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Morphology and properties of organic thin films deposited on semiconducting titanium dioxide

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Abstract

The field of organic electronics has been constantly growing in the past decades. Since many years it is not only the miniaturization that matters, but rather the improvement of devices via utilization of better and better materials. Additionally, replacing an old inorganics with easier accessible, simple to process, better mechanically organics has also been a strong trend. However, one of the difficult challenges along the way is achieving the similar or better electronic parameters. Here, a key role is played by a fundamental research, often on atomic level. They revolve around fundamental processes and interaction in nanoscale, which most often decide of the macroscopic parameters of materials.

This thesis regards investigation of thin molecular layers grown on titanium dioxide semiconductor. As research subjects, two molecules were chosen, i.e. *para*-hexaphenyl (6P) and pentacene's derivative – dihydro-tetra-aza-pentacene (DHTAP). Both of the molecules originate from larger organic families that characterize themselves by their well electronic or absorption properties and exhibit rather high stability. Their characteristic, elongated shape adds another attractive feature in the regard of strong morphological and properties anisotropy. Suitable and proper control of the orientation of such molecules allows for the tuning of some of the substrate material properties.

Within the presented work, a series of experiments were conducted regarding the growth processes of the molecular structures out of the mentioned 6P and DHTAP. A main focus is put into morphology studies by the means of scanning probe microscopy techniques (AFM/STM). Experiments were conducted in both the ultra-high vacuum conditions and in air. Some of the investigation regarded electronic and energetic properties of the formed structures, which were completed with the help of the kelvin-probe force microscopy and thermal desorption spectroscopy. In order to help the reader with a better understanding of the presented data, the dissertation contains a few chapters introducing the field of research, utilized techniques and certain parameters of the conducted experiments.

Streszczenie

Świat elektroniki organicznej to dziedzina prężnie rozwijająca się w ostatnich dekadach. Od lat liczy się już nie tylko miniaturyzacja urządzeń, ale ich usprawnianie za pomocą wykorzystywania coraz to lepszych materiałów. Dodatkowym silnym trendem jest podmiana poszczególnych składowych na elementy organiczne, łatwiej dostępne, lepsze mechanicznie, czy prostsze w obróbce. Jednym z poważniejszych wyzwań na tej drodze jest jednak osiągnięcie podobnych lub lepszych parametrów elektronicznych, co materiały nieorganiczne. Kluczową rolę w osiągnięciu tego celu mają badania podstawowe, często na poziomie atomowym, związane z podstawowymi procesami oraz oddziaływaniami w nanoskali, które najczęściej decydują o właściwościach makroskopowych.

Niniejsza rozprawa dotyczy badań cienkich warstw molekularnych na powierzchni półprzewodnika dwutlenku tytanu. Jako obiekt badawczy wybrano molekuły *para*-heksafenylu (6P) oraz pochodnej pentacenu, czyli dihydro-tetra-aza-pentacenu (DHTAP). Obie rodziny tych molekuł charakteryzują się bardzo dobrymi właściwościami elektronicznymi, czy absorpcyjnymi oraz wykazują stosunkowo wysoką stabilność. Ich charakterystyczny wydłużony kształt dodaje im kolejną atrakcyjną cechę pod względem silnej anizotropii morfologicznej oraz właściwościowej. Odpowiednia kontrola ułożenia takich molekuł daje możliwość decydowania o części właściwości materiału, na którym się znajduje.

W ramach prezentowanej pracy wykonano szereg eksperymentów dotyczących wzrostu struktur z wymienionych molekuł organicznych. Motywem przewodnim są badania morfologii za pomocą mikroskopii bliskich oddziaływań (AFM/STM). Eksperymenty prowadzono zarówno w warunkach ultra-wysokiej próżni, jak i w warunkach normlanych. Część przeprowadzonych badań dotyczyła właściwości elektrycznych i energetycznych powstających struktur, które wykonano przy pomocy technik kelwinowskiej mikroskopii sił oraz spektroskopii termicznej desorpcji. W celu ułatwienia czytelnikowi lepszego zrozumienia prezentowanych wyników, praca zawiera kilka rozdziałów wprowadzających w dziedzinę badań, metody badawcze oraz parametry eksperymentalne.

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Chapter I

Introduction

Within this chapter the field of organic electronics is introduced with a huge emphasis on the organic devices. Families of the investigated molecules are discussed with the explanation of the choices made for the studies subjects. In the fourth section the titanium dioxide substrate and its properties are introduced. Finally, the thesis goals and structure are presented.

1.1 Scientific background

Ever since the famous lecture titled “There’s Plenty of Room at the Bottom” from 1959 presented by the 1965 Nobel Prize Laureate in physics Richard Feynman, the idea of engineering on an atomic level started to attract scientists. Despite the first use of the term “nanotechnology” in regard to the processes occurring on the order of nanometer already in the middle of the 1970s, the next decade was the beginning of a very fast growing field of research in the new small scale. The discovery of fullerenes by Kroto, Smalley and Curl, the idea of the nanoscale “assembler” by Drexler or the rediscovery of carbon nanotubes by Iijima accelerated development in this area even more. The term “nanotechnology” became the name of science and engineering performed in the nanoscale or – to be more precise – in the scale where at least one of the object’s size is lower than 100 nm. [1,2]

In nanotechnology one can distinguish two very basic approaches: “top-down”, where macroscale objects undergo processing in order to reduce their size into nanoscale objects and “bottom-up”, where the manipulation of single atoms and molecules or usage of self-assembly processes leads to the formation of nanoscale structures [3]. Nanotechnology quickly became a useful and constantly developed set of tools for material science and engineering purposes. Whole range of techniques allow for production of nanoscale devices and enhancement of their performance or alteration and improvement of materials’ properties in general.

With these outstanding features nanotechnology accelerated already very rapid development of electronics even further. An ever-growing need of downsizing electronic devices, these new methodologies allowed for reaching new milestones of smaller transistors every few years. Gordon Moore’s wild prediction from 1965 of log-linear relationship between device density and time – later known as “Moore’s law” – was constantly proven to be correct with passing decades. First transistors of a size smaller than 100 nm were produced in the beginning of 21st century. However, it was already known that this process cannot carry on forever, because at some point limitation of size of an atom would be reached. To be worse, with such small device dimensions, quantum effects turned out to cause problems even quicker.

Modern world’s computing devices are based in the vast majority on technology using transistors built of inorganic semiconducting materials. Currently all the electronic industry is built around silicon (Si), because of its good electronic properties accompanied

by high purity production, great stability and accessibility. However, other materials such as germanium (Ge) or III-V type compounds (e.g. GaAs, InSb, InP) received great interest in research throughout the years as potential silicon substitutes, because of their very high charge mobility. With downsizing limitations quickly approaching it seems inevitable to find replacement for silicon as main building material in order to keep improving electronic devices.

Inorganic electronics with its many advantages, such as high speed and performance, ultra-low power and size or high stability in large range of temperatures also has drawbacks. The complicated technology behind manufacturing process often comes with increased costs. Large area production is difficult due to mechanical properties of the materials like stiffness or fragility. During the last two decades the industry's focus strongly shifted towards simplifying manufacture and broadening application possibilities. Since then inorganic electronics began to have a competitor in its organic equivalent, which previously was considered mostly as a "pure research" domain [4]. Chemistry behind organics opens whole range of new possibilities regarding materials' properties and the ability to tune them. Because of these new tendencies, devices consisting of organic molecules such as organic light-emitting diode (OLED), organic thin-film transistor (OTFT) or organic solar cells were created and constantly upgraded [5–7]. Nowadays, they are in use worldwide.

Organic electronics very often relies on a proper utilization of organic thin films. Ultra-thin organic coatings built of a dozen, a few or even a single molecular layer have to be precisely manufactured for devices to have specific parameters. A proper arrangement of the molecules within such films is required as electronic and optoelectronic properties depend on it. Furthermore, the way molecules are adopted on a substrate – an interface – for the organic coatings is even more important. Without a well-defined and high-quality interface utilization of any organic thin film for any electronic purposes is practically impossible. Therefore research focusing on kinetics and early stages of molecular growth processes are very important in regard of organic electronics. Imaging grown molecular structures and studying their properties in nanoscale or molecular level is crucial for a deeper understanding of the base processes during structure formation. Knowledge in this field allows for creating models regarding growth processes in general and, therefore, makes it possible to develop any kind of design and prediction of parameters of devices based on newer organics.

Among others, hydrocarbons as a very wide class of materials have drawn enormous attention of scientists. They can form higher complex structures with basically every other element. Out of all known hydrocarbons one can distinguish a very specific group of small, elongated oligomers. Their anisotropic shapes make them interesting through various possibilities in regard of interface formation. Great examples of such rod-like shaped molecules are oligophenylenes and acenes. Thanks to the conjugated systems within the molecules of these groups they exhibit fine electronic properties. Forcing a specific arrangement of the molecules within nanostructures enhances charge-transport through overlap of π -orbitals. Oligophenylenes and acenes will be discussed in more detail in the following subsections of the chapter.

1.2 Oligo-phenylenes: *para*-hexaphenyl (6P)

Oligo-phenylenes are a group of molecules built of few phenyl rings (Figure 1) each connected with a single covalent bond. Subsequent phenyl rings can be attached either in *ortho*,



Figure 1 – A scheme of a phenyl group.

or *meta* positions (Figure 2) and thus forming *o*-, *m*- or *p*-phenylenes respectively. Out of these three very little attention was brought to *ortho* and *meta* conformations due to the difficulties with synthesis and therefore lack of interest. *Ortho*-phenylenes were very recently discovered to have folding capabilities, which allow for creating three-dimensional complex structures [8]. *Meta*-phenylenes as helical polymers and oligomers can create cross-conjugated systems and they have been studied in regard of pure UV light emission [9,10]. However, most investigated conformation of poly- and oligo-phenylenes over the years have been *para*-phenylenes as electroluminescent materials with high quantum efficiencies [11–13]. Attaching subsequent phenyl rings in *para* position results in the formation of rod-like molecules with inherent π -conjugation. As solubility of *para*-phenylenes decreases dramatically with increase of the molecule's chain length [14,15], great amount of

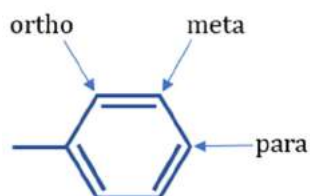


Figure 2 – A scheme of possible substitution positions in a phenyl ring.

research focuses only on short oligomers. Furthermore, the estimated effective conjugation length for oligo(*p*-phenylene)s is about 10 phenyl rings [13,14], what makes longer oligomers less desirable for investigations. A model representative molecule of this large group is a *para*-hexaphenyl (6P) that consists of six phenyl rings (Figure 3a).

Some of the reasons behind huge interest towards *para*-hexaphenyl are its stability in terms of temperature and environment and its synthesis purity [16,17]. This allows for processing in ultra-high vacuum (UHV) conditions at required elevated temperatures as an answer for the molecule's low solubility. *Para*-hexaphenyl tends to arrange into a herringbone molecular structure (Figure 3b) due to strong interaction between negatively-charged π -orbitals pointing out of the phenyl ring planes and the positively-charged edges of neighbouring phenyl rings

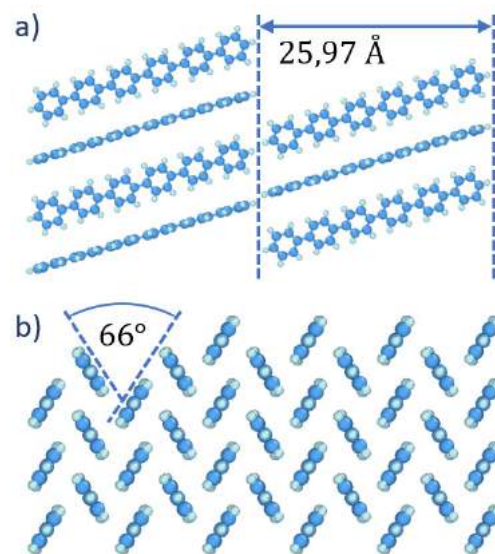


Figure 3 – A scheme of 6P molecules arranged in herringbone structure within molecular bulk crystal.

[15,18,19]. Thus, the unit cell of a bulk 6P crystal is monoclinic lattice of the $P2_1/a$ space group with lattice constants of $a = 8.091 \text{ Å}$, $b = 5.565 \text{ Å}$, $c = 26.264 \text{ Å}$, $\beta = 98.17^\circ$ and layer thickness of 25.97 Å with relative neighbouring molecules' planes tilt of 66° [20,21].

Great attraction towards 6P usage for electronic device purposes originates from its optoelectronic properties. *Para*-hexaphenyl has a fairly large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 3.1 eV [22,23] and exhibits a blue photoluminescence with a high quantum yield of 30% [11,24]. The 6P molecular structures have been investigated with a fairly good success as building blocks of many organic devices starting with OLEDs [22,23,25–28] and OTFTs [29–31], through lasers [32–34] or waveguides [35,36], ending with applications in sensors [37] or even in photo-memory devices [38].

Because the 6P's elongated shape and its anisotropic character of properties, the molecule's relative spatial orientation with respect to the other materials is crucial in the regard of overall system properties. Therefore, huge effort was put into investigating 6P growth processes on various substrates starting with metals, e.g., Cu [39–43], Au [44–47], Ag [48,49] and Al [50], through semi-conductors, e.g., TiO_2 [50–57], GaAs [58–60] and graphene [61–66], ending on dielectrics, e.g., KCl [67,68], mica [50,69–73] or alkali halides [71]. Depending on the substrate type and hence the substrate-molecule interaction, in general, molecules form either islands of various shapes built of “up-right standing” 6Ps (Figure 4a) or elongated nanoneedles built of “flat lying” molecules oriented with their

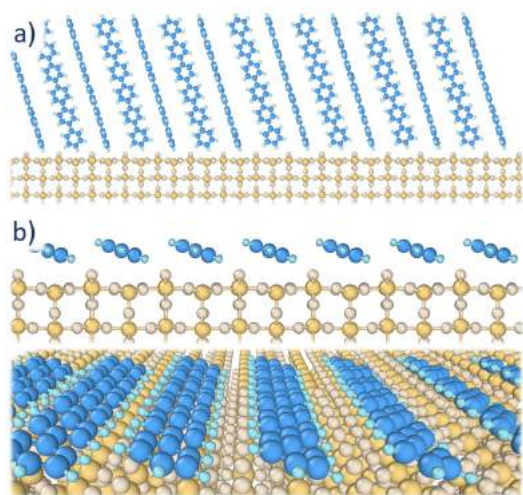


Figure 4 – A ball-stick model representation of 6P molecules on top of $\text{TiO}_2(110)$ surface: a) up-right standing configuration, b) flat-lying configuration.

long axes parallel to the substrate plane (Figure 4b). In addition, in certain cases the formation of these structures can be preceded by a formation of a compact single monolayer of flat-lying molecules. These growth processes can be influenced by substrate surface functionalization, e.g., ion-beam modification [52,54–56,73,74] or parameters of molecular deposition process, such as deposition rate or substrate temperature [47,62,72,75,76]. Therefore, it is possible to control and design the molecules' orientation

on the substrates, which is crucial as properties of 6P structures strongly depend on inner molecular arrangement. However, as mentioned before, a key factor for the utilization of organic films in regard of electronic device purposes is a well-defined interface. Thus studies of morphology and electronic properties of single molecular layers are of great importance.

1.3 Acenes: pentacene (5A) and N-substituted derivatives

Another very interesting family of molecules in terms of applications for organic electronics is a family of acenes – or more generally – polyacenes. These organic compounds are built of linearly fused benzene rings (Figure 5). This arrangement allows for a conjugation of p-orbitals and hence, similarly to oligo-phenylenes, acenes exhibit great electronic properties. Furthermore, the longer the acene chain the lower the HOMO-LUMO gap, the better charge mobilities, the lower reorganization energies. However, lengthening the molecule drastically increases its reactivity and lowers solubility. Moreover, the synthesis and stabilization of longer acenes is much harder and often requires very sophisticated methods and conditions. Beside their electronic properties acenes are often regarded as graphene zigzag nanoribbons, which opens possibilities of the application in spintronics and plasmonics. [77–86]



Figure 5 – A scheme of the general structural formula of acenes.

A five-ring-long representative of acenes – pentacene – with huge attention of scientists over the years, acts as a paradigm elongated molecule for thin film growth and organic electronic purposes [87–91]. Beside the simplicity and purity of its synthesis the most attracting pentacene's property is its temperature-independent fairly high charge carrier mobility, repeatedly reported to be greater than $1 \text{ cm}^2/\text{V}\cdot\text{s}$ [92–94]. Therefore, pentacene has been studied for years in the field of organic thin film transistors [88,90–92,95–97], which could be later functionalized in OLEDs [98–100], organic sensors [101–105], photovoltaics [106,107] or organic memory [108]. Despite pentacene's good charge transport researchers have shown that it could be increased even further. The molecules' packing within its crystal structure turned out to be crucial as it influences π -overlap between neighbours [88,109–111]. Altering the pentacene molecules' mutual arrangement changes electronic properties and hence proper modifications result in overall improvement. However, the enhancement with this approach can only be done up to a point, which, in a way, sets a limit for the molecule's features. Moreover, pentacene's solubility, poor temperature stability and long-term photo-oxidation proneness are also problematic. Therefore, a new approach of substituting the molecule backbone's carbon atoms with heteroatoms or functionalization groups has risen. The new methodology easily gained a lot of attention and it quickly grew into a whole new area of research – pentacene's derivatives.

Among countless modification possibilities, nitrogen-substituted 5A derivatives (family of azaacenes or N-heteroacenes) have drawn a special attention of scientists in the past two decades [112–118]. Replacing C atoms with N atoms and NH groups enhances intermolecular interaction through enabling of the H-bonding between the molecules. Therefore, properties of resulting structures can be undeniably influenced. Altered interaction between the molecules changes intermolecular packing, which – as mentioned before – changes charge mobility through different overlap of π -orbitals. Stronger interactions also improve stability of the structures. An interesting example of azaacenes is dihydro-tetraaza-pentacene (DHTAP or DHTA5). The molecule is a pentacene's derivative with four C atoms replaced by two N atoms and two NH groups with two

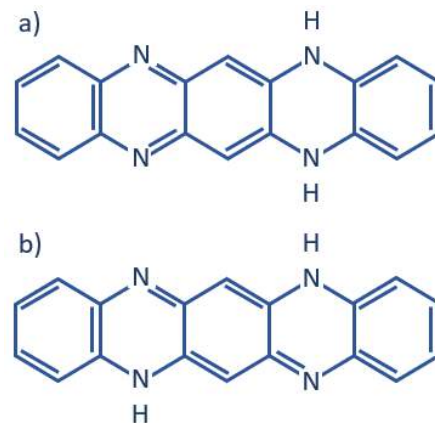


Figure 6 – A scheme of two possible configuration of DHTAP molecule

possible configurations reported: benzenoid 5,14-dihydro-5,7,12,14-tetraaza-pentacene (Figure 6a) and quinonoid 5,12-dihydro-5,7,12,14-tetraaza-pentacene (Figure 6b) [119–121]. It was proven, that the benzenoid configuration is more stable and exhibits better electronic and optoelectronic properties [120–122]. Moreover, the asymmetric distribution of electrons within the molecule due to NH groups built-in on single side of the DHTAP makes the molecule even more interesting. The inner structure of the benzenoid DHTAP results in formation of a built-in dipole moment, which strongly influences the molecule's interactions and thus influences the formation processes of molecular structures. The interface of DHTAP ultra-thin layers grown on metallic and dielectric surfaces was recently investigated in more detail [123–125]. However, not much has been done yet in the regard of semiconductor substrates.

1.4 Titanium dioxide (TiO₂) as semiconducting substrate

As a great substrate for molecular structure growth one can choose semiconducting titanium dioxide. This representative of transition metal oxide exhibits great optoelectronic and catalytic properties [126–131]. There are three main crystal polymorphs of TiO₂ – rutile, anatase and brookite. Only the first two found many applications and were investigated quite intensely. Nevertheless, due to the stability and accessibility, rutile is chosen more often in modern surface science studies and applications. With countless of rutile usage over the years, very recent utilization research concerns electronics [132,133], photocatalysis [134] or photovoltaics [135,136]. However, what makes rutile titanium dioxide one of the most interesting substrate for organic molecules deposition are its electronic properties and its very characteristic features of different crystallographic surfaces.

As non-modified stoichiometric titanium dioxide has a wide band gap of 3 eV [137–139], it requires specific processing in order to enable charge transport within the crystal. Ion beam irradiation and annealing in elevated temperatures reduces TiO₂ by introducing oxygen vacancies and titanium interstitials [131,138]. While the former are responsible for the change of the material's transparency into blue and dark blue colour depending on the concentration, the latter are accountable for *n*-type doping and hence they result in the formation of donor levels close to the conduction band [140,141]. Therefore, the Fermi level is closer to the conduction band, which enhances the overall conductance of the TiO₂ crystal significantly.

If the material is to be considered a good substrate for deposition of organic molecules, the most stable crystallographic surface has to be chosen. In the case of rutile TiO_2 it is (110) surface [142]. This low-index, top layer of the crystal exposes protruding oxygen rows along the [001] direction (Figure 7). This alone makes the surface morphologically anisotropic, which in the case of previously discussed elongated molecules is of great importance. Moreover, the oxygen rows – often referred as “bridging oxygen rows” in literature – possess more electrons than located slightly below titanium rows. This makes the surface even more interesting in the regard of potential organic interface formation.

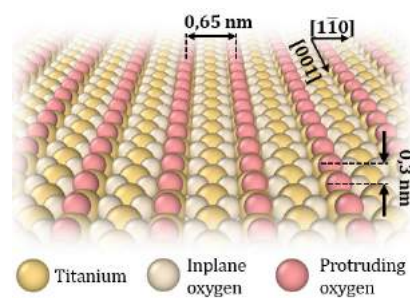


Figure 7 – A ball-stick model of titanium dioxide (110) surface.

1.5 Thesis goals and structure

This work concerns the investigation of thin molecular layers grown in titanium dioxide substrate in the regard of the morphology and properties. Subjects of interest are *para*-hexaphenyl and di-hydro-tetraaza-pentacene. In the case of 6P, with some of the data available in the literature, studies are devoted to unexplored areas of the interface between molecules and the substrate. A postulate of a molecular wetting layer is made, enforcing a direct proof of it. Research involves in-depth studies of the molecules behaviour on $\text{TiO}_2(110)$ with a determination of the interaction between them. In the case of the correct statement regarding the wetting layer, its properties are to be studied. In the instance of DHTAP, a full span of investigation was planned, emphasizing morphology research as little is known of semiconducting substrates. Intended comparison between DHTAP and the pentacene is expected to exhibit rather strong differences due to the built-in permanent dipole moment in the case of former molecules. Dissimilarities are assumed, despite the fact of almost the same 3D structural model of both of the molecules. This dissertation is divided into six chapters, each devoted to a different topic. The first chapter – Introduction – gives an overview of the research field and familiarizes the reader with the area of studies. The second chapter contains a description of the utilized experimental techniques. The following chapter describes equipment, experimental procedures and provides data regarding the research. The fourth and fifth chapters are devoted to the 6P and DHTAP studies, respectively. The last chapter – Summary and conclusions – outlines and recaps findings presented within previous parts of the thesis.

Chapter II

Basis of experimental techniques

The second chapter is written to help the reader better understand the data provided later. Within four sections a full span of utilized techniques are discussed. The main focus is put into the scanning probe microscopy (SPM), as it concerns most of the performed investigations. Scanning electron microscopy (SEM) and low-energy electron diffraction (LEED) techniques are explained, followed by thermal desorption spectroscopy description (TDS) with a great accent on the data analysis methods.

2.1 Preface

The never-ending size reduction trend brings certain consequences and challenges not only in the regard of technology and engineering, but formerly and originally in the case of methodology of research in general. For example, even such fundamental study as imaging in the field of nanoscale turns out to be quite demanding. Due to the nature of light in the visible spectrum range the obtainable resolution for optical microscopy is limited. This fact was discovered already back in the 19th century [143] and later has been known as the Abbe diffraction limit. In order to observe nanoobjects and nanostructures scientists had to develop indirect methods of visualization with a general trend that the smaller the objects the more sophisticated the techniques. One of the breaking points in this matter was the invention, construction and demonstration of the first electron microscope in 1931 by Ernst Ruska and Max Knoll [144]. In the same year they submitted an article about their work regarding geometrical electron optics [145], which was published in the following year 1932 [146]. Knoll's continuation of work led to the first low-resolution images done with scanning of the electron beam [147]. However, the first high-resolution scanning electron microscope was invented by von Ardenne in 1937 [148], which quickened development of this microscopy type allowing for imaging in nanoscale in the following years. Other limit-breaking invention followed tunnelling experiment performed by Gerd Binnig and Heinrich Rohrer in IBM research lab in 1981. Combining electron tunnelling effect with the idea of scanning allowed for designing and building of the first scanning tunnelling microscope [149]. Because of how significant the impact on science of both these techniques was, in 1986 The Nobel Prize in Physics was granted to Ruska, Binnig and Rohrer. In the same year Binnig, together with Christoph Gerber and Calvin Quate published their work regarding another invention of great importance – the atomic force microscope. Its working principles are similar to tunnelling microscope, but it utilizes a vastly different physical phenomena [150]. Electron tunnelling microscopy and atomic force microscopy are the pioneering techniques in a very large group of scanning probe microscopy. It is the first instrumental group of methods to allow for imaging with resolution of distinguishable single atoms in the real space.

Being able to visualize how objects look like is fundamental in regard of research, however, studying any kind of their attributes seems at least equally important. Depending on the research interest, a variety of properties can be investigated, such as

mechanical, electronic, magnetic, thermodynamic, structural, etc. When it comes to the nanoscale, one has to realize that the surface to bulk significance ratio strongly increases and in many cases these should be treated separately. Therefore, in general, experimental techniques can be divided into two main categories depending of the specimen's surface or bulk sensitivity. The following subsections of the chapter will focus on description and explanation of the selected experimental techniques and methods that were used for the research purposes of this work.

2.2 Scanning probe microscopy.

A very wide group of techniques based on two general principles of work – usage of a physical probe and the idea of scanning – make the scanning probe microscopy (SPM). The simplest way to understand the SPM functionality is to imagine describing an object just by feeling it, for example with a hand, without directly looking at it. In SPM the hand is replaced by a probe that has been sharpened as much as possible and that is moved in the range of nanometers over the specimen of interest. During the movement, a set of parameters is constantly measured in a direct or an indirect way. The pre-defined measurement points generally create a 2-dimensional grid, in which every pixel contains data. The whole set is converted into a specific property map afterwards.

The most commonly used scanning methods utilize a line by line zig-zag-shaped movement over the samples (Figure 8). Within this scanning style one can distinguish fast and slow scan directions. The two are differently influenced by some effects that are visible in nanoscale imaging, such as thermal or mechanical drift and therefore one should always use proper scan orientation and carefully analyse received data. Beside the lateral scanning, the most

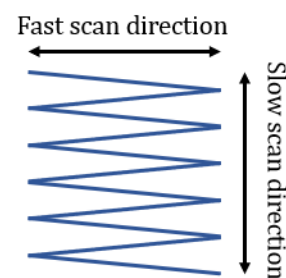


Figure 8 – A scanning pattern scheme

important mechanism is probe positioning over the specimen in the regard of relative distance. Such proper distancing control is executed by a so-called “feedback loop”. An input signal associated with a certain microscopy type and therefore a certain sample-probe interaction is provided to the loop, which is responsible for keeping this signal – so-called “setpoint” – constant. When the probe encounters an obstacle object/structure during scanning, the input signal changes and the feedback loop acts with adjustment of the sample-probe distance so that the input signal goes back to the former state

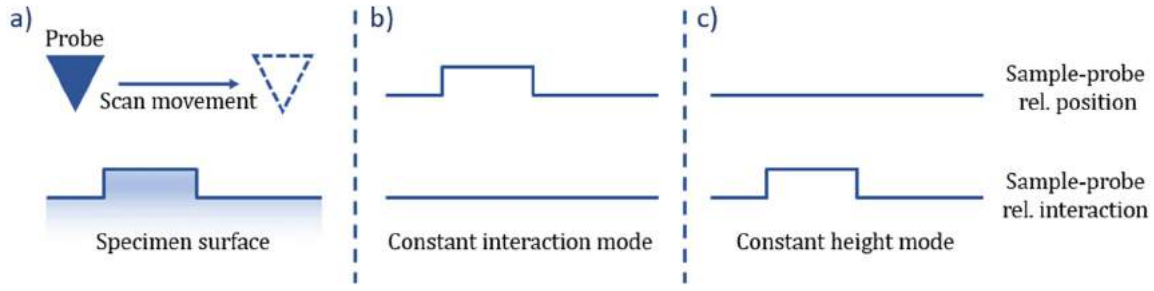


Figure 9 – A scheme presenting working principles of two scanning modes: a) probe movement over the specimen's surface; b) constant interaction mode; c) constant height mode)

(Figure 9a). Such operating process is one of the possible working modes of SPM and is called a constant interaction mode (Figure 9b). Other realization of the imaging process is a constant height mode. In this mode the relative distance between the probe and the sample (as a whole) isn't changed during scanning. Therefore, moving over areas of different heights on the specimen's surface results in different interaction strength/intensity (Figure 9c), which allows for a surface image reconstruction. In both described modes the sample-probe interaction differs depending on the microscopy type. The following subsections describe particular SPM methods used for imaging and certain property mapping.

2.2.1 Scanning tunnelling microscopy.

The first-ever built SPM microscope was the scanning tunnelling microscope (STM). This microscopy type takes advantage of quantum tunnelling effect. Such a phenomenon also occurs for particles and, therefore, can be described as an ability to penetrate through a barrier of a certain width d and potential energy higher than the entity's energy (difference of ΔE):

$$P \propto \exp(-2\kappa d), \quad (1)$$

where

$$\kappa = \frac{\sqrt{2m\Delta E}}{\hbar}. \quad (2)$$

In other words, particles have certain probability to tunnel through vacuum/space without reaching required energy. As the probability is strongly correlated to the particle mass, electrons tend to undergo such phenomenon if the barrier width d is small enough. Bringing two (semi-)conducting materials in a range smaller than 1 nm to each other and

applying a bias voltage between them reduces the barrier's effective height and width heavily enough to induce the tunnelling of electrons. As the process occurs only on the surface, electrons have to constantly move to and from the bulk of the materials. This collective

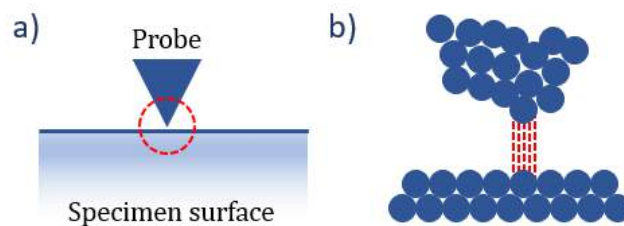


Figure 10 – A scheme visualizing STM probe-sample interaction: 1) overview; 2) sketch of tunnelling process on atomic level

electron movement is classically understood as a current flow and can be easily measured. The tunnelling current I_T is equally proportional to the distance d as in the equation (1) and, therefore, change of d by even 1 Å results in the current change by the order of magnitude. As the “typical atom diameter” is of ~ 3 Å one can imagine that almost all of the tunnelling occurs between 2 closest atoms. Thus, a certain setup can be built in order to measure I_T on the atomic scale (Figure 10). If one of the materials is shaped in the form of a sharp probe it can be used to study the other material's surface via scanning with control of the tunnelling current. Such operating system is what makes the STM.

One has to keep in mind, that for electrons to be able to tunnel from one material to another, there have to be electron filled states on one side and empty states available on the other side. Therefore, materials studied with the STM have to be conducting or, at least, semiconducting. Only then the process can occur and specimen can be investigated via STM. However, considering the above, the received image represents the density of states map of the material's surface, which not always is a plain topography. Furthermore, depending on the specimen material type, morphology, crystallography, etc and probe sharpness, STM imaging can be performed up to the precision of single atoms.

The probes for tunnelling microscopy are typically made out of tungsten (W) and gold (Au) metals or platinum-iridium (PtIr) alloy. These exemplary materials are easy to carve in various ways, so that the probe is cone-shaped and is highly likely to have protruding atom(s) at the very end. Most common techniques involve stretching cuts, electrochemical etching or ion-beam sputtering/sharpening. Gold probes have great properties as the material itself is malleable and doesn't oxidize, which allows to use them in air conditions. However, gold isn't easily etched electrochemically and is rather expensive in comparison to other metals. On the contrary, tungsten is much cheaper and easily undergoes solution etching. It's mechanically very stable and durable and therefore

it is resilient to wear during long-term usage. Its biggest disadvantage is proneness to oxidation on the surface in air conditions, which creates insulating coating on the bare material. Hence, it can work only in ultra-high vacuum conditions. Another great component for STM probes is platinum-iridium alloy. It is rather cheap, malleable and moderately susceptible to chemical etching. In addition, PtIr material can be sputtered with focused ion beam in very controllable manner allowing for preparation of very sharp probes. However, the material isn't as good as tungsten in regard of long-term usage.

2.2.2 Atomic force microscopy.

A considerably different conceptually approach is exploited for atomic force microscopes (AFM). In the micro and nanoscale particles interact with each other through multitude of forces: electrostatic, magnetic, chemical, capillary, van der Waals, etc. When considering a non-magnetic tip-sample SPM setup one can specify long- and short-range categories for these interactions with electrostatic and van der Waals attractive forces acting in larger distances and chemical bonding or Pauli repulsion being sub-nanometer-ranged. A very common expression estimating basic interaction between a sample and an SPM probe (neglecting electrostatic forces) is the Lennard-Jones potential [151]:

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (3)$$

where ε is commonly dispersion energy, σ stands for distance at which $V_{LJ} = 0$ and r represents distance between interacting particles.

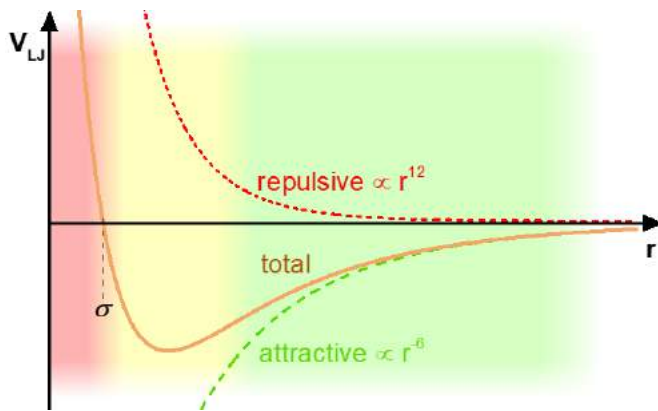


Figure 11 – A plot of Lennard-Jones potential with both the repulsive and the attractive components added. Coloured areas represent working distances for AFM modes as follows: contact AFM (red), tapping AFM (yellow), non-contact AFM (green).

In atomic force microscopy, depending on the chosen distance r , different modes of working regimes can be distinguished. Figure 11 presents plotted graph of the total Lennard-Jones potential with both the repulsive and the attractive components added. Coloured areas are adequate to the appropriate AFM modes (contact, tapping and non-contact), which are described later in this subsection.

With the theory presented above, there is one more challenge to overcome for atomic force microscopy to work – the force measurement. When considering, ideally, atomically sharp probes, then in order to approach the specimen surface without crashing into it, one has to be able to detect forces in the range of nN and pN. On the contrary to STM technique, no direct macroscopic method is available for such subtle interaction. Therefore, a few indirect

alternatives for such control were developed, with optical method being a former and the most commonly used one. The idea behind this approach is to place a sharp AFM probe near the end of a microscopic, flexible cantilever, which on the back-side is reflective to light of a specific, chosen wavelength (Figure 12). Having this prepared, one can use a collimated beam of light with a set of mirrors to aim at the back-side of the cantilever and record the reflected beam with a quadrant photodiode detector. Interaction between the probe and the specimen surface causes the cantilever to bend and, therefore, changes the vertical position of the light spot on the detector. Hence, signals on individual quadrants change and proper arithmetic allows for a cantilever vertical deflection calculation. Using the appropriate distances between the light source, the AFM probe and the detector allows for the detection of sub-nm bending. The cantilever deforms with respect to the Hooke's law:

$$F = -kx, \quad (4)$$

where F is an interacting force, k is a spring constant and x is a deformation length.

AFM probes and cantilevers are most commonly made of silicon (Si), as the technology in the regard of their shape control is most advanced and the material is not expensive. Back-side of the cantilever is often covered with a reflective coating, so that higher amount of the light beam is reflected. For the beam most commonly used wavelength lies in the infrared range. Probe tips themselves can be additionally coated with a specific material for a distinct AFM measurement applications such as conducting, electrostatic, magnetic, etc.

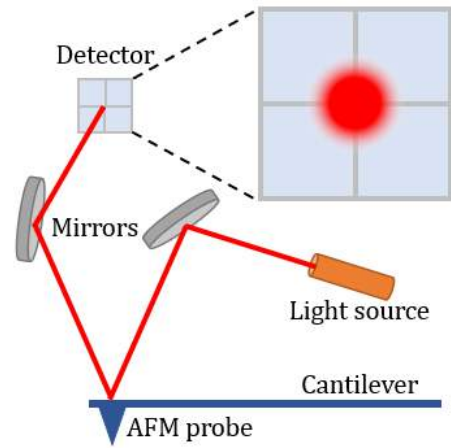


Figure 12 – A scheme presenting common AFM detection system using optical method.

Contact mode atomic force microscopy (c-AFM):

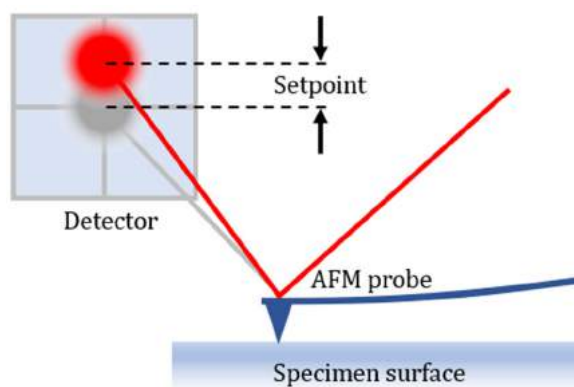


Figure 13 – An exaggerated scheme presenting c-AFM probe-sample setup in an approach position.

The very basic working mode of AFM is the contact mode. It operates in the repulsive interaction regime (red area in the Figure 11), where the probe and the specimen surface are in what is commonly understood as physical contact. During the approach the probe is moved towards the specimen until a user-defined beam vertical deflection setpoint (a chosen repulsive interaction strength) is reached.

In other words, during the movement, when the probe's tip makes contact with the specimen, the cantilever bends and the beam's spot on the detector moves away from a former position (regularly the center) up to a pre-defined value – a setpoint (Figure 13). Choosing a cantilever with known spring constant enables calculation of the interaction force value from Hooke's law (equation 2.4). Due to repulsive force originating from Pauli repulsion, this short-range interaction is limited to the sub-atomic dimensions. Therefore, with probes that are sharp-enough, contact AFM is a technique allowing the atomically-resolved imaging for stiff specimen in proper conditions (ultra-high vacuum and, ideally, low temperatures). However, for more fragile and flexible samples, such as molecular structures, contact mode can be destructive because of the severity of the interaction.

Non-contact mode atomic force microscopy (nc-AFM)

For organics more suitable AFM mode is a non-contact mode. The method takes advantage of the long-range attractive interaction – a van der Waals force (green area in the Figure 11). The force originates from fluctuations of charge density within interacting atoms and molecules, which causes partial polarization and hence the attraction. Unlike in the contact mode, prior to the approach procedure, the cantilever is excited to oscillate at a resonant frequency:

$$f_0 \cong \sqrt{\frac{k}{m}}, \quad (5)$$

where f_0 is the resonant frequency, k is a spring constant and m stands for mass.

Sine-like voltage signal is applied to piezo-electric material connected to the AFM cantilever, which then induces its oscillations. Therefore, on the contrary to contact AFM, the nc-AFM is also called a dynamic AFM. With the probe constantly vibrating, the approach is performed. When the tip of the probe enters the range of the van der Waals attractive force with the specimen, the interaction affects spring constant of the whole system, which ultimately changes

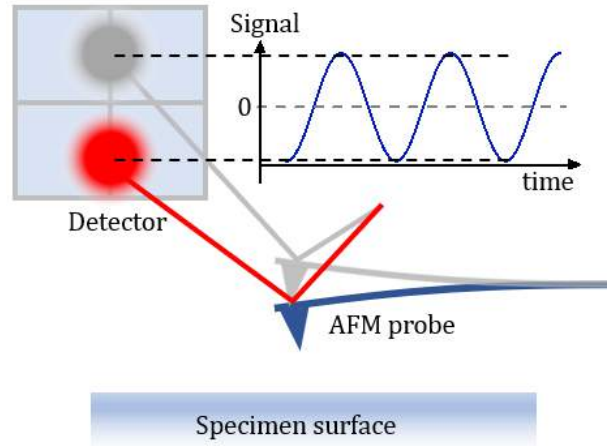


Figure 14 – An exaggerated scheme presenting nc-AFM probe-sample setup with the cantilever oscillating over the specimen.

the resonant frequency (equation (5)) to a new *effective frequency* (f_{eff}). Hence, a change of oscillation amplitude occurs and the phase-locked loop (PLL) tunes the oscillation frequency, so that the amplitude is kept constant. In other words, during the approach a non-zero detuning of resonant frequency ($\Delta f = f_{eff} - f_0$) arises, which acts as a setpoint for non-contact AFM. The higher the detuning, the stronger the probe-sample interaction due to smaller distance between them. The detection system works similarly to the contact AFM (Figure 14). Such working procedure of nc-AFM with a constant oscillation amplitude and changing frequency is called a frequency modulation mode (FM-AFM). Typical oscillation amplitudes for nc-AFM are in order of few nm with a general trend that the smaller the amplitude the better the resolution. As the AFM probe oscillates above the specimen, without going into a physical contact, non-contact mode is a well-suited non-destructive technique for very subtle imaging of fragile molecular structures.

However, such small working amplitudes are not reachable in air conditions, due to large energy losses during every vibration period. Hence, nc-AFM can successfully work only in ultra-high vacuum conditions with addition of sophisticated noise damping systems.

Tapping mode atomic force microscopy (tm-AFM)

The dynamic AFM mode working in ambient conditions is a tapping mode. Similarly to nc-AFM, for tapping AFM the cantilever is excited to oscillate, however, not exactly at resonance frequency, but slightly above it (less often below). Due to the working environment, it is required to drive the oscillation to large amplitudes (several to

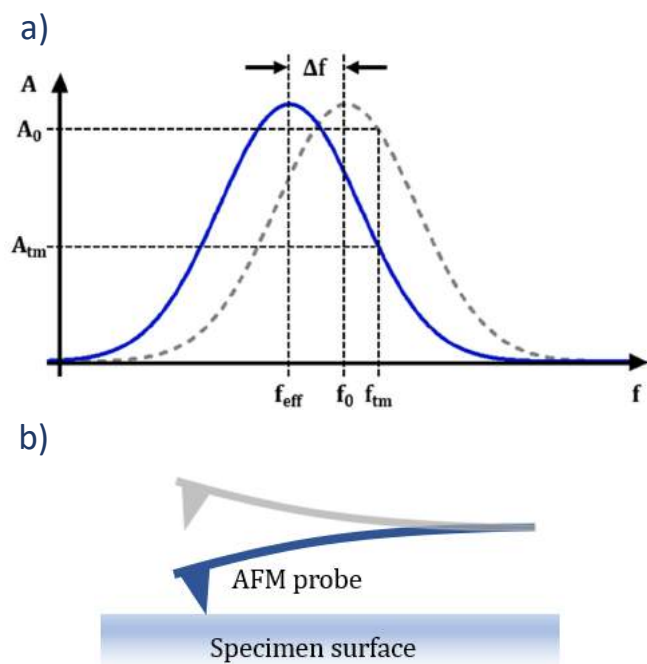


Figure 15 – a) A plot presenting how resonance curve and oscillation amplitudes are affected by probe-sample interaction during approach procedure in tm-AFM; b) an exaggerated scheme of oscillating AFM cantilever in tapping mode with contact shown in maximum deflection.

hundreds of nanometers) in order to attain sufficient stability. In this mode, oscillating frequency is set constant and the amplitude of oscillation acts as a setpoint. During the approach, rising interaction between the tip and the sample affects the resonance shifting the whole curve to the lower frequencies (Figure 15a). Hence, generating oscillations with the former frequency f_{tm} results in the reduction of the amplitude.

Controlling the amplitude allows for setting approach conditions – the mode is also called amplitude modulation mode (AM-AFM).

Due to large energy of the cantilever vibrations, much stronger forces in comparison to nc-AFM are needed to affect resonance sufficiently. Therefore, in the tm-AFM the probe approaches the specimen until at maximum cantilever bend towards the sample they gently contact each other (Figure 15b), meaning they enter repulsive interaction regime. Considering the above one can assign tm-AFM working mode in both the attracting and the repulsive regimes of interaction (yellow area in the Figure 11).

Throughout the years the tapping mode AFM has been successfully used for imaging in air conditions by the means of SPM, including studies for flexible organic structures. However, the mode is not suitable for all molecules as it still can be – to some extent – destructive for the most subtle molecular systems.

Peak force tapping atomic force microscopy (pft-AFM)

In January 2010 BRUKER company published a note about new AFM operational mode that is a peak force tapping AFM [152]. Similar to the regular tapping mode, in pft-AFM the probe is intermittently brought into contact with the specimen for a short period of time. Such mechanism, like in nc- and tm-AFM, eliminates any danger of

damaging the probe during lateral scanning. However, on the contrary to the traditional tapping, the cantilever isn't excited to oscillate with any external signal. Pft-AFM works basing on the direct control of the interaction force between the probe and the sample. As this mode is rather new in comparison to previously described ones and still isn't as popular, it requires a more detailed explanation.

In pft-AFM the whole probe (a cantilever with a tip) moves towards the specimen in sine-like manner. During the movement vertical deflection on the detector is recorded. Starting away from the sample (Figure 16a) the probe approaches the sample. As the tip-sample distance decreases attractive forces bend the cantilever towards the specimen. At a certain moment the force is strong enough and the tip is rapidly brought to contact with the surface – so-called “snap to contact” – and the maximum negative vertical deflection is recorded (Figure 16b). As the progression towards the specimen continues, the cantilever is straightened (Figure 16c) and finally bent in the opposite direction (Figure 16d). The movement continues until a vertical deflection setpoint is reached. At this point a retract procedure starts and the whole process is reversed. Figure 16e presents the overall plot of the vertical deflection in time during a single approach-retract

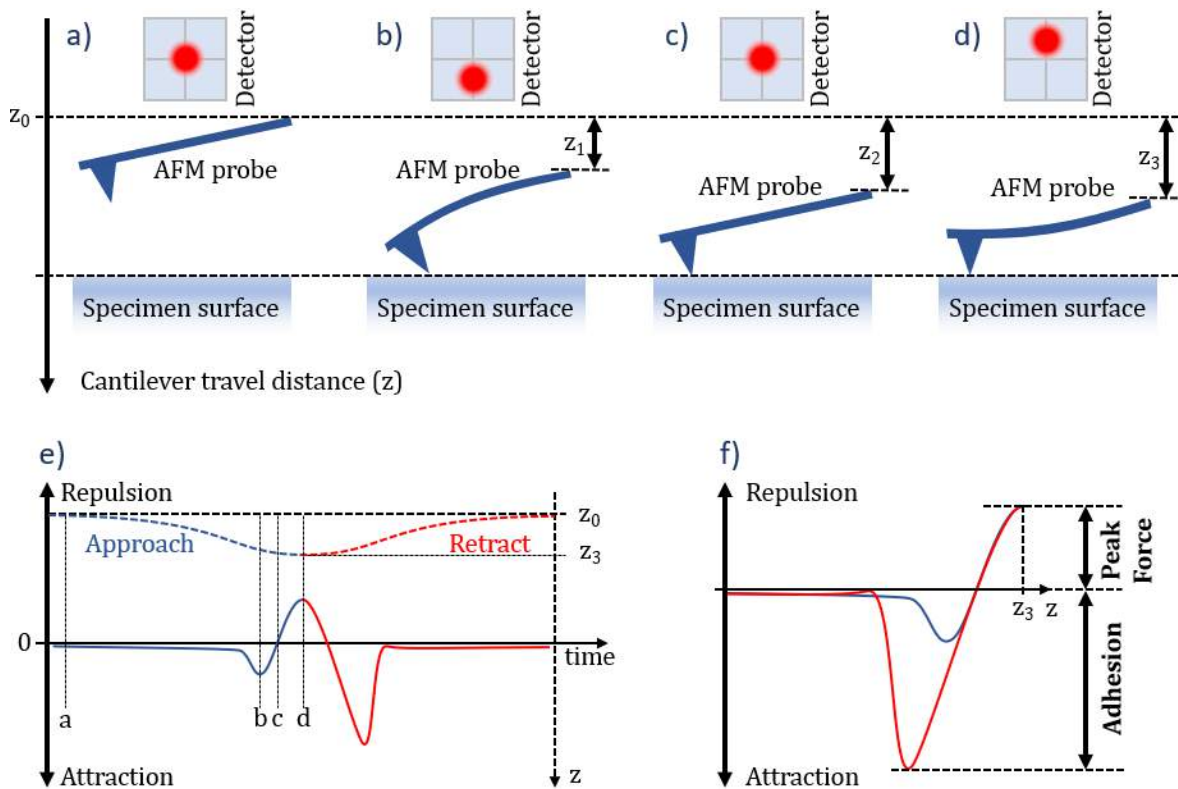


Figure 16 – Peak force tapping AFM working setup: a-d) exaggerated schemes of probe-sample setups during operating procedure; e) plots of vertical deflection (force) and cantilever position in time; f) plot of vertical deflection (force) vs cantilever z position.

cycle. As already established for other AFM modes, using a cantilever with known spring constant allows for direct force calculation from the vertical deflection. Therefore, the setpoint is a direct maximum interaction force between the tip and the specimen surface and hence the *peak force* in the name of the mode. Plotting interaction force vs cantilever position z removes time variable and presents a traditional force-distance curve (Figure 16f). As can be noticed in the Figure 16f higher force is needed to release the tip from the contact with the sample during retraction than for snap to contact within the approach. This fact is correlated to the adhesion, which can be hence directly mapped during peak force tapping measurements. Pft-AFM performs approach-retract movement with a few kHz frequency, which allows for many force-distance curve measurements for each pixel of the map (depending on the scan numerical resolution and speed).

As in the peak force tapping one can set the maximum interaction force, this measurement technique is superior to any other air-condition SPM modes considering subtle, flexible molecular structures imaging. The operation manner makes it possible to use very small setpoints of pN or even, in principle, negative setpoints (approach movement stops before repulsive interaction takes over – in the Figure 16e between lines “b” and “c”). These excellent pft-AFM imaging possibilities will be featured later within this work.

2.2.3 Kelvin probe force microscopy.

One of the important properties in solid state physics surface studies is a work function (ϕ). For particular material it represents energy difference between the Fermi level (E_f) and the level of vacuum (E_v). In other words, a work function is the amount of work needed to extract an electron outside from the surface of a material. This quantity is characteristic for a particular surface depending on the composition of elements, crystallography, molecular compounds, interfaces, etc. The work function is a property of great importance for applications in photoelectronics, organic electronics, electron emitters, vacuum electric field apparatus, contact electrification. As this thesis regards studies of thin organic films and interfaces, a measurement method for this parameter is required.

In 1898 Lord Kelvin observed, that when two metal plates of different materials (zinc and copper in his experiment) are at first brought into an electrical contact and later separated, then an electrical charge is generated [153]. This phenomenon was later explained as the outcome of the work function difference between zinc and copper.

It happens that when two conductive materials of different ϕ are connected electrically, then the former difference in Fermi energy levels is nullified due to electron flow between them (Figure 17). As the electrons move freely in the direction from the higher to the lower Fermi energy, the levels align and the surfaces of both materials become electrically charged with so-called *contact*

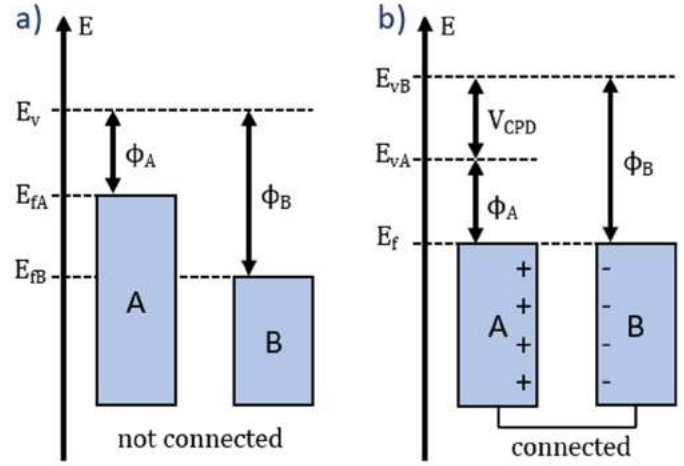


Figure 17 – A scheme presenting vacuum and Fermi energy levels of two conductive materials: a) not connected; b) connected electrically with each other.

potential difference (V_{CPD}) between them (Figure 17):

$$V_{CPD} = \frac{\phi_B - \phi_A}{e}, \quad (6)$$

where ϕ_A and ϕ_B are the work functions of material A and material B, respectively and e is the electron charge. Knowing that it is hence possible to distinguish such difference between any two materials. Furthermore, if ϕ of one of the materials is known, then a direct measurement of absolute value of ϕ for the other material is available.

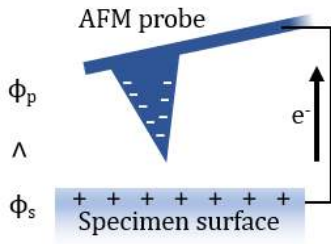


Figure 18 – An exaggerated AFM probe-sample setup with surfaces charged in an exemplary direction due to materials' work function difference.

Considering the above, it is possible to adopt such methodology within the AFM microscopy, where a conductive tip acts as one part of the setup and the specimen as the other. Because the two are electrically connected by the AFM system, electrons move freely between them generating V_{CPD} with the surfaces charging (Figure 18). One can consider such setup as a charged capacitor and, therefore, there is

an electrostatic force F_e interacting between the probe and the specimen. Due to the AFM tip shape F_e is a function of tip-sample effective distance z and can be written as [154]:

$$F_e(z) = -\frac{1}{2} \frac{\partial C(z)}{\partial z} \Delta V^2, \quad (7)$$

where ΔV is a total potential difference between the tip and the specimen surface and $\partial C(z)/\partial z$ is a capacitance gradient.

Because the force F_e is a long-range interaction it participates in the overall tip-sample interaction in nc-AFM and tm-AFM. For heterogenic samples in the regard of lateral surface composition F_e differs depending on the V_{CPD} on particular areas, hence creating false topography map measurement. In order to acquire proper AFM height it is needed to eliminate the F_e force component. Therefore ΔV in equation (7) must equal zero, which can be achieved by applying an external bias voltage V_{bias} consisting of direct (V_{DC}) and alternating (V_{AC}) components:

$$V_{bias} = V_{DC} + V_{AC}\sin(\omega t). \quad (8)$$

Hence, the equation (7) becomes:

$$F_e(z) = -\frac{1}{2}\frac{\partial C(z)}{\partial z}[(V_{DC} - V_{CPD}) + V_{AC}\sin(\omega t)]^2 = \quad (9)$$

$$-\frac{1}{2}\frac{\partial C(z)}{\partial z}\left[\frac{1}{2}(V_{DC} - V_{CPD})^2 + (V_{DC} - V_{CPD})V_{AC}\sin(\omega t) - \frac{1}{4}V_{AC}^2(\cos(2\omega t) - 1)\right].$$

Further, the equation (9) can be divided into three parts:

$$F_{DC} = -\frac{\partial C(z)}{\partial z}\left[\frac{1}{2}(V_{DC} - V_{CPD})^2\right], \quad (10)$$

$$F_{\omega} = -\frac{\partial C(z)}{\partial z}[(V_{DC} - V_{CPD})V_{AC}\sin(\omega t)], \quad (11)$$

$$F_{2\omega} = \frac{\partial C(z)}{\partial z}\left[\frac{1}{4}V_{AC}^2(\cos(2\omega t) - 1)\right]. \quad (12)$$

F_{DC} is responsible for a static interaction on the probe, F_{ω} is used for determination of V_{CPD} and $F_{2\omega}$ can be used for capacitance microscopy [154]. When a proper V_{DC} equal to the V_{CPD}

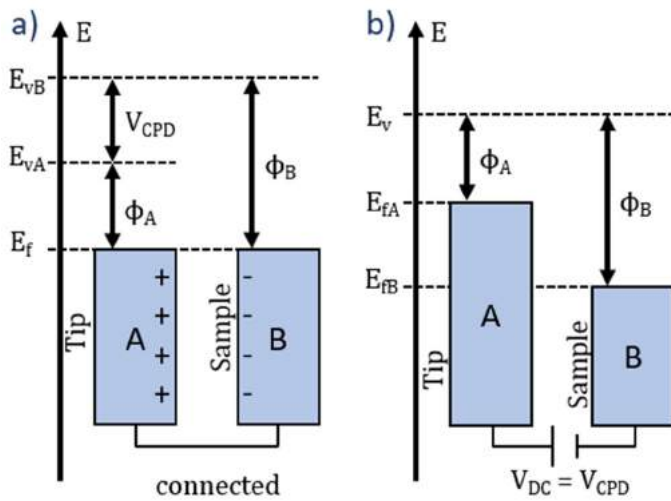


Figure 19 – A scheme presenting energy levels of specimen and AFM tip: a) before; b) after external voltage V_{DC} application.

is found, then polarization illustrated in the Figure 18 is reversed and electrostatic force between tip and the sample is eliminated. This also results in Fermi levels of both the probe and the specimen surface returning to the former energies (Figure 19). Two main methodologies are available for the proper value of external voltage determination in

dynamic AFM modes. One of them utilizes second feedback loop that controls any additional changes in resonance frequency or oscillation amplitude for FM-AFM and AM-AFM, respectively. Thanks to the alternating part of external voltage V_{AC} , a proper direct V_{DC} is found so that mentioned changes are nullified and, hence, V_{CPD} value is determined. Another method that can be used is called a *lift mode* method. In this approach only for every odd line in the fast scan direction the topography is measured (by the means of FM- or AM-AFM). After topography forward and backward line is finished, the probe moves away from the specimen by the specified distance and the external excitation signal is turned off. The probe scans the next forward and backward line following the trace of previously measured topography. During this movement away from the surface, V_{AC} is applied with the frequency ω equal to the resonance frequency f_0 . Therefore, for a non-zero F_e originating from not nullified V_{CPD} , resonance oscillations are induced with a certain amplitude. Hence a proper V_{CD} is found and applied, so that the amplitude goes back to zero – in this case V_{DC} equals V_{CPD} .

Mapping contact potential difference with nanoscale resolution by the means of the described adaptation of AFM is called a Kelvin probe force microscopy (KPFM). However, V_{CPD} map provides only information about lateral differences in the work function, not the absolute values. In order to obtain absolute ϕ , one has to determine the work function of the tip (ϕ_{tip}) beforehand. This can be achieved by V_{CPD} measurement on a specimen with an already known work function value, such as gold monocrystal Au(111) or HOPG (highly ordered pyrolytic graphite) surface with a certain AFM probe. After that, mapping contact potential difference on any specimen with the same tip allows for calculation of the absolute work function.

2.3 Electron beam techniques

Electrons (e^-), due to their properties can be easily produced (meaning extracted from a solid matter), manipulated in the regard of movement and exploited in the field of interaction with other matter. As for now, they are believed to be one of the elementary particles possessing elementary negative charge. An electron of certain energy shot at a specimen shield undergoes a process called scattering. Considering a former electron energy of the keV magnitude, one can distinguish two main types of scattering, i.e. elastic and inelastic. Classification depends on whether the incident primary electron losses

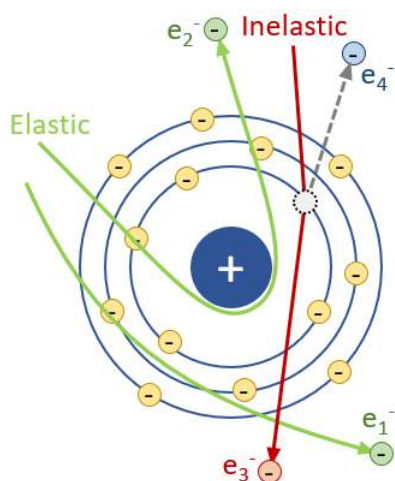


Figure 20 – A Bohr model of an atom with exemplary incident electrons trajectories influenced by scattering: elastic (green), inelastic (red).

energy during the interaction with matter. When the former electron's energy doesn't change, or more specifically ΔE is smaller than ~ 1 eV, one can name it as an elastic scattering. In such a process the electron's trajectory can be either slightly or drastically changed (e_1^- and e_2^- in the Figure 20) due to Coulomb interaction with electron cloud (orbitals) or atomic nucleus, respectively. On the contrary, when the primary incident electron loses energy during scattering (e_3^- in the Figure 20), the process is considered inelastic. The law of conservation of energy requires the lost energy to be transferred,

which can be realised in a various ways. An example of such process is an extraction of an electron from the interacting atom (e_4^- in the Figure 20). A generated electron possesses rather low energy ($E_{\max} \sim \text{few eV}$) in comparison to the former electron. This process can occur either on an outer or inner electron orbital. If the latter takes place, the emptied orbital is quickly filled with an electron originating from the orbital of higher energy, resulting in another transfer of excess energy. This in turn leads to either generating an Auger electron or emission of characteristic X-rays. Energies of both of these are strictly related to the atom element. There are a few other processes connected to the inelastic scattering of incident electrons, i.e. excitations of plasmons or phonons or emission of continuous X-rays (so-called "Bremsstrahlung"), however, these are not important in the regard of this thesis and, therefore, will not be explained.

The presented scattering description concerns a single electron interaction with matter. However, in order to be able to take advantage of products of these processes, there has to be not a single, but a large amount of them. Moreover, it is more useful to use primary electrons of same energy, similar incident trajectory and having them strike at as small area as possible. Therefore, a fitting method concerns utilization of an electron beam that is monochromatic, collimated and has small cross section diameter, respectively. Exposing a specimen to such electron beam generates strong enough signals for detection. Depending on the process, one can produce intensity images, structural images or study atomic composition of the sample. Thanks to the technical possibilities of beam diameter

control to the level smaller than 1 nm, one could expect exceptional resolution of these. However, due to the low-angle scattering of high energy primary electrons, the specimen is penetrated in a wider range than the former beam diameter, creating a so-called “tear drop” interaction volume. Figure 21 presents a schematic overview of origin areas for the particular signals generated with an electron beam. High-energy electrons of primary beam scattered elastically are called “back scattered electrons” (BSE). Low-energy electrons generated from the specimen

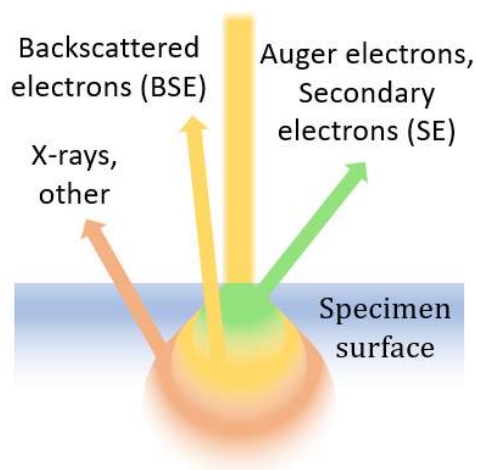


Figure 21 – A Schematic presentation of origin volume areas for particular signals generated from the specimen as a result of electron beam irradiation.

through energy transfer are called “secondary electrons” (SE). Penetration depth and width depends on the primary electrons energy and specimen density (element composition and crystallography). Considering the above, the final obtained resolution is much worse than the beam diameter suggests.

When it comes to the travelling electrons, one has to remember that they interact not only with atoms of the sample, but with any matter in general. Therefore, an electron beam operating in ambient conditions interacts with air, strongly changing particles’ energy and beam collimation/diameter. Electron mean free path in atmospheric pressure (~ 1000 mbar) is less than 100 nm, which results in frequent collisions. Reducing air pressure up to a magnitude of $\sim 10^{-4}$ mbar – high vacuum (HV) conditions – changes mean free path to around ~ 100 m, which is 10^9 times larger than the ambient one. Hence, it is required to produce such environment for a successful electron beam usage.

2.3.1 Scanning electron microscopy

A technique that utilizes the usage of a focused electron beam to investigate a specimen is called scanning electron microscopy (SEM). In SEM the beam is scanned over the specified area, while proper signals are recorded creating a signal intensity map. In order to create a desired electron beam a certain machinery (Figure 22) and procedure is required. Electrons are generated in a so-called „electron gun”, which uses either the thermo-emission or field emission effect. However, such extracted electrons have vastly different energies and movement directions. As the electrons possess charge, they are

susceptible to electric fields, which can be used to accelerate them up to a certain energy. Moving charges also experience a force out of magnetic fields through a Lorentz Force:

$$\vec{F}_L = q\vec{E} + q\vec{v} \times \vec{B}, \quad (13)$$

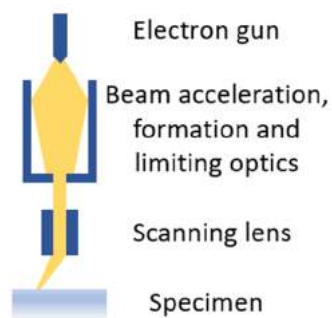


Figure 22 – A basic scheme of a scanning electron microscope.

where q stands for electric charge, v is a charge velocity and E and B are the electric and magnetic fields, respectively. Having that known, the beam can easily be formed with a particular chosen electron energy. Finally, the magnetic lens allows scanning over the specified sample areas. In each chosen place (each pixel) a set of signals is generated depending on the local morphology, element composition, etc. Topography images are usually created by gathering the SE signal with a specifically

designed detector (for example Everhart-Thornley detector). It is possible due to the so-called “edge effect” (Figure 23). The electron beam hitting a flat surface will generate much less secondary electrons than if it was shot at the vertical edge. Hence, depending on the specimen morphology, particular shapes will have different “brightness” (different amount of SE recorded by the detector). This allows for the most commonly utilized imaging in SEM. One has to keep in mind, that such methodology works well only for conducting and sometimes for semi-conducting samples. However, there are some solutions available for less conducting substrates. When it comes to organic structures or organic thin films imaging, electron beam can turn out to be destructive for them either completely ruling out SEM investigation or requiring a very specific conditions.

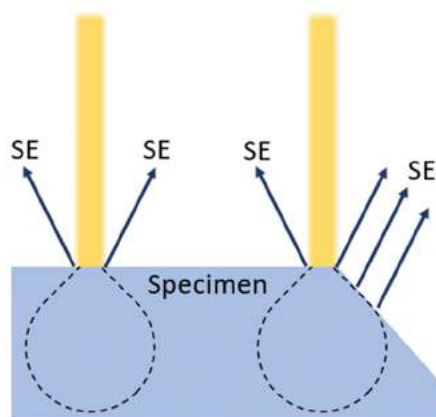


Figure 23 – A scheme presenting difference in electron beam incidence on flat surface and on an edge (“edge effect”).

2.3.2 Low-energy electron diffraction

For molecular growth studies, usually, crystalline surfaces are used as the substrates. In particular, very often monocrystals samples are investigated. In

a crystallographic description, a monocrystal is built of atoms periodically occurring in a 3D space. For such an object, one can define a unit cell, which describes the whole crystal with simple rules of translation vectors. Therefore, most characteristic property of monocrystals is a perfect short-range and long-range ordering. However, preparation of the crystalline surface of interest often requires a lot of effort. Therefore, one needs a methodology to easily control quality of the process on both the small and large areas. A fitting experimental technique for such use is the low-energy electron diffraction (LEED).

In addition to previously defined electrons' properties, they are particles of a very low mass (approximately 1836 times lower than the mass of a proton) and, therefore, their behaviour is strongly correlated to another quantum mechanics phenomenon. In 1924 Louis de Broglie proposed a concept that all matter behaves like a wave [155], which leads to the equation of matter waves (often referred to as de Broglie waves):

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \quad (14)$$

where λ stands for wavelength, h is a Planck constant, p , m and v are the particle's momentum, mass and velocity, respectively. Considering e^- energies ranging between 10 and 200 eV matter wavelength equals a few Å, which is comparable to atomic distances within crystals. Therefore, a beam of electrons pointed at a crystalline specimen will undergo classical diffraction and interference. Similar to the Bragg's law [156], for certain scattering angles θ , the constructive interference of electron wave fronts will occur:

$$\Delta a = d \sin \theta = n \lambda, \quad (15)$$

where Δa is a difference in electrons' travel distance, n is a natural number corresponding to the diffraction order, λ stands for the electrons' wavelength, d equals atomic crystal distancing and θ is the scattering angle (Figure 24a). Taking advantage of the described processes with a proper experimental setup (Figure 24b) allows for the registering of diffraction reflexes. These reflexes

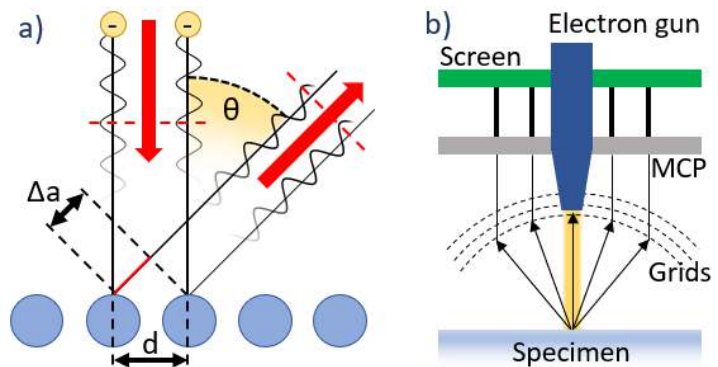


Figure 24 – a) A scheme presenting diffraction of electrons on specimen's atoms; b) a basic scheme of LEED optics.

originate from the specimen's periodicity and represent its pattern in a so-called "reciprocal space", which is a Fourier transform of the real space. In LEED, an electron gun produces a well-defined electron beam that hits the specimen. Scattered electrons go through a set of grids, where the elastically scattered electrons are separated from all of the incoming electrons. A very common method to enhance the signal to noise ratio is the usage of a microchannel plate (MCP), which functions as a particle (electron in this case) amplifier. MCP is built of a set of dynodes that for each incoming particle generate a multiplied number of them. It is very useful for lowest electron energies utilized in LEED as the regular signals are very weak. The last part of LEED setup is a fluorescent screen, which emits light at electron incidence areas, allowing for reflexes pattern observation. As the usual operating electron energies are in the range of 20 – 100 eV only few surface layers are penetrated with the beam. Hence, the retrieved information is strongly surface-related. Intensity of the diffraction reflexes depends on the substrate quality (crystallinity). Therefore, strong signal to noise ratios of the obtained patterns indicate high quality of the substrate (in the regard of atomic ordering). Because some of the electrons are scattered inelastically, the exposure of the samples with subtle molecular structures may lead to their decomposition. However, using small enough electron beam currents and energies of only tens of eV makes it possible to investigate even singular layers of molecules without destroying them.

2.4 Thermal Desorption Spectroscopy

When it comes to the studies of molecular structures grown on particular surfaces, one of the most important property is their stability. This parameter is strongly correlated to the molecule-substrate interaction. When a molecule is deposited on a substrate it can either stick to it (adsorption), move laterally (diffusion) or leave it (re-desorption). Considering the former, one can distinguish physisorption occurring due to weak van der Waals forces and electrostatic forces or chemisorption for strong chemical covalent bonding. Both these processes are characterized by a total binding energy. This parameter is very important in the regard of organic interfaces. One can use a conceptually easy technique of thermal desorption spectroscopy (TDS) for its determination.

The basic idea behind TDS is measuring a desorption rate of molecules while a specimen is being gradually heated. The amount of the emerging molecules is usually recorded by a mass spectrometer calibrated for particular m/q (mass to charge) ratio. During the

temperature increase, the desorption rate rises until there are no more molecules on the sample, which results in the rate drop. With this procedure one can obtain a thermal desorption peak. The process of molecules leaving the substrate can be described by Arrhenius-type equation, which in the case of molecular desorption with a constant heating rate takes a form of Polanyi-Wigner formula [157]:

$$R_{des} = -\frac{d\theta}{dT} = \frac{\nu_n}{\beta} \theta^n \exp\left(\frac{-E_{des}}{kT}\right), \quad (16)$$

where R_{des} is the desorption rate, θ denotes the coverage, T stands for the temperature, ν_n describes a pre-exponential factor (also called as the “attempt frequency”), β is the heating rate, n stands for the order of desorption kinetics, E_{des} is the desorption energy and k is the Boltzmann constant. E_{des} , ν_n and n are often referred to as the kinetic parameters. The order n describes desorption rate dependence of the coverage. There can be either 0th, 1st or 2nd order of the process ($n = 0, 1$ or 2 , respectively):

- In zeroth-order desorption the rate of the emerging molecules is independent of the coverage, i.e. constant for a particular temperature. Curves are asymmetric, with characteristic exponential growth and a rapid drop following the temperature of peak maximum T_m (Figure 25a). With the increase of the coverage, T_m shifts to higher temperatures. This process usually concerns desorption of multilayers;
- in first-order desorption R_{des} is proportional to the θ . Maxima are asymmetric, but T_m is independent of the coverage (Figure 25b). This kinetics is typical for monolayer desorption;
- in second-order desorption the rate is proportional to θ^2 . Recorded curves are nearly symmetric. Increase of the coverage results in the T_m shift to the lower temperatures (Figure 25c). 2nd order desorption usually originates from a recombination happening on the substrate surface.

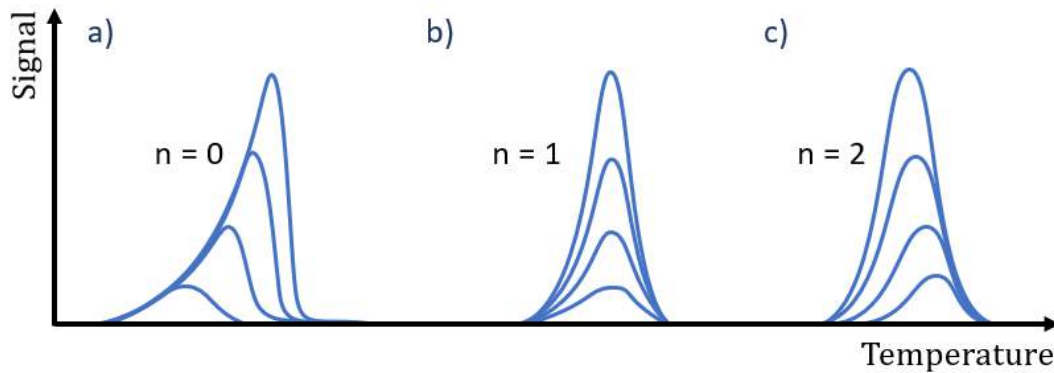


Figure 25 – Plots presenting typical TDS curves depending on the desorption order: a) 0th; b) 1st; c) 2nd.

One of the most important matters when it comes to the TDS is the spectrum analysis. As the primary activity, one must determine the order of desorption curve. Identification can be either a straightforward visual evaluation of the peak shape, if it closely resembles one of the typical shapes (Figure 25), or requires an accurate assessment from Polanyi-Wigner formula. The equation (16) can be written as:

$$\ln\left(\frac{R_{des}}{\Theta^n}\right) = \ln\left(\frac{\nu_n}{\beta}\right) - \frac{E_{des}}{kT}, \quad (17)$$

and, therefore, plotting $\ln(R_{des}/\Theta^n)$ vs $1/T$ will result in a straight line, if a proper n is chosen. If none of the typical kinetic order values produce a linear graph, then there is a strong coverage dependence of the kinetic parameters. However, it has been shown, that in general this method often gives reliable n values, while ν_n and E_{des} are correct only if the kinetic parameters are coverage independent [158].

On the contrary, *leading edge analysis* [159], doesn't require an assumption of ν_n and E_{des} coverage independence and, what is more, even the temperature independence. The method takes advantage of such early stages of desorption, that one can consider coverage and temperature as constant. This approach uses the logarithmic form of Polanyi-Wigner equation:

$$\ln(R_{des}) = n\ln(\Theta) + \ln\left(\frac{\nu_n}{\beta}\right) - \frac{E_{des}}{kT}, \quad (18)$$

and is usually employed for 0th order desorption. Plotting R_{des} vs $1/T$ gives accurate ν_n and E_{des} values, however, a high signal-to-noise ratio in the leading edge region is required.

For 1st order desorption specifically, one can apply *Redhead's peak maximum method* [160]. This approach is based on the position of the desorption curve maximum, where the $d\Theta/dT = 0$. Implementing this into the Polanyi-Wigner equation (16), differentiation with respect to T and applying logarithm for 1st order desorption leads to:

$$R_{des} = RT_{max} \left[\ln\left(\frac{\nu_1 T_{max}}{\beta}\right) + \ln\left(\frac{RT_{max}}{E_{des}}\right) \right], \quad (19)$$

where R is the gas constant and T_{max} is a temperature at which peak maximum occurs. Redhead recognized the linear correlation between T_{max} and E_{des} , from which one can write an equation known as the Redhead's equation:

$$R_{des} \cong RT_{max} \left[\ln\left(\frac{\nu_1 T_{max}}{\beta}\right) - 3,64 \right]. \quad (20)$$

For this method a known ν_1 is needed and it is recommended to perform multiple TDS measurement of different heating rates in order to obtain a correct E_{des} value.

Another approach allowing for rather accurate determination of both the E_{des} and ν_n is the *heating rate variation method* [161], which concerns performing a series of thermal desorption experiments with different heating rates. The position of the peak maximum is dependent of the heating rate and, therefore, plotting the $\ln(T_{max}^2/\beta)$ vs $1/T_{max}$ gives a linear relation, where E_{des} is provided from the slope and ν_n is calculated from the intercept. For the 2nd desorption order a known coverage Θ is required.

The most accurate method is the *complete analysis* [162], however, it is the most time consuming due to the requirement of a series of different experiments and is limited in the regard of application. As the other approaches are accurate enough, this method was not employed within the scope of this work.

Chapter III

Experimental details

In this chapter experimental details are provided. Three sections, i.e. *Apparatus used*, *Substrate preparation procedures* and *Molecular deposition via UHV evaporation* are supposed to define the systems and parameters needed to recreate proceedings within the conducted experiments. When needed, a special attention is brought to crucial details regarding preparation processes. The last section contains information regarding the DFT simulations performed for the needs of this work.

3.1 Apparatus used

Conducted experiments for the purposes of this thesis include utilization of many different techniques that require different environmental conditions. Therefore, not a single, but a few operating research systems were used throughout the work. Most of the studies were done *in situ* in the main ultra-high vacuum system, while the rest of the investigation was conducted in a few other apparatus *ex situ*.

3.1.1 Ultra-high vacuum system

The main, quite large arrangement of interconnected UHV chambers, where the majority of experiments were conducted, is presented in the Figure 26. The system operates with the standard pressure in the range of 10^{-9} – 10^{-10} mbar, where particular chambers can be separated via vacuum valves, keeping each under the nominal pressure. A special load-lock setup is installed, that allows for new sample introduction without a need of venting the whole structure. One of the two main chambers is dedicated for preparation processes, i.e. sputtering with use of an ion gun and annealing. The chamber also contains a few Knudsen cells for organic molecular deposition (*para*-hexaphenyl, pentacene, di-hydro-tetraaza-pentacene), as well as many vacuum-proof glass windows allowing pyrometer installation (IGA 140/23) for a direct temperature control. Within this chamber a quadrupole mass spectrometer (Hiden Analytical's RC PIC QMS with a secondary electron multiplier detector) is equipped, which was used for signal of desorbing molecules detection in thermal desorption spectroscopy experiments. The second large chamber acts as an interconnector between the load-lock and other chambers, while also containing a OCI Vacuum LEED/Auger device. Finally, the third chamber has an UHV Omicron RT-AFM/STM microscope, equipped with a $6 \times 6 \mu\text{m}^2$

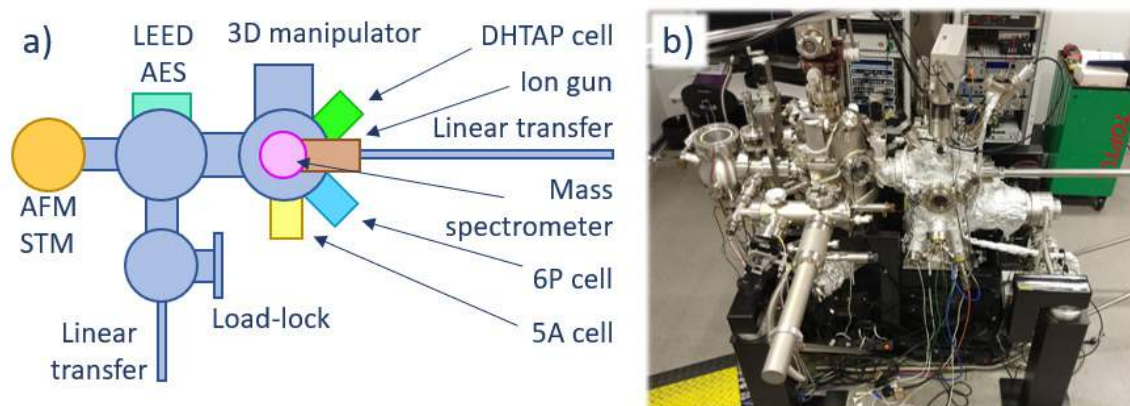


Figure 26 – The UHV system: a) schematic overview; b) a photograph of the actual system.

scanner, which allowed for the *in situ* specimen SPM imaging. The microscope is placed on a platform isolated from the whole UHV apparatus by the magnetic damping system, which significantly neglects high-frequency noise. For STM both the tungsten and the platinum-iridium probes were used, while for AFM and KPFM silicon cantilevers of f_0 frequencies ~ 90 kHz and ~ 270 kHz were utilized.

3.1.2 Scanning electron microscope

An external HV chamber contains a scanning electron microscope SEM Quanta 3D FEG (Figure 27a). The microscope is equipped with a Schottky electron emitter and optics capable of the acceleration of electrons in the range of 200 eV – 30 keV. The utilization of separate detectors for high-energy back-scattered electrons (semiconductor disc) and low-energy secondary electrons (Everhart-Thornley detector) allows for simultaneous TOPO and COMPO imaging with the regular electron beam current of tens of pA. Additional apertures for elevated beam currents (a few nA) are adopted for EDS analysis. Possible magnifications are in the range of 0,5 – 1000k. The microscope has an additional ion gun column (FIB – Focused Ion Beam), which enables both the ion beam imaging and ion beam processing within the chamber. For the purposes of this work, the ion beam was mostly used for the STM PtIr probes preparation. The working pressure is in the range of 10^{-4} – 10^{-5} mbar. Furthermore, a non-standard load-lock system is installed, allowing quick sample exchange, without the need of whole chamber venting.

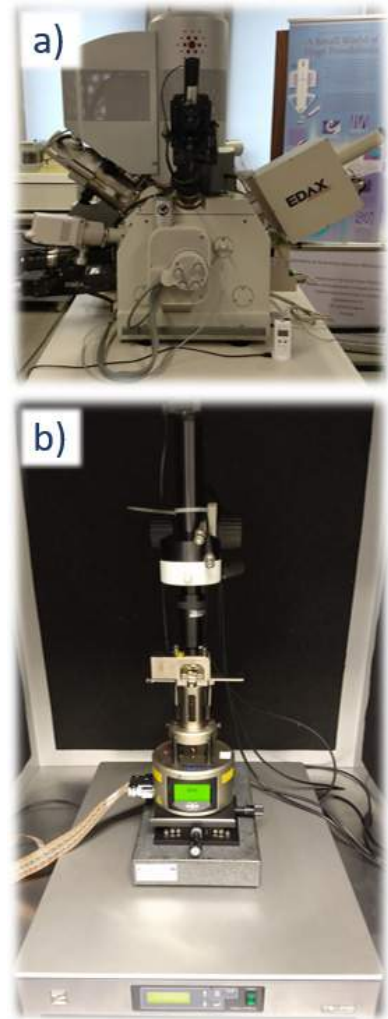


Figure 27 – Photographs of the: a) scanning electron microscope apparatus; b) AFM microscope working in the ambient conditions.

3.1.3 Ambient AFM microscope

In addition, a second microscope was used for the nanoscale imaging in ambient conditions after air exposure of the samples. The ambient AFM is a BRUKER MultiMode 8 extensible microscope, equipped with a $125 \times 125 \mu\text{m}^2$ scanner (Figure 27b). Installed hardware allows for all of the AFM invented modes imaging, however, for the purposes of this work only c-AFM, tm-AFM, pft-AFM and AM-KPFM were used. The microscope is placed on an active vibration isolation table and a set of different heavy platforms for external vibrations reduction. The whole system is covered with a thick box neglecting sound noise.

3.2 Substrate preparation procedures

Preparation processes include all of the activities concerning the $\text{TiO}_2(110)$ monocrystal cleaning, processing and quality check, together with STM probe chemical etching and sharpening. The following subsections describe experimental details regarding these proceedings in both the ambient conditions and vacuum environment.

3.2.1 Substrate preparation – atomically flat surface

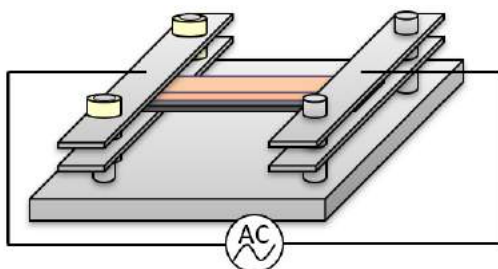


Figure 28 – A scheme of TiO_2/Si “sandwich” mounted on a sample holder dedicated for current heating.

Titanium dioxide samples used for the experiments were 1-side polished pieces of $10 \times 3 \times 0,5 \text{ mm}^3$ rutile monocrystals bought from MaTecK company. The first steps of preparation, before UHV introduction, required rinsing in isopropanol with usage of an ultrasonic cleaner. Such a processed crystal was mounted on an Omicron sample holder with a Si/SiO₂ wafer underneath (Figure 28). Each sample edge was placed on electrically separated electrodes, which allows voltage application and the current flow through it. The specimen, mounted this way, were introduced to the main UHV system via the load-lock system, where after transferring to the preparation chamber a series of procedures were conducted. As a first step in the UHV, samples were outgassed via heating up to the temperature of 750°C for 1 hour. After that, a number of cleaning cycles was performed, which include multiple ion sputtering and high-temperature annealing steps performed in turns one after another. Ion bombardment concerned noble gas ions Ar^+ of 1 keV

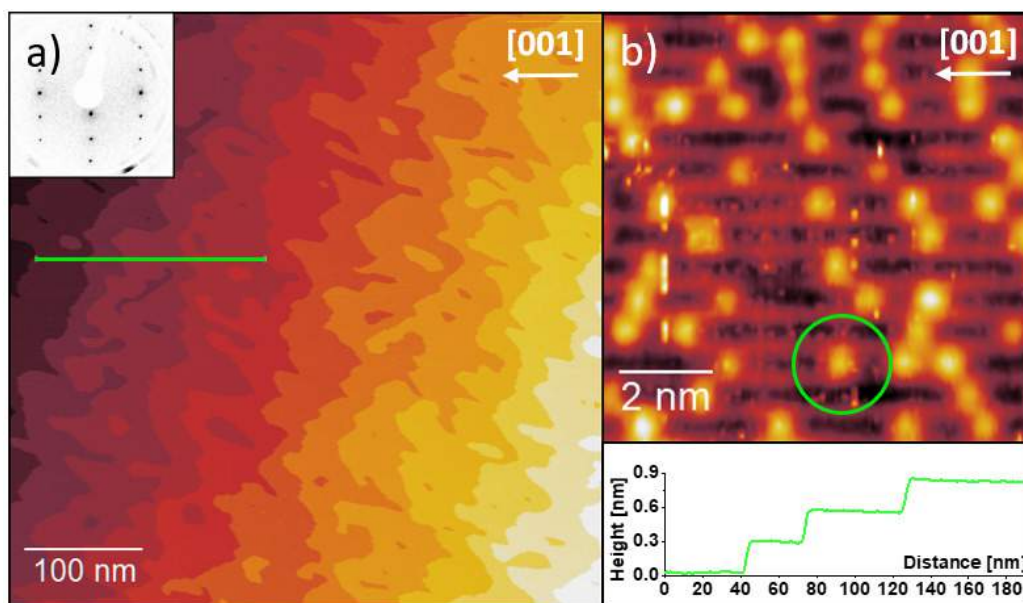


Figure 29 – a) A STM image of flat, terraced TiO₂(110) surface ($U = +1.7$ V; $I = 25$ pA) with the corresponding LEED pattern inset ($E_e = 108$ eV) and a cross section profile taken across green line; b) a HR-STM image of TiO₂(110) surface presenting the atomic row structure.

irradiation at an incidence angle of $\alpha = 60^\circ$ (off normal) and the total fluence of $\sim 10^{16}$ ions/cm². For the current flow heating, in order to obtain a homogenous temperature across the sample an alternating voltage was used. Annealing was performed at the temperature $T = 750$ °C for 20 minutes in each cycle. Cleaning cycles were conducted up to a point of reaching the desired atomic terrace structures (in most cases large compact terraces) imaged with STM (Figure 29a) and/or a high-quality LEED pattern was received (inset in the Figure 29a). Better resolved STM imaging reveals the structure of the substrate surface atomic rows (Figure 29b). As the positive BIAS voltage of $U = +1,7$ V is applied to the sample rather than the tip, the empty states of TiO₂(110) surface are imaged. This results in titanium atoms appearing as bright rows and oxygen atoms being dark. The bright and round features located on the dark rows are the oxygen vacancies occupied by the OH⁻ groups (exemplary one marked with a green circle). They originate from the dissociation of adsorbed water molecules always present in UHV chambers in residual amounts.

3.2.2 Anisotropic surface morphology formation

Some of the experiments concerned not flat, terraced TiO₂(110), but ion-modified surface in the form of ripples in order to investigate influence of a strong morphological anisotropy and an increased concentration of step-edges. Such samples were prepared

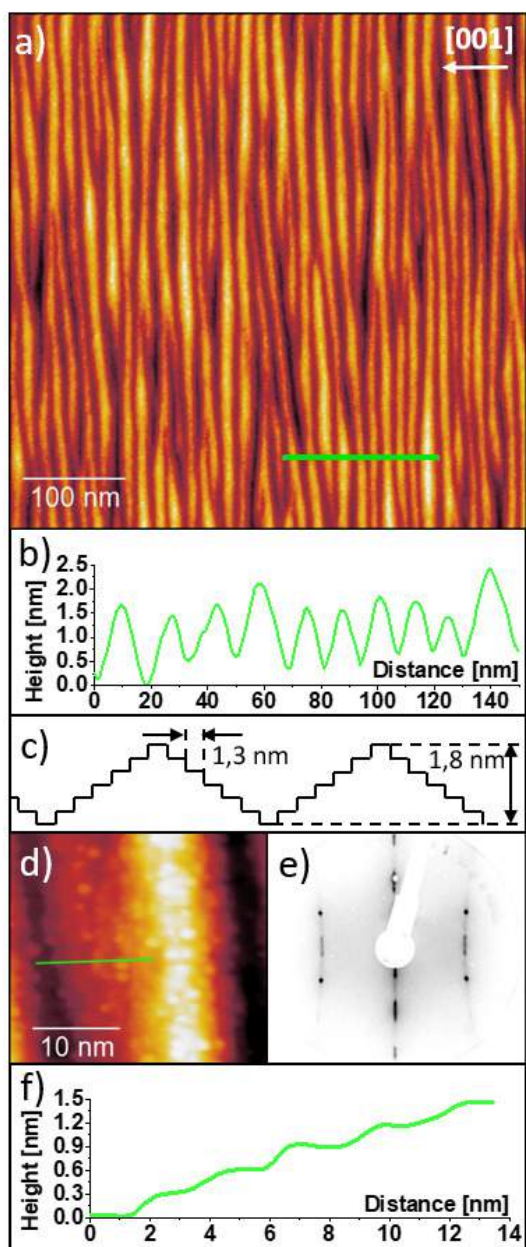


Figure 30 - A rippled $\text{TiO}_2(110)$ substrate: a) An STM image of exemplary rippled $\text{TiO}_2(110)$ surface ($U = 1.7$ V; $I = 15$ pA); b) a cross section profile from the marked area in a); c) scheme presenting stepped structure of ripples; d) an STM image of smaller area depicting stepped structure of ripples; e) a LEED pattern for the described specimen; f) a cross section profile from marked area in d).

similarly as in the previous subsection of the chapter, however, instead of the number of cleaning cycles, a grazing-angle ion bombardment was conducted, resulting in a modulated surface structure (Figure 30a). Depending on the incidence angle, a total ion fluence and the incidence correlation to the substrate's [001] atomic rows direction, different ripples in the regard of depth were achieved (modulation amplitude in the range of 1 – 3 nm). The obtained ripple period was rather similar and equalled 16 ± 2 nm. Therefore, shallow ripples with amplitude of about 1 nm consisted of 3-4 substrate terraces with average width of $\sim 2,6$ nm. Likewise, deeper ripples of 2 and 3 nm in height were built of 6-7 and 10-11 steps with average widths of $\sim 1,3$ nm and $\sim 0,85$ nm, respectively (Figure 30b-d,f). For such preparation, the grazing angles were in the range of $75 - 80^\circ$ (off normal), while the total fluence varied from $5 \cdot 10^{16}$ to $5 \cdot 10^{17}$ ions/cm². In the regard of the substrate's [001] direction, the incidence was either perpendicular or parallel. The sputtering of atoms for the former orientation is much stronger than that for the latter. Therefore, the grazing angle and the total fluence had to

be controlled very carefully. Also, the sputtering rate of Ti and O atoms are different, which requires the TiO_2 crystal to be kept at elevated temperature ($T = 500^\circ\text{C}$) in order to maintain both the stoichiometry and crystallinity of the surface. A fine crystallographic order was confirmed by a high quality LEED pattern (Figure 30e).

3.2.3 STM probes preparation

The probes for scanning tunnelling microscopy were prepared via chemical etching process, which quality was later verified with the SEM microscope. Both the tungsten and the platinum-iridium wires were processed with the diameter of 0,125 mm each. For tungsten etching a 3M NaOH solution in distilled water was prepared. Etching occurred through applying a direct voltage of 5V with the tungsten being a positive electrode and a counter-electrode of a gold wire in the form of a loop being a negative one. Setup was prepared in such a way, that the etched wire of interest would fall down into a small spiral making sure that the tip is not damaged (Figure 31a). The fallen piece had to be cleansed in water and immersed into isopropanol until the mounting on a proper holder and the introduction into the UHV system. However, it was recommended to check the probe with SEM and immediately move it into the UHV.

PtIr probes were etched with a different setup, where the wire was submersed into a 3M CaCl_2 solution (Figure 31b). Gold counter-electrode was utilized and an alternating voltage of 8V was applied until a cut-off current limit of 30 mA was reached. The final etched wire was outside of the solution. Contrary to the tungsten wires, platinum-iridium etched wires

can be kept in ambient conditions for longer periods of time before introduction into UHV chambers as STM probes. Sometimes, PtIr mounted probes were further processed in the SEM chamber with a focused ion beam. Carefully chosen sputtering parameters allowed for the preparation of very sharp tips (Figure 31c).

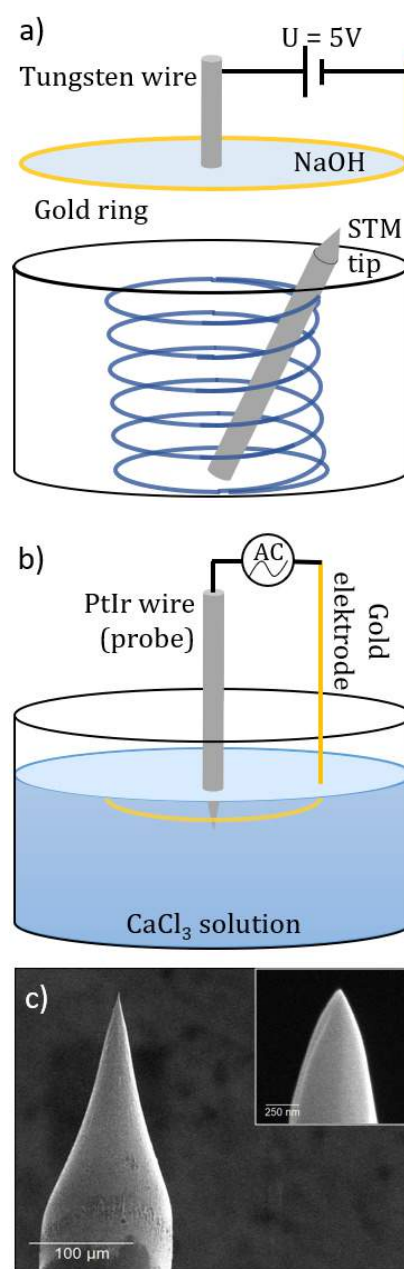


Figure 31 – a-b) Exaggerated schemes of setups for chemical etching of tungsten (W) and platinum-iridium (PtIr) wires; c) SEM images of FIB-processed PtIr tips.

3.3 Molecular deposition via UHV evaporation

Deposition was conducted via organic molecular beam epitaxy (OMBE). The titanium dioxide surfaces were exposed to the beam of molecules evaporated from a particular Knudsen cell. For each molecular cell (6P, 5A and DHTAP) the flux was measured and calibrated with the usage of a quartz microbalance (QMB) as a function of changing resonance frequency f_{QMB} in time [Hz/s] due to a change of its total mass. Further AFM and SEM imaging experiments, accompanied by the TDS spectra allowed for the calculation of the coverage as a function of f_{QMB} and thus as a function of time. Standard flux used for *para*-hexaphenyl deposition ranged from 0,15-0,20 ML/min, while for 5A and DHTAP a flux of 0,5 ML/min was applied. Here, a ML stands for a monolayer of flat-lying molecules, which is greatly different than a monolayer of up-right standing molecules due to their strong anisotropic shape. Such parameters required molecular cells to operate at the temperatures of 215, 140, 155 °C for the 6P, 5A and DHTAP, respectively. For all of the molecules different TiO₂(110) substrate morphologies were investigated as well as a wide span in terms of the coverage (range of sub-monolayer to a few multilayers). Specific parameters for each experiments are described in the following chapters dedicated to the results. OMBE was performed while keeping the substrate at room temperature for 6P and 5A deposition or at an elevated temperature for DHTAP growth.

Due to the specimen mounting system (sample holder presented in the Figure 28) and the current flow heating method, a special procedure had to be carried out during molecule deposition for TDS experiments. As the current flows not only through the sample, but

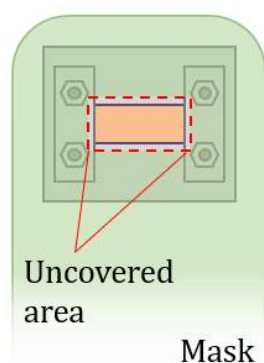


Figure 32 – A basic scheme of a mounted sample (top view) covered with a mica mask.

also through the holder, both of them are heated during any temperature proceedings. Therefore, any amount of molecules deposited on the holder result in additional signal recorded by the MS during TDS, which leads to incorrect spectra received. The usual methods in such cases concern either the sample-spectrometer distance reduction and covering of any irrelevant areas during thermal desorption or a proper restriction of deposition areas during deposition. In the used UHV system only the second method, which required preparation of a mask with a properly shaped and positioned hole (Figure 32), was possible. Such cover was made out of mica, since an insulating material

was required – some depositions were performed at elevated substrate temperatures and the mask had to be as close to the specimen as possible, often leading to physical contact between them. The difference between results obtained from depositions with and without proper covering are later presented and discussed in chapter five.

3.4 Density functional theory – simulation details

Calculations were performed by prof. dr hab. Mariusz Krawiec from the Institute of Physics of Maria Curie-Skłodowska University in Lublin. They concern the *para*-hexaphenyl molecules on titanium dioxide substrate. The energetically optimized structural model of the interface was received, as well as the value of adsorption energy per molecule. From the DFT charge redistribution within both the molecules and the substrate were obtained. In addition, density of state (DOS) maps were simulated for comparison with the STM experimental data.

The van der Waals corrected exchange–correlation functional (vdW-DF) available in the Vienna ab initio simulation package (VASP) [163,164] and the spin-polarized DFT with the projector augmented waves (PAW) [165,166] were used for first-principles calculations. For all calculations, the optB86b-vdW implementation of the vdW-DF method was used [167–169]. An energy cut-off restriction of 700 eV was set for the plane-wave basis. The Brillouin zone was sampled by a $2 \times 8 \times 1$ Monkhorst–Pack k-points grid, including the Γ point [170]. A criterion of 10^{-6} eV was chosen for the total energy convergence. A slab of 4 atomic layers had been used for the titanium dioxide substrate modelling with a vdW-DF level surface unit cell of $29,62 \times 6,45 \text{ \AA}^2$ – $\text{TiO}_2(110)$ (10×2) – containing 302 atoms in total. In order to avoid interaction between surfaces in the slab, a vacuum region of $16 \text{ \AA}$ was added. A conjugate gradient method was utilized for the atomic positions relaxation with the exception of atoms in the bottom layer, where atoms were fixed at their bulk ideal positions. A requirement of the maximum force in any direction was set to be smaller than $0,01 \text{ eV/\AA}$.

Chapter IV

***Para*-hexaphenyl structures grown on TiO₂(110)**

The following chapter is dedicated to the study of the *para*-hexaphenyl interface with the TiO₂(110) surface. In the first sections a summary of general 6P growth modes is presented. The main focus of the chapter is provided in the second and the third sections regarding the morphology of the 6P wetting layer. The last section is a description of the studies and findings about electronic and energetic properties. Experimental results are supported by the presented DFT simulations.

4.1 Differently shaped structures of *para*-hexaphenyl on TiO₂(110)

The formation of particular 6P structures grown on titanium dioxide strongly depends on the substrate's morphology and the overall deposition coverage [52–57]. Naturally anisotropic TiO₂(110) induces a single observed orientation of flatly lying molecules. Therefore, a proper preparation of the substrate surface in regard of certain parameters greatly influences the type and shape of the resulted structures. *Para*-hexaphenyl can either form more or less anisotropic islands or strongly elongated nanoneedles with a possible “2-dim” molecular wetting layer underneath. The following subsections describe attributes of the grown 3-dim-6P structures and aspects that affect the growth processes, as well as introduce the idea of a single complete primary layer.

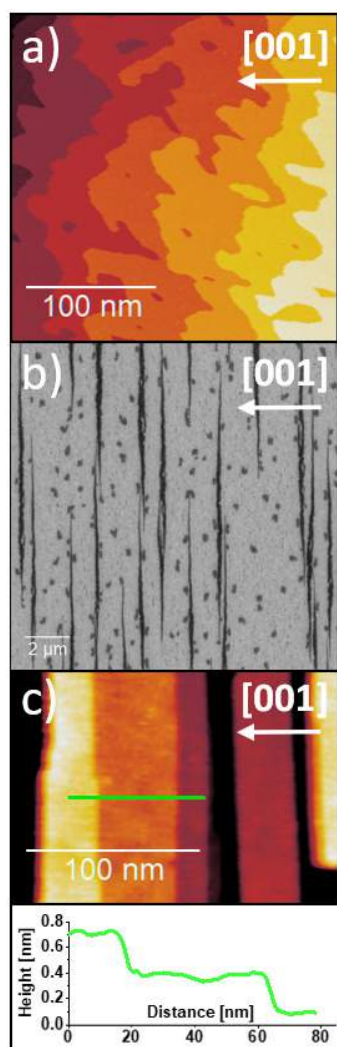


Figure 33 – Exemplary images of 6P nanoneedles on TiO₂(110): a) STM substrate image; b) SEM nanoneedles image; c) AFM of nanoneedles' top layers with a cross section profile taken along the marked line.

4.1.1 Layered crystalline 6P nanoneedles

Deposition of a few MLs of *para*-hexaphenyl molecules on atomically flat (terraced) TiO₂(110) (Figure 33a) leads to the formation of strongly elongated nanoneedles. Figure 33b presents SEM image of described structures with their dark contrast originating from transparency to the primary high energy electrons and blocking of the substrate's secondary electrons. Nanoneedles are regularly μm-long, hundreds of nm-wide and a few nm-high entities with their long axes perpendicular to the [001] direction (substrate's atomic rows direction). XRD studies by Koller *et al* revealed the crystal inner structure of the needles [171]. It was shown that the single adopted crystalline orientation of 6P is (20 $\bar{3}$). Therefore, a layer by layer growth of the structures was expected. More detailed AFM investigation of the nanoneedles indeed displays their layered structure (Figure 33c). Average layer height equals 0,36 nm, which originates from the bulk tilt of the molecules of about $\pm 34^\circ$ with respect to the substrate plane. One can also notice, that the 6P molecular long-axis orientation with respect to the substrate is parallel to the atomic rows.

Further studies of the coverage dependence of the resulted structures show non-uniform distribution of the needles across the substrate with the increase of deposited molecules. Instead of even occurrence raise, so-called “bunches” or groupings are formed with the central needle being the longest and the highest and the outer needles the smallest. The “bunching process” was described in detail by Wrana *et al* [53].

4.1.2 Islands of 6P on the ion-modified titanium dioxide

Modification of the $\text{TiO}_2(110)$ surface morphology to the form of nanoripples (Figure 34a) influences and drastically changes molecular lateral diffusion and structures growth processes. Increase of the substrate height modulation amplitude in a certain area enlarges the amount of step-edges concentration, which results in the lowering of the average molecule-substrate interaction due to the enforcement of the over-the-edge molecular arrangement. Thus, with steep-enough ripples the overall molecule-substrate interaction becomes lower than the molecule-molecule interaction causing the formation of a different type of 6P structures – the islands (Figure 34b). They are built of molecules with their long axes perpendicular to the substrate’s plane and, therefore, can be called “up-right standing” islands – their average height of 2,7 nm complies with the 6P molecules length (Figure 34c).

The island’s shape strongly depends on the average ripple depth as it strengthens the surface diffusion anisotropy [52,54]. The general trend is the larger the ripples’ amplitude, the more elongated the islands. A further rise in the 6P coverage leads to the increase of the islands’ occurrence and vertical growth of consequent “up-right standing” levels on top of each other, instead of a full and compact single layer on $\text{TiO}_2(110)$.

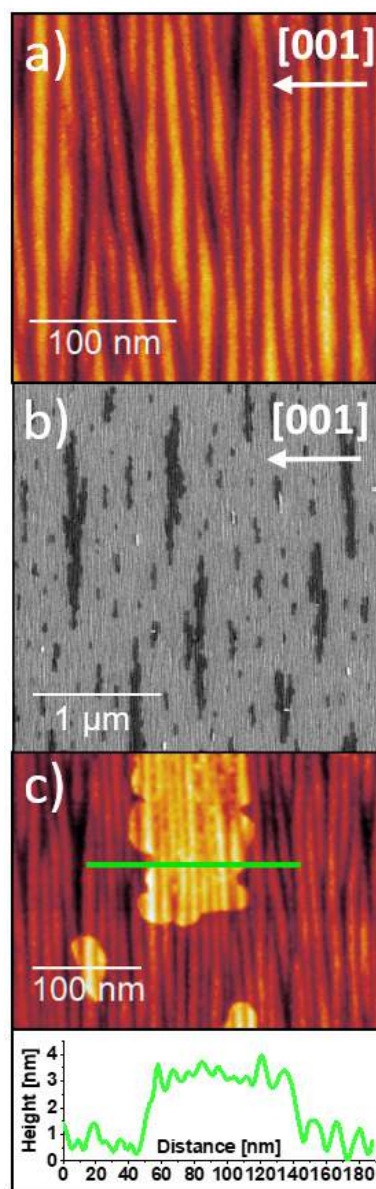


Figure 34 – Exemplary images of 6P islands on rippled $\text{TiO}_2(110)$: a) STM substrate image; b) SEM islands image; c) Air-AFM of 6P islands with a cross section profile taken along the marked line.

4.1.3 Indication of a 6P molecular wetting layer existence

As described in the chapter III, molecular deposition takes place in the UHV system. *In situ* imaging can be performed up to an area of $6 \times 6 \mu\text{m}^2$ due to scanner limit. Therefore, in order to obtain larger scale pictures samples were often moved out of the primary UHV setup and imaged either with SEM or with ambient AFM microscopes. While investigating 6P/TiO₂(110) samples exposed to air conditions, one could notice the existence of additional structures around 6P nanoneedles (Figure 35a). A similar effect was observed for some of the samples with up-right standing 6P islands (Figure 35b). These structures have been considered to be formed as a product of the degradation of a 6P molecular wetting layer during ambient conditions exposure [51,53,55,56]. Such process can be called as “*de-wetting*” of the very first 6P monolayer. The structures don’t possess any distinctive shape and they are rather round with a regular height of a few nm and lateral diameter of tens of nm. However, their mean size and distancing differs depending on the TiO₂(110) surface roughness. An additional interesting effect can be observed in the areas nearby nanoneedles or islands. Some of the areas close to the former 6P structures are empty of the newly-formed clusters (green arrow markings in the Figure 35a-b), often referred to as “*crystallites*” [53,54,57]. This fact can be explained by an idea of the de-wetting molecules diffusing towards the needles/islands and expanding them during air exposure. Effects of such a process are visible in a change of the nanoneedles height by a few nm and an increase of islands’ lateral dimensions in comparison to the *in situ* obtained images. Furthermore, for the latter, one can distinguish an inner part of the island that belongs to the primary growth in UHV and the outer part originating from the

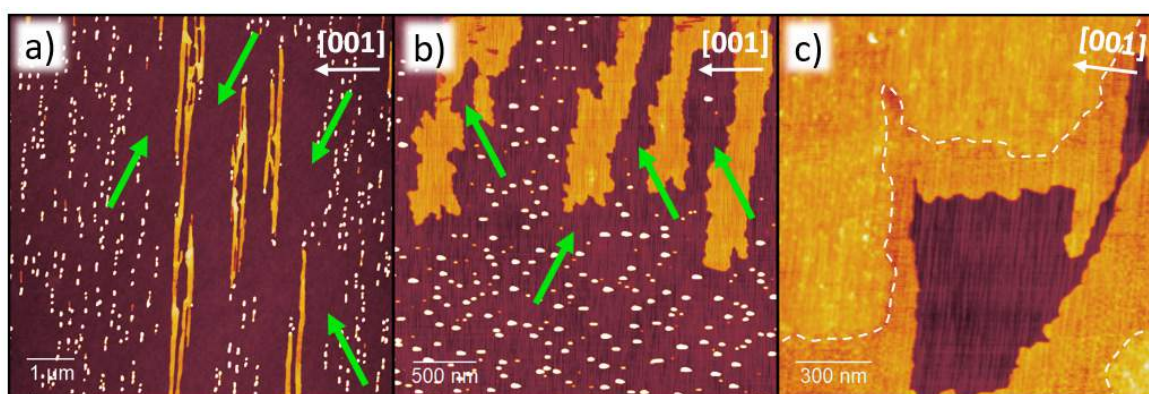


Figure 35 – Tm-AFM images of para-hexaphenyl molecules on TiO₂(110) in air conditions: a) nanowires with 6P clusters nearby separated by denuded zone; b) 6P islands with clusters nearby separated by a denuded zone; c) 6P islands with outer rim of different origin.

de-wetting (white dashed lines in the Figure 35c). Areas empty of the de-wetting clusters are called “*denuded zones*” or “*depletion zones*”. Some of the morphologically modified substrate $\text{TiO}_2(110)$ samples with 6P islands lack the described de-wetting structures, which originates from the lack of the wetting layer. Details of this fact are described in the following subsection of this chapter. However, despite the indirect proof of the wetting layer existence in general, it wasn’t previously investigated in detail. Such research seems crucial as the interface between 6P and $\text{TiO}_2(110)$ is of great importance when it comes to the electronic properties.

4.2 First look at the 6P molecular wetting layer

In order to get a direct proof of the 6P wetting layer existence – its image – a few experiments were carried out with atomically flat $\text{TiO}_2(110)$ prepared with a dozen of cleaning cycles. Coverages of little over a single layer were used, while deposition was performed on the substrates kept at room temperature. Samples were investigated with both the STM and the LEED. The following subsections focus on the general appearance of the wetting layer and the ordering of the molecules within it.

4.2.1 STM morphology of the monolayer

Figure 36a presents an STM image of a flat $\text{TiO}_2(110)$ monocrystal covered with a single layer of *para*-hexaphenyl molecules. Differences in contrast of large areas originate from the substrate's terraced structure – not from additional layers of the molecules. On the image, one can distinguish single molecules flatly lying on the $\text{TiO}_2(110)$ surface with their long axes oriented parallel to the $[001]$ direction. The molecules are closely packed, side by side, forming so-called “*molecular stripes*”, as the ones marked with the dashed green lines. These stripes are on average parallel to the $[1\bar{1}0]$ direction (perpendicular to the substrate's atomic rows) with slight deviations originating from the possible small shifts between the adjacent molecules. The displacements are equal to a multiple constant of $1/12^{\text{th}}$ of the molecule's length (Figure 36b). This is equivalent to the shift of at least one half of a phenyl ring (Figure 36c). The average width of the molecular stripes is $2,90 \pm 0,05$ nm, which is slightly larger than the length of the 6P

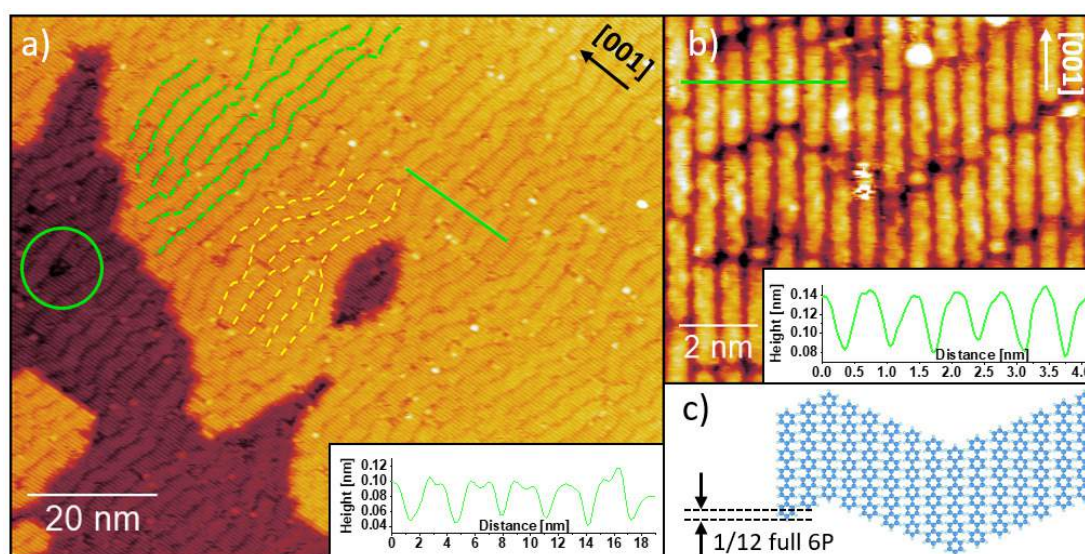


Figure 36 – STM images of *para*-hexaphenyl monolayer on top of $\text{TiO}_2(110)$: a) an overview of large area with depicted important features; b) small area scan with individual molecules/phenyl rings visible; c) scheme of neighbouring molecules displacement (top-view).

molecule – van der Waals dimensions $\sim 2,72 \times 0,65 \text{ nm}^2$ [172,173]. Periodicity in the $[1\bar{1}0]$ direction equals 0,65 nm and is exactly the same as the molecule's width and the distancing between the substrate's protruding oxygen rows. Therefore, such alignment visible in STM is strongly favourable.

The irregular, meandering shapes of the molecular stripes are strictly correlated to the $\text{TiO}_2(110)$ surface terrace structure. The *para*-hexaphenyl molecules, that are in frontal contact with the substrate's step-edge, resemble the contour of the edge line creating a similarly shaped stripe (Figure 36a). The curvature propagates over the particular terrace, as depicted by the yellow dashed lines. Having that in mind, it is obvious that the contact areas of differently shaped stripes occur, resulting in the wetting layer defects. An example of such irregularity is a truncation-like defect, where the stripes' shape forces termination of one stripe between the neighbouring ones. In such areas the space between the "closing stripes" along the $[001]$ direction is too small to fit a whole 6P molecule (green circle in the Figure 36a). Interestingly enough, the molecule-free area is not occupied by differently oriented 6Ps, but is rather kept empty. This observation means that any different flat orientation of the *para*-hexaphenyl molecule than parallel to the $[001]$ direction is greatly unfavourable. Other defects visible on the STM images stem from the substrate defects present prior to the molecular deposition.

Behaviour of the 6P molecules near the $\text{TiO}_2(110)$ step-edges is excellently visible on the areas with small titanium dioxide terrace islands. Figure 37a presents such

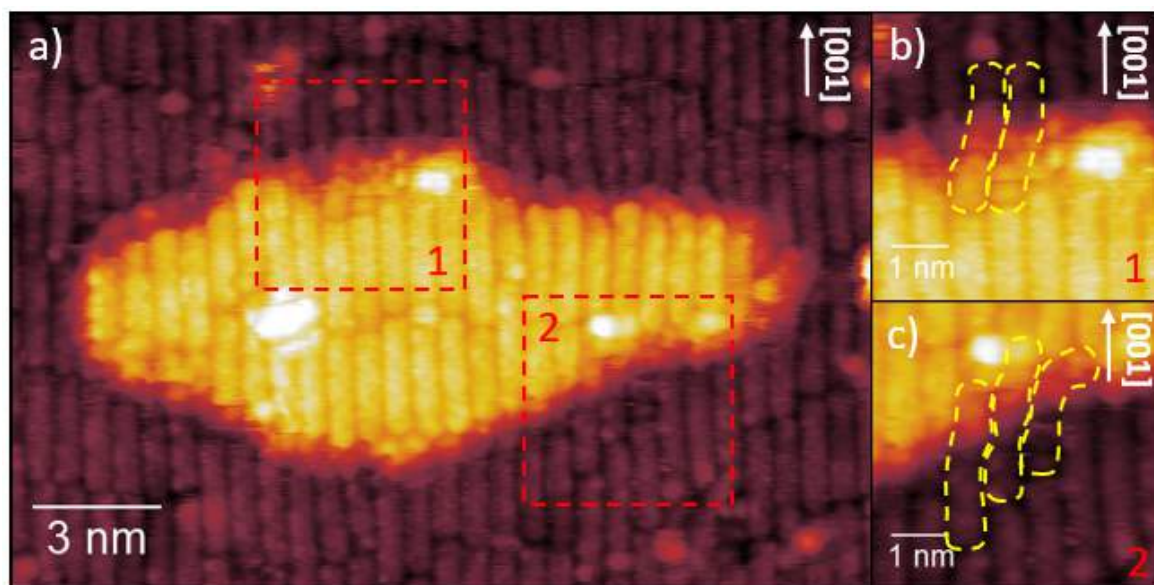


Figure 37 – STM images of *para*-hexaphenyl molecules on top of $\text{TiO}_2(110)$: a) an overview of a substrate terrace island; b-c) selected small areas (1, 2) of a) with individual over-the-edge molecules depicted by yellow dashed lines.

a region covered with *para*-hexaphenyl molecules. Within the lower substrate terrace one can clearly observe the already discussed frontal adhering on both sides of the higher terrace. On the upper terrace, the molecules fill the substrate as tight as possible along the [001] direction. However, due to the island's dimensions in this direction, it can't always accommodate an integer number of 6Ps. Therefore, some of the molecules bend over the step-edge in order to maintain the correlation with the substrate's atomic rows (Figure 37b-c). The twist in the perpendicular direction $[1\bar{1}0]$ stems from the crystallography of titanium oxide. Atomic rows of the subsequent higher/lower terraces are shifted by a half of the $[1\bar{1}0]$ lattice constant with respect to the former terrace. As the resolution in the Figure 37 allows for distinguishing particular phenyl rings within the 6P molecule, one can easily recognize, that the molecules can hang over the step-edge via any of its building blocks. All these observations, once again, confirm the strong interaction between the *para*-hexaphenyl and the substrate's atomic rows.

4.2.2 A Short-range and a long-range order within the wetting layer

A great technique for pattern investigation and crystalline-like structures studies is LEED. It provides information averaged over larger areas, while still being sensitive to short-range ordering. For molecular layer studies – especially a molecular monolayer – one has to utilize electron energies of ~ 20 eV with as small a beam current as possible. This is required so that the signal comes from the very first specimen layers and the molecular structures are not destroyed or degraded by the electrons. Figure 38a shows an obtained LEED pattern for *para*-hexaphenyl monolayer on $\text{TiO}_2(110)$ with the substrate's reflexes (0,1) and (0,-1) depicted by yellow colour and the 6P's satellite reflexes around them marked with blue colour. The LEED experiments that have been performed, allowed for observation of only the first additional reflexes from spot splitting as the signals were very weak. The profile presented within Figure 38a enabled deducing the periodicity in [001] direction of 5,82 nm, which is equivalent to roughly double the STM molecule's length. Hence, one can assume that the constructive interference of the scattered electrons occurs between every second molecular stripe and not every nearest neighbouring stripe.

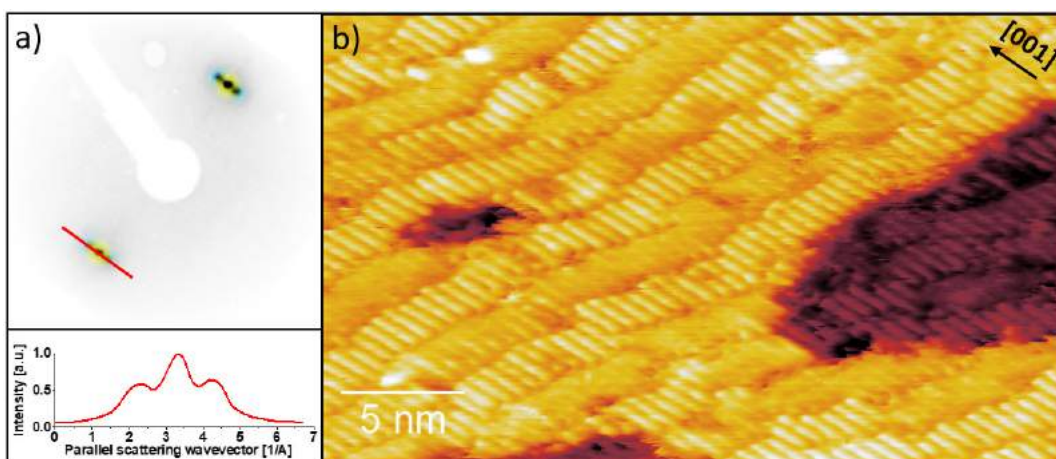


Figure 38 – Para-hexaphenyl molecular stripes differences: a) LEED pattern of a 6P wetting layer; b) STM image exhibiting stripe dissimilarities.

Further STM imaging indeed revealed differences in the appearance of the consecutive 6P stripes. Figure 38b presents such inequality of adjacent stripes. In general, one can clearly distinguish singular molecules in every second stripe, while the other half of the stripes appears to be more blurred and smeared out. Such a visual appearance can be explained by the differences in the arrangement of the 6P molecules with respect to the $\text{TiO}_2(110)$ substrate and an unsymmetrical STM probe. Nevertheless, such images are in line with the obtained periodicity from LEED patterns.

Considering the perpendicular direction of $[1\bar{1}0]$ no additional diffraction maxima originating from a different than the substrate's periodicity were found. This is in line with the wetting layer periodicity in this direction measured with STM. From such an observation one can conclude that within the stripes the molecules are distributed and oriented similarly with respect to the $\text{TiO}_2(110)$ surface.

4.2.3 The limiting factor for the wetting layer formation

As already mentioned, the 6P wetting layer can also arrange itself on a much more sophisticated $\text{TiO}_2(110)$ surface in regard of morphology, i.e. on the ripples. Even a strong modulation of the substrate's surface doesn't prevent a formation of the monolayer. Despite a high concentration of the titanium dioxide step-edges, the wetting layer can still be assembled, as shown via previously discussed degradation process due to air exposure (Figure 35b). However, clusters from degradation don't emerge on every rippled specimen, indicating that the WL doesn't always form. When preparing rippled samples, one has to realize that the topographic modulation can be differently oriented with respect to the materials' crystallographic directions. Considering the above and the

6Ps' strong correlation towards the [001] direction, it makes the ripples' crystallographic orientation crucial. Within the scope of this work only two extreme cases of parallel and perpendicular orientations with respect to the substrate atomic rows were investigated. On a $\text{TiO}_2(110)$ rippled along the [001] direction, 6P forms a wetting layer almost regardless of the surface modulation (Figure 39), as the molecules can fit even very narrow terraces [56]. Considering such oriented ripples with average depth of ~ 2.5 nm and average terrace width of ~ 1.1 nm (Figure 39), one or two molecules should still easily fit the narrow shelves with their long axes aligned with the substrate's atomic rows, forming the wetting layer. It is proven by the clusters formation after air exposure, as presented in the Figure 39b. The compact character of the wetting layer grown on ripples was directly observed for shallow ripples with average modulation amplitude of ~ 1 nm and atomic terrace width in the range of a couple to about 10 nm (Figure 39c-d). Similarly, as presented in the previous subsection, 6P molecules show very strong correlation to the [001] direction, with a tendency for bending at the $[1\bar{1}0]$ step-edges if forced by the frontal neighbours (green arrow markings in the Figure 39d). Molecules at the very top

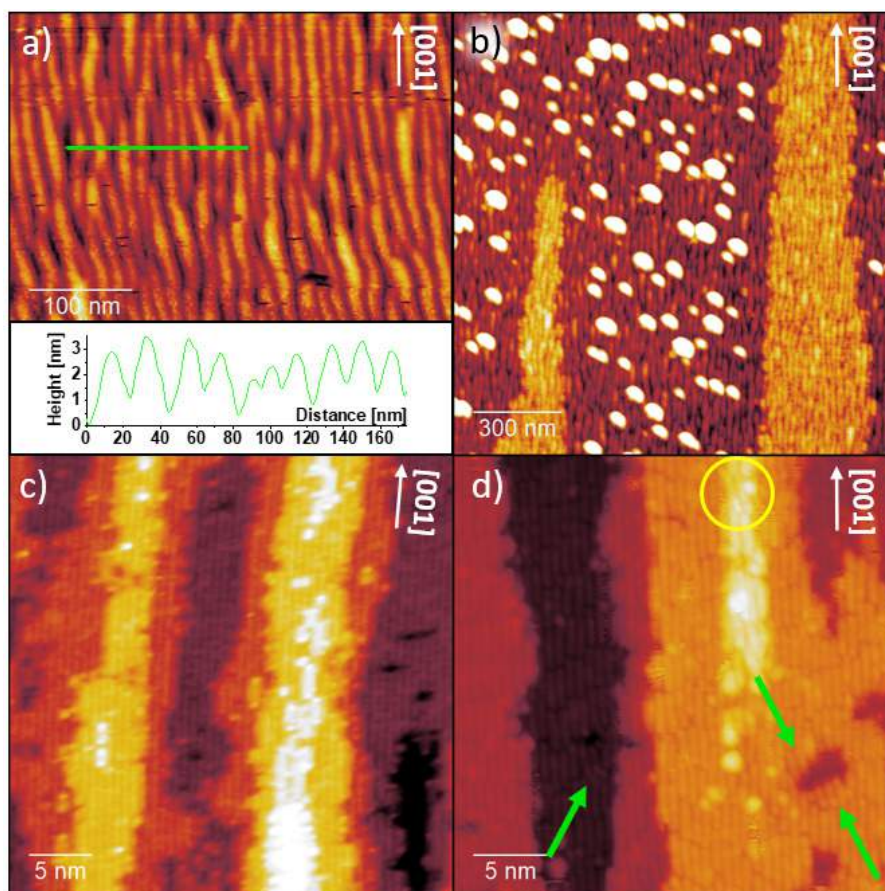


Figure 39 – Para-hexaphenyl wetting layer formation on the $\text{TiO}_2(110)$ rippled along substrate atomic rows direction: a), c) STM images of deep/shallow substrate ripples; b) a tm-AFM image of 6P islands with de-wetted clusters around them; d) molecularly-resolved STM of the 6P WL on the shallow $\text{TiO}_2(110)$ ripples.

areas are sometimes slightly rotated, which most probably stems from the very narrow character of the terraces, i.e. “1-2” substrate atomic rows (yellow circle in the Figure 39d). For the perpendicular orientation of the ripples, the surface modulation – and hence the step-edge concentration – plays a key role when it comes to the monolayer assembly (Figure 40). Terraces that are too small ($< 2,6$ nm) don’t fit whole 6P molecules (Figure 40b), which would require either over-the-edge bending or a different adsorbing orientation. While the former was observed and presented, the latter was proved and discussed as not occurring in previous subsections. However, the bent and twisted molecules developed only to fill the gaps in the well-ordered and compact layer, not as stand-alone entities or general features. Therefore, on ripples perpendicular to the substrate’s atomic rows direction with too narrow step shelves, 6P wetting layer is not formed. In such cases deposited molecules create meta-stable layer of mobile 6P molecules – a so-called “2D lattice gas” [56]. Further increase of molecular coverage leads to the formation of up-right standing islands. Lattice gas preserves its form until air exposure, when very mobile molecules are forced into certain conformations by the interaction with adsorbates. During such reformation two processes take place. Molecules in the close neighbourhood of up-right standing islands formed already in the UHV during molecular deposition adjoin them, resulting in their lateral expansion. Broadened parts of the islands differ from the former areas (white line marking in the Figure 40d), similarly to the development during de-wetting of the compact monolayer. Concurrently, 6Ps that were farther away from the initial islands, form small up-right standing islands on their own (Figure 40c). The described process results in bimodal island size distribution.

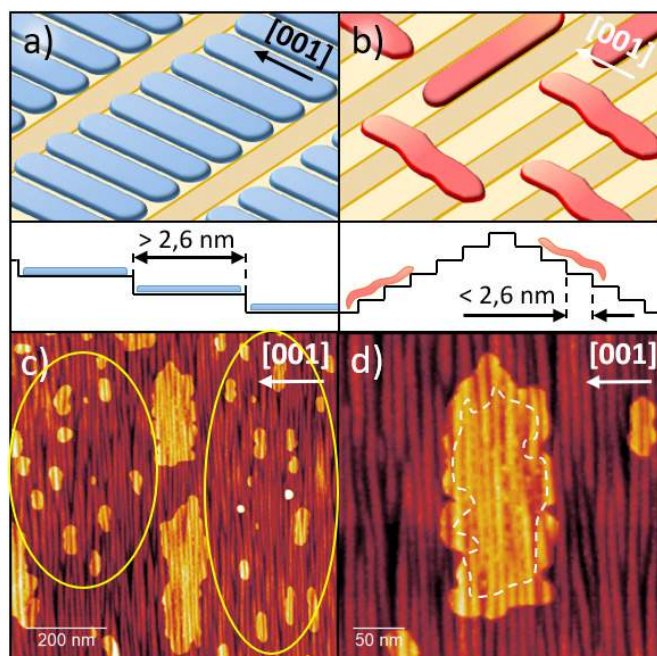


Figure 40 – Para-hexaphenyl molecules on the $\text{TiO}_2(110)$ rippled perpendicular to the substrate atomic rows direction: a), b) exaggerated schematic images presenting 6P molecules lying on ripples; c) *tm*-AFM image of two types of 6P islands – large grown in the UHV and small grown during air exposure; d) *tm*-AFM image of the former 6P islands with marked outer areas originating from expansion during air exposure.

4.3 In-depth studies of the 6P/TiO₂(110) interface

As the inner structure of the 6P molecular wetting layer on titanium dioxide remained unknown, further investigation was needed. In order to reveal more information regarding the interface additional experiments were carried out with sub-monolayer and monolayer coverages. The former took advantage of a possibility to uncover the buried substrate topography and the latter was continued until a high-resolution STM images were obtained. This part of the work was supported by the DFT simulations regarding both the structural model and the density of states (DOS) appearance of the 6P molecules on TiO₂(110).

4.3.1 A sub-monolayer 6P coverage STM

In order to investigate the exact position of the 6P molecules over the TiO₂(110) atomic rows a sample was prepared with a coverage of 0,4 ML. Figure 41 shows STM image of such surface. Molecules, visible as bright features, are clearly longer than previously measured 2,9 nm. Such appearance can be explained by the molecules' movement along the [001] direction with the protruding oxygen rows acting as rails. The mobility can either originate from the room temperature energy or, alternately, be a result of STM imaging itself. Nevertheless, the periodicity in the $[1\bar{1}0]$ direction of 0,65 nm is preserved. Within the image, one can select areas, where the substrate surface is revealed (yellow circle in the Figure 41). By drawing a cross section profile for such a region perpendicular to the molecules' long axes, one can determine whether the 6P's center of mass lies over the titanium rows or the oxygen rows. Because of the positive BIAS of

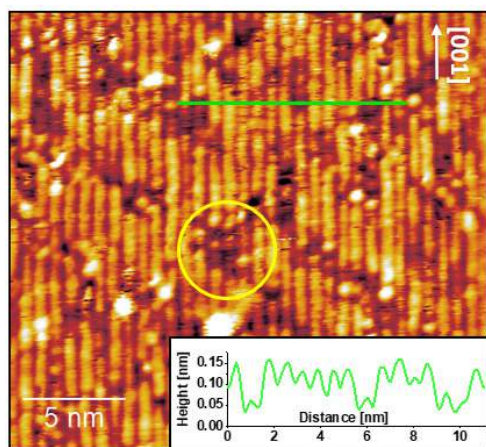


Figure 41 – STM image of 6P/TiO₂(110) specimen with the sub-ML coverage of the molecules.

+1,7 V being applied to the specimen, STM probes the empty states of the TiO₂(110) substrate. This results in Ti atoms appearing as bright (“higher topographically”) and O atoms being dark (“lower topographically”). Hence, the presented cross section profile in the Figure 41 shows, that 6P molecules lie over the Ti (5f) atoms. During imaging only the movement along the [001] direction was observed with no hopping over the oxygen rows along the $[1\bar{1}0]$ direction.

Within the same experiment it was found that the molecules' mobility is mostly a thermally activated process. On the sample, an area that contained a step-edge roughly perpendicular to the surface atomic rows was chosen. This particular area was scanned many times, one after another, with only one chosen slow scan direction – from the bottom to the top. With such a procedure the molecules “pushed” through scanning would have moved towards the step-edge, where they would have gathered and anchored. However, no such behaviour was observed during the experiment (Figure 42a-c). The number of molecules being in frontal contact with the upper terrace edge didn't increase and the distribution of moving molecules along the oxygen rows looked roughly the same. Therefore, one can assume, that the 6Ps' movement does not originate from the STM scanning (tip-induced) or, at least, it is not the major component.

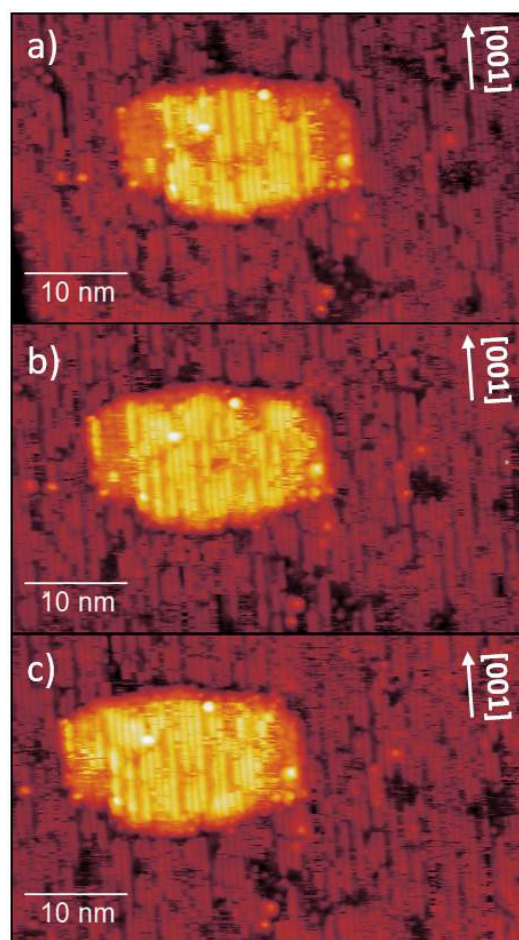


Figure 42 – STM images of consecutive STM scans of the same area with constant slow scan direction (upwards): a) first scan; b) third scan; c) fifth scan.

4.3.2 HR-STM of 6P at the monolayer coverage

Figure 43 presents the HR-STM images of the 6P wetting layer supported by the corresponding DOS maps from the DFT calculations. The sample was imaged with two different sample BIAS applied to the specimen, i.e. +1,3 V (Figure 43a) and +1,8 V (Figure 43b). On the experimental images one can clearly distinguish single phenyl rings within the molecules. On the provided DFT data subsequent phenyl rings of 6P molecules appear as bright, two-lobed structures that are rotated by a 90° with respect to each other. Same effect is visible on the STM images, however, it is not as clear as in the simulations – vertical lobes are distinguishable much easier than the horizontal ones. What is more, for the +1,8 V sample BIAS (Figure 43b) a clear non-uniform contrast of the molecules is visible with one side along the short axes appearing brighter than the other side.

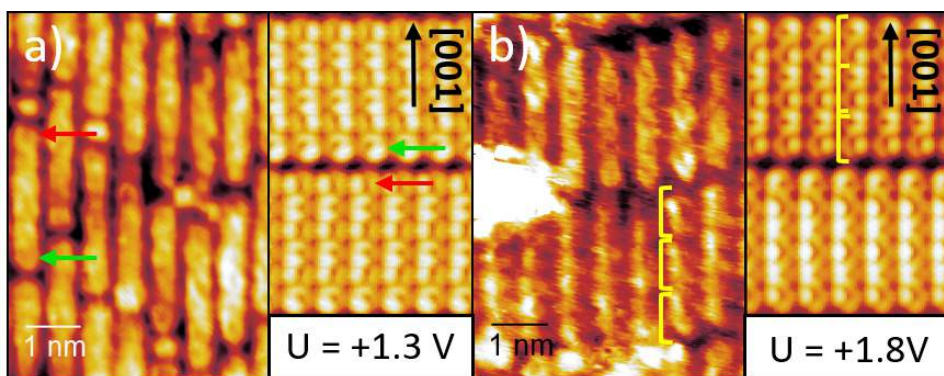


Figure 43 – HR-STM images of $\text{TiO}_2(110)$ covered with a compact layer of 6P molecules: a) image taken with sample BIAS = + 1.3 V; b) image taken with sample BIAS = + 1.8 V.

Such a look is different for the +1,3V (Figure 43a), where the molecules appear to be more “flat”. In addition, one can observe, that the contrast of the neighbouring molecular stripes is, on average, different, which was already noted in the previous subsections. In the Figure 43 it is visible for both the STM image and the DFT DOS maps.

Performed simulations revealed the energetically optimized structural model of the 6P molecules on the $\text{TiO}_2(110)$ substrate (Figure 44). The relaxation lead to the molecular distancing of 0,645 nm and 2,96 nm in the $[1\bar{1}0]$ and the $[001]$ directions, respectively. These values are in a great agreement with the presented STM measurements. As clearly visible in the Figure 44, a non-planar 6P conformation is adopted with the 6Ps’ short axes

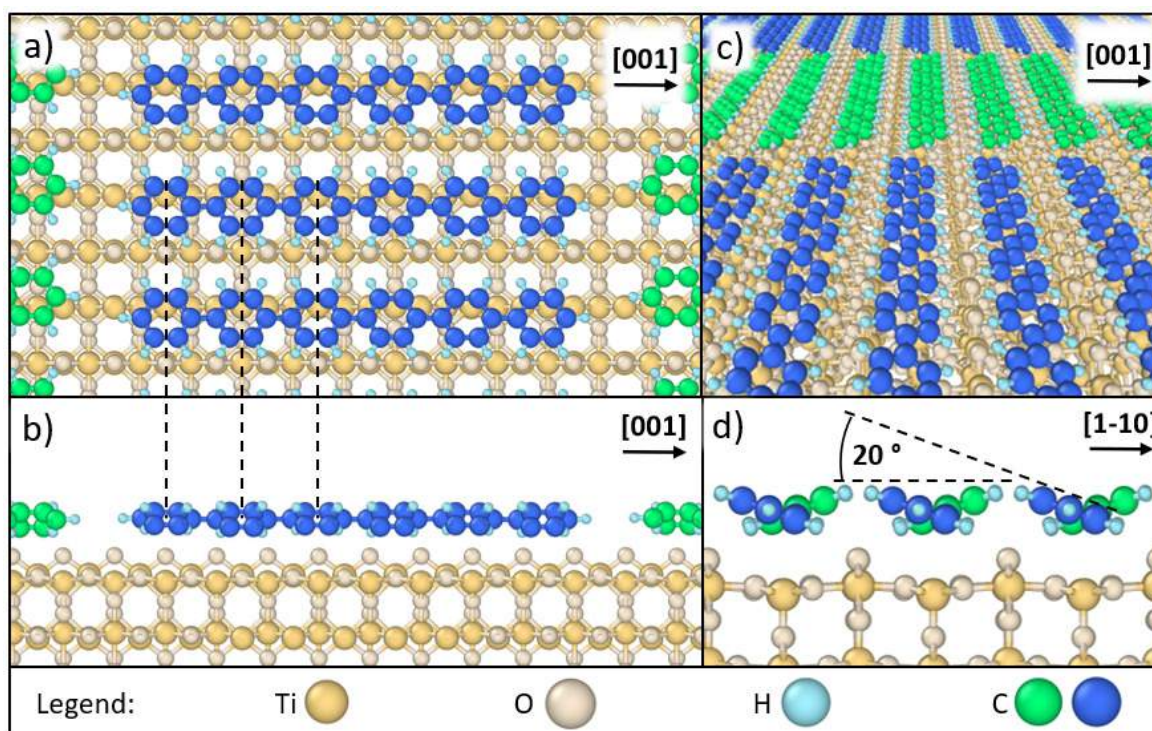


Figure 44 – Structural model of 6P molecules within the wetting layer on $\text{TiO}_2(110)$ obtained with DFT simulations: a) top view; b) side view showing positioning of the molecules over substrate atoms; c) perspective view; d) front view showing tilting of the molecules with respect to the substrate plane.

tilt of 20° with respect to the substrate plane. This fact explains the non-uniform STM contrast of the molecules. Furthermore, as depicted by differently coloured 6P molecules in the Figure 44, a configuration of alternately tilted molecules of the neighbouring stripes is energetically the most favourable. Thus, the 6P wetting layer has a rectangular unit cell of a $5,92 \times 0,645 \text{ nm}^2$, which is in excellent agreement with the previously presented LEED results – $5,82 \times 0,65 \text{ nm}^2$. The optimized structural model allowed for determination of the molecule placement over the substrate's Ti atoms along the [001] direction (Figure 44b). As can be observed, the neighbouring phenyl rings are positioned over different Ti atoms in regard of the substrate's unit cell. However, every second phenyl ring within the molecule lies over a similar substrate's Ti atom. Thus, such a feature has a direct impact on the STM imaging with a described two-lobed appearance of the phenyl rings (Figure 43). This difference is best visible on the outermost rings of the molecules, as they have to be positioned over dissimilar Ti atoms (arrow markings in the Figure 43a). Furthermore, one can group phenyl rings into pairs, creating 3 equivalent segments within a 6P molecule, which is also sometimes distinguishable in the STM data (green markings in the Figure 43b).

The theoretical and experimental data provided, shows the same information in regard of the 6P/TiO₂(110) interface inner structure. Therefore, one can conclude that the presented findings greatly represent the real conformation.

4.4 Characterization of the interaction within the 6P/TiO₂(110) interface

When considering material surface properties, adsorbing molecules on top cause changes in many aspects. Molecules themselves are bound with the substrate by a certain energy, depending on the interaction nature. Electron states of the developed interface can be vastly different than the former ones. Therefore, the specimen work function of the TiO₂(110)/6P interface can be modified with respect to the bare TiO₂(110). The following subsections present the experimental and simulated data regarding these matters.

4.4.1 Electronic properties

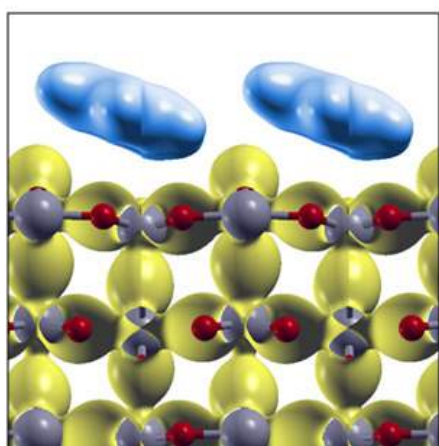


Figure 45 – Charge density isosurface of the 6P/TiO₂(110). System calculated with DFT at the isovalue of $3 \times 10^{-5} \text{ e}/\text{\AA}^3$.

With the DFT simulations, the nature of a molecule-substrate interaction within the studied interface was investigated. The bonding between *para*-hexaphenyls and the titanium dioxide substrate is primarily non-covalent, which can be seen in a presented image of a calculated isosurface of the charge density (Figure 45). Within the interface, due to a total interaction, a charge redistribution in both the TiO₂(110) and the 6Ps occur. The analysis determines the existence of a small charge transfer from 6P molecules to the

substrate of 0,26 e⁻/molecule. As molecules donate electrons from H atoms, the overall molecular tilt induces different participation in the charge-transfer of particular hydrogens. H atoms that are closer to the substrate surface donate more electrons than the top-most ones. This results in an asymmetry of charge within the molecules and, thus, the emergence of a small dipole moment of 0,09 D towards the TiO₂(110). Moreover, the substrate surface experiences a transfer from Ti to O atoms with the strongest changes affecting elements positioned directly under 6P molecules. Titanium atoms become less positively charged, while oxygen atoms' negative charging is increased. However, the in-surface O atoms are slightly more negatively charged than the O atoms from the substrate's protruding atomic rows – the latter are positioned between the molecules. Yet, the ion interaction between 6P and TiO₂(110) is very limited and the overall interaction is dominated by van der Waals forces.

The already mentioned electron redistribution and induced dipole moment should affect the surface work function by a slight decrease. KPFM measurements allowed for work functions determination for both the bare substrate and the $\text{TiO}_2(110)$ covered with the 6P monolayer. For the two, the experiments were carried out separately, one after the other, due to the sub-monolayer coverages being unstable with the molecules distributed uniformly among the surface, rather than forming monolayer islands. After the KPFM performed on a bare $\text{TiO}_2(110)$, the 6P molecules were deposited in excess to ensure the growth of a full, compact wetting layer. This led to the formation of small nanoneedles, which did not affect the monolayer measurements. Throughout the series of KPFM imaging the tip was calibrated on a reference of a cleaved HOPG sample, which has a well-defined work function of ~ 4.5 eV [174,175]. Therefore, it was possible to determine the absolute work function values for the investigated surfaces. Figure 46a-b shows the KPFM morphology and the CPD map of the $\text{TiO}_2(110)$ covered with 6P molecules. *Para*-hexaphenyl monolayer lies in between the nanoneedles, however, due to the imaging resolution it is not distinguishable. The attached histogram for the WF map (Figure 46d) indicates a clear difference between the values from the monolayer areas and the nanoneedles (multilayer) areas. Prior measurements of a bare $\text{TiO}_2(110)$ WF allowed for

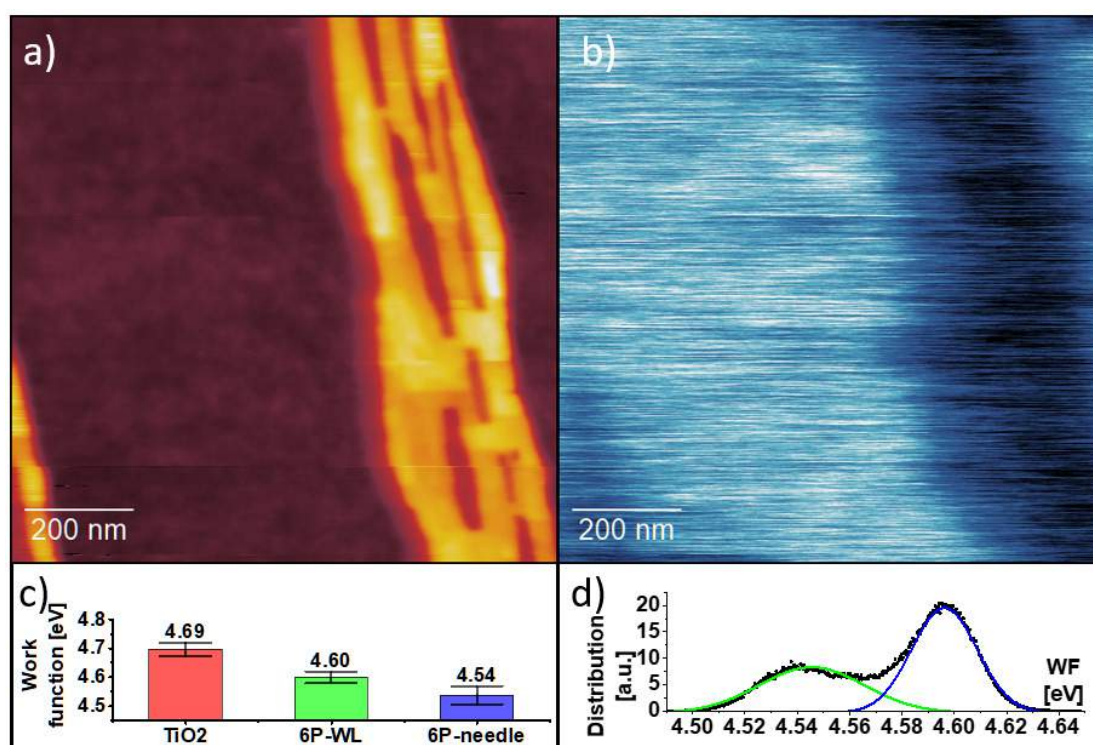


Figure 46 – KPFM images of $\text{TiO}_2(110)$ with a multilayer coverage of 6P: a) topography; b) work function map; c) work function values for a bare $\text{TiO}_2(110)$, one covered with 6P wetting layer and 6P nanoneedles; d) work function distribution histogram.

comparison of the values (Figure 46c). One can conclude, that covering titanium dioxide surface with 6P wetting layer lowers the surface work function by 97 ± 22 meV. Work function of a multilayer is even smaller ($4,54 \pm 0,03$ eV), however, no investigation regarding nanoneedles' height was performed. The ultraviolet photoelectron spectroscopy WF for a bulk *para*-hexaphenyl yields a value of $\sim 4,45$ eV [44], which is not far off from the measured nanoneedle WF. One could argue, that higher nanoneedles – built of more 6P layers – would result in a smaller deviation from the bulk WF.

4.4.2 Adsorption/desorption energy studies

As another outcome from the performed DFT simulations, the adsorption energy was computed. The value per single 6P molecule within the wetting layer equals $E_{\text{ads}}^{\text{WL}} = 4,06$ eV, while the calculated adsorption energy for multilayer (nanoneedles) equals $E_{\text{ads}}^{\text{N}} = 2,71$ eV. Similarly to the previous investigations, an experimental technique was utilized to confront these values, by the means of thermal desorption spectroscopy. A series of experiments was performed in order to calibrate the setup and retrieve proper data. Four different 6P coverages were studied from the range of 1,46 to 3,65 ML of 6P. Thermal desorption was carried out by heating with a constant rate of ~ 1 K/s. As the singly ionized 6P molecules possess the mass-to-charge ratio of $m/q = 458$, it is out of range for the utilized mass spectrometer. Therefore, the second strongest signal was registered of doubly ionized molecules (6P^{2+}). This, however, significantly lowered

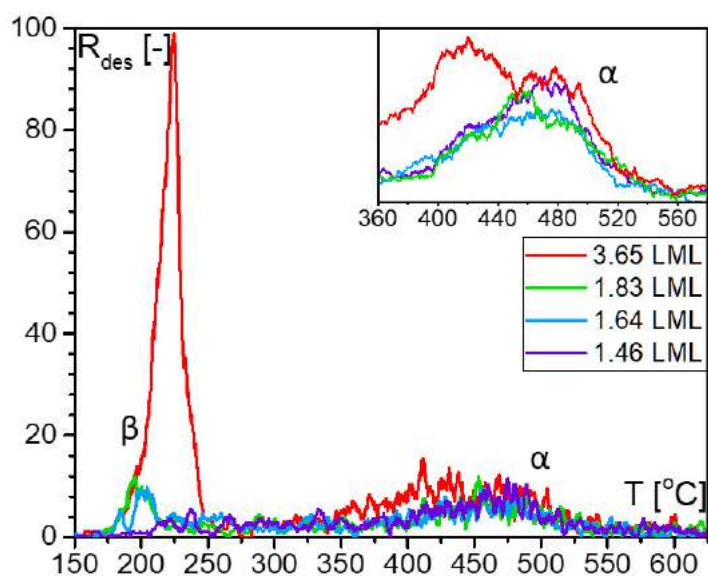


Figure 47 – Smoothed TDS spectra (10 adjacent points) of 6P desorption from $\text{TiO}_2(110)$ for different former coverages with added inset for the α -peak.

sensitivity throughout the experiment. In order to analyse desorption spectra, the received data was plotted as a desorption signal against the sample temperature (Figure 47). Within the graphs, one can distinguish two desorption peaks, that originate from different molecular structures. The left-most desorption peak (β) at temperatures between 170 and 250 °C can be associated with

the multilayer desorption (nanoneedles), as its shape exhibits a sharp drop right after the maximum value – characteristic for 0th order desorption. Right-most, broad peak (α) in the temperature range of 400 to 500 °C (inset in the Figure 47) arises from the desorption of the wetting layer, as it is the only desorption maximum for low coverages. The average maximum position of the α -peak doesn't change for higher coverages and the signal magnitude is roughly the same. The increased signal in the temperature range of 370 – 440 °C for the 3,65 LML spectrum is an experimental artefact, which will be discussed in more detail in chapter five. Conversely to the wetting layer peak, the β -peak arises for higher coverages and significantly enlarges with increase of 6P deposition amount.

For the multilayer desorption β -peak, the *leading edge analysis* was employed (equation (18)). A graph of $\ln(R_{\text{des}})$ vs $1000/T$ was plotted for the 3,65 LML coverage (Figure 48Figure 49). For the linear fit, a range above average signal noise of the spectrum and below desorption rate drop was chosen. From the slope of the fitted line, the desorption energy of $E_{\text{des}}^{\text{N}} = 2,27 \pm 0,26$ eV was calculated, which is slightly lower than the DFT value ($E_{\text{ads}}^{\text{N}} = 2,71$ eV). However, the DFT “multilayer” value was calculated for the second layer of 6Ps, where molecules most probably still interact with the TiO₂(110) substrate. Moreover, the experimental value fits the literature value for 6P multilayer desorption of $2,4 \pm 0,1$ eV [176] very well. From the intercept of the *leading edge analysis* linear fit, pre-exponential factor of $\nu_1 = 2 \cdot 10^{25(2)} \text{ s}^{-1}$ was determined, as the signal-to-noise ratio was good enough. This value was used for the *Redhead peak maximum method* utilized for the α -peak of the WL. The parameter is not strictly established for the α -peak due to signal's weakness, however, it is still a better estimation than the most commonly used $\nu = 10^{13} \text{ s}^{-1}$, which was used by Redhead for diatomic gases [160]. For rod-like molecules like the *para*-hexaphenyl or pentacene experimental pre-exponential factors are closer to the $10^{20} - 10^{25} \text{ s}^{-1}$ range [176,177]. Nevertheless, the *Redhead analysis* allowed for the determination of the WL desorption energy of $E_{\text{des}}^{\text{WL}} = 3,75 \pm 0,41$ eV, which is in a good agreement with the DFT value (4,06 eV).

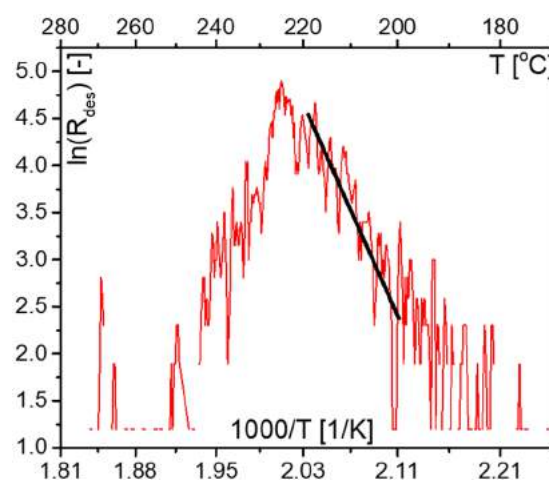


Figure 48 – A leading edge analysis graph for the raw (not smoothed) desorption spectrum of 3,65 LML 6P.

Chapter V

Dihydro-tetraaza-pentacene as pentacene's derivative with a permanent dipole moment – molecular structures growth on titanium dioxide

In chapter V a broad span of studies regarding pentacene's derivative with four carbon atoms replaced by nitrogens is described. The growth of the structures and their development is studied for the set of experimental parameters, i.e. substrate temperature during deposition, substrate surface roughness and anisotropy. In the second section a huge emphasis is put into in-depth studies of the molecular wetting layer. In the last section non-morphological properties are investigated by the means of TDS, KPFM and SEM.

5.1 Multilayer coverage growth

An overview of the grown structures at multilayer coverages is a good first step during any molecular growth investigation, as it gives a general idea of the processes and growing modes. Also, potential applications often utilize molecular layers of rather large thickness, therefore, it is self-evident to present such overview. This section of the chapter also presents results on certain parameters influence on the growth processes, i.e. substrate temperature during deposition, initial substrate surface state and differences in total molecular coverage. Furthermore, the determination of the optimal UHV deposition parameters is crucial in order to obtain well-defined structures with high repeatability. Up to now no studies regarding the DHTAP growth on the $\text{TiO}_2(110)$ surface were done, therefore, any information for the research could only have been obtained from the investigation concluded on different substrates [123–125]. However, pentacene molecular growth on $\text{TiO}_2(110)$ was already investigated [178], thus one could presume some kind of similarities for the DHTAP molecules. Nevertheless, with the new molecule-substrate system, it was required to perform a full span of studies in regard of mentioned dependencies. The following subsections describe the deposition parameters deduction and report on the growth of DHTAP 3D molecular structures.

5.1.1 Substrate temperature dependence on the resulting DHTAP structures

Matković *et al* have shown that an increase of the sapphire substrate temperature during DHTAP deposition results in significant lateral diffusion enhancement and hence, the enlargement of the formed molecular structures [124]. With this knowledge, a series of UHV deposition and *ex situ* SEM imaging experiments were performed on terraced $\text{TiO}_2(110)$ samples. For each specimen the total coverage was about 2 MLs, while the deposition was held with different substrate temperatures ($T_{\text{substrate}}$). It has been found that similarly to the sapphire substrate, DHTAP structures grown on $\text{TiO}_2(110)$ surface differ while considering $T_{\text{substrate}} = \text{RT}$, $T_{\text{substrate}} = 110\text{ }^\circ\text{C}$ and $T_{\text{substrate}} = 125\text{ }^\circ\text{C}$ during OMBE (Figure 49). The room temperature deposition results in the formation of a large amount of small structures ($\sim 100 - 500\text{ nm}^2$) separated by distances of $\sim 100\text{--}150\text{ nm}$ (Figure 49a). Whereas, the deposition performed with the substrate at $110\text{ }^\circ\text{C}$ leads to the formation of structures resembling bent or twisted wires of lengths from hundreds nm to even a few μm (Figure 49b). They are, on average, ~ 20 times larger laterally than the structures that grow at room temperature. Their mean separation is a distance of

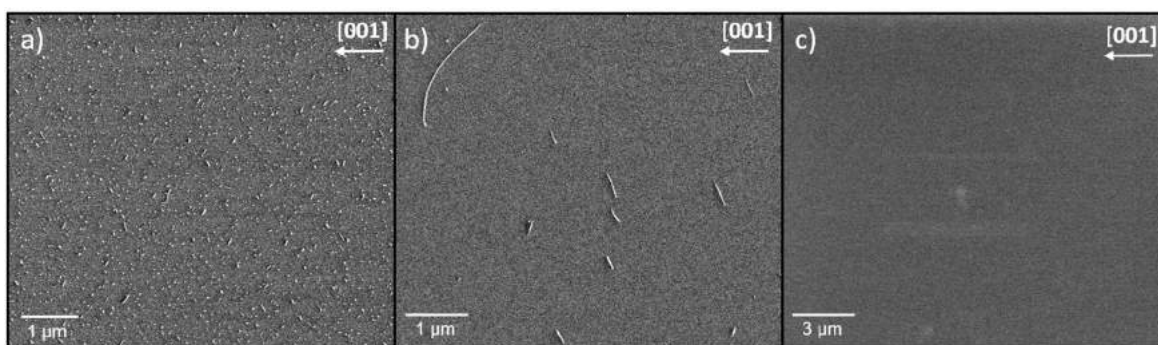


Figure 49 – SEM images of DHTAP structures grown on $\text{TiO}_2(110)$ with substrate kept at different temperatures during deposition process: a) room temperature; b) 110 °C; c) 125 °C.

a few μm , which is the result of the increased surface diffusion. They don't possess any particular shapes beside their elongation, nor are correlated to the substrate's crystallographic directions. Additionally, for the deposition at the $T_{\text{substrate}} = 110\text{ °C}$, one can notice the existence of only a single type of structures – the wires – differently than for the RT deposition. For the deposition at the $T_{\text{substrate}} = 125\text{ °C}$, no 3-dimensional structures were found (Figure 49c), which leads to the assumption that at such substrate temperature the redesorption process takes over the adsorption resulting in the lack of molecular growth. One could argue, that the molecules formed structure(s) indistinguishable by SEM, however, it will be later proven otherwise.

With the findings regarding the influence of the substrate temperature during DHTAP deposition, it was decided to perform all of the following experiments with the $T_{\text{substrate}} = 110\text{ °C}$ during the molecular epitaxy.

5.1.2 The aspect of the $\text{TiO}_2(110)$ substrate surface crystallinity

It has been found that the $\text{TiO}_2(110)$ substrate surface quality in regard of crystallinity strongly influences 3D structures growth. When considering investigated terraced titanium dioxide surfaces, they can exhibit different LEED patterns in the aspect of signal-to-noise ratios (Figure 50). The most clear diffraction reflexes are, for sure, associated with the high quality of the substrate on atomic

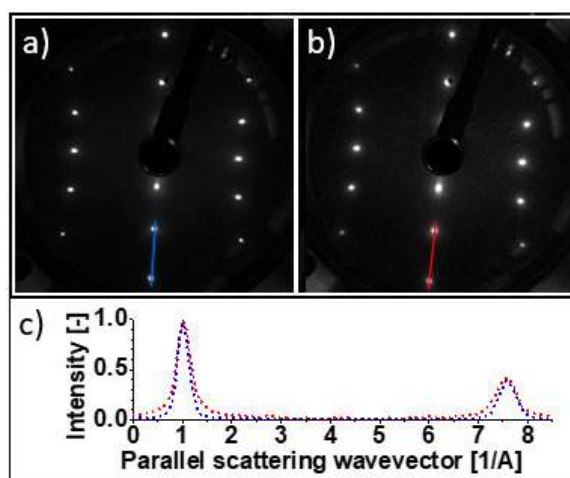


Figure 50 – LEED patterns for terraced $\text{TiO}_2(110)$ substrate with: a) higher; b) lower signal-to-noise ratios; c) cross section profiles along marked lines.

level (Figure 50a). Slightly worse patterns with broader diffraction spots and higher average noise originate from more defected and/or rougher $\text{TiO}_2(110)$ surface morphologies (Figure 50b). In most cases, LEED differences are correlated to the number of performed cleaning cycles [179].

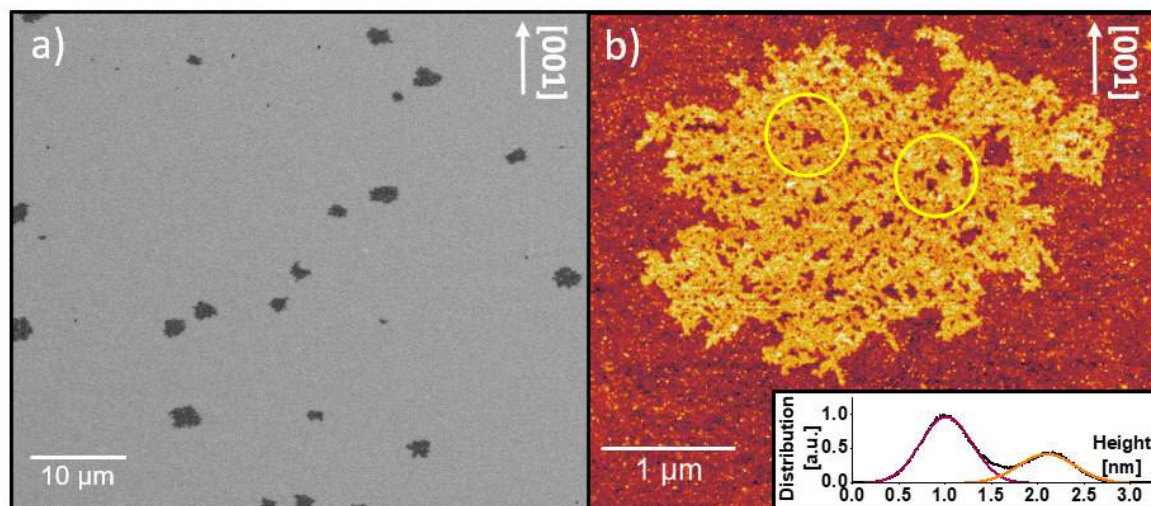


Figure 51 – Images of DHTAP islands grown on flat $\text{TiO}_2(110)$ at $T_{\text{substrate}} = 110^\circ\text{C}$ and 2ML coverage: a) SEM; b) tm-AFM.

For titanium dioxide crystals exhibiting a very clear LEED pattern prior to the deposition, structures different than elongated wires form – islands (Figure 51). The general shape of these islands is very complicated with fractal-like outer rim. Even within closed areas one can notice an existence of holes (exemplary yellow markings in the Figure 51b). The islands' lateral dimensions are of 1-3 μm , on average, with a slight elongation along the $[1\bar{1}0]$ direction of the substrate surface. The average height of the islands is about 1,1 nm, as presented in the height distribution of tm-AFM image (Figure 51b). This value is much smaller than the DHTAP molecule's length of 1,6 nm [124]. In comparison, on a sapphire substrate DHTAP, the up-right standing islands' average height has been reported to be $\sim 1,3$ nm [124], while the molecule's STM length on the $\text{Au}(111)$ substrate has been reported to be 1,43 nm [123]. Furthermore, height of the up-right standing islands of pentacene has been found to equal $\sim 1,5$ nm [180]. One could associate the observed 1,1 nm height to a large tilt of the molecules' long axes with respect to the substrate surface plane normal of $35\text{-}45^\circ$. Such a high angle shouldn't be favourable energetically, however, it could be explained by a single preferred frontal orientation of the molecules with respect to the substrate. As the DHTAPs possess a built-in dipole moment, due to differently modified benzene rings (N atoms and NH groups – Figure 52a), anti-parallel

conformation of neighbouring molecules within a packed structure is expected. However, such mutual arrangement disfavours any shifts between the molecules, since reducing the distance between the most negative part of a DHTAP and the most positive part of the neighbouring DHTAP (Figure 52b) is the most beneficial energetically. Therefore, the anti-parallel configuration cannot lead to the stated strong tilt with respect to the substrate plane. Considering the fact that $\text{TiO}_2(110)$ outer layer exhibits protruding oxygen rows of an average negative charge, the overall charge of the (110) surface is negative. Hence, one could expect the

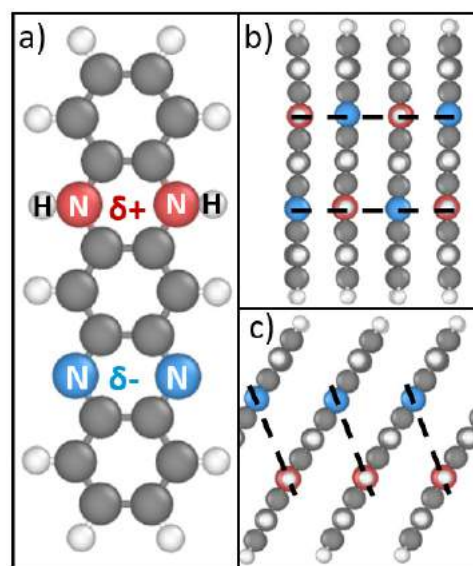


Figure 52 – Structural models of DHTAP molecules: a) overview on the molecule; b) side-view of vertical anti-parallel arrangement; c) side view of tilted parallel configuration.

standing dipolar DHTAP molecules to face the surface with their positive fronts. With such configuration the molecules should tilt with respect to the substrate's normal direction in order to reduce the distances between N atoms and NH groups (Figure 52c). Moreover, as the negative parts of DHTAPs move closer to the negative $\text{TiO}_2(110)$, the repulsion increases stopping further tilting. Such process could explain the observed island height of 1,1 nm. Furthermore, considering the proposed conformation, attracting interaction acts only in the vertical direction with respect to the substrate plane. Then, the lateral

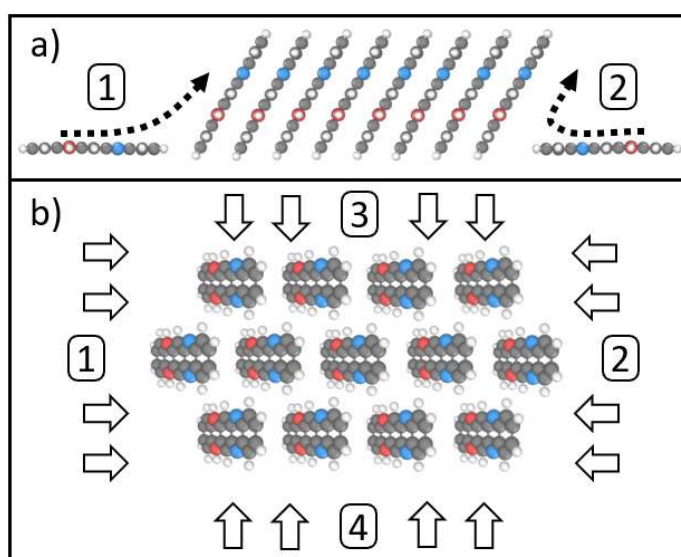


Figure 53 – Schematic models of DHTAP island with marked different adsorption sides: a) side view; b) top view.

interaction between the molecules is repulsive, which could contribute to the splitting of islands during their growth, leading to the observed complicated shapes. However, the mechanism behind the formed fractals, could also originate from the existence of an unfavourable adsorption side of the islands (Figure 53a). There must be a clear difference in

energies required for molecules to adjoin an island when facing it from the “slope side” (position “1” in the Figure 53) or the “cavity side” (position “2” in the Figure 53). What is more, molecules could face encountered islands either with their “positive” or “negative” front (considering two extreme cases). However, in both cases the cavity side is much less favourable energetically than the slope side. The other sides of the islands (positions “3” and 4” in the Figure 53b) are symmetric and adsorption of new molecules shouldn’t be inhibited there.

5.1.3 A coverage dependence of the DHTAP grown structures

Structure development for a larger amount of deposited molecules was studied. With the knowledge from the previous subsections of the chapter, two extreme cases of the substrate surface initial state were investigated – atomically flat, terraced surface exhibiting very clear LEED pattern (Figure 57a) and intentionally ion-beam roughened substrate with no diffraction spots obtained (Figure 57b). For both cases, an increased coverage of about 3 times as much of DHTAPs with respect to the previously presented results (~6 MLs in total) was used for the deposition. Figure 55 and Figure 56 show obtained molecular structures, exhibiting a strong influence of the substrate morphology on the growth process. These observations are in agreement with the previous findings

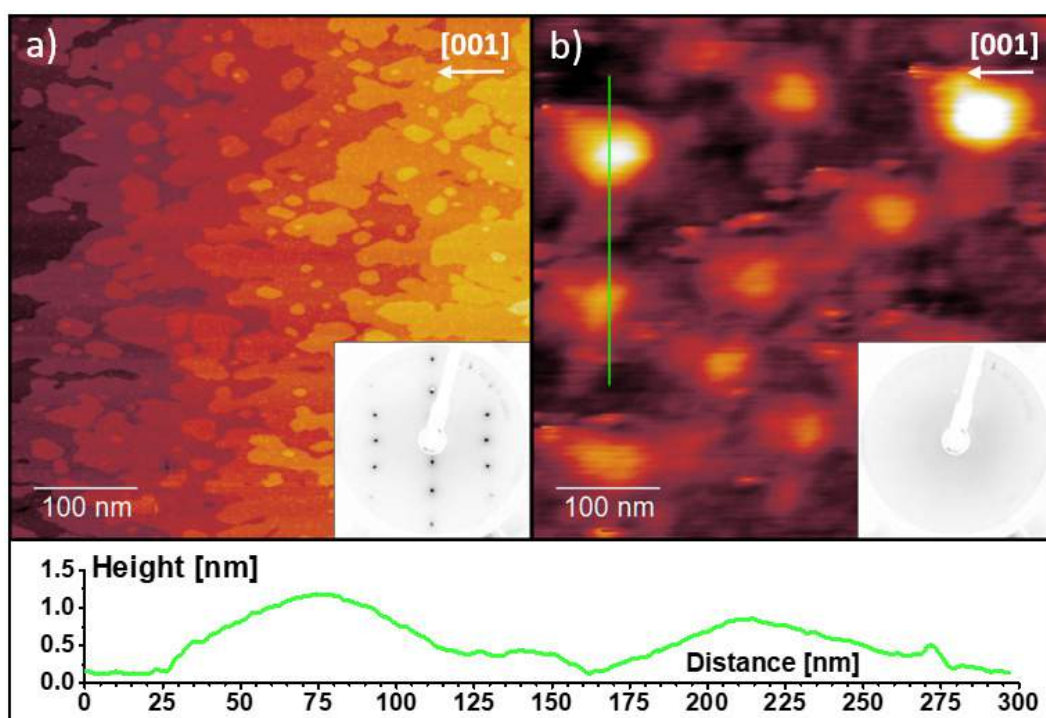


Figure 54 – SPM images of the initial state of $\text{TiO}_2(110)$ surfaces for the coverage dependence studies: a) STM of atomically flat morphology with a corresponding clear LEED pattern; b) NC-AFM topography of ion-roughened surface with a corresponding lack of diffraction pattern.

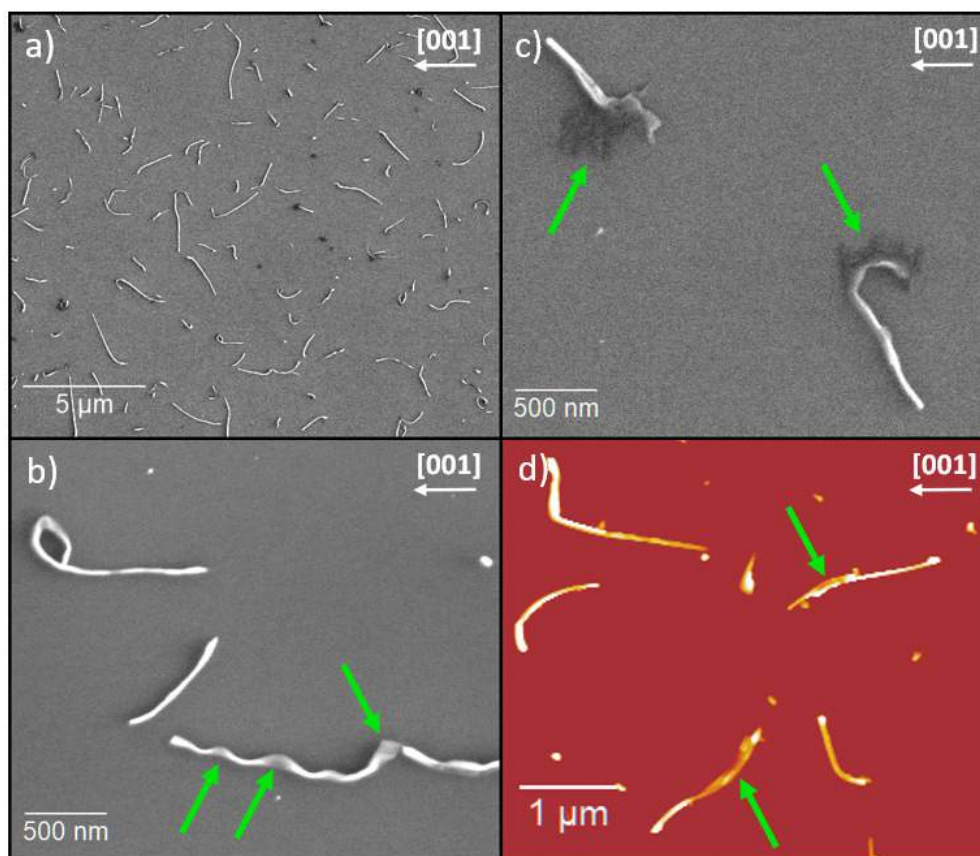


Figure 55 – Images of the high coverage (6 MLs) of DHTAP on $\text{TiO}_2(110)$: a) SEM overview image; b) SEM image showing ribbon-like appearance; c) SEM depicting anchoring of ribbons; d) *tm*-AFM overview image.

in regard of the substrate roughness. In both cases of the substrate surface, overall results of the increased molecular coverage are the enlargement of the lateral dimensions of the structures, as well as the increase of the average density of the structures quantity. Such development is expected when the amount of deposited material (molecules) is enlarged. As for the case of the roughened substrate, DHTAP wires are much longer and statistically more twisted than in the case of 2 ML coverage. Careful imaging and analysis showed a very interesting appearance of some wires, which at certain parts looked more like flat, folded ribbons (green arrows in the Figure 55b). Some of the wires on one of their ends are clearly connected to different, much more laterally expanded structures – they look as if they were anchored at these ends (green arrows Figure 55c). The *Tm*-AFM revealed a height range of the wires to be 20 - 100 nm (Figure 55d). The images also show that wires are often built of different segments (green arrows Figure 55d). The AFM imaging of these structures was quite challenging, because of their height and, most importantly, their folded/twisted shapes. Hence, unfortunately, no better images showing their substructure were obtained.

On the other hand, on flat, highly-crystalline $\text{TiO}_2(110)$ substrate fractal and isotropic, 2-4 μm in size, structures of different SE contrast are grown (Figure 56a). *Ex situ* AFM measurements revealed that the contrast differences originate from a multi-level character of the structures (Figure 56b). Cross section profile yielded an average step height of 1,1 nm (Figure 56b), which is consistent with the previously stated molecular tilt of 35-45° angle of their long axes with respect to the substrate plane. One can make an interesting observation that for some of the islands their central parts are built of a single layer of molecules (green arrow markings in the Figure 56a). However, as these islands grow laterally they also start growing vertically forming multi-level structures.

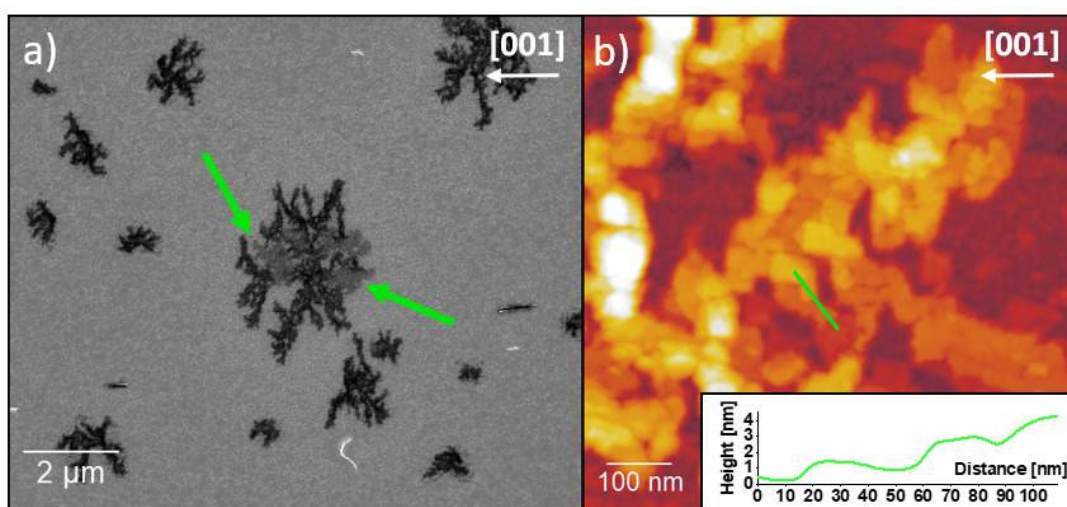


Figure 56 – Images of molecular structures developed after high coverage (6 MLs) deposition of DHTAP on atomically flat, fully crystalline $\text{TiO}_2(110)$: a) SEM overview image; b) tm-AFM image with a cross section profile inset.

5.1.4 Substrate step-edge concentration influence on the resulting molecular structures – the case of ripples

Findings presented previously regarded specimens with the substrate surface being either flat, terraced-like and more or less crystalline or roughened with no crystallinity maintained. Therefore, an interesting route for the following experiments seemed to be an investigation of growth processes on substrate surface that is, in a way, a combination of the two – on the ripples. As shown in previous chapters, ripple-like morphology regards lowering of the surface terrace widths leading to an increase of the surface step-edge concentration. Such surface modification can be obtained via ion sputtering at the grazing incidence angle. However, in order to maintain a local surface crystallinity, the process has to be conducted at elevated substrate temperature. In the

following, the results of an investigation of DHTAP structures growth on $\text{TiO}_2(110)$ rippled-surface with variable width terraces are shown.

A change of average terrace width from the previously investigated ~ 50 nm (Figure 54a) to the average width of ~ 10 nm (Figure 57a) already influences the growth process. Deposition of about 2 MLs on such surface leads to the formation of slightly more elongated islands built of tilted molecules (Figure 57b-c) than for the case of 50 nm terraces (Figure 51). As a parameter to compare island lateral dimensions, average length-to-width ratio (LWR) was chosen. Islands grown on $\text{TiO}_2(110)$ substrate of both mentioned terrace widths are elongated in the $[1\bar{1}0]$ direction (Figure 51 and Figure 57). However, the average LWR increases from the former $\sim 1,5$ to the new value of $\sim 2,5$ for more narrow terraces, due to the morphological anisotropy parallel to the $[1\bar{1}0]$ direction (perpendicular to the substrate atomic rows). The change of the LWR doesn't affect the island's height of 1,1 nm, which is associated with the single layer of tilted molecules.

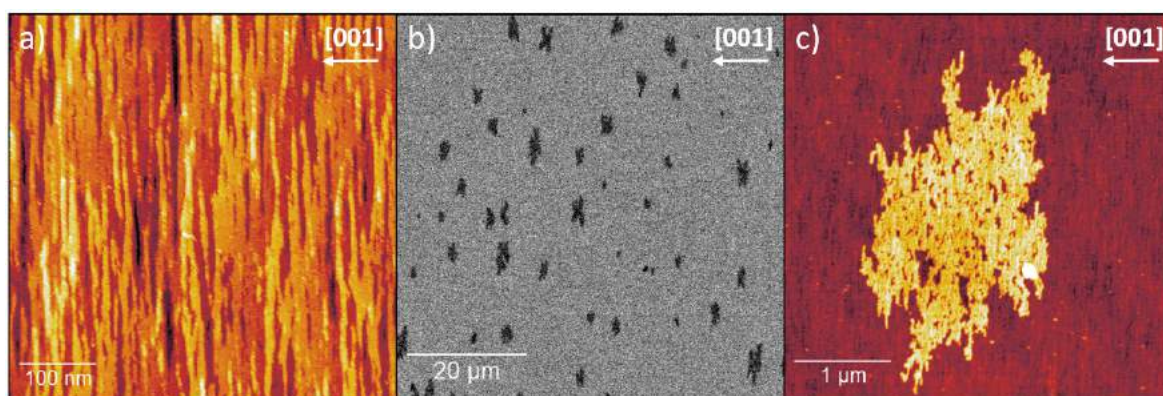


Figure 57 – Images of the DHTAP islands on shallow ripples of $\text{TiO}_2(110)$: a) STM image of substrate ripples prior to the deposition; b) SEM overview image of the grown islands; c) tm-AFM image of a DHTAP island.

For the further investigation, ripples of narrower terraces were produced with the ion-beam irradiation (Figure 58a, dFigure 56). For this part of the study a coverage of 6 MLs was chosen. The investigated substrate topography concerns ripples built of 3-4 and 8-9 atomic terraces with average widths of $\sim 2,5$ nm and ~ 1 nm, respectively. However, it is worth to note that the orientation of the ripples is along $[001]$ direction i.e. parallel to the $\text{TiO}_2(110)$ surface atomic rows. DHTAP structures grown on such substrate morphologies are much different from the previously shown, due to the strongly influenced surface anisotropy and step-edge concentration, as presented in the Figure 58 (6MLs of DHTAP grown on atomically flat substrate surface was added for comparison). Starting with the rippled substrate surface with a terrace width of 2,5 nm, DHTAP molecules form 5-10 μm long and 2-6 μm wide multi-layered islands (Figure 58e-f). The observed shapes are

strictly connected to the surface diffusion anisotropy originating from the rippled topography. For the investigated case islands are elongated in $[001]$ direction, on the contrary to the case of the terraced $\text{TiO}_2(110)$ substrate (Figure 58h). Therefore, the strong morphological anisotropy outmatches the slight preference towards the islands' elongation in the $[1\bar{1}0]$ direction. Similarly to the structures grown on the flat substrate, some of the islands have their central parts built only of a single, rather compact layer of molecules, while the outer parts are multi-level and fractal-like. As for the substrate with the highest concentration of atomic step-edges, a drastic difference in the shape of the formed structures is observed (Figure 61a-b). In the investigated case, the average ripple

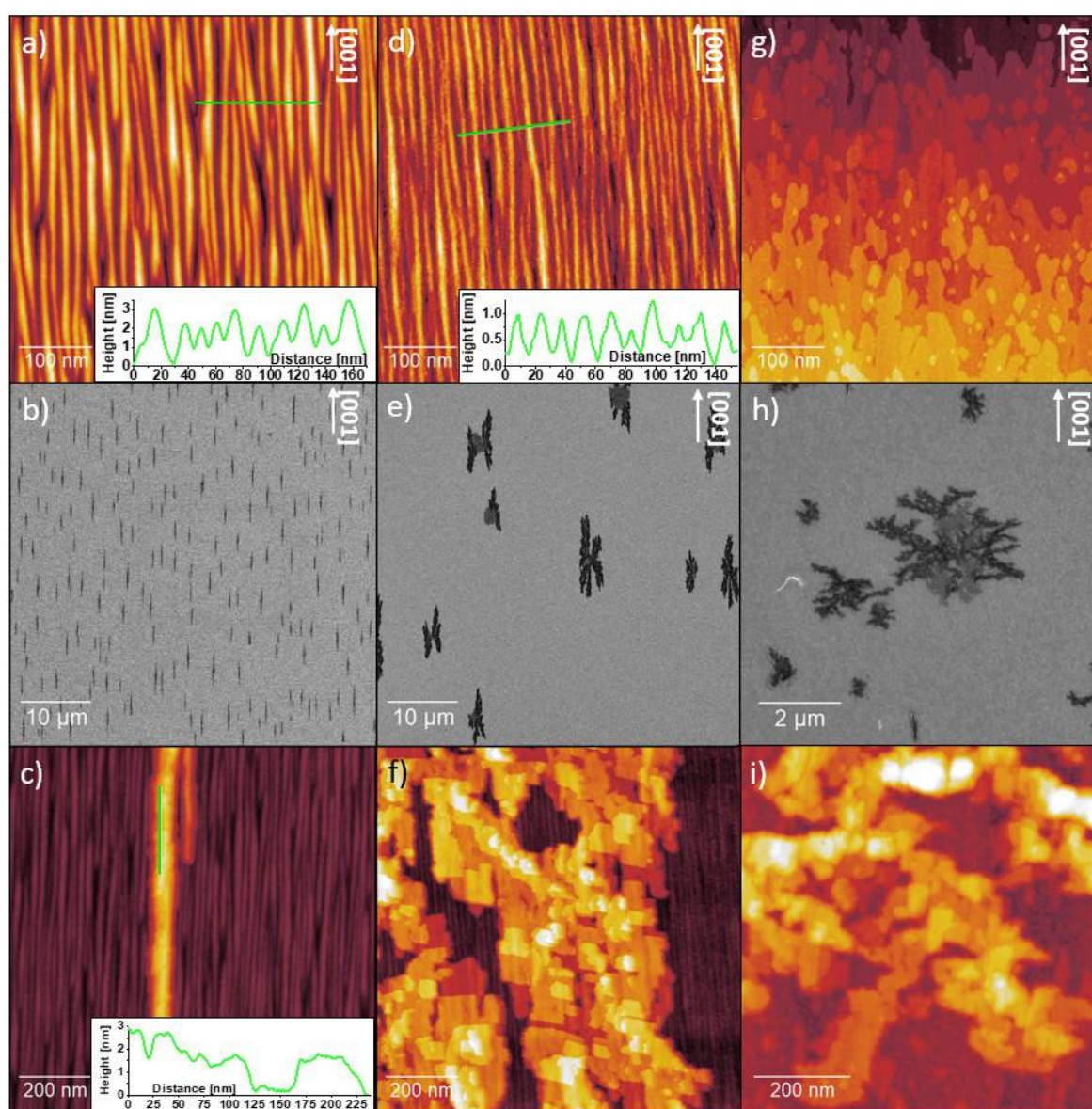


Figure 58 – $\text{TiO}_2(110)$ substrate morphology initial state influence on the grown DHTAP islands: b-c) SEM and tm-AFM images for structures on deep $\text{TiO}_2(110)$ ripples; e-f) SEM and pft-AFM images for islands on shallow $\text{TiO}_2(110)$ ripples; h-i) SEM and tm-AFM images for DHTAP on atomically flat $\text{TiO}_2(110)$.

lengths are increased, together with the average topography modulation amplitude. Therefore, the lateral diffusion is greatly influenced creating a very strong diffusion anisotropy. In addition, the average size of the structures is reduced, while their quantitative density is increased. In comparison to the case of moderate ripples (2,5 nm terrace width), the length to width ratio is increased by a factor of 20, as the presented structures are statistically 3-6 μm long and about 100 nm wide. One could compare these extremely elongated structures to the wires/ribbons that form on rough, non-crystalline $\text{TiO}_2(110)$. However, the SE contrast for these structures is dark, which is similar to the DHTAP islands and contrary to the wires. Tm-AFM investigation revealed a step-like structure on top of the structures with average step height of 1,1 nm, which is the same as for the molecular islands. Considering all these findings, even for the ripples of 2,5 nm topography modulation DHTAP islands of tilted molecules are formed.

A very interesting structural feature was observed with a careful AFM investigation of the multi-layer fractal islands grown on moderately deep ripples (1 nm). Following the yellow dashed lines in the Figure 59a, one can notice a step-edge occurrence within the area of supposedly the same level/layer of DHTAP molecules. For comparison reasons and a different perspective, a view of a 3D image representation was added to the Figure 59. Such shape of the layers could be explained by helical/screw-like growth process. However, no similar appearance was found on the multi-level islands grown on atomically flat $\text{TiO}_2(110)$. Therefore, the presented feature should not be considered as purely DHTAP structural property, but also as an outcome of the substrate morphology. The mechanism behind the fractal-like lateral shapes most probably plays some role in the process of the shown growth. The edge of a single molecular layer adhering a ripple hill

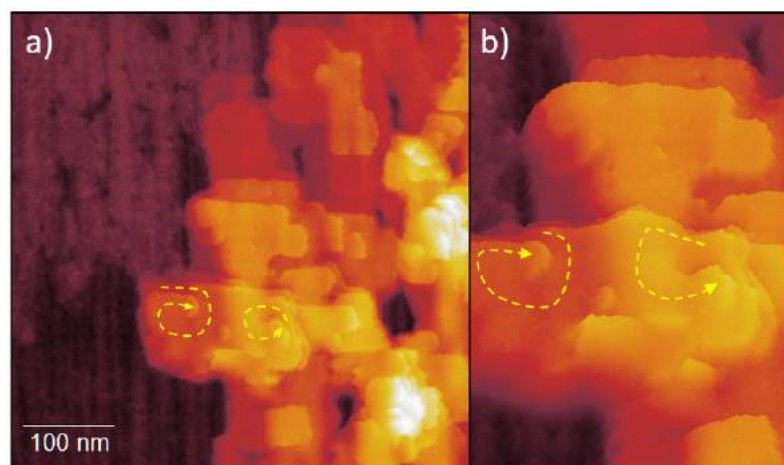


Figure 59 – Multi-level DHTAP islands on top of rippled $\text{TiO}_2(110)$ substrate: a) pft-AFM image; b) 3D representation of (a).

can expand upward and then along the top. Such expansion can lead to encountering of the molecules from the valley and, therefore, growing a layer on top of them. The process can continue leading to the formation of the mentioned additional step-edges within an island originating from a single layer (marked areas in the Figure 59a). The presented mechanism is only hypothetical, as the exact arrangement of the molecules within a multi-layer structure is only stated basing on the consecutive layer heights. Furthermore, as proposed before, the tilted single molecules should be repulsive to each other, which could lead to a more complicated helical growth. Consecutive molecules may experience rotation with respect to each other causing more of a rotation-like growth. However, such a process is less probable as the molecules would have to break from a crystallographic order to undergo such formation. Nevertheless, the obtained observation of helical/screw-like growth is very interesting and uncommon for such small molecules as pentacene or its derivatives.

At this point it seems relevant to highlight a great resolution obtained with pft-AFM mode. As shown in the Figure 63a and Figure 59 molecular step-edges are clearly visible with a standout frayed look. It has to be stated that this isn't an imaging artefact, but the true island edge shape, as the consecutive images of the same area are identical, together with forward-backward scans. For such sophisticated and delicate structures as multi-layers islands of "upright" molecules it is not always easy to have a proper imaging in ambient conditions without causing damage to the structures, especially if their edges are not compact and stable. As presented in the chapter II, peak-force tapping AFM can be set to

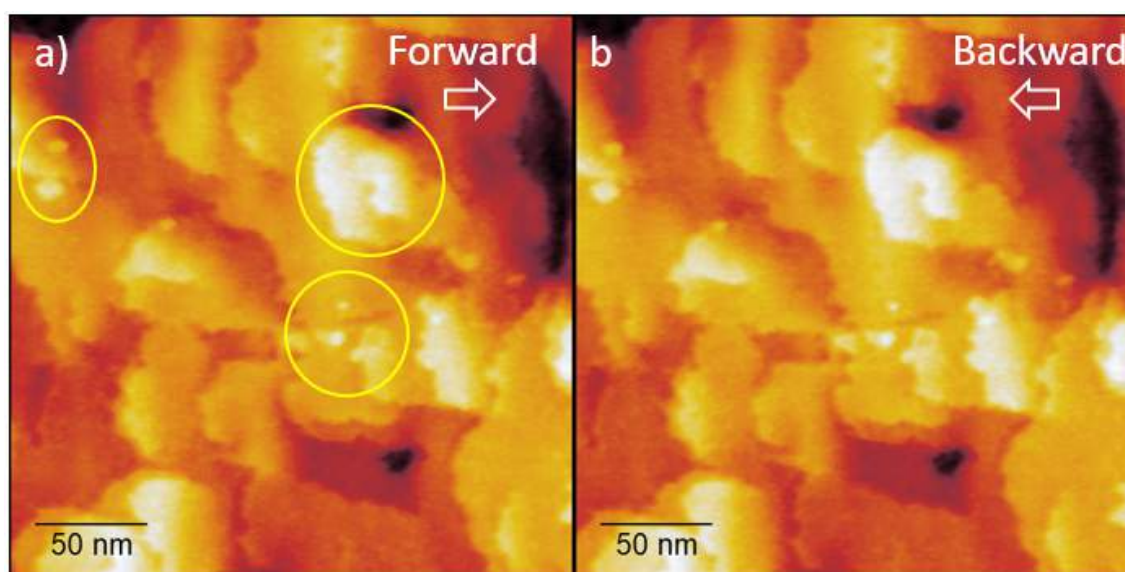


Figure 60 – A pft-AFM image of multi-level DHTAP islands on top of rippled $\text{TiO}_2(110)$ substrate: a) forward; b) backward height maps.

probe really small forces in order to keep the structures intact. If the tip is sharp enough, really small structural features like defects or mentioned frayed edges of a few nm lateral dimensions can still be shown, even in air environment.

5.1.5 Indication of a wetting layer existence

Similarly to the *para*-hexaphenyl molecules described in the chapter IV, there is a particular indication of the existence of an additional structure not resolved with air-AFM, nor SEM. However, unlike to the 6P wetting layer, this structure is not straight-up decomposed with an exposure to the ambient conditions. It has been found that the de-wetting can be induced by an electron beam. Imaging an area between DHTAP

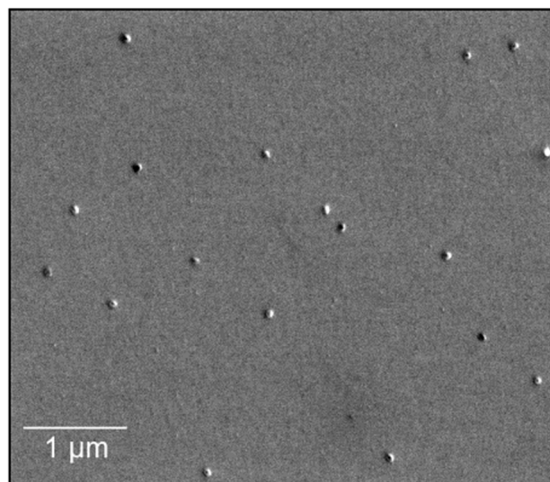


Figure 61 – A SEM image $\text{TiO}_2(110)$ after DHTAP deposition showing clusters formation originating from electron beam interaction.

islands with SEM leads to the formation of clusters, as shown in the Figure 61. The process occurs after a single scan with a “strong” beam (high current $I = 4 \text{ nA}$, electron energy $E_e = 10 \text{ keV}$, pixel size $px = 5 \times 5 \text{ nm}^2$ and dwell time $DT = 30 \mu\text{s}$) or a few (3-5) scans of the same area with a “weak” beam ($I = 17 \text{ pA}$, $E_e = 2 \text{ keV}$, $px = 5 \times 5 \text{ nm}^2$, $DT = 30 \mu\text{s}$). Such clusters are somewhat similar to the 6P crystallites associated with the degradation of a wetting layer. In order to confirm that the emerging clusters are not just an SEM imaging artefact, a contact mode AFM with a high operating setpoint of $1 \mu\text{N}$ was performed with a very stiff AFM probe cantilever ($k = 36,8 \text{ N/m}$). The same area of $500 \times 500 \text{ nm}^2$ was scanned four times with the idea of moving the molecules with the AFM tip (Figure 62a-d). After that a single larger scan of $2 \times 2 \mu\text{m}^2$ was performed with a lower setpoint of 35 nN (Figure 62e). No additional topography features to the $\text{TiO}_2(110)$ terraced structure was observed with the exception of a much more blurred belt-shaped zone of $\sim 1 \mu\text{m}$ (marked with blue dashed lines in the Figure 62e) – the expanded area of first four scans. In addition to the vertical deflection of the AFM cantilever, the horizontal deflection was monitored, which is associated with the friction between the tip and the sample (Figure 62f-g). One can notice a clear difference in contrast, when considering a former area of $500 \times 500 \text{ nm}^2$. The contrast inversion originates from the forward and

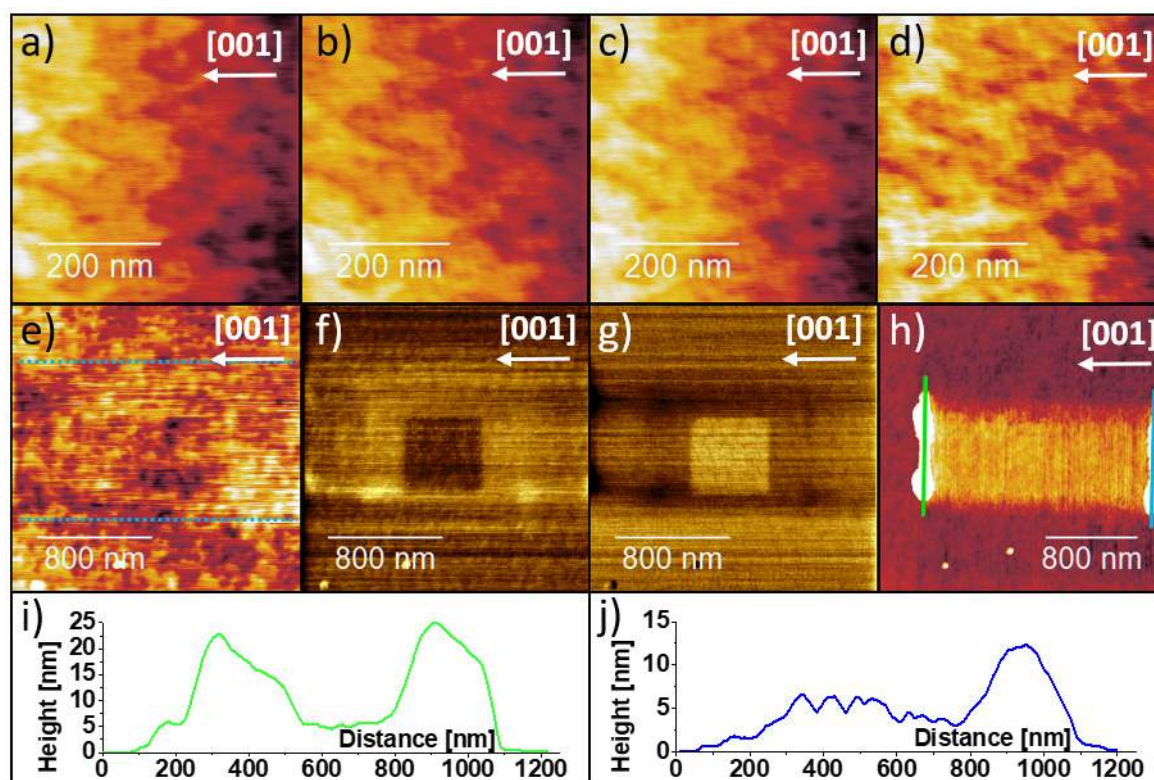


Figure 62 – c-AFM experiment on the area supposedly covered with DHTAP molecules: a-d) consecutive $500 \times 500 \text{ nm}^2$ c-AFM scans of the same area; e) $2 \times 2 \text{ }\mu\text{m}^2$ c-AFM scan with the same central point; f-g) horizontal deflection maps for (e); h) $2,5 \times 2,5 \text{ }\mu\text{m}^2$ tm-AFM scan; i-j) cross section profiles for the marked lines in (h).

backward scan mapping and the relative changes of horizontal deflection. Differences in friction of the former area suggest that something could have been moved away, which caused the changes. It was assumed that despite the low force setpoint, the fifth scan (Figure 62e) potentially pushed the gathered material farther away. Therefore, a tapping-mode scan was performed for the area of $2,5 \times 2,5 \text{ }\mu\text{m}^2$ (Figure 62h). The imaging revealed mounds of material at the fast scan direction borders of the $2 \times 2 \text{ }\mu\text{m}^2$ contact mode scan. A rather compact morphology of the aggregations instead of smeared out/torn clusters suggests tip-induced movement of whole segments. Such behaviour indicates a very strong molecule-molecule interaction. The mounds of molecules are asymmetric in terms of mutual average height and height distribution within each of them (Figure 62i-j). Their calculated total volume is of about $\sim 2 \cdot 10^6 \text{ nm}^3$. With the reported height of flat-lying DHTAP molecules between 1,1 nm and 1,4 nm [123,125] considered material amount should cover an area of $\sim 1,5 \text{ }\mu\text{m}^2$, which is roughly the area of brighter contrast in the Figure 62h. Therefore, it can be assumed that DHTAP molecules form a full single layer during the UHV deposition.

5.2 Molecular arrangement within the DHTAP/TiO₂(110) interface and the DHTAP 3D structures.

When comparing the findings regarding an additional, not-resolved DHTAP structure to the 6P growth process, one could assume an existence of a molecular wetting layer. Therefore, a further investigation with a higher resolution had to be performed. For such purposes *in situ* UHV-STM studies have been performed for a sub-mono- and a mono-layer DHTAP coverages. Another unresolved topic was the inner structure of the DHTAP islands and ribbons. Some of the additional experiments regarded this issue. The following subsections are dedicated to the determination of the molecular arrangement within the structures grown on the TiO₂(110) substrate.

5.2.1 Arrangement of individual molecules on TiO₂(110)

In order to investigate the orientation of the DHTAP molecules on top of the TiO₂(110) substrate, an experiment with a flat, terraced-like titanium dioxide surface and the molecular coverage of 0,4 ML was prepared. *In situ* UHV-STM imaging resulted in images of DHTAP molecules on top of the substrate (Figure 63a). Molecules appear to be parallel with their long axes to the [001] direction of the atomic rows. Most of the molecules are smeared out due to a high mobility at the room temperature. Also, a tip-induced movement of the molecules cannot be excluded as a reason for the presented look. An interesting observation is that the DHTAPs appear as molecules, which are either asymmetric and immobile or symmetric, mobile (elongated) and wide or

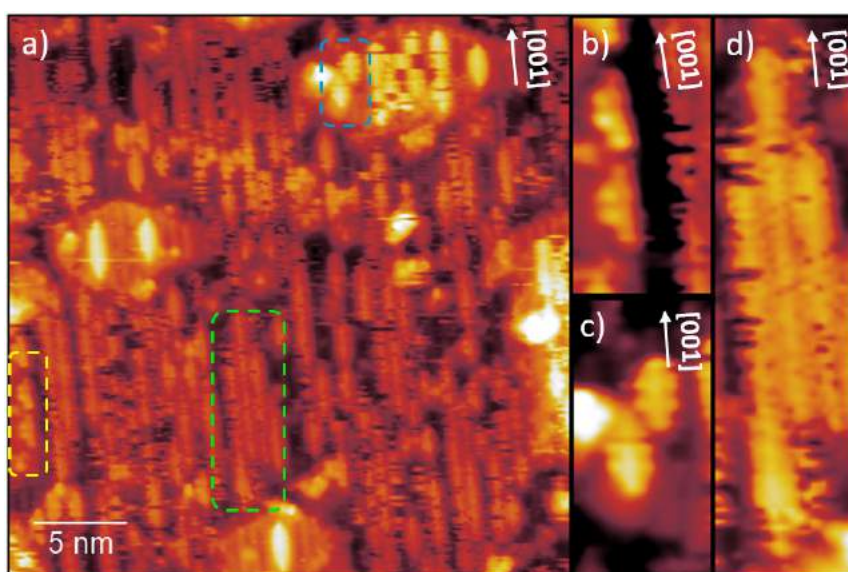


Figure 63 – STM images of DHTAP molecules on TiO₂(110) at sub-ML coverage: a) an overview; b-d) extracted areas of interest.

narrow (yellow, blue and green dashed ovals in the Figure 63a, respectively). The asymmetric configuration is the most clearly resolved and is characterized by a trapeze-like shape with two clear maxima on the shorter side (Figure 63b). As already mentioned, molecules with such appearance are not mobile and stick to a single adhesion point and possess the length of $\sim 1,7$ nm and width of $\sim 0,8$ nm. This is slightly larger than the 1,6 nm of the vdW length [124] and the reported STM length of 1,43 nm on the Au(111) substrate [123]. However, the latter concerns the length within a closely packed layer that can be influenced by a bending of the DHTAP molecule, which has been proven to occur with DFT calculations for Cu(110) substrate [125]. In the case of $\text{TiO}_2(110)$ the unburied substrate allows to determine that the longer part of molecule lies over the bright titanium rows, while the shorter part tops the dark protruding oxygen rows.

Some of the DHTAP molecules appear as wide, symmetric and elongated features, unless the [001] direction movement is inhibited by other molecules or a step-edge (Figure 63c). In such cases, molecules are much wider with the dimensions of ~ 1 nm, while having the same STM length of $\sim 1,7$ nm (measured for the “blocked” molecules). For molecules to appear like this it is required to have empty neighbouring atomic rows. A more careful observation shows that the central part of the molecule is similar to the long side of the trapeze-like shape described before, however, with the two maxima visible on both sides. From the distinguishable substrate surface, one can deduce that the longest part of the molecule lies over the titanium atoms, while the sides top the protruding oxygen rows.

Some of the wide and symmetric molecules are smeared along [001] direction resulting in the elongated lines with no additional features within (Figure 63d). Such appearance concerns mobile molecules surrounded by other DHTAPs on the neighbouring atomic rows (along the $[1\bar{1}0]$ direction). Their average width is $\sim 0,65$ nm, which is consistent with the periodicity of the substrate in the $[1\bar{1}0]$ direction. What is not intuitive and interesting is that the molecules are mobile despite having neighbours around and move along [001] direction in groups. From such an observation one can guess that the molecule-substrate interaction is very weak.

The distinctive feature of the trapeze-like molecules in relation to the differently appearing ones is their lack of mobility and their asymmetric shape. The molecules appear as if they were tilted along their short axes with respect to the substrate. Considering the stable positioning, one could assume that they are anchored to the $\text{TiO}_2(110)$ surface at some adhesion sites. This asymmetric look is in a good agreement with the DFT-simulated

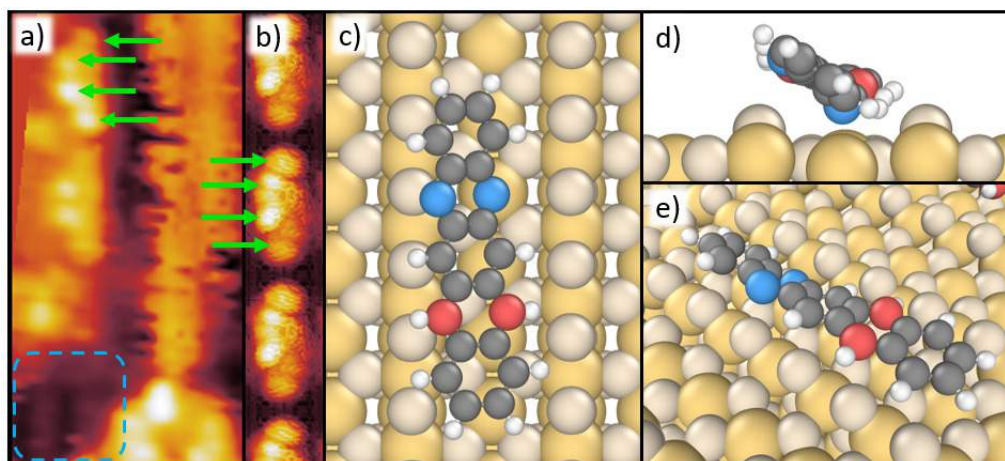


Figure 64 – DHTAP molecule on $\text{TiO}_2(110)$: a) An STM image; b) DFT simulated DOS map; c-e) DFT-optimized structural models.

density of the state map for energetically optimized structural configuration of a single DHTAP molecule on $\text{TiO}_2(110)$ substrate surface (Figure 64). Both the STM and DFT images exhibit clear maxima similarly located over the molecules, as marked by green arrows in the Figure 64. Furthermore, the simulated structural model reveals the exact molecule's positioning over the substrate's atoms (Figure 64c-d). The DHTAP molecule is tilted with its short axis in respect to the substrate plane, while also being twisted along its long axis (Figure 64d-e). The positive parts of the molecule (NH groups) favour the substrate's negative oxygens, while the negative parts (N atoms) prefer close neighbourhood of the positive titanium atoms. Comparison of the STM images and the DOS maps with the Figure 64c-d leads to the conclusion that the brightest maxima in the experimental image originate from atoms located over oxygen rows. Careful inspection of the Figure 64a (area marked with dashed blue line) allows for the same observation – drawing straight lines from the marked $\text{TiO}_2(110)$ substrate atomic rows.

5.2.2 A complete DHTAP wetting layer

As the single molecules on top of the $\text{TiO}_2(110)$ exhibit a high mobility in the room temperature, it was required to study a system with higher molecular coverage. Figure 65 shows the STM appearance of an almost complete single layer of DHTAP molecules (~ 1 ML) with a terrace contrast originating from the substrate. The very first observation one has to make is that the molecules are no longer oriented with their long axes parallel to the $[001]$ direction. A careful STM analysis yields new configurations concerning DHTAPs lying along the $[1\bar{1}0]$ direction or rotated by the angle of $(36 \pm 6)^\circ$ in both ways from $[1\bar{1}0]$ direction. Due to a drift effect during imaging, it is not intuitive to notice all

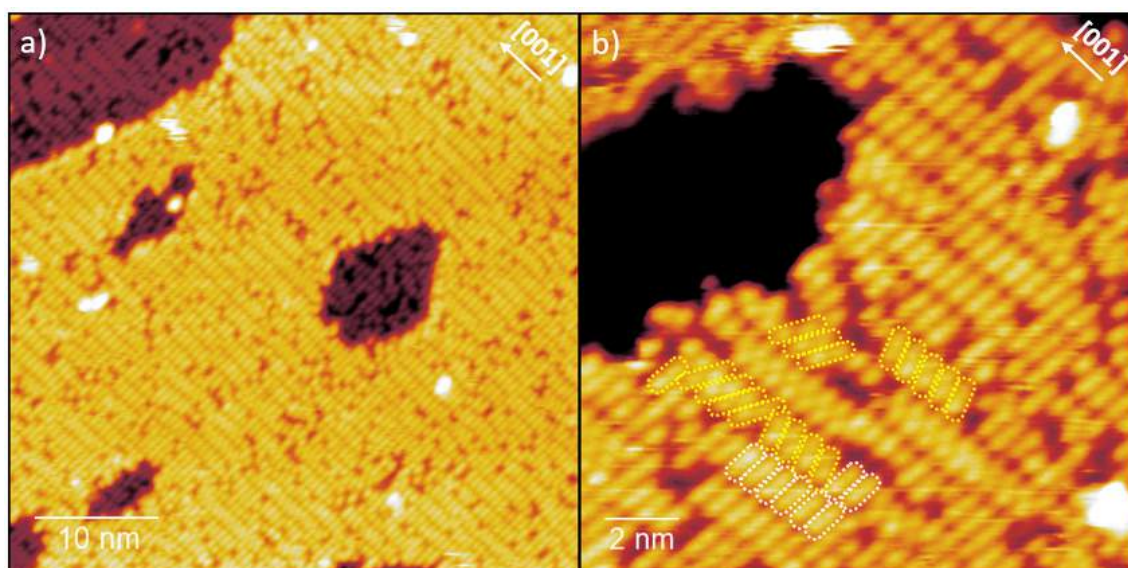


Figure 65 – STM images of an almost complete single layer of DHTAP molecules on $\text{TiO}_2(110)$ terraced crystalline substrate.

three conformations, however, they can be recognized as marked with the yellow ovals in the Figure 65b (for comparison reasons molecules parallel to the $[1\bar{1}0]$ direction were marked with white ovals).

The molecules are arranged into a form of stripes that are exactly parallel to the $[001]$ direction. Within such a compact layer the molecules look as if they were built of two segments. The STM-determined molecule's length equals 1,3 nm or 1,4 nm for the $[1\bar{1}0]$ orientation and the 36° rotated orientation, respectively, with the average width of 0,6 nm. However, the unit cell dimensions of the wetting layer are $1,3 \times 0,6 \text{ nm}^2$ regardless of the molecules' conformation. With the DHTAP length of 1,3-1,4 nm one has to assume some kind of bending along the molecule's long axis, similar to the one reported for $\text{Cu}(110)$ [125]. The bending, in turn, can be a result of electrostatic interaction between the substrate and the negative rings consisting of N atoms and positive rings that have NH groups. The periodic positive-negative character of the $\text{TiO}_2(110)$ along the $[1\bar{1}0]$ should cause the interaction and, hence, a flexure. Unfortunately, it wasn't possible to determine an exact positioning of the DHTAP molecules above the substrate's atoms with the performed STM investigation.

The 0,6 nm periodicity in the $[001]$ direction suggests that the molecules adopt exactly double the period of the atoms within the substrate's oxygen rows. As the consecutive substrate atoms are equivalent, one should be able to find mismatches when comparing molecules from the neighbouring stripes. Considering the $[1\bar{1}0]$ orientation first, it is rather easy to find either head-to-head frontal facing of the molecules from the

subsequent stripes or the in-between orientation with the molecules from one stripe being shifted by a single lattice constant of 0,3 nm in [001] direction with respect to the neighbouring stripe (Figure 66a). The described head-to-head in-between configurations occur also for the consecutive stripes of 36° rotated molecules or the combination of the $[1\bar{1}0]$ molecules and the rotated molecules (Figure 66b-c).

Despite the unusual arrangement of the molecules within the wetting layer, there has to be a mechanism behind such behaviour. In order to find an explanation, one can start with a comparison to the pentacene's wetting layer. Lanzilotto *et al* have shown that 5A molecules adopt orientation parallel to the [001] direction, even within a complete monolayer [178]. While pentacene is a similar molecule to the DHTAP in regard of structure and dimensions, it doesn't possess a permanent dipole moment that its derivative has. This fact has to be considered as a major contributor towards the behaviour discrepancy when studying such strongly anisotropic substrate as $\text{TiO}_2(110)$. Starting from

small coverages of DHTAPs, the molecules align with the titanium dioxide atomic rows. Some of the molecules stick to the adhesion sites, while a greater majority diffuse freely along the [001] direction. With the increased coverage the molecules tend to form groupings that are still very mobile despite being stabilized by each other. Such an observation depicts very low molecule-substrate interaction. Finally, with a further molecular coverage increase, the molecules are packed more closely, which leads to a larger molecule-molecule interaction. As the interaction becomes larger than the substrate-molecule interaction, the molecules find another local minimum of energy in the form of a rotated orientation (either 54° or 90° with respect to the former conformation). It has to be dictated by the electrostatic interaction of the DHTAPs' dipole moment with the substrate's positive Ti atoms and negative O atoms. As the molecular deposition process takes place with the titanium dioxide at elevated temperature, the DHTAPs have additional energy to undergo such rearrangement.

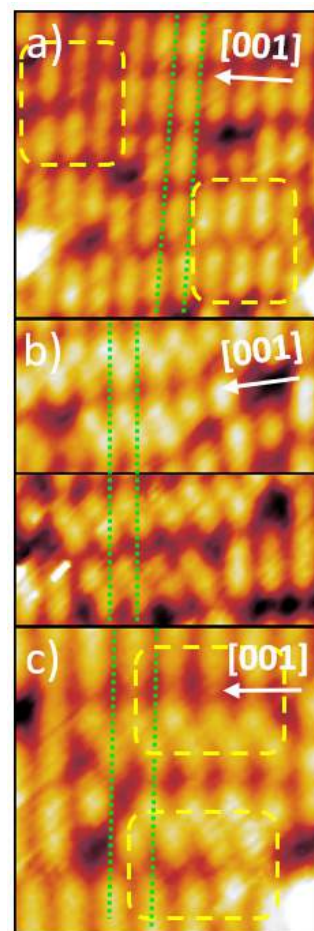


Figure 66 – STM images of DHTAP at the ML coverage with different stripe-to-stripe molecule arrangement.

5.2.3 Initial stages of the 3D islands' growth

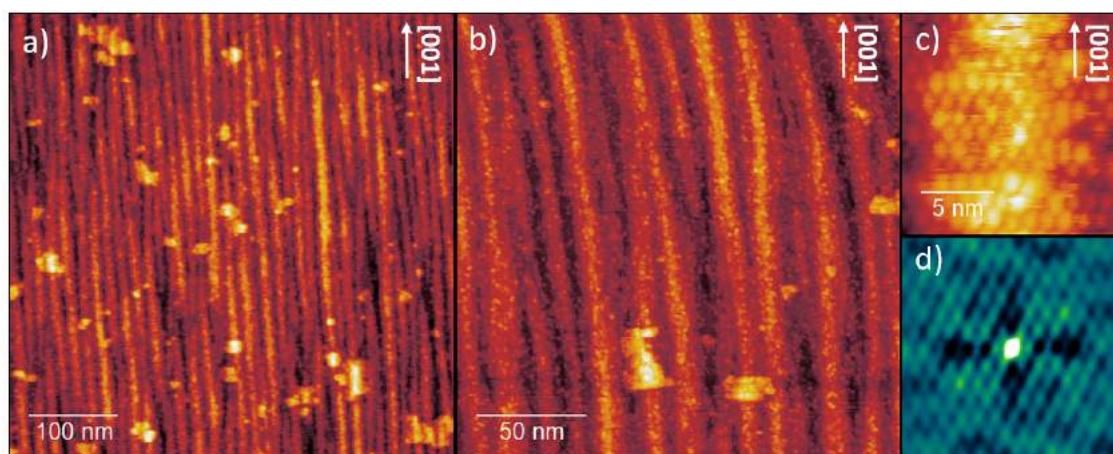


Figure 67 – UHV images of small DHTAP islands on rippled $\text{TiO}_2(110)$: a) nc-AFM overview; b) STM overview; c) STM on top of a larger island; d) 2D-selfcorrelation of (c).

While the DHTAP/ $\text{TiO}_2(110)$ interface has been resolved, the inner molecular structures of 3D islands or ribbons remained unknown. In order to investigate the DHTAP arrangement in such cases a rippled $\text{TiO}_2(110)$ sample was prepared and a coverage of 1,5 ML of the molecules was used. The grown structures were imaged *in situ* with nc-AFM and the STM. As the result small DHTAP islands emerged with the lateral dimensions ranging from a few nm up to about 50 nm (Figure 67a). Cross section profile analysis revealed that the average island height depends on the island's size with a general trend of the height increase with their size up to the 1,1 nm (Figure 68), as shown in previous sections for the large islands. Such a feature can originate from the fact that the molecules within larger islands stabilize themselves mutually. STM imaging lead to the same conclusion regarding the islands' height and yielded similar values (Figure 67b). Such observation is of a great importance, as it indicates a good vertical conductivity by the

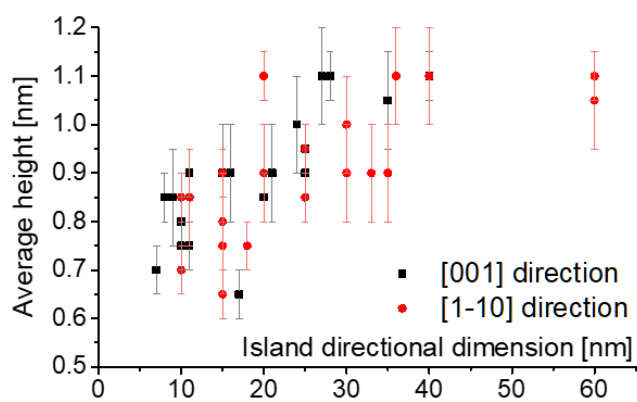


Figure 68 – Plots of average DHTAP island height vs its dimensions in crystallographic directions of the substrate surface.

substrate-molecule interface and the molecule itself. Further STM investigation gave better resolved images of the islands with the distinction of single molecules within (Figure 67c). Average STM-measured molecule dimensions range from 1,1 to 1,4 nm in [001] direction and equal ~ 1 nm in $[1\bar{1}0]$ direction. 2D self-correlation yielded hexagonal

unit cell with translation vector of 1,05 nm (Figure 67d). Large width of the molecules can be correlated to the wide appearance of the lying molecules presented before. Considering the proposed parallel facing of the substrate by the molecules with respect to the built-in dipole moment, DHTAPs should be mutually repulsive and, hence, could appear similarly wide to the flatly lying molecules. As for the molecules' increased [001] dimension, one can correlate it to the lower measured island height in these cases and, therefore, a stronger tilting towards the substrate plane. Nevertheless, presented findings show a clear ordering within the 3D islands.

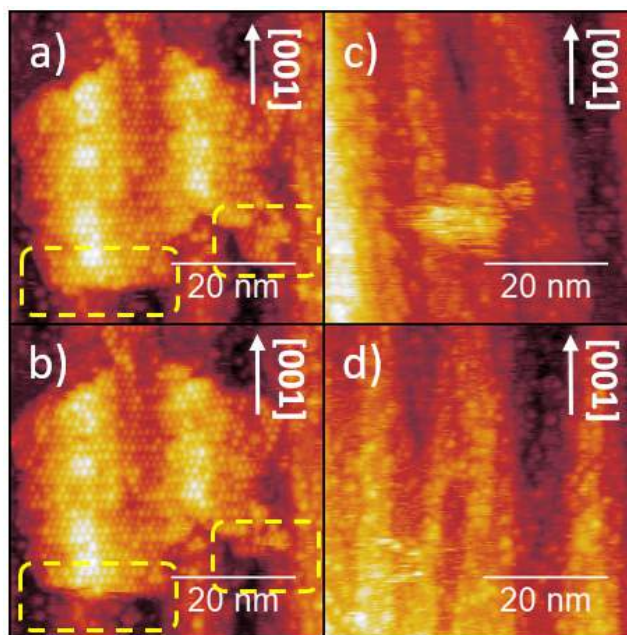


Figure 69 – Consecutive STM images of two different areas with small DHTAP islands: a-b) decomposition of island's edges; c-d) movement of the whole island.

An additional interesting aspect can be observed during continuous imaging of the same island with the STM. As the chosen island is imaged multiple times, molecules on its edges tend to detach and diffuse away (Figure 69a-b). Thus, it is very probable that the small islands are unstable. Such fact was further confirmed by decomposition and movement of a whole small island with just a single STM scan, as shown in the Figure 69c-d. An island present in the bottom half of the Figure 69c decomposes and moves away from the former area (Figure 69d).

5.2.4 Inner structure of molecular ribbons

The remaining DHTAP structures grown on $\text{TiO}_2(110)$ that required investigation were the elongated twisted ribbons. As already stated, they form on rough, non-crystal titanium dioxide surface with no correlation to the substrate crystallographic directions. A fact not mentioned before is that sometimes they grow out of the well-described 3D islands, as if they were anchored together (Figure 70). This may indicate that the ribbons are crystalline and their growth is only dictated when the molecule-substrate interaction is very low. In such cases the lateral diffusion coefficient should also be rather high, especially at the elevated substrate temperature that the molecular deposition takes

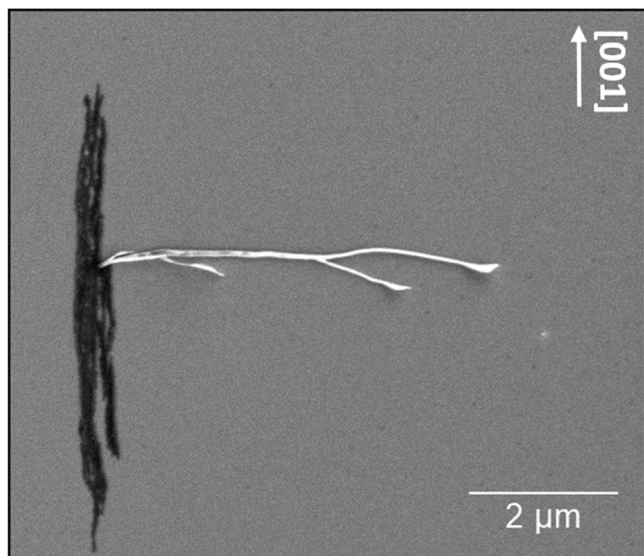


Figure 70 – SEM image showing DHTAP ribbon growing out of a 3D island.

place at. Considering the above, together with the layered vertical structure of the islands and the helical growth possibility, one could assume ribbons as the ultimate multi-level structure oriented parallel to the substrate plane. Unusually folded and twisted shapes could be correlated with the fractal nature of the DHTAP structures and the helical growth. As an indirect proof for such process, DHTAP total

material within ribbons can be compared to the material amount building the wetting layer and the islands. Calculating a total volume of ribbons (Figure 55Figure 54) vs a total volume of 3D islands (Figure 56) from the similar areas, the values are close to each other after adding the amount of molecules needed to cover this area with WL (islands part). This comparison is equal within a tolerance of 10%. Therefore, the proposed growth mechanism of the inner structure of the ribbons is possible.

5.3 Electronic properties of the DHTAP/TiO₂(110) interface

Within this section of the chapter, studies regarding thermal desorption energy of DHTA layers and their work function are presented, together with an observation of the overall structures stability against the exposure to ambient conditions. The experimental findings are compared with the properties of the pentacene's structures.

5.3.1 Desorption energy of DHTAP molecules in comparison to the case of 5A

With no data available in literature regarding mass spectrometry of DHTAP, a full span QMS spectrum of DHTAP molecules evaporated from the molecule K-cell kept at 155 °C (the deposition temperature) was obtained (Figure 71). What can be clearly noticed, the highest signal-to-noise ratio was acquired for the m/q ratio equal to 284, which is a single ionized DHTAP molecule. However, the spectrum around the main maximum exhibits other peaks at m/q equal to 281, 282, 283, 285 and 286 (red arrow markings in the Figure 71). These maxima can be related to the molecules, which adopt additional hydrogen atoms at rings with nitrogens or losing them mostly at NH groups. Rather high values for peaks at masses lower than 284 can be also the result of the molecule decomposition/dissociation in the QMS electron ionizer. Maxima at lower m/q ratios (~ 270 , 256, 230) are most probably a result of the DHTAP molecules losing nitrogen atom(s) or a fragmentation at the nitrogen positions. For all of the further TDS experiments mass = 284 was chosen as the measured signal.

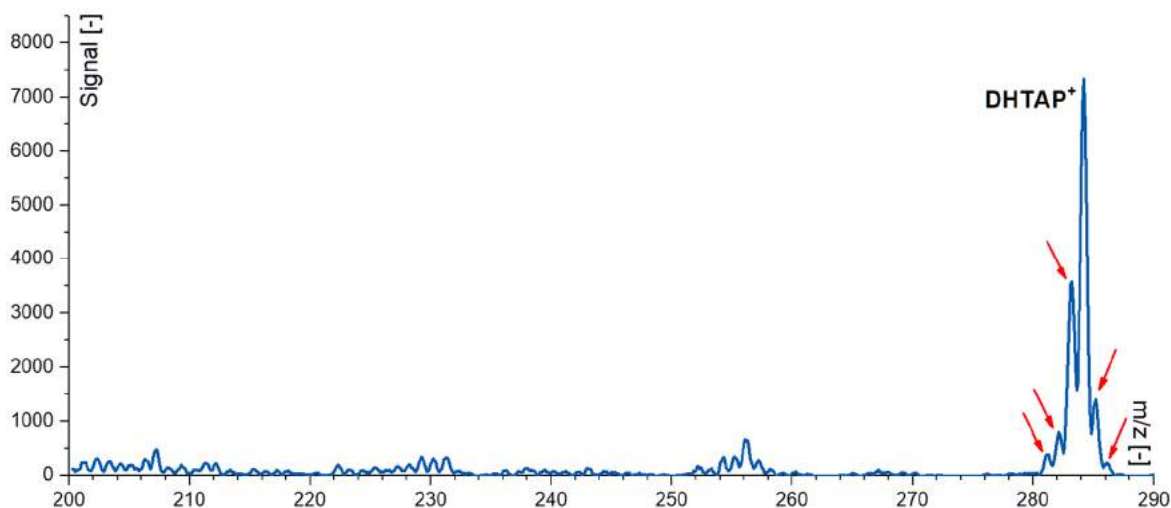


Figure 71 – Mass spectrum for DHTAP molecules measured directly from its deposition cell.

In order to determine the desorption energy for DHTAP molecules, a series of TDS experiments was performed with different initial molecular coverage. As indicated before, molecular deposition required a special care when preparing samples for thermal desorption due to the sample mounting system and the utilized heating method. The organic molecular beam epitaxy in the UHV system takes place with a whole sample holder placed in a broad molecular beam, resulting in deposition of the molecules on both the sample and the holder (Figure 72a). As the holder heats up together with the specimen crystal, the desorbing molecules originate from the whole sample mounting system, which strongly influences MS recorded signal (Figure 72c). Therefore, a masking system was used in order to make sure that the molecules are deposited only on the titanium dioxide crystal surface (Figure 72b). As clearly visible in the Figure 72c, the received TDS spectrum from a sample without the mask exhibit three desorption maxima of high intensity. Two of them originate from material desorbing from the sample holder (blue arrow markings in the Figure 72c), as they are not present on the spectrum obtained from the sample prepared with a usage of the mask.

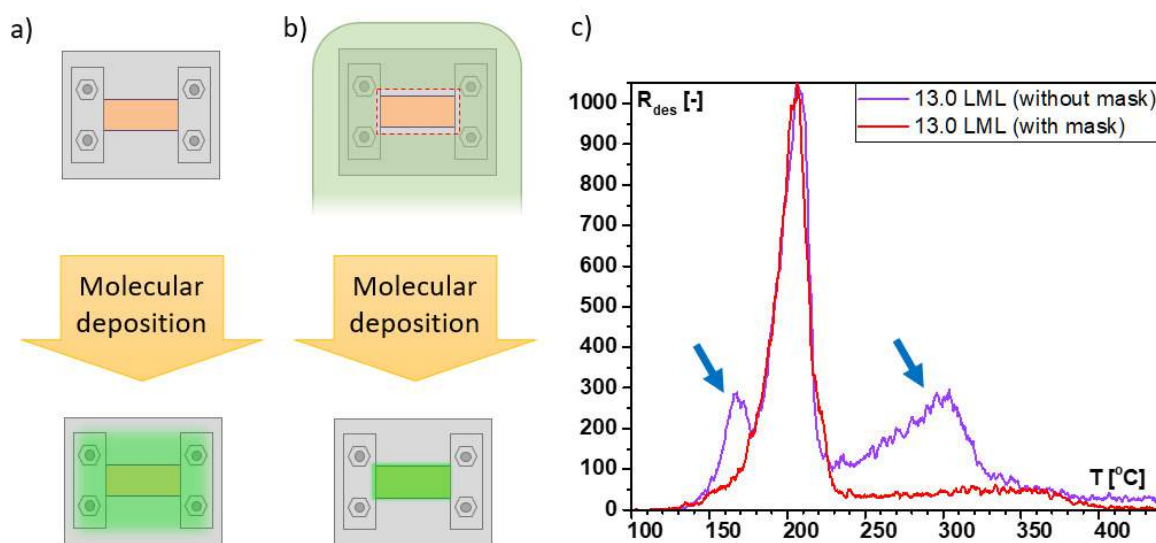


Figure 72 – Masking system utilization during molecular deposition: a-b) basic schemes of deposition areas for molecules without masking system (a) and with masking system (b); c) Smoothed TDS (7 adjacent points) spectra obtained for desorption of 13 MLs of DHTAP from $TiO_2(110)$ with different molecular deposition procedure.

Having that known, a properly prepared series of specimen with different DHTAP molecular coverage was investigated via TDS. Figure 73 shows spectra for a constant heating rate of $\beta = 1$ °C/s. Data is presented in graphs of recorded signal as the function of temperature. For the low coverage of ~ 1 LML one can notice an emerging peak maximum

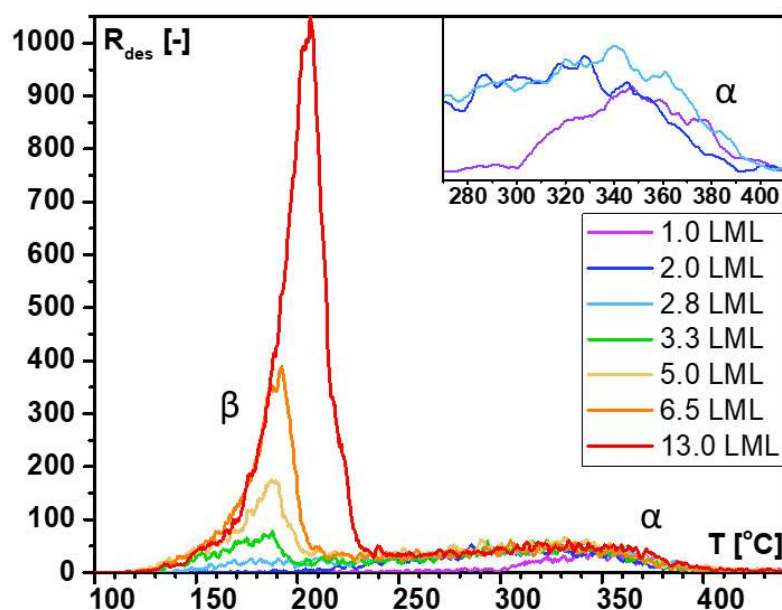


Figure 73 – Smoothed TDS spectra (7 adjacent points) for desorption of DHTAP molecules from $\text{TiO}_2(110)$ substrate with multiple different initial coverages. The inset presents data only for three lowest molecular coverages.

(α) at the temperature range of 300-400 °C. With the increasing coverage, another peak emerges (β) for the lower temperatures (150-250 °C). These maxima are related to the monolayer (α) and multilayer (β) desorption. For the *leading edge analysis* of the β -peak a $\ln(R_{\text{des}})$ vs $1000/T$ graph was plotted from the raw data (Figure 74). A linear fit was employed for the TDS spectrum of the highest coverage (13 MLs). While data points for the 6,5 MLs coverage fit well with the linear dependency, the data for lower coverages deviates from it. This originates from the differences in the exponential growth of the MS signal for coverages ≤ 5 MLs. The analysis yielded a desorption energy of multilayer $E_{\text{des}}^{3D} = 1,16 \pm 0,05$ eV and the pre-exponential factor $\nu_0 = 1,6 \cdot 10^{15(1)} \text{ s}^{-1}$. Using the ν_0 for multilayer, the Redhead analysis for the 1st order α -peak of the wetting layer was applied resulting in the desorption energy of $E_{\text{des}}^{\text{WL}} = 2,03 \pm 0,07$ eV.

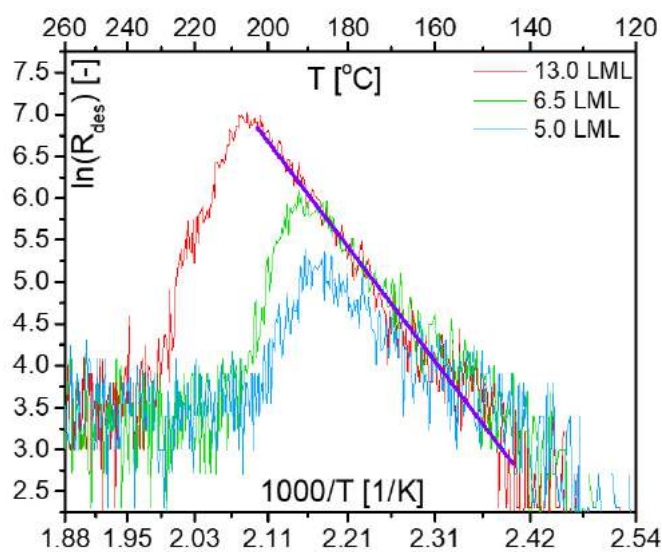


Figure 74 – A leading edge analysis graph for the multilayer desorption spectra of DHTAP.

In order to verify received values and test the correctness of v_0 usage for the WL desorption, TDS experiments were performed for the same coverage of ~ 1 ML and with varied sample heating rate constant in the range of 0,99 to 9,76 °C/s. The results are shown in the Figure 75a. A general shift of the α -peak position to the higher temperatures with the increasing heating rate can be observed. From the equation (16) in the case of the 1st order desorption one can notice that a peak maximum occurs when:

$$\frac{d^2\Theta}{dT^2} = n \cdot \Theta^{n-1} \cdot \frac{d\Theta}{dT} + \Theta^n \cdot \frac{E_{des}}{kT_{max}^2} = 0. \quad (21)$$

With the usage of equation (16) again for the $d\Theta/dT$, the fact that $n = 1$ and some rearrangements one can conclude with:

$$\frac{E_{des}}{kT_{max}^2} = \frac{1}{\beta} \cdot v_1 \cdot \exp\left(-\frac{E_{des}}{kT_{max}}\right). \quad (22)$$

Taking natural logarithm of the above equation and some further rearrangements yield:

$$\ln\left(\frac{T_{max}^2}{\beta}\right) = -\frac{E_{des}}{kT_{max}} + \ln\left(\frac{E_{des}}{k \cdot v_1}\right). \quad (23)$$

Therefore, plotting $\ln(T_{max}^2/\beta)$ vs $1/T_{max}$ should result in a straight line with E_{des} obtainable from the slope and v_1 from the intercept. Figure 75b presents the calculated data with a fitted linear function. Hence, the determined $E_{des}^{WL} = 2,10 \pm 0,09$ eV, while the $v_1 = 7,72 \cdot 10^{15(1)} \text{ s}^{-1}$.

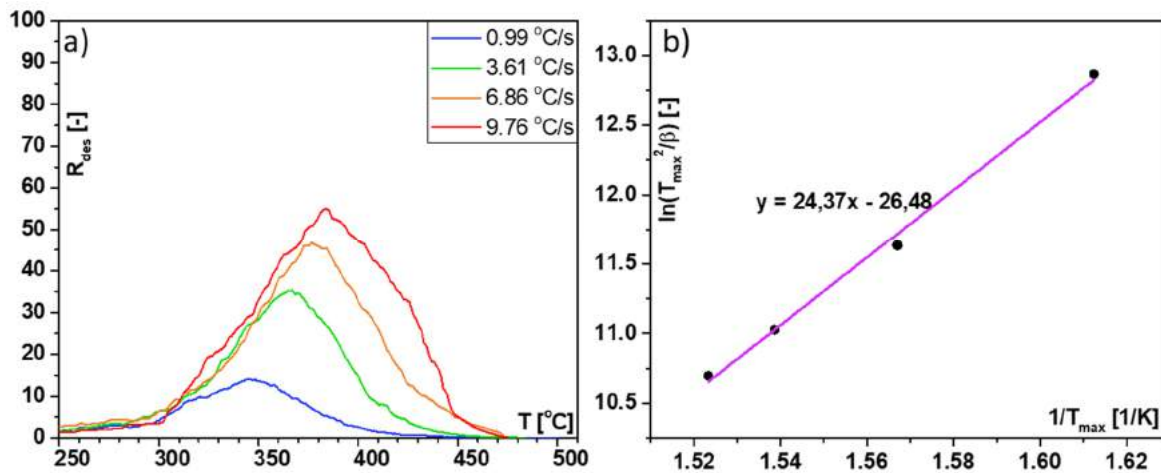


Figure 75 – Heating rate variation TDS procedure: a) smoothed desorption spectra (10 adjacent points) for different heating rates with similar nominal coverage; b) $\ln(T^2/\beta)$ vs $1/T$ plot with a linear fit.

Collected data for different heating rates additionally allowed for a broader Redhead equation utilization as it contains dependence on the heating rate (equation (20)).

All calculated values for α -peak are presented in Table 1. Average $E_{\text{des}}^{\text{WL}}$ from the Redhead analysis were calculated as weighted averages. All of the values are very close to each other and, therefore, it proves that the evaluation of the desorption energy is correct. Another observation one can make is that a leading-edge analysis allows for a good estimation of the pre-exponential factor.

Table 1 – Calculated desorption energies and pre-exponential factors from different analytic methods.

Method	B [°C/s]	$E_{\text{des}}^{\text{WL}}$ [eV]	ν [s ⁻¹]
Redhead analysis	0,99	$2,03 \pm 0,07$	$1,6 \cdot 10^{15 \pm 1}$ adopted from the leading-edge analysis
	3,61	$2,02 \pm 0,13$	
	6,86	$2,03 \pm 0,17$	
	9,76	$2,03 \pm 0,07$	
	Weighed average	$2,03 \pm 0,04$	
Heating rate variation	All	$2,10 \pm 0,09$	$7,72 \cdot 10^{15 \pm 1}$

In order to evaluate the influence of the DHTAP's molecule built-in dipole moment on the determined values, TDS experiments for pentacene were performed. An investigation was carried out for a constant heating rate of ~ 1 °C/s and different initial coverages in the range of 0,5 to 5 LML (Figure 76). On the contrary to the DHTAP spectra, three peaks emerge for a multilayer coverage. Left-most maximum (β) emerges for temperatures in

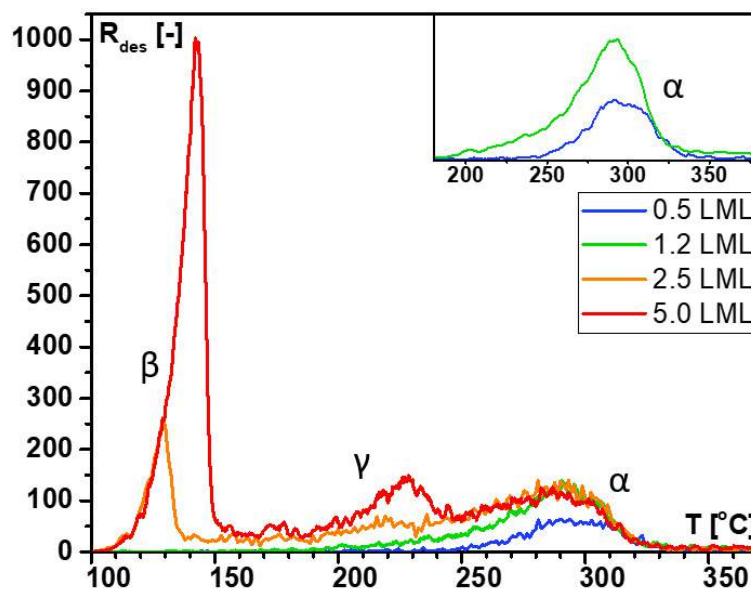


Figure 76 – TDS spectra for desorption of pentacene molecules from $\text{TiO}_2(110)$ substrate with multiple different initial coverages.

the range of 100 – 150 °C with the shape of 0th order desorption (multilayer). Right-most peak (α) appears in the temperature range of 250 – 330 °C and originates from the desorption of a monolayer. The third peak (γ) emerges for higher coverages for the temperatures 200 – 250 °C. Usually, additional peak(s) between a monolayer and multilayer are attributed to a reconstruction within a wetting layer [176,181]. However, they often appear already for coverages in between a single layer and many layers – prior to the multilayer maximum. Additionally, for the 5A molecules, no reconstruction within the wetting layer on TiO₂(110) was observed [178]. Moreover, in the presented spectra one can notice, that γ -peak emerges only for the highest coverages. One could correlate its existence to the desorption of a second flat-lying layer from the substrate. Considering Stranski-Krastanov growth [182] in the meaning of small islands of layer by layer growth for 5A/TiO₂(110), higher coverage enlarges the islands, increasing the percentage of the substrate covered with a “second layer”. However, such hypothesis was not confirmed nor denied by any other experiments. It is also possible, that the γ -peak originates simply from a not fully covered sample holder with the masking system.

Similarly to the TDS for DHTAP/TiO₂(110) a leading-edge analysis was performed for the β -peak, followed by the Redhead analysis for the α -peak. Determined desorption energy for the multilayer equals $E_{\text{des}}^{3D} = 1,64 \pm 0,05$ eV with the pre-exponential factor estimated for $\nu_0 = 9,1 \cdot 10^{22(1)} \text{ s}^{-1}$. The desorption energy accords well with the literature data of 1,59 – 1,63 eV [183,184]. A pre-exponential factor for pentacene multilayer desorption from Au(111) was reported to be $\sim 10^{19} \text{ s}^{-1}$, which is smaller than the value from the performed experiments. The Redhead analysis for both the 0,5 and 1,2 LML coverage spectra yielded a weighted average desorption energy of $E_{\text{des}}^{\text{WL}} = 2,73 \pm 0,08$ eV. In comparison to DHTAP, one can immediately notice that the energies for both desorption maxima are higher for pentacene, while occurring at lower temperatures. This is strongly correlated to the huge difference of the pre-exponential factor of the energy probing frequency. It can be clearly observed while comparing rate of the exponential growth for β -peaks between the two molecules. Desorption energies from the wetting layer differ by 0,65 eV. Lower energy for DHTAP molecules corresponds to the previously described very low molecule-substrate interaction.

5.3.2 Influence on the TiO₂(110) work function by the DHTAP and 5A monolayers.

As the interfaces of DHTAP and pentacene with titanium dioxide are vastly different in regard of both the morphology and the energies, one could expect a different change of the substrate work function when covered with the respective wetting layers. A series of KPFM measurements were performed consisting of bare TiO₂(110) WF determination, HOPG tip calibration and WL/TiO₂(110) interface measurement. Figure

77 presents exemplary topography and WF maps for DHTAP series with histograms for particular images. In comparison to the TiO₂(110) surface, the interface with DHTAP exhibits a change in the work function of $\Delta\phi_{\text{DHTAP}} = -0,25 \pm 0,04$ eV. For the pentacene WL, the change is larger and equals $\Delta\phi_{5A} = -0,36 \pm 0,03$ eV. Such difference can be

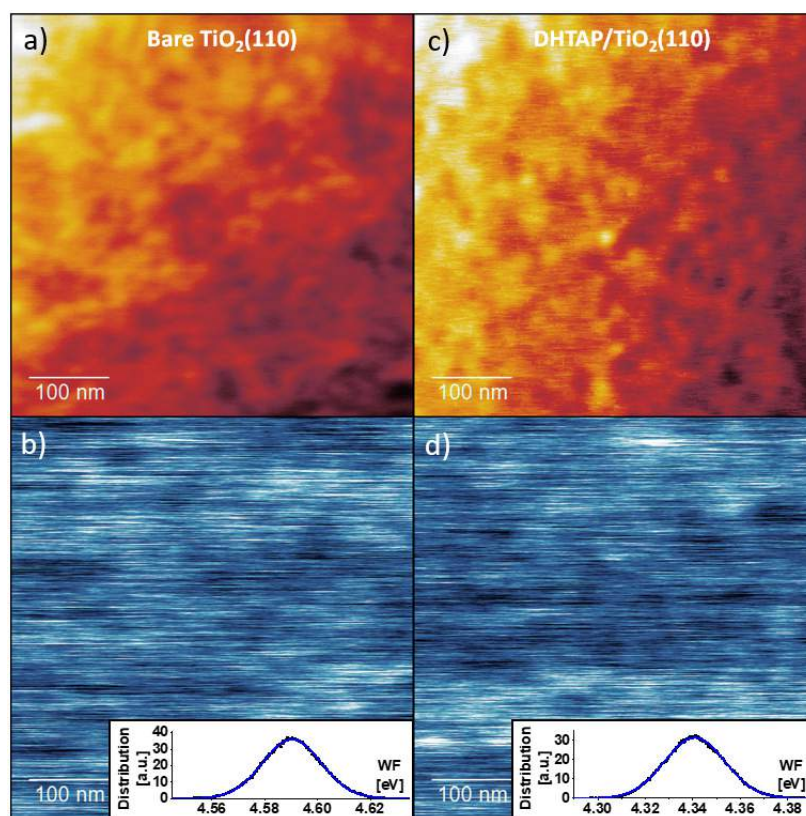


Figure 77 – Work function determination for bare TiO₂(110) substrate and DHTAP/TiO₂(110) interface: a,c) KPFM topographies; b,d) recalibrated work function maps.

again contributed to the molecule-substrate interaction. Additionally, the dipolar character of the DHTAP goes in line with the TiO₂(110) substrate character, especially in the case of perpendicular lying orientation with respect to the surface atomic rows. The presented difference encourages similar studies regarding any primary molecules modification with implementation of permanent dipoles as a tool for WF tuning.

5.3.3 Ambient stability of the DHTAP structures.

It has been shown that on sapphire substrate up-right standing islands of DHTAP are not stable in time and decompose in timeframes of days/weeks [124]. However, no data is available regarding the stability of other DHTAP structures. Here, some of the

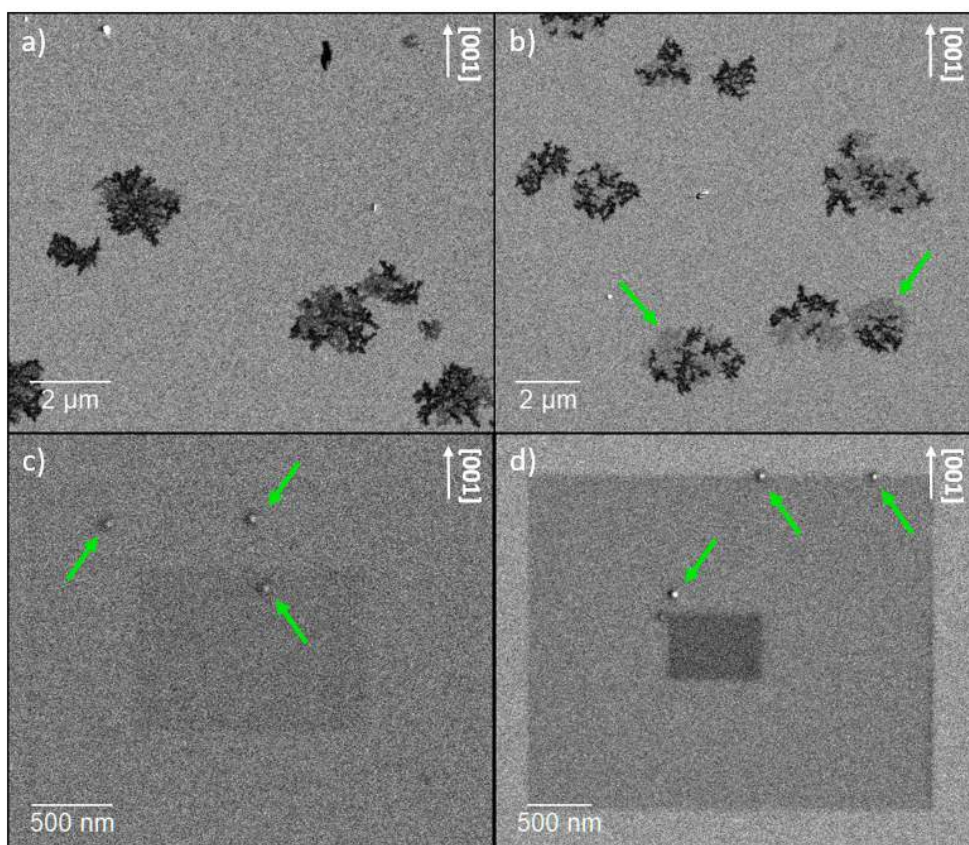


Figure 78 – SEM images of DHTAP structures on $\text{TiO}_2(110)$ after air exposure: a) 3D islands at the day of the exposure; b) 3D islands after 2 weeks in air conditions; c) wetting layer indication at the day of the exposure; d) WL indication after a month in air conditions.

DHTAP structures were tested against the time storage at various time-scales. It was found, that similar to a sapphire substrate, the DHTAP islands change in equivalent periods of time, losing their sharp edge-lines and SEM contrast (Figure 78a-b). As for the wetting layer, it seems to be stable in air conditions, which is indirectly proven by forcing the decomposition with SEM imaging (Figure 78c-d). The wetting layer still exists after

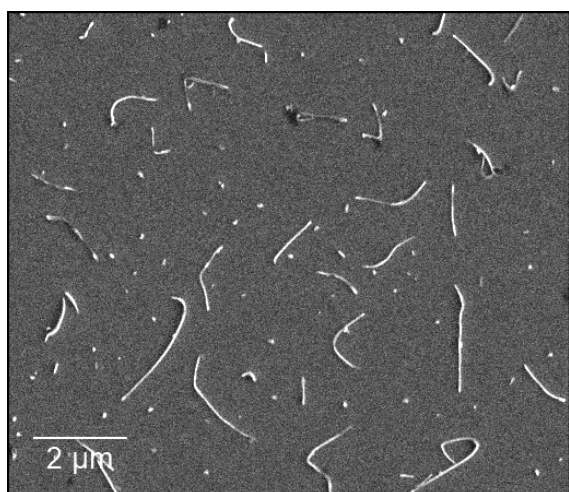


Figure 79 – SEM image of DHTAP ribbons after six months in air conditions

exposure to the ambient conditions, which makes it very stable despite the very low molecule-substrate interaction.

The twisted nanoribbons laterally don't change. Even after a long period of six months in air conditions, they preserve their bent and folded shapes (Figure 79). The visible uniform contrast within structures suggests none or very little degradation occurrence.

Chapter VI

Summary and conclusions

Within the last chapter a summary of conducted studies is presented, together with conclusions drawn from the investigated molecules comparison.

6.1 *Para*-hexaphenyl

Within this work, the general growth modes of 6P on differently prepared titanium dioxide surfaces have been recapped. Most importantly, a formation of the molecular wetting layer has been directly proven. *Para*-hexaphenyl forms a compact monolayer of closely-packed side-by-side molecules with their long axes parallel to the substrate's protruding atomic rows. The correlation with the [001] direction is so strong, that no other orientation is adopted, even in extreme cases of morphological alteration. The wetting layer perfectly resembles the substrate's periodicity perpendicularly to the atomic rows. 6Ps form, so-called, molecular stripes roughly along the $[1\bar{1}0]$ direction. Within the stripes the molecules are tilted by their long axes with respect to the substrate plane by an angle of 20° . Despite a very strong interaction in such conformation, its character stems mostly from the van der Waals attraction. Rather high thermal desorption energy of the molecules have been determined both experimentally ($3,75 \pm 0,41$ eV) and theoretically (4,06 eV), which are in a good agreement with each other. Finally, an influence on the surface work function was investigated via KPFM measurements yielding a change of about -0,1 eV for the 6P/TiO₂(110) interface. One could conclude, that *para*-hexaphenyl forms a well-defined, compact and ordered interface with the TiO₂(110) surface, which is crucial for any application purposes. Unfortunately, the interface lacks stability in air conditions.

6.2 Dihydro-tetraaza-pentacene

For the DHTAP molecular growth it has been shown, that on titanium dioxide various growth processes can occur. Substrate crystallinity is of great importance when it comes to the formation of fine structures. Despite the fact of TiO₂(110)s' strong morphological anisotropy and a non-uniform surface charge distribution environment, which for the case of dipolar molecules like DHTAP should be crucial, the molecule-substrate interaction is very weak. A few different configurations of lying molecules are found when increasing coverage from a single molecule up to a full monolayer. On the contrary to the structurally equivalent pentacene, DHTAP forms a wetting layer built of molecules lying perpendicularly to the [001] direction. Such a fact most probably stems from the dipolar character of the molecule. With the further increase of the coverage, the molecules form fractal-like 3D multi-level islands of strongly tilted molecules. In some cases a helical/screw-like growth is observed. A very low molecule-substrate interaction

was confirmed by the desorption energies of molecules from both the multi- and mono-layer regimes (1,19 eV and 2,07 eV, respectively). In comparison, the pentacene's desorption energies for similar circumstances are much larger and equal 1,64 eV and 2,74 eV, accordingly. However, despite the very low mentioned energies, the DHTAP wetting layer remains stable in air conditions for long periods of time. As the molecules are dipolar, such layer could exhibit interesting electrical parameters. On the contrary, the 3D islands are vastly unstable and decompose within first weeks in air environment. Another interesting study within this work was a difference of the surface work function shift when comparing DHTAP and 5A wetting layers on TiO₂(110). The DHTAP/TiO₂(110) interface shows a lower WF of about 0,25 eV in comparison to the bare titanium dioxide, whereas the TiO₂(110) covered with pentacene wetting layer has a lower WF of about 0,36 eV than the bare substrate. In some particular electronical cases such a difference could play a crucial role. Concluding the above, DHTAP exhibits some great properties, however, it is also problematic in the case of large structures.

6.3 General conclusions

With the two rod-like molecules investigated in terms of thin-film growth on titanium dioxide, one can draw some overall conclusions, due to similarities and differences between the 6P and the DHTAP. As both of the molecules are elongated any surface with morphological anisotropy should affect their behaviour. It is indeed observed, that on TiO₂(110) both molecules energetically favour parallel orientation with respect to the substrate's atomic rows. However, with enough neighbouring molecules, in the case of DHTAP, the perpendicular configuration is adopted. The strong molecule-molecule interaction enforces rearrangement of the molecules from parallel orientation to the one rotated by 90 degree with their long axes. In the case of *para*-hexaphenyl no such process occurs, indicating a much stronger molecule-substrate interaction. It is indeed confirmed by the thermal desorption energies difference in favour of the 6P by a huge offset of 2 eV. The mentioned rotational rearrangement also doesn't occur for pentacene on TiO₂(110). The determined desorption energy for the 5A is also higher than for the DHTAP by almost 0,7 eV, which again, accords with the adopted configuration conclusion. Another premise for the differences in molecule-substrate interaction is the growth of up-right standing islands or, more precisely, circumstances at which they are

formed. In the case of 6P, a high concentration of substrate step-edges is needed to force the growth of islands, which in the case of DHTAP is not necessary.

An interesting observation concerns the stability of the molecule-substrate interface in air conditions. The *para*-hexaphenyl wetting layer is immediately decomposed when exposing it to the air environment, while the DHTAP monolayer remains stable. It is rather unintuitive considering previous findings regarding interaction energies. Therefore, one has to assume, that DHTAP molecules stabilize themselves when in a compact, adherent layer, preventing a degradation.

As for the mechanical properties of the investigated molecules throughout the experiments, it was observed that 6P molecules are able to lie over the titanium dioxide step-edges, while DHTAP molecules are not. Such a fact can originate from the interconnection between the consecutive segments of molecules. In the case of *para*-hexaphenyl, a single bonding between phenyl rings makes the whole molecule flexible, allowing for a certain bending/twisting in order to maintain coherency with the substrate atomic rows, when lying over the step-edge. The DHTAP molecule, similarly to the pentacene, is built of benzene rings that are fused together, making whole molecules rather stiff. During imaging, no occurrence of over-the-edge configuration was found for the DHTAP.

Publications authorship and co-authorship

1. *In situ study of redox processes on the surface of SrTiO₃ single crystals*
D. Wrana, C. Rodenbücher, **W. Bełza**, K. Szot, F. Krok
Applied Surface Science, 432 (2018) 46-52,
2. *Fabrication of ion bombardment induced rippled TiO₂ surfaces to influence subsequent organic thin film growth*
M. Kratzer, K. Szajna, D. Wrana, **W. Bełza**, F. Krok, C. Teichert
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3. *Initial stage of para-hexaphenyl thin-film growth controlled by the step structure of the ion-beam-modified TiO₂ (110) surface*
K. Szajna, M. Kratzer, **W. Bełza**, A. Hinaut, D. Wrana, T. Glatzel, C. Teichert, F. Krok
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4. *Kelvin probe force microscopy work function characterization of transition metal oxide crystals under ongoing reduction and oxidation*
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7. *Tuning the electronic properties of a clean TiO₂ surface via repeated sputtering and annealing: A KPFM and LC-AFM study*
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