artificial antiferromagnetic (AF) coupled multilayers can be used as an electrode in MTJ’s [132, 133].

In this work we used as bottom electrodes artificial AF coupled Co/Ru/Co multilayers. For the top electrode we used simple Co layers, which were capped with aluminium,
tantalum or Ru thin films, in order to prevent oxidation of the magnetic film (see Fig. 5.4).

**Antiferromagnetic coupled multilayers**

Experimental studies on Co/Ru/Co multilayers revealed that the interlayer coupling oscillates between ferromagnetic (FM) and antiferromagnetic (AF) when the thickness of the Ru interlayer is varied [132, 133]. AF-coupling was observed between two Co layers with thicknesses of $d_1 = 120$ Å and $d_2 = 40$ Å, separated by a 6 Å Ru layer. In Fig. 5.6 the theoretical, in-plane magnetization as a function of applied field for such a system is displayed. The loop is characterized by three different regions. First, the plateau at low fields corresponds to an antiparallel alignment of the Co magnetizations due to the AF-coupling. The magnetization direction of the thinnest layer points opposite to the field direction. Further, the plateau is followed by a gradual increase of the magnetization corresponding to a rotation process in which both Co layers participate. Finally, at sufficiently large applied fields ($> H_2$) the AF-coupling is fully broken and the magnetization of both Co layers is parallel to the field. The fields $> H_1$ and $> H_2$ at which the rotation of the layer magnetizations commences and ends, respectively, are given by [132]:

$$
\mu_0 H_1 = -2J_c \left( \frac{1}{d_1 M_{s1}} - \frac{1}{d_2 M_{s2}} \right),
$$

(5.16)

$$
\mu_0 H_2 = -2J_c \left( \frac{1}{d_1 M_{s1}} + \frac{1}{d_2 M_{s2}} \right),
$$

(5.17)

where $J_c$ denotes the coupling strength (in J/m$^2$), $\mu_0$ the magnetic permeability of vacuum and $M_{s1(2)}$ the saturation magnetization of layer 1 (2). For the AF coupled layers, $d_1 = 120$ Å, $d_2 = 40$ Å and $M_{s1} = M_{s2}$, the ratio of the fields $H_1$ and $H_2$ at which the rotation of the magnetization of the two Co layers commences and ends, has a value of $H_1/H_2 = 1/2$. 

![Figure 5.6: Theoretical magnetization curve of two AF-coupled ferromagnetic layers, having different layer thicknesses and in-plane magnetization orientation. The arrows indicate the magnetization directions of these layers schematically.](image)
5.3. Results and discussion: Magnetic characterization

Figure 5.7: (a) Measurement of both the ellipticity $\varepsilon$ and the rotation $\psi$ of an anti-ferromagnetically coupled Co 120 Å/Ru 6 Å/Co 40 Å structure as a function of external magnetic field. (b) Projection of the magnetization of both magnetic layers on the y-axis in arbitrary units as a function of magnetic field. (c) The angle between the magnetization direction and the x-axis versus the applied magnetic field for both Co layers. (d) The relative angle of the magnetization directions of the two layers versus the applied field. Insets show the corresponding magnetization directions of both layers at different field values (in (b): side view, in (c) top view).

Figure 5.7 shows the magnetic properties of an AF coupled Co/Ru/Co multilayer stack, measured by means of MOKE. In Fig. 5.7 (a) we represent the rotation and ellipticity experienced by the incident light as a function of the applied field. We can see that the measurements resemble the expected behavior. The theoretical value $H_1/H_2 = 1/2$ is in agreement with the values determined from Fig. 5.7 (a): $H_1 \approx 0.09$ T and $H_2 \approx 0.18$ T.

In the present measurement configuration (see Fig. 5.5), MOKE measures the projection of the magnetization on the y-axis. For a system with two magnetic layers, the
measured change in ellipticity $\varepsilon$ and rotation $\psi$ of the reflected light can be written as:

$$\varepsilon = e_1 M_{y1} + e_2 M_{y2}$$  \hspace{1cm} (5.18)

$$\psi = r_1 M_{y1} + r_2 M_{y2}$$  \hspace{1cm} (5.19)

with $e_n$ and $r_n$ being constants, and $M_{y1(2)}$ the projection of the magnetization on the $y$-axis of the lower (upper) Co layer. The lower 120 Å Co layer is represented by layer 1 and the upper 40 Å Co layer is represented by layer 2 in this figure. In general, $e_1 \neq e_2$, $r_1 \neq r_2$ and also $e_n \neq r_n$.

From Fig. 5.7 (a) it becomes clear that the ellipticity measurement is most sensitive to the thin Co layer (2), evidenced by the non-monotonous jump around zero field. The rotation measurement most strongly probes the thick Co layer (1), since the measurement changes monotonically with field.

Assuming for the two Co layers a single magnetic domain structure and a completely anti-parallel magnetization alignment for low fields ($< 0.05$ T) and a parallel magnetization alignment for high fields ($> 0.30$ T), the coefficients $e_n$ and $r_n$ from equations (5.18) and (5.19) can be calculated from Fig. 5.7 (a). Then, by combining the ellipticity and rotation measurements, $M_{y1}$ and $M_{y2}$ can be separated, as shown in figure 5.7b. Notice that $M_{y1,2}$ are the projection of the magnetization on the $y$-axis in arbitrary units. In Fig. 5.7c the same information is shown as in Fig. 5.7b, but then transformed to an angle with respect to the x-axis by taking the arccos of $M_{y1,2}$. This enhances features near $90^\circ$, but also enlarges small scaling errors and noise resulting in the more than $90^\circ$ values. It was assumed that the total magnetization remains constant, while it rotates. At $\sim 0.1$ T a spin flip transition occurs, suddenly rotating the thick layer (1) $\sim 25$ degrees away from the field direction. The relative angle of the magnetization directions of the two layers is displayed in figure 5.7 (d).

Altogether, we demonstrated that the Co/Ru/Co trilayer displayed the proper behavior to serve as a magnetic layer in our OMTJ’s.

Magnetic properties of thin Co films deposited on molecular films

In this subsection we discuss the magnetic behavior of Co films grown on thick molecular films. The films were deposited via two different deposition methods: magnetron sputtering and e-beam evaporation. For the MOKE experiments we used wedge-shaped samples, which were made under UHV conditions by slowly withdrawing a shutter at a constant speed, during deposition. A schematic drawing of a wedge-shaped sample is shown in Fig. 5.8 (a). By measuring the magnetization loops at different points on the wedge, information on the magnetic properties of ferromagnetic films of different thicknesses can be obtained.

An example of a hysteresis loop measured with MOKE is plotted in Fig. 5.8 (b). The magnetic field was applied in the plane of the film surface. One of the parameters that can be extracted from the magnetization loops is the coercive field ($H_c$). Another parameter is the saturation value of the MO signal ($\theta_{sat}$), which is a measure of the magnetic moment. $\theta_{sat}$ will be further referred to as magnetic moment ($M$).
Figure 5.8: MOKE measurements on Co thin films deposited on a PTCDA layer. (a) Schematic drawing of a wedge-shaped sample; (b) Hysteresis curves measured using the MOKE; $H_c$ is the coercive field; $\theta_{sat}$ is a measure of the magnetic moment of the sample; (c)-(h) Experimental values, obtained using the MOKE, of the coercive field $H_c$ (c,e,g) and magnetic moment $\theta_{sat}$ (d,f,h) in Co films, plotted as a function of the thickness of the Co films. Substrates: (c,d) Magnetic properties of Co films deposited by sputtering on Si(001)/SiOx substrates. In (e,f) the Co films were grown by magnetron sputtering and in (g,h) by e-beam evaporation on 2000 Å PTCDA films.

First we discuss the magnetic properties of thin Co films deposited on Si(001) substrates with a native oxide. The evolution of the $H_c$ as a function of Co film thickness is displayed in Fig. 5.8 (c). Up to a thickness ($d_1$) of 15 Å $H_c$ is zero, then it rises steadily...
up to a thickness of about \( \sim 30 \, \text{Å} \) and above this value it decreases at a slower rate. This behavior is similar with previous results by published by Camarero et al. in the case of Co/Cu(111) system [134]. The initial increase of \( H_c \) has been attributed to the reduced dimensionality, associated with the changes in the Curie temperature of the films. For larger thicknesses, three-dimensional behavior sets in, and the variation of \( H_c \) with Co coverage was explained by the influence of this parameter on the structure and dynamics of magnetic domain walls.

In Fig. 5.8 (d) we represent the magnetic moment of Co layers versus thickness. The magnetic moment was normalized to the value measured for a thickness of 100 Å. We can see a decrease in the magnetic moment as the thickness of the film is decreased. At a thicknesses around \( d_o = 7 \, \text{Å} \) it drops to zero, indicating that a fraction of the deposited Co is not contributing to the magnetic signal in our experiment. SQUID measurements performed on a 12 Å thick Co film, indicated a magnetic moment of \( 7.5 \pm 0.2 \cdot 10^{-7} \text{emu/mm}^2 \), a value that is expected from a film thickness of about 5 Å. This means that a magnetic dead layer of about 7 Å of Co is formed. This value matches with the thickness \( d_o \) determined from the MOKE experiments.

Thus, we obtained a thickness range 7 to 15 Å with a finite magnetic moment and a vanishing \( H_c \) at a thickness \( d_o \) of 7 Å. Up to a thickness of 7 Å the Co layers are magnetically dead, whereas in the range 7 – 15 Å the films are superparamagnetic or soft magnetic.

The magnetic properties of Co films deposited on PTCDA layers showed different behavior from those deposited on silicon films. Figures 5.8 (e, g) represent plots of the \( H_c \) versus Co thickness, for Co layers deposited by evaporation and sputtering, respectively, on a 2000 Å thick PTCDA film. For the two deposition methods, we represent in Fig. 5.8 (f, h) the magnetic moment (M) as a function of Co thickness. Just like for the films grown on silicon substrates, we normalized the magnetic moment to the one a 100 Å thick film. Notice the scattering between points in the dependence of the \( H_c \) and magnetic moment versus Co thickness for the sputtered Co layers (Fig. 5.8 (e, f)).

A key observation is that the magnetic moment of the Co vanishes to zero at much larger thicknesses when PTCDA layers are used as substrates. A vanishing thickness \( (d_o) \) of 17 Å and 35 Å for the evaporated and sputtered films, respectively, was measured. We note that the value for \( d_o \) could be reproduced within 10% when the same batch of PTCDA material was used. However, \( d_o \) was found to change every time the evaporation cell was refilled, which hindered a more systematic study. The dependence on refilling of the K cell points at a subtle dependence on the purity of the organic film.

Interestingly, the coercive field of the Co/PTCDA system is larger than in the absence of the PTCDA film. Moreover, in contrast to \( d_o \), the coercive field showed large statistical variation from sample to sample even within the same batch of PTCDA material. For example, for 100 Å thick films, it varied in the case of sputtered layers from about 5.5 up to 12 kA/m (\( \mu_0 H_c = 7 \) to 15 mT), thus always larger values than the case of silicon substrate (around 2.4 kA/m). This observation might provide an attractive way of establishing different switching fields for top and bottom electrode.
The increased value for $d_\circ$ is attributed to the diffusion of the metallic atoms into the molecular film. When the atoms interdiffuse through the organic layer, their atomic moments are randomized (being in the paramagnetic state) and no longer contribute to the magneto-optical signal. The fact that the vanishing thickness for the evaporated Co films is smaller than that corresponding to sputtered layers is consistent with the lower kinetic energy of Co atoms in the evaporation process.

Increased coercive fields have been registered for Co films grown on Alq3 layers [29], but also for various magnetic films of increased roughness [135–138]. In the latter case, the increased coercive field has been attributed to domain wall pinning. AFM images recorded on 100 Å thick Co films deposited on PTCDA revealed similar morphologies with the PTCDA film (see for example Fig. 3.13 (a) from chapter 3). This is a clear indication that not only the roughness of the Co film is increased, but also the lateral size of the grains. Thus, we think that in our Co-PTCDA system, the increased coercive field should be attributed both to shape anisotropy of the Co grains and domain wall pinning.

To resume this section, we showed that the magnetic properties of Co films is sensitive to the presence of molecular films. Our measurements indicate that we deal with diffusion of Co metal particles into the molecular film. Apparently, when Co films are deposited by magnetron sputtering the interdiffusion is stronger than when e-beam evaporation is used.

5.4 Results and discussion: Transport Characterization

In this section we present the experimental results of transport measurements on magnetic tunnel junctions with organic barriers.

First, we discuss the results of the experiments performed on PTCDA based OMTJ's. Junctions could be successfully prepared for organic layer thicknesses above 500 Å, using e-beam evaporated electrodes. We note that electrodes prepared by magnetron sputtering mostly lead to electrical shorted devices when 500 Å organic films were used. This is a confirmation that indeed metallic films deposited by sputtering interdiffuse stronger into molecular films than the e-beam evaporated ones. Typical electrical behavior of PTCDA-based OMTJ’s with e-beam evaporated electrodes is shown in Fig. 5.9. The current density versus bias voltage measured at a temperature of 30 K and zero magnetic field (Fig. 5.9 (a)) shows a clear non-linear behavior. The differential resistance (dV/dI) versus voltage (Fig. 5.9 (b)) is similar to conventional MTJ’s and provides a direct indication of tunneling. However, unlike expectations for an ideal tunnel junction, a strong temperature dependence of the junction is registered (see Fig. 5.9 (c)). These junctions showed no measurable magnetoresistance.

Next, we discuss the TERPY based junctions. For these type of junctions, the electrodes were prepared by magnetron sputtering. Similar to the PTCDA based OMTJ's we encountered problems with interdiffusion of the top electrode. Out of all prepared junctions, only few resulted in electrically non-shorted devices with a reasonable resistance. In Fig. 5.10 we show the results of electrical measurements of a Ru (35 Å)/Co
Figure 5.9: (a) Current density versus voltage for a PTCDA (500 Å) based OMTJ’s with Co top electrode prepared by e-beam evaporation. The characteristic is measured at 30 K and zero magnetic field. (b) Normalized differential resistance (dV/dI) versus voltage; (c) Junction resistance versus temperature. 

Figure 5.10 (a) represents the current-voltage characteristic measured in zero magnetic field and at a temperature of 5 K. This curve shows a clear nonlinear behavior, which may be taken as a sign of tunneling. Despite of the fact that the top and bottom electrode are of the same material, the curves are asymmetric around the zero voltage. At 5 K, the asymmetric nonlinear curve was fitted with a Brinkman dependence, resulting in the following barrier characteristics: barrier width, $d = 19.2 \, \text{Å}$, average barrier height, $\bar{\varphi} = 2.3 \, \text{eV}$, and barrier asymmetry, $\Delta \varphi = 2 \, \text{eV}$. Remarkably, the fitted barrier thickness is much smaller than the nominal thickness of the TERPY layer (600 Å).

In Fig. 5.10 (b) the magnetoresistance (MR) measurement is displayed. The curve
5.4. Results and discussion: Transport Characterization

Figure 5.10: (a) Current density as a function of bias voltage for a Ru 35 Å/Co 120 Å/Ru 6 Å/Co 40 Å/TERPY 600 Å/Co 200 Å OMTJ at 5 K; (b) Magneto-resistance curve; (c) Histogram representing the different measured values of the switching fields. $H_1$-$H_4$ are defined in figure (b); (d) MR as a function of applied bias voltage at 5 K; (e) Junction resistance (in MΩ) as a function of temperature.
was measured at 5 K and a bias voltage of 14 mV. A clear MR effect is observed. At high negative fields, the magnetizations of both electrodes are parallel, pointing to the left, as indicated by the arrows in the figure. As the magnetic field is swept towards positive values, at a certain value $H_3$ one of the electrodes is switching its magnetization. An antiparallel alignment of the top and bottom electrode is achieved and the resistance of the junction increases. As the field is increased further, the other electrode also switches (at a field $H_4$), and the two electrodes have again a parallel alignment of the magnetization, leading to a decrease in the resistance. Scanning the magnetic field in the reverse way, results in changes in the orientation of the magnetization of the two layers and the resistance is changed again, at magnetic fields defined by $H_1$ and $H_2$. Taking into consideration that the bottom electrode is an AF coupled multilayer, this behavior is surprising. Moreover, the switching fields and the the absolute value of the magnetoresistance varied randomly each time the MR measurement was repeated. The histogram shown in Fig. 5.10 (c) indicates the limits observed for the four different switching fields, measured at different times. The relative change in magnetoresistance varied up to 7%.

The MR was found to depend strongly on the applied bias. In figure 5.10 (d) the measured MR (squares) as a function of bias voltage is shown. At an applied bias of 50 mV the MR was already reduced to only 1%. Also the temperature dependence of the MR was found to be strong. At temperatures above 30 K no MR was registered.

Figure 5.10 (e) illustrates the temperature dependence of the junction resistance $R_J$. The resistance was measured at a current of 1 nA in zero magnetic field. The junction resistance decreases up to temperatures of about 200 K, and keeps approximately constant above 200 K. Notice that junction resistance at 300 K is only half of the value measured at 5 K.

A qualitative analysis of this dependence can be made in terms of the expected temperature dependence (see Eqs. 5.14 and 5.15) for a tunnel junction. Because of the weak variation of the resistance above 200 K we can assume that the inelastic processes are negligible and the only contribution to the resistance is given by the elastic tunneling component. We assume further that the polarization of the electrodes does not vary significantly, and the polarization related term in Eq. 5.14 is considered as a constant. Thus, we can assume a dependency of the type described by Eq. 5.15. The fit for the temperature dependence based on parameters determined from fitting the IV characteristic is plotted in Fig. 5.10 (e) with a dotted curve. We can see that this analysis predicts a much weaker dependence than experimentally observed. This suggests the presence of an additional current mechanism that has a stronger temperature dependence.

Altogether, in the TERPY based MTJ’s we have been able to measure a 7% magnetoresistance at 5 K. However, the transport properties of these junctions showed several features that deviate from those of conventional inorganic MTJ’s. First of all the switching fields observed in the magnetoresistance curves were not corresponding to the expected behavior. We measured MR curves showing sharp switching from parallel to antiparallel alignment. Moreover, the switching fields were irreproducible at
successive measurements. Secondly, unlike the IV characteristics (not shown), the observed MR showed a strong bias and temperature dependence. Finally the electrical properties of our junctions could not be reproduced in latter attempts.

A possible explanation for the behavior of our TERPY junction is that the actual tunneling takes place via Co clusters formed in the TERPY barrier. A possible configuration of the actual device formed is indicated in Fig. 5.11. We conjecture that clusters are formed in the barrier by diffusion of the sputtered Co electrodes. The tunneling takes place via clusters which are closest to the bottom electrode. The distance \( d \) in Fig. 5.11 roughly corresponds to the effective barrier thickness, as determined from Brinkman’s equation. This assumption is in agreement with the fact that the organic MTJ’s could not be fabricated reproducibly, because diffusion is a random motion and therefore the Co clusters are formed by chance.

As discussed above, the MR curve is not in agreement with the magnetic behavior of the electrodes and the TMR switches discretely at ‘random’ applied fields (see Fig. 5.10 (d, e)). The observed MR is consistent with our assumption of tunneling via a Co cluster. Such a cluster could have a Curie temperature smaller than that of the electrode itself. It is therefore possible that the Co cluster is ferromagnetic and becomes superparamagnetic when the temperature is slightly raised. Due to the very rough structure of the top electrode, we expect that its magnetization is nonuniform at the interface with TERPY, as indicated by the domains 1 and 2 in Fig. 5.11 giving rise to fringe fields. These fringe fields affect the magnetization of the Co clusters. Because the structure of the domains is microscopically different each time a magnetic field is applied, the parallel and antiparallel orientation of the microscopically formed junction is never achieved at the same applied field, which explains the random applied fields at subsequent measurements.

We discuss next the strong bias dependence of the MR. It seems that the spin sensitivity of the tunnel current is quenched when a bias voltage is applied. This might be an indication that we have actually measured a temperature rather than a bias dependence of the MR. If it is really the case that the total tunneling current passes through the Co particle, most power should be dissipated as heat in or near the Co particle. In addition to the creation of phonons, this thermal energy might be sufficient to randomly change the direction of magnetization of a Co particle, i.e. drive the particle in the superparamagnetic state. If this process occurs, the time average of the remanence is zero and no magnetic behavior of the Co clusters is observed. It is
possible that the strong decrease of the TMR for increasing bias is due to this process. We note that a similar argument can be used to explain the vanishing of MR at 30 K.

If we assume that all energy is dissipated as heat, we are able to estimate the temperature of the Co cluster. For this, we consider for the power dissipated into the device the equation based on Fourier’s law of heat conduction:

\[ P = A \kappa \frac{\Delta T}{d} \]  \hspace{1cm} (5.20)

with \( A \) the device area (in our case, cluster area), \( \kappa \) thermal conductivity, \( \Delta T \) the temperature change due to the power transfer, and \( d \) the effective barrier thickness. We assume an area for the Co cluster in the order of 1 to 10 nm\(^2\) and a barrier thickness of about 10 nm. Typical values for the thermal conductivity of organic semiconductors are around 0.1 W/m K at room temperature \([105]\). At 50 meV the resistance of the device is in the order of 10 M\( \Omega \), corresponding to a power of about \( 2 \times 10^{-10} \) W. With these values, an increase in temperature in the order of 2 to 20 K is determined. The estimated \( \Delta T \) has an order of magnitude close to the temperature of 30 K, at which a complete quench of the MR effect is observed, indicating that heating induced effects can not be excluded.

It must be noted that while the hypothesis qualitatively describes the difference between the macroscopic magnetization switching of the electrodes and the local MR data, as well as the extreme temperature dependence, it is very difficult to actually prove its correctness, because OMTJ’s could not be fabricated reproducibly.

5.5 Conclusions

In conclusion, we investigated the magnetic and electrical properties of several hybrid organo-metallic magnetic junctions. The magnetic properties of Co films showed a strong dependence on the presence of the organic interlayer and thickness of the top electrode. Two different deposition methods for the Co have been investigated: e-beam evaporation and sputtering. We have provided evidence that metals interdiffuse stronger in the molecular films when deposited by magnetron sputtering. Despite the strong interdiffusion of the top electrode in the organic layer, we have been able to produce a promising MR of 7% at 5 K, for the TERPY-based OMTJ’s. At the moment a good reproducibility of the results is lacking, which we attribute to the interdiffusion of the metallic contacts into the molecular films.
Bibliography


Summary

The revolution in (semi)conducting organic materials has been one of the highlights in physics over the past decade. Molecular and polymeric thin films are projected to be used as active elements in a wide range of electronic and optoelectronic applications. Among the main driving forces for such plastic electronics are the low-cost processing and the chemical tunability. Potential applications include ultrathin organic light emitting diodes for (flexible) flat displays, field-effect transistors, sensors and many other.

Although intensively studied both in industrial and academic environments, the intrinsic limits of molecular materials is an open issue. Pushing the limits of these materials and devices is a major scientific challenge with enormous implications for the electronics industry. In this thesis we explored novel hybrid molecular - metallic structures with a magnetic functionality for “spintronic” applications. Spintronics is a new branch of electronics in which electron spin, in addition to charge, is manipulated to yield a desired outcome. The spintronic devices are particularly attractive for memory devices (MRAM’s) and magnetic sensors applications.

It has been suggested that molecular materials would provide an attractive alternative, not only in view of the general advantages of plastic electronics, but particularly, also because of the intrinsically low spin-orbit scattering due to the low mass of atoms involved. Despite these challenging opportunities, from materials and preparation point of view a large number of issues still have to be solved. Some of them have been addressed in this thesis.

One of the crucial requirements for the realization of molecular spintronics is to obtain control over the ordering and morphology of molecular layers. This aspect is generally considered as one of the decisive parameters for achieving molecular electronics with high carrier mobilities. Since spintronic devices are extremely sensitive to the magnetic properties of the outermost atomic layers, our choice was to work with deposition of molecules under ultra-high-vacuum environment, rather than using “wet” techniques under ambient atmosphere. Obtaining ordered organic molecules on ferromagnetic materials represents a challenge, since the high reactivity of these type of substrates tends to decompose molecules, such as happening for thiols, or lowers surface mobility as to hinder molecular ordering.

In Chapter 3 of this thesis we investigated the structural properties of two novel molecular - ferromagnetic systems. We demonstrated that long-range ordering of these
molecules can be obtained when the substrate is exposed to small amounts of oxygen (Perylene-tetracarboxylic-dianhydride (PTCDA) - Ni(111)) or when a proper molecule-substrate combination is chosen (PTCDA - Co, pentacene - Co, and pentacene - Ni(111)). Very promising is our finding that pentacene tends to grow in an almost layer-by-layer fashion, producing ordered terraces of few µm in lateral size even on polycrystalline Co.

Another aspect addressed in this thesis is the electronic properties of thin molecular films in bulk and at interfaces with ferromagnetic metals. Proper functionality of the molecular spintronic devices requires appropriate electronic properties. These are determined, on the one hand, by intra-molecular properties such as transport gap, electron affinity, as well as inter-molecular overlap of molecular orbitals. Also the alignment of the energy levels of the molecular systems with respect to the Fermi level of the metal and the nature of interaction at these interfaces play an important role for the charge injection into the molecular films. We analyzed the electronic properties of thin pentacene films and of its interfaces with Co and Ni(111) by means of ultraviolet photoelectron spectroscopy (UPS). We found a difference of 1.4 eV between the ionization potential of the gas phase and the solid state, which we attribute to a change in the local environment and charge redistribution in pentacene. Despite the fact that the ionization potential of pentacene is very close to the work function of the two studied metals, an increased barrier for the hole injection at these two interfaces was found. We attributed these observations to hybridization between molecules and substrate.

Besides the production of large area, pinhole-free and well-ordered layers, a strict requirement consists of preventing interdiffusion when depositing top electrodes on a organic film. While this process has been studied extensively for polymer LEDs, the requirements may be even more stringent in the present case, since diffused atoms may act as spin scattering centers. We studied the magnetic properties of Co layers deposited by two different deposition methods (magnetron sputtering and evaporation) on PTCDA. We demonstrated that the presence of the molecular film influences the magnetic properties of Co (such as magnetic moment and switching behavior). This might provide an attractive way of establishing different switching fields for top and bottom electrodes. Moreover, we have evidence that Co particles interdiffuse more strongly into the molecular film when sputter deposition is used instead of evaporation.

As a potential application of organic materials in spintronics, we investigated the so-called magnetic tunnel junctions, with a barrier made out of molecular constituents. We have been able to produce a promising magnetoresistance (MR) of 7% at 4 K with junctions based on [2,2'; 6',2"] terpyridine-4-yloxy-hexanoic acid (TERPY) deposited in UHV conditions, although still hampered by a poor reproducibility, severe interdiffusion and a full quenching of MR above 30 K.
Samenvatting

In het afgelopen decennium is de ontwikkeling van (half)geleidende organische materialen een van de hoogtepunten in de academisch en industriële wereld geweest. Moleculaire en polymeer dunne films kunnen worden gebruikt als actieve elementen in een breed gebied binnen elektronische en opto-elektronische toepassingen. De belangrijkste redenen voor de toepassing van deze plastic elektronica zijn de lage productiekosten en de mogelijkheid tot het aanpassen van processen met behulp van chemie. Enkele mogelijke toepassingen zijn ultradunne lichtgevende diodes voor (flexibele) platte schermen, veld-effect transistoren en sensoren.

Hoewel de intrinsieke limieten van moleculaire materialen in zowel de industriële als de academische omgeving grondig bestudeerd zijn, blijft dit een open kwestie. Het verleggen van de grenzen van deze materialen en toepassingen is een grote wetenschappelijke uitdaging met belangrijke gevolgen voor de elektronische industrie. In dit proefschrift hebben we nieuwe moleculaire - metallische structuren met een magnetische functionaliteit voor “spintronica” onderzocht. Spintronica is een nieuwe vorm van elektronica waarbij de elektron spin in combinatie met de lading aangepast wordt om een gewenst resultaat te bereiken. Vooral voor geheugentoepassingen en magnetische sensoren zijn spintronische onderdelen bijzonder geschikt.

Er is gesuggereerd dat moleculaire materialen aantrekkelijke alternatieven bieden voor spintronische componenten, zowel vanuit het oogpunt van de algemene voordelen van plastic elektronica, als ook in het bijzonder de lage spin-baan wisselwerking vanwege de lage massa van de betrokken atomen. Alhoewel er in het moleculaire spintronicagebied tal van uitdagende mogelijkheden liggen, moeten er vanuit de materiaal- en proceskant nog vele problemen opgelost worden. Een aantal van deze problemen worden besproken in dit proefschrift.

Een van de cruciale eisen om moleculaire spintronica mogelijk te maken is het verkrijgen van controle over de structuur en morfologie van de moleculaire lagen. Dit aspect wordt in het algemeen gezien als een van de beslissende parameters voor het verkrijgen van moleculaire elektronica met hoge mobiliteit van de ladingdragers. We hebben gekozen om te werken met depositie van moleculen in een ultrahoog vacuum (UHV) omgeving, in plaats van gebruik te maken van de nat-chemische technieken bij normale atmosferische omstandigheden vanwege de gevoeligheid van de magnetische eigenschappen van de buitenste atoomlagen bij spintronische componenten. Vanwege de hoge reactiviteit ontleden moleculen bij dit soort substraten, zoals bijvoorbeeld
bij thiolen, of zorgt het verlagen van de oppervlaktemobiliteit voor verhindering van geordende moleculaire structuren. Dit maakt het verkrijgen van geordende organische moleculen op ferro-magnetische materialen tot een ware uitdaging.

In hoofdstuk 3 van dit proefschrift hebben we de eigenschappen van twee nieuwe moleculaire - ferromagnetische systemen onderzocht. We hebben laten zien dat het mogelijk is om ordening van moleculen op grote schaal te verkrijgen wanneer het substraat blootgesteld wordt aan kleine hoeveelheden zuurstof (perylene - tetracarboxylic - dianhydride (PTCDA) - Ni(111)) of wanneer de juiste molecuul-substraat combinatie gekozen is (PTCDA - Co, pentaceen - Co en pentaceen - Ni(111)). Onze bevinding dat pentaceen bijna laag-voor-laag kan groeien, met geordende terrassen van een paar µm grootte, zelfs op polycrystallijn Co, is veelbelovend.

Een ander aspect wat wordt besproken in dit proefschrift is de elektronische eigenschappen van dunne moleculaire films in de bulk en op het grensvlak met het ferromagnetische materiaal. Voor het goed functioneren van de moleculaire spintronische onderdelen zijn geschikte elektronische eigenschappen nodig. Deze eigenschappen worden aan de ene kant bepaald door intra-moleculaire eigenschappen zoals transport gap, elektronenaaffiniteit en intermoleculaire overlap van de moleculaire orbitalen. Ook de uitlijning van de energieniveaus van de moleculaire systemen met het Fermi-niveau van het metaal en de interactie aan het grensvlak zijn van belang voor de ladingsinjectie in moleculaire films. Door middel van ultraviolet fotoelektronspectroscopie (UPS) hebben we de elektronische eigenschappen van dunne pentaceen films en de grensvlakken met Co en Ni onderzocht. We hebben een verschil van 1.4 eV gevonden tussen gasfase en vaste stof, welke we toeschrijven aan de verandering in de lokale omgeving en de ladingsverdeling in pentaceen. Alhoewel de ionisatiepotentiaal van pentaceen heel dicht bij de werkfunctie van de twee bestudeerde materialen ligt, is er toch een verhoogde barrière voor de gateninjectie gevonden. Deze waarnemingen schrijven we toe aan hybridisatie tussen moleculen en het substraat.

Naast de productie van grote oppervlakken, pinhole-vrije en goed geordendelagen bestaat een strikte eis tot het voorkomen van interdiffusie bij depositie van de bovenelektrodes op organische films. Alhoewel dit proces uitgebreid bestudeerd is voor polymeer-LED’s, zullen de eisen wat strenger zijn in het huidige geval omdat gediffundeerde atomen zich kunnen gedragen als spinverstrooiing centra. Met twee verschillende methodes (magnetron sputteren en opdampen) hebben we de magnetische eigenschappen van Co lagen op PTCDA bestudeerd. We hebben gedemonstreerd dat de aanwezigheid van moleculaire films invloed heeft op de magnetische eigenschappen van Co (zoals het magnetisch moment en schakelgedrag). Dit zou een aantrekkelijke mogelijkheid tot het verkrijgen van verschillende schakelvelden voor boven- en onderelektroden kunnen bieden. Verder hebben we bewijs gevonden dat Co deeltjes sterker in de moleculaire film diffunderen, wanneer sputterdepositie gebruikt wordt in plaats van opdampen. Als mogelijke toepassing van organische materialen in spintronica hebben we de zogenaamde magnetische tunneljuncties met een barrière van moleculair materiaal onderzocht. Het is ons gelukt om een veelbelovende magnetoweerstand (MR) van 7 % bij 4 K te realiseren, met juncties gebaseerd op [2,2'; 6';2"] terpyridine-4-yloxy-hexanoic acid
(TERPY) gedeponeerd in UHV condities, alhoewel slecht reproduceerbaar, er sprake was van hoge interdiffusie en de MR volledig verdween boven 30 K.
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List of publications

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Growth and Photoemission of EuO
P. Steeneken, M.V. Tiba, H.T. Tsjeng, and G.A. Sawatzky, in preparation
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