1. Introduction

1.1. Motivation and Outline

The concept of molecule has historically been developed in the field of chemistry and for a long time molecules have almost exclusively been investigated by chemists. However, the development of powerful investigation tools as well as quantum theory allowed the scientists to gain a deep understanding of the physics at the molecular scale. Hence molecules started to be in the focus of physicists too.

Nature shows how much complexity can be borne in a very small space. A molecule is a remarkable example of an extremely small structure which has well defined characteristics and properties. Miniaturization is not only observed in nature but has been a constant trend in the technology development of our times. Researchers have continuously tried to engineer smaller and smaller devices. However so far the approach to miniaturization has mostly been quite different than the one used by nature. Scientists and engineers have mainly tried to shrink the size of objects which already exist and work at a larger scale. This approach proved to be very successful, nevertheless it is clear that there are limit to it. In fact scaling down processes which work at the macro- or micro-scale is going to face fundamental physical limits. For instance the ultimate limits for lithography processes employed in the silicon based electronics are not far from being reached[1].

The novelty of *nanoscience* consists in studying the properties and functionalities of nanoscale structures, often already known from chemistry or biology. Their understanding may lead to identify structures which can be directly used for applications or teach how to engineer new objects with the desired properties. Although very difficult, such an approach has a great potential. As pointed out by Richard P. Feynman in his famous talk “There’s plenty of room at the bottom – An invitation to enter a new field of physics” gaining the ability to control and address single atoms and single molecules would allow to extraordinarily accelerate most miniaturization processes.

Among the systems available in nature organic molecules look very appealing as they are small but simultaneously complicated and structured enough to comprise interesting functionalities. Therefore, in this thesis the attention will be focussed on organic molecules adsorbed on suitable supports with a relevance for potential applications in the field of *molecular electronics*.

The use of very small functional units poses many technological challenges. Among them a very relevant one is the difficulty to handle and interconnect different units which are needed to assemble any useful device. However, the observation of nature offers a very brilliant approach to this issue. Practically all systems in nature are somehow capable to self assemble.

One of the goals of *nanoscience* is to understand and profitably use self assembly to form nanostructures with the desired functionalities. The smart combination of the so called *bottom up* approach (letting different substructures organize in more complicated ones) with the *top down* approach (scaling down system working at macro- and/or microscale) constitutes one of the most important peculiarities of *nanoscience* and *nanotechnology.* Of course understanding and reproducing the conditions necessary to address the self assembly in a desired way is a difficult task. Nevertheless, in recent years, the potential of such an approach triggered a lot of research in this direction. In particular, STM revealed itself to be a powerful tool to address, analyze and modify self assembled molecular structures as well as single atoms.

In this thesis different nanoscale structures have been produced, studied and combined. All the structures described have been produced following a *bottom up* scheme. As shown in the following, this indeed limits the control on the growth process. On the other hand, it has to be stressed that, due to this approach, the nanostructures investigated can be produced in a virtually countless number and in a comparably fast and cheap way. Exploiting this research direction looks therefore very important in order to open a way to the application of *nanotechnology* to any device of practical interest in everyday life.

1.2. Experimental Techniques

The experimental work described in this thesis has been carried out mainly by means of scanning tunnelling microscopy (STM), photoelectron spectroscopy (PES) and low energy electron diffraction (LEED). In this section a brief introduction about the working principles and some of the practical aspects of these instrumental techniques is given.

1.2.1. Scanning Tunnelling Microscopy

Introduction

Scanning Tunnelling Microscopy is a powerful tool invented at the IBM Zurich Research Laboratory in 1981 by Gerd Binnig and Heinrich Rohrer[2]. Very soon after its invention STM proved to be an extremely useful tool for the investigation of surfaces and in 1986 Binnig and Rohrer were awarded the Nobel Prize.

The STM working principle relies on the quantum mechanical tunnelling of electrons through a potential barrier between a conductive sample and a sharp metallic tip placed very close to each other (typically a few Å). A bias is applied between the tip and the sample and a tunnelling current is measured to flow across the tip-sample gap. The tip is then scanned over the sample by means of piezo-electric tubes. While moving the tip, the sample corrugation induces a variation of the sample-tip distance and therefore of the tunnelling current. The tip can be scanned on the sample at a fixed z-position above the sample while measuring the current (*constant height* mode). Alternatively a feedback system can be used to adjust the tip-sample distance in order to keep the tunnelling current constant. In this second mode (*constant gap* or *constant current*) the most important signal recorded is the z-displacement of the tip needed to keep the current constant.

One of the key aspects of STM is the very strong dependence of the tunnelling current on the tip-sample distance. This implies that only the very end of the tip apex and a very small portion of the sample are significantly involved in the tunnelling process. Such a localized interaction is crucial in order to obtain a high spacial resolution. Binnig and Rohrer could observe for the first time features such as monoatomic steps, surface reconstructions[3] as well as atomic resolution of metal[4][5] and semiconductor[6] surfaces in real space.

The invention of STM turned out to be a landmark point in the advancement of surface science, allowing for the first time real space investigation of surfaces at the atomic scale. Moreover it triggered the development of a whole family of scanning probe microscopies (SPM) such as atomic force microscopy (AFM)[7], magnetic force microscopy (MFM)[8], electrostatic force microscopy (EFM)[9] and scanning near field optical microscopy (SNOM)[10][11].

A brief theory of STM

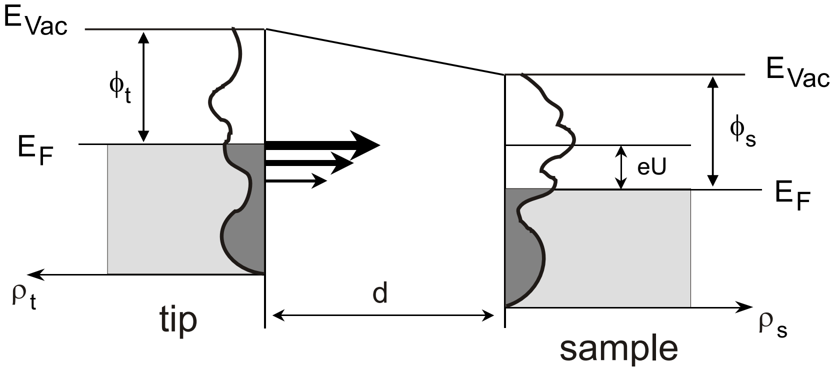

Figure 1.1.: Schematic 1-dimensional diagram of a tip-sample junction. In this representation a positive bias U has been applied to the sample. The size of the horizontal arrows indicates the different transmission coefficients (and therefore of the tunnelling probabilities) for electrons of different energies.

Developing a precise theory of the tunnelling process at the tip-sample gap is not feasible as very little is known about its detailed geometrical and chemical configuration. Overviews on this problem and the possible approaches to solve it are given in different books[12][13] as well as in review articles (see for example ref. [14]).

Despite this complexity, most of the aspects of scanning tunnelling microscopy can be explained considering the simple theory developed by Bardeen[15]. In this theory the specific geometry of the tip-sample junction is neglected and the tunnelling junction is modelled as a 1-dimensional system (fig. 1.1).

From basic quantum mechanics it follows that the probability for an electron with energy

E to tunnel through a potential barrier of energy E_{bar} (with $E_{bar} > E$) is

$$T = e^{-\frac{2d\sqrt{2m(E_{bar}-E)}}{\hbar}} \tag{1.1}$$

where m and d are the electron mass and the barrier width, respectively.

In the approximation proposed by Bardeen the net tunnelling current between tip and sample measured while applying a bias U will simply be

$$I = \frac{4\pi e}{\hbar} \int_0^{e\cdot U} \rho_{\mathrm{s}}(E)\rho_{\mathrm{t}}(e\cdot U - E)T(E, e\cdot U, d)dE \tag{1.2}$$

where ρ_{s} and ρ_{t} are the density of states of the sample and of the tip while $T(E, e\cdot U, d)$ is the transmission coefficient from the tip to the sample for an electron with energy E. For this extremely simplified 1-dimensional model, as described in eq. 1.1, the transmission coefficient will be

$$T(E, e\cdot U, d) = e^{-\frac{2d\sqrt{2m(E_{bar}-E)}}{\hbar}} = e^{-\frac{2d\sqrt{2m}}{\hbar}\sqrt{\frac{\phi_{\mathrm{s}}+\phi_{\mathrm{t}}}{2}-\frac{e\cdot U}{2}-E}} \tag{1.3}$$

where ϕ_{s} and ϕ_{t} are the work function of the sample and of the tip. It is important to note that the expression 1.2 is just the integral of the transmission coefficient over the density of states of the tip and of the sample (indicated by the arrows in fig. 1.1) laying in the energy window allowed for tunnelling. This window corresponds to the energy range where the occupied states of the tip and the unoccupied states of the sample overlap each other. In the simplified model presented here, tip and sample have a perfectly symmetric role. Thus, the whole discussion applies the very same way for negative sample bias (i.e. for electrons tunnelling from occupied states of the sample to unoccupied states of the tip).

In reality the geometries of tip and sample are different and such an asymmetry significantly affects the system. As stated before, this complicates the situation significantly and makes it almost impossible to develop a first principles theory. Nevertheless many attempts have been made to treat the problem with approximations closer to the real situation. Among those the so called s-wave-tip model developed by J. Tersoff and D. R. Hamann[16][17] is definitely one of the most important. It models the tip apex as a little metal sphere, thus implying that only s-states of the tip take part in the tunnelling process. For low biases (much smaller than the tip work function ϕ_{t}), the current turns out to be proportional to the Fermi local density of states (LDOS) at the center of the sphere $\mathbf{r_0}$

$$I \propto eU\rho_{\mathrm{s}}(E_{\mathrm{F,s}})\rho_{\mathrm{t}}(E_{\mathrm{F,t}}, \mathbf{r_0})\, e^{-\frac{2d\sqrt{2m}}{\hbar}\sqrt{\frac{\phi_{\mathrm{s}}+\phi_{\mathrm{t}}}{2}}} \tag{1.4}$$

It is interesting to note that in this approximation the dependence of the current from the tip is expressed only by the factor $\rho_{\mathrm{t}}(E_{\mathrm{F,t}}, \mathbf{r_0})$ which remarkably is just a constant. Therefore, in the frame of the Tersoff and Hamann theory, the variations of the tunnelling current while scanning the tip on the sample turn out to depend only upon local properties of the sample and not on the tip.

STM data handling

In STM the tip is typically scanned over a sample and the signal of interest is recorded at a fixed time/space interval. As the tip is usually raster scanned over a squared area, the natural output of an STM measurement is a two dimensional data array. While scanning more than one signal can be acquired, thus for each measurement different arrays can be generated. In the *constant current* mode (used throughout this thesis) the tunnelling current is kept constant by the feedback and the most interesting signal is the z-displacement of the tip. This signal is often called *topography* although it carries also information about the electronic structure of the sample surface. In addition to the z-displacement, the current signal can also give out useful information because of the limited reaction speed of the feedback. In fact, when the tip gets over a protrusion, a variation of the tip-sample distance and therefore of the tunnelling current is needed in order to induce the feedback reaction. Working with an integral feedback, the current signal represents the derivative of the topography and therefore highlights all the rapid variations of the z-displacement signal. Besides these considerations, the current signal is also very interesting in order to evaluate the efficiency of the feedback and for this reason is also called *error signal*. In certain experiments, also performed in this thesis, the bias voltage is changed repeatedly while scanning. For this kind of measurements the acquisition of the bias voltage is also very useful in order to keep track of its variations.

The two dimensional data arrays obtained as output of STM measurements are generally shown in an image format by using a color coding. Consequently very often for STM measurements the expression *STM images* is used. In practice each point of the array is converted to a pixel with a color corresponding to the recorded data value of the array. The most common code is the greyscale one, where bright and dark tones of grey are used for high and low values of the recorded signal. Other colored codings are also used, always according to the same convention about bright and dark tones.

If not explicitly otherwise indicated, all STM images reported throughout this thesis are topography images. Generally the data shown in the images are either raw data or processed through a plane subtraction. This is not the case for some of the images showing periodic structures. In some of these cases, in order to improve the resolution of a periodic structure, a so called *averaging procedure* has been employed. By using a special algorithm (developed by R. Hoffmann at the Institute of Physics of the University of Basel) it is possible to sample several copies of the unit cell of the periodic structure present in the image. The output of the procedure consists in an average of all the unit cells sampled from the original image. Another relevant filtering procedure employed for some of the images is the so called *flattening*. This procedure operates on the original data line by line. A polynomial of first order is fitted to each scan line of an image and successively it is subtracted to the original data. This procedure is specially useful to enhance the contrast in images which present significantly different z-displacements in different areas. For instance it is very helpful for images where the bias voltage is changed while scanning.

In order to emphasize specific features, the acquired data can also be presented in a so called pseudo 3D view. In addition to a color, an elevation is assigned to each point of the array. The resulting 3-dimensional structure is then represented in a perspective view.

1.2.2. Low Energy Electron Diffraction

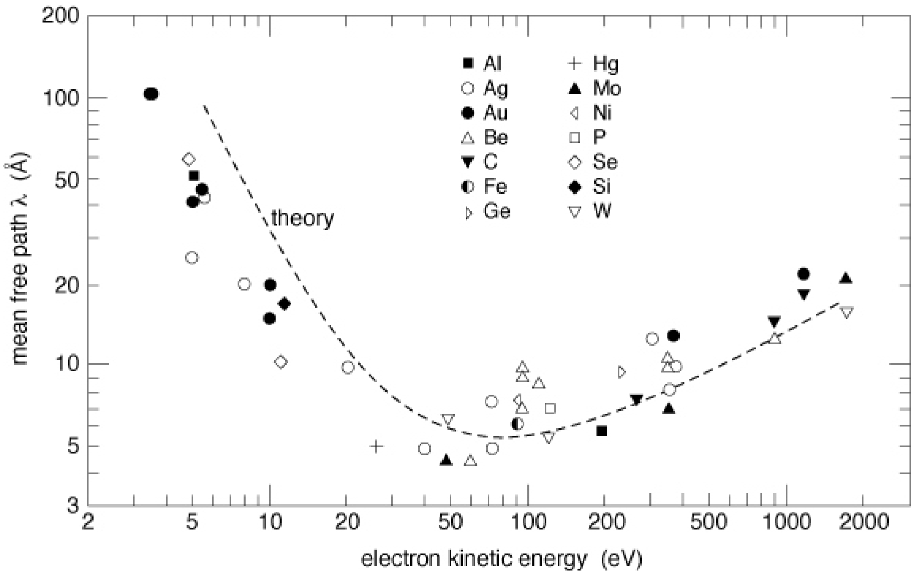

Figure 1.2.: Universal curve of electron mean free path. Adapted from ref. [18] and reference therein.

Along STM, another important experimental technique used in this thesis is low energy electron diffraction (LEED). The development of LEED was guided by Germer[19] some thirty years after his original experiment[20]. This technique relies on the observation that the de Broglie wavelength for electrons with low energy (in the order of tens of eV) is in the same range of the size of typical periodic structures studied in surface science (for example for electrons of $E = 10$ eV the de Broglie wavelength is $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = 3.88$ Å). This makes low energy electrons very well suitable for diffraction experiments on surfaces.

In LEED a beam of electrons, accelerated to the desired energy (from few to some hundreds eV), is directed towards the sample perpendicularly to its surface. The backscattered, diffracted electrons are then collected on a fluorescent screen placed in front of the sample surface (on the same side as the electron source). To ensure that only electrons that underwent an elastic process are collected, an energy filter is set in a way that only the electrons with an energy close to the one of the incident beam, are allowed to reach the fluorescent screen.

If the surface under investigation is characterized by some periodic structure this will be reflected in the diffraction pattern formed by the electrons collected on the screen. In detail it can be shown that such a pattern is the Fourier transformation of the periodic structure of the surface. More precisely the intensity recorded on the screen is proportional to the modulus of the reciprocal representation of the surface structure. For this reason the problem of inverting from LEED images to the direct space is not trivial and there is no direct method to solve it. Moreover, only a cut of the reciprocal surface can be imaged through the fluorescent screen. In order to face these problems a big number of software tools have been developed, allowing to simulate the LEED pattern obtained from almost any possible periodic surface structure. In this thesis the LEEDSIM software by CreaPhys GmbH (Reinhardtsgrimma, Germany) has been used to simulate some of the LEED patterns observed.

A very important aspect of LEED is its very pronounced surface sensitivity. In fact the diffraction pattern obtained from LEED carries exclusively information of the periodic structures present in the few topmost layers of the sample. This is crucial in order to observe phenomena such as surface reconstruction or self assembly of adsorbate ultra-thin films.

This extreme surface sensitivity is achieved because of the very short mean free path of electrons in matter (not more than a few nanometers). This implies that only electrons penetrating a very short distance into the substrate can be elastically backscattered. Moreover, the mean free path of electrons does not depend much on their kinetic energy (fig. 1.2), thus allowing a great freedom in tuning the wavelength of the incident electrons. This property makes electrons very suitable for surface science investigations and indeed, besides LEED other powerful surface science techniques based on the short electron mean free path have been developed. Comprehensive overviews on LEED and its applications have been published in several books and articles (see for example the book of Van Hove *et al.*[21] or the review paper from Heinz[22]).

1.2.3. Photoelectron Spectroscopy

Another important experimental technique employed in this thesis is photoelectron spectroscopy (PES). As LEED, photoelectron spectroscopy is a non local method as it gives information integrated over a macroscopic area of the sample. The basis of this technique is the so called photoelectric effect discovered already in 1887 by Hertz[23] and theoretically explained in 1905 by Einstein[24]. This effect simply consists in the emission of electrons from a surface upon irradiation with electromagnetic radiation.

Given the frequency ν of the incident radiation, an electron emitted from the surface will have the kinetic energy

$$E_{kin} = h\nu - E_b - \phi \tag{1.5}$$

where E_b is the binding energy of the emitted electron (measured relatively to the Fermi energy) and ϕ is the work function of the sample.

In photoelectron spectroscopy, the excitation radiation is chosen to be monochromatic. Therefore, for each electron, it is possible to measure the energy of the level from which it has been emitted just by measuring its kinetic energy. The electrons emitted from the sample are collected on a detector which allows to measure the number of electrons for each kinetic energy $N(E_{kin})$. This allows to map the density of states (DOS) of the sample (fig. 1.3).

In order to excite the electrons from their bound states in the sample, different sources of electromagnetic radiation, operating at various energies, can be used. Generally two regimes are identified: X-ray photoelectron spectroscopy (XPS) for energies $h\nu \gtrsim 100$ eV and ultraviolet photoelectron spectroscopy (UPS) for energies $h\nu \lesssim 100$ eV. Although conceptually

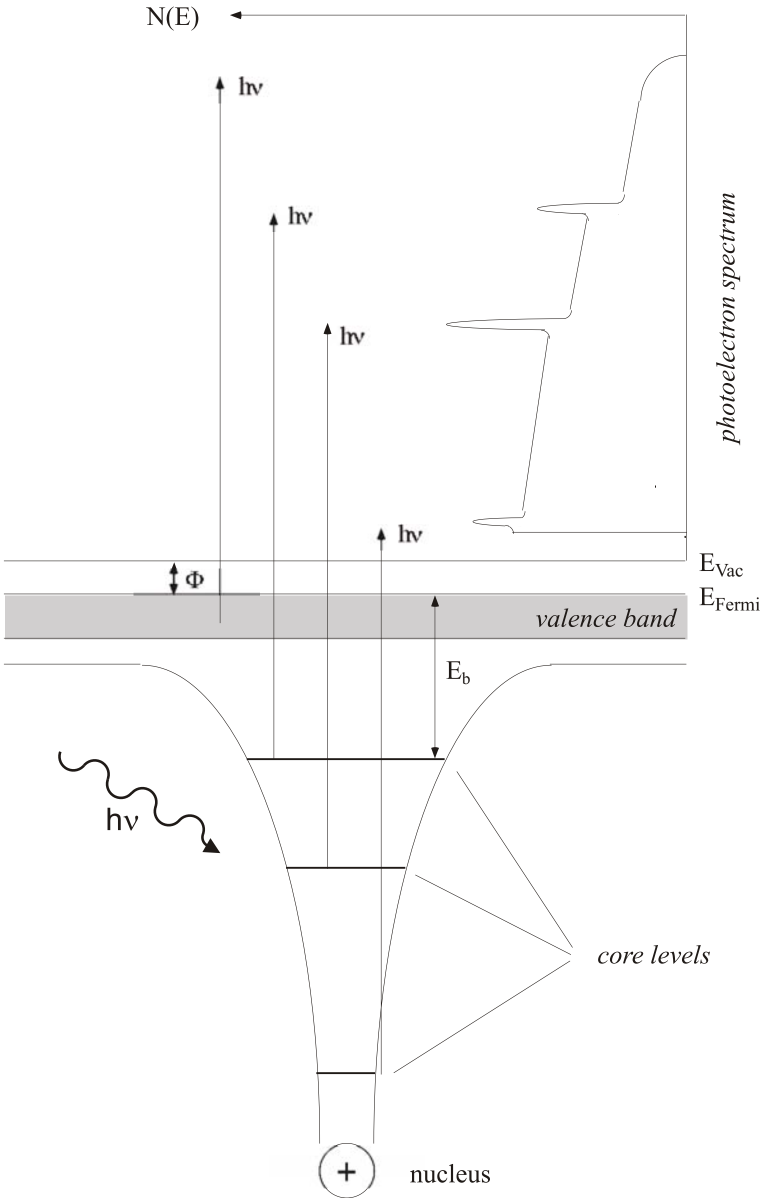

Figure 1.3.: Schematics of photoelectron spectroscopy measurement principle, showing the relation between the DOS of the sample and the photoelectron spectrum.

extremely similar, XPS and UPS measurements offer different kinds of information about the sample.

XPS allows to investigate the energy range corresponding to the atomic core levels and therefore gives information about the chemical composition of the sample. The intensity of the different peaks can be evaluated in order to determine the sample stoichiometry at the surface. Moreover, different chemical environments often induce slight modifications of the core level positions. These modifications, also known as *chemical shifts*, can be detected by XPS and can be interpreted in terms of the interactions between the different chemical species present at the surface. This information is of special interest when investigating adsorbates as it allows to evaluate the adsorbate coverage and to learn about its interaction with the substrate.

The states investigated by UPS are the ones close to the Fermi level. The interpretation of these spectra is very interesting although more complicate than for the ones obtained by XPS. These low energy states are in fact very sensitive to the interactions between different compounds. UPS is therefore very useful to study the adsorption of molecules on surfaces as it allows to get deep insight in the molecule-substrate and molecule-molecule interactions. Moreover, by UPS it is possible to get a direct measurement of the sample work function and its change upon various surface modifications[25].

Common to UPS and XPS as well as to LEED, as described before, is the very high surface sensitivity due to the short electron mean free path. Electromagnetic radiation can penetrate deep into the sample but only electrons emitted in a region very close to the surface can leave it and reach the detector. Given the relevant role of photoelectron spectroscopy in surface science, a very large number of publications treat this topic in detail. For a comprehensive overview on the subject see for example the book of S. Hüfner[26].

1.3. Instrumental Set-Up

1.3.1. The UHV System

An extremely important requirement to study surfaces at the atomic or molecular scale is the ability to precisely control the conditions of the surface under investigation. In this perspective, ultra high vacuum (UHV) is a fundamental tool which allows to keep surfaces free of contaminations. All the experiments presented in this thesis have been performed in the NANOLAB at the Institute of Physics of the University of Basel. NANOLAB is a massive vacuum system consisting of seven chambers, each with a dedicated pumping system composed by turbomolecular, ion getter and titanium sublimation pumps. The base pressure for the system is in the low 10^{-10} mbar range. A fast entry air lock allows to insert or remove samples, STM tips as well as evaporation sources from the system, without breaking the vacuum. Two schematic representations of the NANOLAB multi-chamber system are shown in figs. 1.4 and 1.5. Samples are mounted on customized VG stubs that can be transferred through the entire vacuum system. The sample holders are equipped with a tungsten filament allowing to heat up the probe up to ca. 1100 K.

For the cleaning of metallic samples standard sputtering/annealing procedures have been employed[27]. For this purpose a sputtering gun operating with Ar gas is installed and the annealing of samples is performed by using the stub filament or by resistively heating the entire sample manipulator.

For the experiments described in this thesis it has been crucial to reliably deposit various molecules as well as NaCl on different substrates and with submonolayer precision. A flexible evaporation system has been specifically developed for the deposition of organic molecules. It is located in a dedicated chamber in order to keep the rest of the UHV system clean.