

Design and optimalization of large-area molecular junction for charge transport measurements of self-assembled monolayers

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Preface

It is very hard to image today's world without electronics. Computers and mobile phones are an inherent element of both professional and private parts of our lives. Contemporary silicone-based electronics has some limitations such as incompatibility with flexible substrate. Emerging field of organic electronics seems to be a perspective alternative to the standard electronics, due to its unique features. There is no evidence so far, that organic electronics can compete with the standard approach in high-end applications, but for low-end ones it certainly can. Even today, most of the displays in smartphones are made in organic light-emitting diodes (OLED) technology. Perhaps in the future the market of organic electronics will be even more pronounced.

In low-end applications the low costs of processing are of the highest priority. Instead of single molecules, self-assembled monolayers (SAMs) can be used, where the functionality is still incorporated in the molecular structure, but the processability is much less demanding. SAMs can be formed by immersing the substrate in a solution containing precursor molecules which spontaneously bind to the substrate, forming a densely-packed monolayer. Moreover, only small quantities are required to cover a large area. For instance, using only 1 g of dodecanethiol a densly-packed SAM on gold can cover an area of ca. 0.5/m². Comprehensive knowledge about the structure and electronic transport properties are needed for using SAMs in organic electronics.

This thesis is a summary of author's research conducted during his studies of Physics at the Jagiellonian University in Cracow. During that time author designed and fabricated large-area molecular junctions, which can be used for investigating the charge transport properties across a SAM. The first chapter provides a reader with basic information concerning organic electronics which is a general context of further work. The second chapter is an introduction which gives basic notions and theoretical models describing the physics of SAMs. The third chapter reviews current methodology for measuring the conductance of SAMs. The main experimental work concerning large-area molecular junctions is presented in the fourth chapter. In the appendix, one can find author's article concerning the structure SAMs, which has been published recently in the Journal of Physical Chemistry C.

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Chapter 1

Organic electronics

The invention of a transistor by John Bardeen and William Schockley in 1947 and later on the invention of Integrated Circuit (IC) by Jack Kilby in 1958 have changed irreversibly the face of the world. Both of these inventions have been acknowledged by the Nobel Committee with The Nobel Prize in Physics (Bardeen-1956, Kilby-2000). Apart from obvious advantages of the silicon-based electronics, this approach has some serious limitations such as natural incompatibility with flexible substrates. For some applications, flexible electronics is highly desired and organic electronics seems to be an interesting alternative fulfilling this demand.

This chapter is devoted to organic electronics in order to establish the general frame of reference for further discussion. Beginning of this chapter provides a reader with general knowledge concerning organic electronics i.e. historical background and motivation for using organic molecules in contemporary electronics. Finally, some interesting applications are discussed to illustrate the progress in the field of modern organic electronics.

1.1 Historical background

Organic electronics dates back to 1862, when Henry Letheby for the first time obtained a partly conductive material which was most probably polyaniline (PANI). Since then, electrical transport behavior has been sought very intensively, but the true breakthrough came much later with an extensive studies of polyacetylene [1] by Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid for which they were awarded The Nobel Prize in Chemistry (2000). Their pioneering work in the field of organic electronics led to synthesis of many polymers of a great practical importance such as poly(phenylene vinylene) (PPV) used in organic light-emitting diodes (OLEDs) or poly(ethylenedioxythiophene) (PEDOT) used in organic photovoltaic cells (OPVs).

The class of organic molecules showing self-assembly behavior such as deoxyribonucleic acid (DNA) or self-assembled monolayers (SAMs) are of special importance for practical applications. Electrical transport properties of DNA has been studied since 1960s [2]. The idea that DNA strands could have conducting properties comes from the work of Jacqueline K. Barton in 1993 [3] which started a hot debate upon conductivity mechanism trough DNA molecules. It was reported that DNA is electric conductor, semiconductor, insulator [2] or even superconductor [4]. Those apparently contradictory

results were explained by a very large phase space of probing and preparation conditions of DNA samples.

Electric properties of SAMs have been studied for a relatively short time. First experiments incorporating two monolayers of alkanethiolates sandwiched between mercury drops comes from the work of Krzysztof Słowinski, Harold Fong and Marcin Majda [5] from 1999. Later on, some other techniques has been established such as deposition of metal films by thermal evaporation or using the tips of scanning-tunneling microscopy (STM) or conductive probe atomic force microcopy (CP-AFM) as an electrode [6]. Each of the employed techniques possess some advantages, however, exact values of conductivity obtained with different approaches show significant differences [7]. Nevertheless, character of electrical transport through SAMs seems to be confirmed as quantum tunneling [6]. More information about SAMs can be found in the chapter 2.

1.2 Motivation for using organic molecules in electronics/photonics

Stereotypical view on polymers (plastics) is that they are somehow the opposite of metals. Many of polymers do indeed insulate, but it is not the general characteristic of organic substances. It is possible to synthesize transparent (80% at wavelength of 550nm) polymer films with conductivity as high as 3000 S/cm which is comparable to to widely used inorganic films of indium tin oxide (ITO) [8].

Electrical conductivity of polymers is strongly connected to the presence of conjugated double bonds along the backbone. Each double bond consist of a strong, chemical and well-localized σ bond and a weak, delocalized π bond (remaining p_z electron after sp^2 hybridization of carbon atoms). Addition of dopants partially removes π electrons which increase their mobility along the chain. Interchain electronic transport is governed by rather complicated interplay of band-like transport, hopping mechanism and tunneling [9]. In addition, mobility of carriers is also decreased by the presence of grain or domain boundaries which leads to more localized states. Those effects makes the electron mobility dramatically lower for organic conductors as compared to inorganic ones, so it is unlikely that organic electronics will replace conventional materials for the high-speed applications in the nearest future. However, electronics based on polymers possess some unique features which are highly desired in some fields.

One of the most important drawbacks of inorganic electronics is their complicated and expensive production based on UHV (Ultra High Vacuum) techniques. It takes significant amount of money and time in order to make a specialized circuit which, in a sense of profitability, limits the production only to large quantity. Organic materials overcome this problem as they can be prepared from solution, avoiding expensive UHV production line. As a consequence, using organic materials, even complex electronic circuits could be printed using slightly modified inkjet printer. That open the opportunities for completely new applications such as radio-frequency identification (RFID) tags on every item without a major increase of their price. Even today, OLED displays are dominating in the mobile phones. In consequence, global market studies forecasts bright future for printed electronics with the revenue of 96 billion US dollars in 2020 [10].

Another important aspect of organic electronics is its compatibility with the substrate. (Poly)crystalline silicon is a rigid material with high-temperature processing needed to obtain suitable electronic properties. Bending of silicon crystalline structure results in damaging device. This all limits the silicon-based electronics only to rigid substrates. In contrast, organic electronics is free of this



Figure 1.1: (a) Strong σ bonds in the phenyl ring. (b) Delocalized π bonds in the phenyl ring. Both those bonds results from sp^2 hybridization.

limitations and it could be safely applied on flexible substrate [11]. SAMs' application in organic electronics consist of a couple of existing solutions as OLEDs [8] or organic field-effect transistors (OFETs) [12] as well as more forward-looking ones such as molecular memories [13] or nanoparticle-based electronics [14].

In conclusion, organic electronics may have electronic performance not as good as this based on silicon, but good enough for a whole new range of applications where conventional electronics has always been too expensive. In combination with flexible substrates and printing possibility organic electronics emerge as an interesting alternative to silicon-based electronics.

1.3 Applications of organic electronics

The number of possible devices based on organic electronics is growing rapidly nowadays mainly driven by low fabrication costs, mechanical flexibility and good compatibility with other materials. This section briefly describes three most promising organic electronics applications which have already stepped from laboratory into industry: (1.3.1) organic light-emitting diodes (OLEDs), (1.3.2) organic photo-voltaics (OPVs) and (1.3.3) organic field-effect transistors (OFETs).

1.3.1 Organic light-emitting diodes (OLEDs)

OLED's principle of operation is similar to LED's. Electric carriers are injected into the semiconductor region which results in radiative recombination. Importantly, for OLED's radiative recombination takes place in the whole region of organic semiconductor and not just on the junction as for LEDs. That increases vastly the active region of the diode. In case of organic semiconductors the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are used as the equivalence to conductance band and valence band, respectively. Energy difference between HOMO and LUMO states is correlated with the wavelength of emitted light. By proper choice of the material, it is possible to obtain OLEDs emitting light in visible region.



Figure 1.2: Schematic energy band diagram of an OLED. Effective work function of the anode could be modified using SAMs with different dipole moment orientation. The right-hand side of the picture represents the orientation of dipole moments for various SAMs on the anode.

Carrier injection barriers for OLEDs are determined by the difference between work functions of electrodes and HOMO or LUMO levels. That energy barrier strongly affects emission efficiency of the device [15]. By coating an electrode with SAMs of different dipole moments it is possible to tune the effective work function of an electrode to HOMO/LUMO level of the organic semiconductor to lower injection barrier (see Fig. 1.2). In combination with the simple micrometer-range lithographic techniques such as microcontact printing (μ CP) technique such approach enables a local modification of the desired regions of an OLED [16].

The major advantage of OLEDs over LEDs is compatibility with flexible substrates. That feature enables design of a completely different kind of devices such as roll-up displays. Moreover, OLEDs seems to have much faster response time, better power efficiency and higher contrast ratios which makes them a serious competitor to LCD display technology [17]. However, there are still some issues which should be overcome in order to exploit the true potential of OLEDs. One of the main obstacle is short lifespan and vulnerability to moisture. This means that OLEDs should be carefully designed against water damage and other environmental factors.

1.3.2 Organic photovoltaics (OPVs)

OPVs work in a reverse way to OLEDs. Organic semiconductor is sandwiched between transparent electrode with a high work function, in most cases ITO, and anode with a low work function. That sets up an electric field inside semiconductor (see Fig. 1.3a). When photon of suitable energy is absorbed in the bulk of organic semiconductor, an excited state is created and confided with a molecule or region of polymer chain. This excited state can be treated as an electron-hole pair bound by electrostatic interaction (exciton). Exciton can be broken up by the effective electric field brought up by electrodes of different work functions. Electron/hole are further pulled by cathode/anode and that results in a creation of voltage and current in a circuit.



Figure 1.3: Models and the corresponding schematic energy band diagrams for three types of OPVs. (a) Single layer organic semiconductor cell. (b) Planar bilayer cell. Photoinduced electron is transferred from electron donor polymer into electron acceptor region. This can happen only in the neighborhood of the interface. (c) Bulk heterojunction morphology. The area of interface between two organic semiconductors is vastly increased in comparison to bilayer cell.

Using OPVs with single organic semiconductor, apart from its simplicity, is not the most effective approach. Often the electrons made of excitons recombine with the holes rather than reach the electrode. To deal with this problem bilayer OPVs has been developed where two layers of organic semiconductors with different electronic structure are stacked (see Fig. 1.3b). If the exciton is formed at the interface of both semiconductors electron can be transferred into electron accepting semiconductor with lower LUMO level and then to anode [18]. That approach seems to be much more effective than the single layer strategy.

The polymer films needs to be about 100 nm thick in order to absorb enough light and excitons usually decays within ca. 6 nm [18]. That means that only excitons formed very close to an interface have a chance to diffuse across the film. To deal with that problem, bulk heterojunction approach has been introduced [19] (see Fig. 1.3c). This strategy involves dissolving both organic semiconductors in the same solvent and casting a blend. In this way it is possible to obtain an inhomogeneous film consisting of two semiconductors with larger interface area.

In order to utilize the broader spectrum of light, tandem OPVs are constructed, in which two solar cells of different absorption are stacked together. So far, the highest reported efficiency of such organic solar cells is 8.62% [20]. This efficiency is quite low in comparison to traditional multi-layer solar panels (ca. 30%), but large scientific attention (see Fig. 1.4) in this field suggests further improvements.

SAMs start to play an important role in the organic solar cell field. Firstly, introduction of SAMs onto electrodes enables tuning the work function [21] to improve photoinduced charge transport and in a consequence, dramatically improve the efficiency of OPVs [22]. Secondly, SAMs has recently been used for light-harvesting in artificial photosynthetic system which may be used as an efficient light-to-current convertor in molecular devices [23]. Finally, bio-SAMs are also used as a convenient interface between inorganic electrodes and biological systems in the photosynthetic fuel cells and bio-sensing applications [24].

The main reason why contemporary solar cells are not so widely used as a power source is their



Organic solar cell publications

Figure 1.4: The number of OPV's scientific publications in the last decade. Search done using Thomson Reuters ISI Web of Knowledge.

high costs of manufacture. Harvesting reasonable power from a solar panel requires large-area devices to be built. This, together with a high price of defect-free semiconductors makes inorganic solar cells quite expensive. However, OPVs are much cheaper and its production does not employ sophisticated processing. Furthermore, natural compatibility with flexible substrates together with a small weight makes those solar cells very attractive for many home applications. OPVs are already commercially available. In 2008 Konarka Technologies started production of polymer solar cells on commercial scale. The foldable organic solar cells with efficiency of 5% can already be purchased.

1.3.3 Organic field-effect transistors (OFETs)

The first organic field-effect transistors (OFETs) [25] were indeed hybrid systems consisting of inorganic silicone/silicone dioxide and organic semiconductors used for channel formation. This approach seemed to be the most straight-forward as the silicone technology was readily available. Even today, it is still used in benchmark test devices [26]. Nevertheless, fully organic transistor technology, which possess all the advantages of organic electronics such as low costs and flexible substrate compatibility, is emerging. Recently, transparent and flexible OFET design has been reported [27] which can be used as a multi-modal sensing device with a wide range of applications.

Apart from sensing applications, OFET technology is also rapidly progressing in the other fields

of modern electronics. In digital electronics, it is now possible to make a flexible printed organic NAND flash memory [28]. The concept of printing electronics surely would dramatically decrease the costs of manufacture and enable reaching the applications in which electronics used to be too expensive. One of this applications could be organic RFID tags which have a potential to replace conventional barcodes, or other identification systems used in logistics. Those devices has already been implemented using OFETs. Furthermore, there are also public-domain SPICE (Simulation Program with Integrated Circuit Emphasis) libraries for simulation OFET-based circuits [29].

The problems with a low mobility of carriers (as mentioned in the section 1.2) seems to limit OFET applications to non-analog ones. This, however, is only partially true as there are successful attempts in analog circuits design such as digital-to-analog convertor (A/D) or delta-sigma modulator [30]. New methods of preparation and synthesis of organic compounds enable to achieve the higher carrier mobility [31].

Due to different conduction mechanism in organic semiconductors carriers move mainly by hopping, and band-like transport can only be observed at low temperatures [26]. Organic semiconductors, due to weak intermolecular interactions, are basically molecular solids. This results in a broader number of effects through which the dielectric layer isolating the gate can affect the carrier transport properties in OFETs. Probably the most important parameters influencing the performance of OFETs are semiconductor morphology and interface's roughness which are affected by dielectric film.

SAMs in OFET applications can bring a way to increase the mobility of carriers. It was reported, that introduction of octadecytrichlosilane SAM on the silicone dioxide gate insulator results in 20fold improvement in the mobility of carriers in polyfluorene copolymer [32]. Another import issues concerning the performance of OFETs are the source and drain contact resistance. The metal work function needs to be tuned to semiconductor's ionization energy for efficient charge injection, which can be fulfilled by covering the contacts with SAMs of suitable dipole moment [33]. SAMs are also used in OFET-based bio-sensor applications for immobilization of given molecules such as DNA on the gate electrode [34, 35].

Chapter 2

Self-assembled monolayers (SAMs)

Introduction of a surface breaks the translational symmetry in a crystal, which results in a different properties of the surface in comparison to the bulk material. The surface science has drawn a significant attention due to a large scope of applications. The usage of SAMs enables tailoring the properties of a surface to suit a given application. This chapter gives general information about SAMs. First, the structure of SAMs is discussed together with a brief description of the most important molecules used for the SAM's preparation. Secondly, the most remarkable applications of SAMs are given. Finally, theoretical models of a charge transport mechanism across SAM are presented.

2.1 Structure

One can define SAM as a quasi-two dimensional system of spontaneously well-ordered molecules, chemisorbed on the substrate. The thickness of SAM is well-defined and lies in the range 1-3 nm with spacing between molecules ca. 0.5 nm. Typically, one can divide SAM molecule into three parts, depicted in the Fig. 2.1. Head group is the part of SAM which binds chemically to a substrate, terminal group which defines properties of the functionalized surface and spacer chain which separates both of those groups.

The most important molecules forming SAMs are thioles, carboxylic acids and silanes which enables formation of SAMs on metals (Au, Ag, Cu, Ni), semiconductors (Si, GaAs) or isolators (mica, glass). Common precursors of SAMs with corresponding substrates are presented in the Table 2.1. Thioles on Au (111) has been used as a model system in the most structural research of SAMs [7, 36-38], probably due to the high stability. A selene analogs of thioles, id est. selenolates, seems to be a perspective alternative for thioles due to even higher stability [39].

A spontaneous self-organization of SAMs is driven by mutual van der Waals or dipol-dipol interactions between neighboring molecules. The energy of this interaction is a complicated function of a spacer chain's length, chemical composition and packing density of the monolayer. In case of hexadecanethiol (C16) SAM the intermolecular interaction of a given molecule with its closest neighbors is ca. 1.1 eV. The molecules forming SAM are typically not normal to the surface, but



Figure 2.1: Schematic representation of molecules forming SAM.

Substrate	Precursor	Binding with the substrate
Au	RSH (thiol)	RS-Au
Au	ArSH (thiol)	ArS-Au
Au	RSSR (disulfide)	RS-Au
Au	RSR (sulfide)	RS-Au
${ m Si/SiO}_2$	$RSiCl_3(trichlorosilane)$	Si-O-Si (siloxane)
${ m Si/Si-H}$	RCOOH (carboxyl)	R-Si
Metal oxides	RCOOH (carboxyl)	$RCOOMO_n$

Table 2.1: Common substrates and corresponding SAMs' precursor molecules after Ref. [40]. R corresponds to alkane and Ar corresponds to aromatic hydrocarbon.

tilted by some angle as schematically depicted in the Fig. 2.1 and denoted as α . Tilt angle depends on the spacer chain, head group and substrate as well. For C16/Au α is about 35°C.

SAMs can be prepared by incubation a substrate in a solution containing precursor molecules, which can chemisorb on the surface. Typically, the concentration of precursors is quite low (ca. 1 mM) and it takes a couple of hours to prepare a well-organized monolayer. Alternatively, a substrate can be exposed to a vapor of reactive molecules.

In fact, the process of SAM's formation can be divided into two stages [41]. During the first stage, which lasts a couple of minutes, precursor molecules chemisorb on the surface and thickness of SAM reaches about 80-90% of completely formed monolayer [42]. A contact angles measured during this step reaches close values to the final ones. This stage is dominated by interactions of the head group with the substrate and takes longer time for less diluted solutions. At the next stage, molecules spontaneously organize due to intermolecular interactions. This process is governed by mobility of molecules at the surface and interactions between SAM's molecules. The process of SAM's formation is depicted on in the Fig. 2.2.

The kinetics of the first stage of SAM's formation can be described by means of the simple Langmuir model. This approach, however, leads to significant discrepancies with reality as it denies to take into consideration molecule-molecule interactions and unequal probabilities of adsorption for each molecule. It was shown [43], that addition of a dipole moment increasing the intermolecular interactions, leads to a divergence with the Langmuir model. The probability of adsorption is not



Figure 2.2: Schematic representation SAM's formation process. At the first stage, which lasts a couple of minutes, precursor molecules binds chemically with the substrate. Next, mutual interactions of the chains leads to organization of the chemisorbed molecules. This stage is spontaneous and lasts a couple of hours.

uniform on the surface. SAMs tend to grow by nucleation with domains formed in the neighborhood of surface defects [44]. Moreover, a process of SAM formation runs not only through mentioned above stages, but rather through a couple of intermediate stages. It was observed [37, 45, 46], that at the beginning the flat phase is formed which is then transformed through the coexistence with some transitive phases into the final stable phase. All that issues together with a large quantity of molecules taking part in a SAM formation process led to the extremely complicated system, virtually impossible to be accurately described theoretically, for the time being. Also, computer simulations of SAMs denies to give much of the insight as they are mostly based on the experimental results [47-49]. Recent simulations employing the Monte Carlo algorithms presents the proper reconstruction of the SAM formation, but only for simple alkanethioles [50]. Experimental work is the main source of knowledge about more complex SAMs.

Alkanethiol $(CH_3 (CH_2)_n SH)$ SAMs has been probably the most widely studied systems because of their stability and versatility. Those molecules form a well-ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure on Au(111) substrate [7], but aromatic molecules seems to be more desired in the field of organic electronics. However, the structure of purely aromatic SAMs seems to be quite defective with smaller domains than in the case of their aliphatic analogs. This problem could be solved by using a hybrid aromatic-aliphatic SAM. The addition of a carbon chain makes molecules more flexible, introducing new degrees of freedom which results in a better quality coverage.

Another interesting aspect of SAMs structure is the coexistence of different phases. Polymorphism of SAMs can be controlled (to some degree) by changing parameters of their formation, such as the temperature of incubation. Fig. 2.3, 2.4, 2.5 shows some exemplary results of author's STM studies of ω -(4'-methylbiphenyl-4-yl) alkaneselenolates $CH_3(C_6H_4)_2(CH_2)_nSe^-$ (BPnSe, n = 2 to 6) on Au(111) substrate, which has been recently published [51]. The whole article can be found in the Appendix.

2.2 Applications

By introducing a monolayer one can significantly change the properties of the surface. Moreover, molecules of SAMs tend to organize spontaneously, without any further external influence. Those properties seems to have a wide application also in many fields beyond organic electronics.



Figure 2.3: STM data for BP4Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a-d) STM images taken with different resolutions. In (e-f) heights profiles A and B are taken along lines depicted in (c). In (g-h) heights profiles C and D are taken along lines depicted in (d). In (a-d) α , β and γ symbols mark different phases. In (c) the rectangular box marks the commensurate rectangular $5 \times 2\sqrt{3}$ unit cell of β -phase with dimensions marked in the height profiles presented in (e) and (f), respectively. In (d) the oblique box marks the incommensurate oblique $2 \times 1.2\sqrt{3}$ unit cell of γ -phase with dimensions marked in the height profiles presented in (g) and (h), respectively.



Figure 2.4: STM data (error signal) for BP4Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. In (a-b) yellow lines in the γ -phase mark the very regular boundaries of the translational domains with their separation distances of ca. 3.5-3.6 nm depicted in (a) and measured along one of the $\langle 11\overline{2} \rangle$ directions. To enable tracking relative shift of the γ -phase structure between subsequent translational domains in (a-b) short white lines mark every second molecular row with separation distance of 1.0 nm (indicated in white) measured along one of $\langle 11\overline{2} \rangle$ directions. Red lines in (ab) are shown to track the effect of the periodic cancelation of the relative translational shift after every fourth domain boundary (numbered I-IV).



Figure 2.5: Schematic illustration of the different structures observed at elevated deposition temperature (333 K) for BPnSe SAMs on Au(111) with n = odd (upper panel) and n = even (lower panel). Figures in the right and left columns show schematically the top view and the side view of the structures, respectively. For all structures herringbone arrangement of phenyl rings was assumed. Open circles in the top view correspond to gold atoms at the Au(111) surface, light and dark grey filled circles correspond to Se atoms with the exact adsorption sites taken arbitrary. In the upper panel (n = odd), the commensurate oblique $(2\sqrt{3} \times \sqrt{3})$ R30° unit cell is marked by the *a* and *b* basis vectors (~ 0.216 nm^2 /molecule). In lower panel (n = even) three different phases are shown with: (1) α -phase for which only the *b* basis vector is defined whereas the distance a is irregular (shown by different values of $a: a_1 \approx$ 0.63 nm, $a_2 \approx 0.73$ nm and $a_3 \approx 0.53$ nm, $\sim 0.260-0.275 \text{ nm}^2/\text{molecule}$; (2) commensurate β -phase described by a rectangular $5 \times 2\sqrt{3}$ unit cell (~0.375 nm²/molecule) and (3) incommensurate (in *a* vector direction) γ -phase described by the oblique $2 \times 1.2\sqrt{3}$ lattice (~0.26 nm²/molecule).



Figure 2.6: Friction coefficients for Au and Si substrates coated with different SAMs. On Au: HDT-Hexadecanethiol, BPT- biphenylthiol, BPTC- cross-linked biphenylthiol. On Si: DHBp- dihydroxylbiphenyl [41].

In the fields of lithography, SAMs can be utilized in a twofold manner. On the one hand, SAMs can be used as a masking material, protecting given parts of a substrate against chemical etching. On the other hand, SAMs can be used for selective adsorption of other organic or inorganic molecules. The SAM's lithography consist of several methods enabling the global or local surface modification with resolution in the range of nanometers [52]. Locally, SAMs can be applied with the dip-pen nanolithography (DPN), which uses an atomic force microscope (AFM) to write SAM molecules with a 30-nanometer linewidth [53]. A tip of an AFM is immersed in solution containing SAM molecules and by moving it close to a surface it is possible to write SAMs on the surface, just like in case of ordinary dip pen. Globally, one can apply SAMs on a substrate using easy and fast method of micro-contact printing (μ CP) [54]. This method utilizes polymer stamp with a given pattern covered with solution of SAMs. Short physical contact with a substrate is sufficient to cover suitable parts of the surface with SAMs and obtain the resolution of ca. 200 nm. Recently, it was also shown that it is possible to make a subtracting patterning using μ CP of SAMs [55]. In this case, polydimethylsiloxane (PDMS) stamp was activated by oxygen plasma and used for removing the SAMs from the surface. The covalent interactions formed at the stamp-substrate interface are strong enough to remove not only SAMs, but also substrate's atoms beneath, enabling to achieve 40 nanometer patterns.

In the field of nanoeletromechanical structures (NEMS) design, tribological parameters like friction or wettability play a crucial role. SAMs can be used as a convenient coating in order to tailor those parameters for specific needs. Fig. 2.6 shows the dependence of different SAM coating on the friction coefficient. It was also shown [56], that one can design surfaces that exhibit dynamic and reversible transition between hydrophobic and hydrophilic states, triggered by a change of an electric potential.

Another field of SAM's application is the biosensor design. A functionalization of noble metal's surface by SAM provides a simple route to functionalize electrodes by organic molecules and use them to immobilize given molecules of interest. For example, recently SAMs were used for controlling bacterial adhesion [57]. Application of an electric potential changes the surface of SAMs to be bacteria attractive or repellent which enables to study bacteria adhesion dynamics in real-time.

All mentioned above applications require a comprehensive knowledge about basic properties of SAMs, like proper methodology of their formation, influence of different head group or electronic transport properties. The main aim of this thesis is to build a testbench which would enable studying electronic conductance in the context of future applications, especially in the field of organic electronics.

2.3 Charge transfer mechanism

Several experiments [58-63] clearly shows charge tunneling through the SAM monolayer due to its small thickness (1-3 nm). The efficiency of charge tunneling through SAM depends on the HOMO-LUMO gap which can range from ca. 8-10 eV for aliphatic SAMs to ca. 4 eV for aromatic SAMs (see [67]). The mechanism of charge transport seems to be in most cases the coherent tunneling with hole tunneling theoretically more probable than electron tunneling [64]. The tunneling current density J is described by the Simmons model of tunneling trough rectangular barrier [65]:

$$J = \frac{e}{2\pi h d^2} \left[\left(\varphi_B - \frac{eU}{2}\right) \exp\left[-\frac{2\sqrt{2m}}{\hbar} \alpha d\sqrt{\varphi_B - \frac{eU}{2}}\right] - \left(\varphi_B + \frac{eU}{2}\right) \exp\left[-\frac{2\sqrt{2m}}{\hbar} \alpha d\sqrt{\varphi_B + \frac{eU}{2}}\right] \right],$$
(2.1)

where *m* is the electron mass, *d* is the barrier width, φ_B is the barrier height, *U* is the applied voltage and α corresponds to a parameter describing the barrier's shape (for rectangular barrier $\alpha = 1$). Equation (2.1) can be simplified depending on the applied voltage *U*. For $eU \ll \varphi_B$:

$$J \approx U \frac{e^2 \alpha \sqrt{2m\varphi_B}}{\hbar^2 d} \exp\left[-\frac{2\sqrt{2m}}{\hbar} \alpha d\sqrt{\varphi_B}\right],$$
(2.2)

where J is a linear function of U. For $eU \approx \varphi_B$ we can make following appoximation: 9)

$$J \approx \frac{e}{2\pi h d^2} \left(\varphi_B - \frac{eU}{2}\right) \exp\left(-\frac{2\sqrt{2m}}{\hbar} \alpha d\sqrt{\varphi_B - \frac{eU}{2}}\right),\tag{2.3}$$

where J is exponent of U. In both approximations, relation J(d) is exponential. In the case of electrode-molecule-electrode d junction parameter d corresponds to the length of molecule. Equations (2.2) and (2.3) can be written in more convenient forms:

for
$$eU \ll \varphi_B$$
: $J \sim d^{-1} \exp\left(-\beta_0 d\right), \beta_0 = 2\alpha \hbar^{-1} \sqrt{2m\varphi_B}.$ (2.4)

For
$$eU \approx \varphi_B$$
: $J \sim d^{-2} \exp\left(-\beta_U d\right), \beta_U = \beta_0 \sqrt{1 - \frac{eU}{2m\varphi_B}}.$ (2.5)

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Figure 2.7: Schematic representation of the effect of the image potential on the rectangular barrier φ_B . The barrier $\varphi(x)$ given by (2.8) incorporates the image potential.

In the low voltage regime β_0 is independent on U and is a property of the junction. By measuring the current density J as a function of carbon chain length for both aliphatic and aromatic SAMs it was shown that tunneling is more effective in case of aromatic molecules ($\beta_0^{aromatic} \approx 0.62$, $\beta_0^{aliphatic} \approx 0.92$)[58].

The model of rectangular potential barrier tends to describe well the experimental results only in the regime of small voltages (up to $\pm 0.2 \text{ V}$). Recent experiments [66] show, that for higher voltages ($\pm 1 \text{ V}$) effective electron mass should be introduced ($m_e \rightarrow m_e*$) and shape of the barrier should be revised ($\varphi_B \rightarrow \varphi(x)$) which incorporates the image potential V_i . The interaction of an electron from one electrode with its image from the second leads to induction of the image potential V_i at distance x from metal electrode which can be approximated as:

$$V_i = -1.15\lambda \frac{d^2}{x (d-x)},$$
(2.6)

where:

$$\lambda = \frac{e^2 \ln 2}{8\pi\varepsilon_0\varepsilon_r d}.\tag{2.7}$$

Here ε_0 is the permittivity of vacuum and ε_r is the relative dielectric permittivity of the SAM. The induction of image the potential V_i changes the shape of the barrier. The barrier height at distance x is then given by:

$$\varphi(x) = \varphi_B - eU\frac{x}{d} - 1.15\lambda \frac{d^2}{x(d-x)}.$$
(2.8)

The effect of the image potential is to reduce the area of the potential barrier by reducing its height and rounding off the corners. Schematic representation of the effective barrier $\varphi(x)$ given by eq. (2.8) is presented in the Fig. 2.7.

The experimental values of the effective electron mass $m_{e^*} \approx 0.28m_e$ and mean barrier height $\overline{\varphi_B} \approx 5 \text{ eV}$ for alkanedithiols [66] are consistent with the theoretical predictions [67] $(m_{e^*} \approx 0.29m_e, \overline{\varphi_B} \approx (E_{LUMO} - E_{HOMO})/2 = 5.1 \text{ eV}).$



Figure 2.8: Schematic representation of different tunneling mechanisms together with corresponding current-voltage characteristics after Ref. [42]. (a) The elastic tunneling. (b) The inelastic tunneling as a result of excitation of vibrational state of energy $h\omega$ which changes the current-voltage characteristic for the voltage $U = h\omega/e$. (c) The resonant tunneling trough electron state of SAM leading to a change of the current-voltage characteristic. (d) The theoretical explanation of the NDR observed for some SAMs. The tunneling electron forms a polaron state which lies below the Fermi level of the anode, leading to current blockade in the junction.

For the above reasoning the Fermi levels of both electrodes lies in the band gap of the SAM (see Fig. 2.8a). This however, does not mean that the SAM is not taking part in this process. The inelastic scattering of electrons on SAM's molecules (see Fig. 2.8b) was also observed recently [68]. This effect increases the effective current density as another channel for electron tunneling. The increase of the current density is very subtle and can be only observed at cryogenic temperatures as a peak on the second derivative of current-voltage characteristic (d^2I/dU^2) . Inelastic tunneling is a threshold process which can be observed only for energies equivalent to excitations corresponding to a given vibrational state of molecules $(eU \ge h\omega)$. Peaks on the d^2I/dU^2 characteristic over a wide range of voltage correspond to a complete spectrum of excited vibrational states of a given molecule. This approach, called Inelastic Electron Tunneling Spectroscopy (IETS), enables to identify the chemical composition of a sample [69] and also gives much of the insight into electron transfer mechanism [70].

Another tunneling mechanism is predicted when Fermi level of an electrode is tuned with the molecular free state (see Fig. 2.8c-d). This mechanism is often described as resonant tunneling and its current-voltage characteristic is quite different than in the case of inelastic tunneling. It can be observed [71] by analysis of derivative dI/dU which reveals peaks for certain voltages. The obtained experimental results are consistent with theoretical calculations [72]. Furthermore, negative differential resistance (NDR) which was observed for some SAM systems [73] opens a new range of applications of SAMs as the memory elements or electronic switches. NDR can lead to complete blockade of the tunneling current as shown schematically on Fig. 2.8d. This effect is not fully understood, but the latest theoretical considerations predict that NDR behavior occurs due to formation of polaron in the SAM's region. If polaron state is lower than the Fermi level of the anode, then electrons cannot reach the anode which results in a blockade of the junction [68]. Working devices utilizing the SAMs for molecular memory arrays has been constructed [74]. A vast review of using SAMs for memory applications can be found in [75].

Chapter 3

SAMs in molecular junctionsshort review

As already pointed, electron transport properties of SAMs are crucially important from the point of view of organic electronics applications. This chapter describes various experimental techniques used for studying electron transport properties of SAMs. Considering that SAMs can be spontaneously formed on different metal substrates such as Au or Ag, their contact with bottom electrode is very easy. In contrast, connecting SAMs with the top metal electrode is challenging task since thermal evaporation of a metal on top of SAMs usually leads to a short circuiting due to easy penetration of metal atoms through thin organic monolayer. To deal with this issue, some more advanced techniques has been developed. The most important techniques can be classified into three groups: STM/AFM, hanging drop and large-area junctions. Each of those groups of techniques are described below.

3.1 STM/CP-AFM

STM is a workbench fundamentally designed for measuring small currents with a tremendous accuracy. That is why it can be also used for studying electron transport properties of SAMs (see Fig. 3.1a). One of the advantages of this approach is that it enables to measure both current and morphology at the atomic level simultaneously. This implies that single molecules can be, theoretically, addressed and measured. In reality, however, densely packed structure of SAMs prevents it as the tip size and morphology are unknown. To deal with this issue aromatic SAMs, showing higher conductivity, can be inserted into a matrix of aliphatic SAMs [76]. Nevertheless, probed molecules anchor to surface at defect sites or grain boundaries which introduce the uncertainty connected with different tip-molecule distance.

The main disadvantage of this approach results from the STM principle of operation. Information about the tip-sample distance is measured by means of tunneling current magnitude. This means, that the tip-molecule distance and tunneling current across SAMs are indistinguishable. Furthermore, additional tip-molecule gap and small number of molecules taking part in this process limits the usage of STM for measuring only highly conducting SAMs. For molecules exceeding 14 carbon



Figure 3.1: Schematic representation of STM/CP-AFM testbench. (a) STM tip is brought over the SAM to measure tunneling current. (b) CP-AFM tip is brought to contact with SAM via a nanoparticle.

atoms in length the obtained current is too low for accurate measurements.

Conducting probe atomic force microscope (CP-AFM) can also be used for measuring the conductivity of SAMs. With this technique it is possible to bring the tip into contact with molecules which reduces the extra tunneling gap and increases the measured current (see Fig. 3.1b). On the other hand, CP-AFM tip is coated with metallic layer which makes it larger in comparison with STM tip. Possible circumvention of this problem can be achieved by deposition of metal nanoparticles on the SAM, finding them with AFM and then bringing the tip to the contact [77]. As the size of nanoparticles can be measured accurately, the contact area is well-defined. Disadvantages of this technique are uncertainties of tip-nanoparticle contact resistance and other side effects such as charging of nanoparticles.

CP-AFM, in contrast to STM, can also be used for studying other effects affecting conductivity of SAMs. By changing the coating of CP-AFM tip it is possible to study the influence of metal work function on the electron transport of SAMs. Furthermore, by using functional groups which shows affinity to the coating of a CP-AFM tip one can study the differences between chemisorbed and physisorbed contacts [78].

3.2 Hanging drop

As mentioned earlier in section 1.1, the first measurements of electronic properties of SAMs consisted of a hanging drop of mercury as the top electrode. In this approach, a mercury drop was coated with SAM and brought to contact with another SAM formed on metal substrate. In this way, the junction Hg-SAM-SAM-metal has been introduced (see Fig. 3.2a). The simplicity of this technique allows to obtain large quantity of data needed for statistical interpretation of results. However, working with toxic mercury vapors for a long time may result in health problems. Another drawback is the adsorption of mercury by gold through the defects of SAM, when the metal bottom electrode is used. Also, the interface between SAMs on both electrodes burdens the experiment with some additional resistance.



Figure 3.2: Schematic representation of a liquid metal testbench. (a) Hg-SAM-SAM-metal junction. (b) EGaIn-Ga2O3-SAM-metal junction.

Recently, mercury has been altered with gallium-indium eutectic (EGaIn) which is a non-toxic and moldable liquid metal in the room temperature [79]. EGaIn under ambient conditions is covered by a thin (ca. 4 nm) layer of gallium oxide (Ga_2O_3). This insulating layer is the analog of SAM chemisorbed to Hg drop in the previously mentioned technique (see Fig. 3.2b). Measurements using EGaIn approach enables to obtain large quantity of data needed for statistical analysis. Obtained results using EGaIn certainly gave much of the insight into the electron transfer mechanism of SAMs [80-82].

3.3 Large-area molecular junctions

Evaporation of metal electrode directly on the SAM leads to a mass shorts formation, even for very small devices. It was recently proposed [83] to solve this problem by separating SAM and the top metal electrode by an interlayer of highly-conductive polymer (PEDOT:PSS), which prevents penetration of the SAM by metal atoms during thermal evaporation of the top metal electrodes (see Fig. 3.3). Such procedure of making junctions is more complicated, but it possess some advantages over previously mentioned techniques. Firstly, the bottom electrode is spin-coated with a photoresist and by using a standard photo-lithography it is possible to obtain holes of a given dimension. SAMs are implanted only inside the holes in the photo-resist layer which defines the area of the junction. Finally, PEDOT: PSS is spin-coated over SAM and metal electrode is evaporated at the top of the junction. The top metal electrode ensures a good electrical contact with probes, but also act as a shadow mask for etching away redundant PEDOT:PSS between neighboring devices using reactive plasma etching (RIE). Photo-lithography is widely used in electronics industry and enables to make thousands of junctions at once with a yield of nearly 100%. The encapsulation of SAM protects it very efficiently from degradation and junctions may work after many (888) days in air [84]. Another important merit of large-area junction is that it enables to study electronic transport properties of SAMs in a typical configuration used in organic electronics' devices such as OLEDs or OFETs. Recently, it was demonstrated that this kind of junctions can be made on



Figure 3.3: Schematic representation of large-area molecular junction. SAMs are grown in the holes made using a standard photo-lithographic techniques. The conductive layer of PEDOT:PSS polymer prevent diffusion of metal atoms during evaporation.

flexible substrates with the excellent stability [11].

Nevertheless, introduction of the PEDOT:PSS-SAM interface raises some uncertainties concerning the nature of this junction [85]. Hydrophobicity of PEDOT:PSS can lead to incompatibility of this approach with some SAMs. The current densities observed for those junctions are larger than measured using most of other techniques (larger by factor of ca. 10³). Explanation of this phenomenon is not clear, but it was suggested that it comes from a partial dissolution of the SAM in the polymer film [82]. One of the recently proposed solutions to these problems is interchange of PEDOT:PSS with a multilayer graphene [86]. Another ambiguity concerning this type of junction is the fact that the substrate is treated chemically during a photo-lithography process. The process of developing a photo-resist or its residues can affect the structure of SAM and measured electrical characteristics.

Taking into account flaws and merits of different techniques, large-area junction approach has been chosen for studying electronic transport properties of SAMs, mainly due to its attractiveness from the point of view of organic electronics. Below, one can find detailed description of author's work on design and built of proper testbench needed to study electrical transport properties of SAMs in large-area molecular junctions.

Chapter 4

Design and characterization of the largearea molecular junction

In this chapter the complete procedure of building a large-area molecular junction is presented. The section 4.1 presents the overview of the junction fabrication. In the later sections (4.2, 4.3, 4.4), devices are fully characterized by means of various experimental techniques (AFM, IRRAS, contact angle measurements) and key parameters of fabrication are underlined and discussed. Finally, the section 4.5 presents the results of conduction mesurements for 1-dodecanethiol (C12), 1-hexadecanethiol (C16) and 1-docosanethiol (C22) SAMs, used for verification of the proper design of the large-area molecular junction. Photographs showing samples during the fabrication process has been shown in the Fig. 4.1.

4.1 Process overview

Procedure of building the junction can be divided into a couple of stages:

1. The bottom electrode evaporation

Ultra flat silicon substrate with 1 μ m layer of silicon oxide is cleaned with pure ethanol and blown dry with nitrogen. Next, samples are positioned in a home-built sample holder with a shadow mask and put into a vacuum chamber. Prior to the bottom electrode deposition, samples are heated to 100 °C for at least 3h in the vacuum ca. 10⁻⁶ mbar. That results in surface reorganization and desorption of water and organic contamination. Before evaporation of gold electrode, the samples are cooled to room temperature and 5 nm layer of chromium is deposited (rate: 0.1 Å/s) to increase the gold adhesion. After that, gold layer of 150-200 nm is deposited (rate: 3 Å/s).

1. Vertical tunnel fabrication

Negative photo-resist (ma-N 1410, Micro Resist Technology) is spin-coated at an initial speed of 500 rpm for 5s and final speed of 1500 rpm for 30s (thickness ca. 1.3 μ m). Pre-bake of photo-resist is done on a hotplate at 140 °C for 5 min. This step is crucial in order to evaporate the solvent and obtain a continuous layer. Subsequently, the photo-mask containing spots with the diameter of 100 μ m, is placed in contact with the sample and UV exposure is done using mercury vapor lamp for



Figure 4.1: Photographs taken during fabrication of junctions. (a) Samples after evaporation of bottom electrode. (b) Complete sample. (c) Samples with connected probes.



Figure 4.2: The overview of the large-area molecular junction construction. (a) Au bottom electrode is vapor deposited on the Si substrate. Next, photo-resist is spincoated. (b) Vertical tunnels are defined in the insulating layer during the process of photolithography. (c) SAM is formed on bottom electrode after cleaning with RIE (removal of residues of the photoresist process) and conductive polymer PEDOT:PSS is spincoated over the whole sample. (d) Top Au electrode is evaporated and the residual layer of PEDOT:PSS is removed using RIE.

15 min. Developing process is made by rinsing the sample in the developer (ma-D 533/s, Micro Resist Technology) for 1 min. Finally, samples are rinsed in distilled water, to remove the residues of the developer, and blown dry with nitrogen.

1. SAM formation

In order to make the photo-resist insoluble in ethanol, hardbake is done in oven at 200 °C for 2 h. To reduce pattern reflow, heating is done with temperature ramp from room temperature up to 200 °C during 1 h and then the samples are kept at 200 °C for another hour. After cooling down the samples to the room temperature, oxygen RIE (Zepto Plasma Cleaner, Diener Electronics) is performed (power: 40 W, preasure: 0.7 mbar, time: 4 min) to clean the bottom electrode from residues of the photo-resist. The experiment with infrared reflection absorption spectroscopy (IRRAS) showed that this step is crucial and needs to be optimized. Too short time of plasma cleaning results in a poorly organized SAM, due to the substrate contamination. Moreover, too aggressive treatment can lead to the gold oxidation (see Fig. 4.5). Immediately after RIE samples need to be put into the ethanolic solution containing precursors of SAM (concentration ca. 1 mM) in order to reduce the contamination of the substrate. The samples are stored in the solution for at least 20 h to obtain a well-organized SAM. For experiments alkanethiols were selected due to existing data for those molecules in the scientific literature.

1. The top electrode fabrication

In order to enhance wetting properties of PEDOT:PSS (AI 4083, Ossila) a small quantity of nonionic surfactant (Capstone FS-3100, DuPont) is added into PEDOT:PSS filtered with 0.2 μ m glass microfiber filters (5 droplets per 5 ml of PEDOT:PSS) and mixed with a magnetic stirrer for at least 1h. After organization of SAM the samples are rinsed thoroughly with ethanol and blown dry with nitrogen. Immediately after that, PEDOT:PSS is spin-coated at the initial speed of 500 rpm for 10 s and at the final speed of 1500 rpm for 110 s (thickness ca. 100 nm). Instead of standard drying using a hotplate, drying is done in vacuum as increased temperature can lead to desorption of SAM from the surface. To prevent the formation of holes in the layer vacuum chamber is pumped slowly to 0.1 mbar and kept for 1 h. Finally, 150-200 nm layer of gold is deposited (rate: 3 Å/s) through the shadow mask and the redundant PEDOT:PSS layer between paths is etched away using RIE (power: 100 W, preasure: 0.2 mbar, time: 3 min). For electrical measurements spring-loaded contacts (5099-D, Phoenix Mecano Company) are mounted on the pads. The current-voltage characteristics are recorded using the Keithley 2400 source meter under ambient conditions.

Obtained results of current density J for 1-dodecanthiol (C12), 1-hexadecanethiol (C16) and 1docosanethiol (C22) shows good agreement with previous experiments [11]. This clearly shows the robustness of the large-area molecular junction technique. To the best of author's knowledge, only three groups [11, 83, 87] has managed to fabricate large-area molecular junction, but using sophisticated lithographic equipment and in a very clean environment. In this project, fabrication of the junctions was done outside a clean room and without a mask-aligner or a glove-box.

4.2 Bottom electrode characterization

The sample holder and shadow masks for evaporation of both electrodes were designed by the author. Stainless steel plates of thickness 0.5-1 mm (see Fig. 4.3) were cut using laser and then



Figure 4.3: Design of the sample holder. (a) The bottom plate. (b) The holder for four samples. Notches in the corners were made for easier access to the samples while mounting (c) The bottom electrode shadow mask. (d) The top electrode shadow mask. (e) The top plate. (f) The plexi-glass cover for attaching the probes to junctions. Golden spring-loaded probes has been mounted in the marked places.

polished. The alignment of both electrodes is ensured by stacking the plates and then screwing them together. Paths of both electrodes were designed wide enough (1.5 mm) in order to reduce the risk of misalignment. Large pads (5 mm) ensures an easy access to the probes. Moreover, pads from bottom and top electrode are situated not directly above each other to prevent possible shorts during the probe's connection.

In order to attach probes to the junctions, a poly(methyl methacrylate) (PMMA) plate was designed which could be mounted on top of the sample holder. Spring-loaded contacts (5099-D, Phoenix Mecano Company) with the resistivity lower than $10m\Omega$ has been mounted inside the holes drilled in the PMMA plate. Loading force of the probes can be adjusted with nuts of the mounting screws.

Fabrication of the bottom electrode of the large-area junction is done by physical vapor deposition (PVD) process in a home-built vacuum chamber. The thickness of evaporated metal shows high angular dependence. Theoretically, if mass m of metal has been evaporated from a source of small area dA then dm will be emitted into the solid angle $d\Omega$:

$$dm = \frac{m}{\pi} \cos \alpha d\Omega, \tag{4.1}$$



Figure 4.4: Geometric situation during evaporation of metal.

where α is the relative angular position of the substrate (see Fig. 4.4a). π is just the normalization factor as:

$$\int_{\Omega} d\Omega \cos \alpha = \pi.$$
(4.2)

So, the matter flux emitted into the solid angle is given by:

$$\phi(\alpha) = \frac{dm}{d\Omega} = \frac{m}{\pi} \cos \alpha = \phi_0 \cos \alpha.$$
(4.3)

The impingement rate R on the substrate depends also on the source-substrate distance r and the tilt angle of the substrate relative to the source β :

$$R = \frac{\phi \cos \beta}{r^2} = \frac{m \cos \alpha \cos \beta}{\pi r^2}.$$
(4.4)

In the case of infinite, plane substrate (see Fig. 4.4b) one can assume $\alpha = \beta$ and $r = h/\cos\alpha$ which yields:

$$R\left(\alpha\right) = \frac{m}{\pi h^2} \cos^4 \alpha. \tag{4.5}$$

Typically, for controlling the film thickness during PVD process quartz oscillators are used. An oscillator is put near the substrate and while evaporating the resonant frequency is changing. This change can be calibrated for the evaporated film thickness. However, equation (4.5) suggests a very strong angular dependence on the film thickness. As substrate and crystal oscillator were not in the same place, the thickness of evaporating layer has been mapped in the sample holder. Evaporated film thickness has been measured using AFM (Park Scientific Instrument Autoprobe CP II) in contact mode. After evaporation of gold, without adhesive promotion of chromium, the samples



Figure 4.5: (a) Typical AFM image of the scratch made on Au surface with the line denoted as A. (b) Height profile along the line A from (a).

were gently scratched with tweezers. Typical scratch obtained with this method is presented in the Fig. 4.5. For all AFM data analysis a freeware tool WSxM has been used [89]. This analysis enabled to accurately establish the bottom electrode thickness and its uniformity. In the fabricated junction the Au thickness was in the range of 150-200 nm.

As previously suggested [90], the surface roughness can have a major impact on the electrical conductance of the molecular junction. In order to characterize the quality of the evaporated Au layer, AFM studies has been made. The samples were fabricated using the procedure listed in 4.1 up to SAM formation (after the first RIE). Then, bottom electrode inside the tunnel in the photo-resist layer has been studied with AFM in contact mode. Typical result is presented in the Fig. 4.6. This analysis showed that typical RMS roughness of gold electrode is ca. 2.9 nm for area of $1\mu m^2$.

One of the mentioned ambiguities of large-area molecular junction is the substrate chemical cleanness after the process of photo-lithography. In order to investigate this issue thoroughly, infrared reflection absorption spectroscopy (IRRAS) studies has been made. Measurements were performed using a dry-air-purged FTIR spectrometer (Nicolet 6700, Thermo Scientific) with a liquid nitrogencooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. Spectra was measured at the resolution of 2 cm⁻¹ and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with SAM and R_0 is the reflectivity of the reference (perdeuterated C16 SAM). Typically, 1000 scans were averaged to yield spectra with acceptable signal-to-noise ratio.

IRRAS spectra of reference sample of C16/Au was compared with spectra of samples where C16 had been formed in the vertical tunnels of diameter of 1 cm. Photo-lithography process was performed using the same procedure as in the case of junction fabrication. During this experiment the substrate was not cleaned using RIE. The results are shown in the Fig. 4.7.

The C-H stretching region (see Fig. 4.7b) is sometimes described as a fingerprint region for alkanethiolbased SAM. Peaks positions and their relative heights, in this region, are indication of a well-defined structure of SAM [92]. The IRRAS spectra of C16 on photo-lithographed Au substrate is clearly



Figure 4.6: (a) Typical AFM image of Au surface inside the vertical tunnel in the photo-resist layer with the line denoted as A. (b) Height profile along the line A from a. (c) Histogram of height for the AFM image presented in a.



Figure 4.7: IRRAS spectra of C16/Au for the reference sample and the sample after photo-lithography (without RIE). (a) Wide range spectrum. b) The C-H stretching region. The vertical dotted and dashed lines correspond to methylene and methyl vibrational modes. Mode assignments are given in Tab. 4.1.

Mode description	Abbr.	Peak freq. (cm-1)	Direction of transition dipole moment
			in molecular coordinates
methyl asym (ip)	r^{-}	2964	ip of CCC backbone, \perp C-CH3 bond
methyl sym	r_{FR}^+	2937	C-CH3 bond
methylene asym	d-	2920	\perp backbone plane
methyl sym	r^+	2877	C-CH3 bond
methyl sym	r^+	2877	C-CH3 bond

Table 4.1: C-H stretching peak assignment table [91]. Abbreviations used: asym=asymmetric, sym=symmetric, ip=in plane, FR=Fermi resonance splitting component.



Figure 4.8: IRRAS spectra of C16 on RIE cleaned Au surface for different times of exposure (2-7 min) and reference spectrum of C16/Au. (a) Wide range spectrum. (b) The C-H stretching region. The vertical dotted and dashed lines correspond to methylene and methyl vibrational modes, respectively. Mode assignments are given in Tab. 4.1.

different than for C16/Au, especially in the C-H stretching region (see Fig. 4.7b). This experiment confirmed that RIE cleaning of the bottom electrode is necessary as contamination of the substrate leads to the ill-defined monolayer.

The parameters of cleaning the substrate has to be carefully chosen as too aggressive oxygen plasma treatment can lead to gold oxidation. In order to optimize plasma cleaning parameters, the power of the generator was set to 40 W and oxygen pressure of 0.7 mbar, which correspond to a gentle cleaning, and the effect of RIE exposure time has been studied with IRRAS. Samples, prepared using the same procedure as in the previous experiment, were treated with RIE for time in range (2-7 min) before formation of C16 SAM inside vertical tunnels. The results of this experiment are shown in the Fig. 4.8.

Comparison of positions and relative heights of peaks in the fingerprint region enabled finding optimal time of exposure (4 min) for other parameters (power: 40W, pressure: 0.7 mbar) of the oxygen RIE. This experiment also revealed that proper formation of SAMs is quite sensitive to RIE parameters (see Fig. 4.9). This issue seems to be omitted in the previous reports. Effectiveness of RIE can varies for different devices as well as for different positions in a vacuum chamber. Approach presented above is a simple and fast test, giving much insight into the structure of SAM in the



Figure 4.9: IRRAS spectra of C16 on RIE cleaned Au surface for different times of exposure in the C-H stretching region. Dashed line on each plot shows reference spectrum C16/Au. a) 2min. b) 4min. c) 5min.



Figure 4.10: (a) Wedge-shape edge profile of negative-photoresist in case of over-esposure. (b) Pyramidal edge profile positive-photoresist in case of over-esposure.

junction which is crucial for a well-defined experiment.

4.3 Vertical interconnection characterization

For photo-lithography a negative photo-resist (maN-1410, Micro Resist Technology) has been chosen due to different edge profile in case of over-exposure (see Fig. 4.10). Negative photo-resist cross-links due to the UV radiation which makes it insoluble in developer. Over-exposure of negative photoresist leads to a wedge-shape profile (see Fig. 4.10a). This type of edge profile seems to be safe for junction performance, as there is a continuous path from top to bottom electrode. On the other hand, a pyramidal edge profile (see Fig. 4.10b) of positive photo-resist can lead to breaks in connection between the electrodes.

Photo-masks were fabricated using a commercial image-setting machine on polyester, transparent foils in the form of dots with diameter of $25 - 100 \,\mu$ m. The shape and area of blackened spots on the masks were investigated using the optical microscope (see Fig. 4.11). For reference, the pictures of calibration grating with a well-defined spacing has been taken with the same optical setting. Analysis of those images reveled, that the shape of dots is certainly deformed, but its area seems to match the design.

Photo-resist chosen for experiments shows a high absorption in the range of 300-400 nm (see Fig. 4.12b). In order to ensure that material used as a photo-mask are compatible with the photo-resist, the absorption of light in the range of 300-400 nm of both blackened and transparent parts



Figure 4.11: Optical images of dots on polyester film used as a photo-mask in the process of photolithography. a) spot of diameter approx. 100 μ m. b) spot of diameter approx. 25 μ m.



Figure 4.12: (a) Relation between photo-resist's thickness and spin speed during spin-coating process. Vertical line is used as an eye-guide for the speed 1500 rpm which was used for making junctions. (b) UV/vis absorption of both unexposed and exposed photo-resist. Vertical lines shows the wavelength of i-line (365 nm) and h-line (405 nm) of mercury vapor lamp used for exposure. Data has been taken from specification of photo-resist (ma-N 1410, Microresist Technology).

the photo-mask was measured using a light detector. Results clearly show a major change of light transmittance between blackened and transparent parts of photo-masks (see Fig. 4.13) making masks compatible with chosen photo-resist.

In order to ensure a stable electrical insulation between top and bottom electrode, the photo-resist thickness of ca. 1.3 μ m has been chosen. This thickness corresponds to spin-casting with the initial speed of 500 rpm for 5s and the final speed of 1500 rpm for 30s (see Fig. 4.12a). This has been confirmed with AFM images of the vertical tunnels after the process of photo-lithography (see Fig. 4.14 and Fig. 4.15).

AFM measurements of vertical tunnels of diameter $\sim 100 \ \mu m$ and $\sim 25 \ \mu m$ revealed that effective area of the junction is decreased by ca. 20% by the wedge-shape profile. This has been taken into account during calculation of current density J from current-voltage characteristics of the junction.

Another important step during large-area junction fabrication is the photo-resist pre-bake process which makes a photo-resist more etch-resistant and more adhesive to the substrate. In case of too



Figure 4.13: Light transmittance analysis of different parts of photo-masks. (a) Blackened part which defines the area of the junction. (b) Other part of the mask which needs to be transparent enough to cause the photo-resist to cross-link.



Figure 4.14: (a) Typical AFM image of the vertical tunnel of diameter ca. 100 μ m with the line denoted as A. (b) Height profile along the line A from (a).



Figure 4.15: (a) Typical AFM image of the vertical tunnel of diameter ca. 25 μ m with the line denoted as A. (b) Height profile along the line A from (a).

mild pre-bake, the layer of photo-resist can be damaged which can result in a short-circuiting of the junction (see Fig. 4.16a). Moreover, the temperature of the pre-bake process and its duration time affect further developing process. These three parameters should be optimized simultaneously. In order to solve this problem, devices without vertical tunnels have been fabricated (without photomask) for (1) different pre-bake temperature, (2) pre-bake duration time, (3) UV exposure time and (4) developing time. For such devices current-voltage characteristics has been measured using the Keithley 2400 source meter (see Fig. 4.16). This experiment showed that pre-bake done at the temperature of 140 °C for 5 min with UV exposure of 15 min and developing time of 1 min leads to creation of a continuous and highly-insulating layer of the photo-resist. Afterwards, this procedure has been verified by fabrication of vertical tunnels and measuring their profile with AFM.

Obtained current-voltage characteristics during the previous experiment showed also that ca. 1.3 μ m layer of photo-resist is indeed sufficient to provide good insulation of the both electrodes. Typically, the current lower than 0.1 nA was measured in the voltage region of -1 V to 1 V (see Fig. 4.16b) which correspond to the source meter accuracy. On the other hand, the small resistance of ca. 2.5 Ω measured while short-circuit formation (see Fig. 4.16a) means that the parasitic resistance is negligible in comparison to the resistivity of the SAM.

4.4 Top electrode characterization

As mentioned before, the layer of highly-conductive polymer PEDOT:PSS prevent gold atoms penetration through the monolayer during evaporation process. In order to study the properties of PEDOT:PSS-SAM interface, contact angle measurements has been performed. First, the contact angle of PEDOT:PSS on the C12/Au was measured (see Fig. 4.17a). This measurements revealed that the solution of PEDOT:PSS does not wet well the alkyl-terminated SAMs on gold substrate (contact angle: $\sim 90^{\circ}$). In order to increase the wettability of PEDOT:PSS solution on alkanethiol SAM, small amount (5 droplets /5 ml) of non-ionic surfactant (Capstone FS-3100, DuPont) was added. That resulted in a major decrease of contact angle ($\sim 20^{\circ}$) as presented in the Fig. 4.17c.



Figure 4.16: Typical *I-V* characteristics for: (a) a short circuit, (b) an open circuit. Note different current scale on (a) and (b).



Figure 4.17: Contact angle measurements of: (a) PEDOT:PSS on C12/Au, (c) PEDOT:PSS with a small amount of surfactant FS-3100 on C12/Au. (b) Change of the surface tension of distilled water due to addition of surfactant FS-3100. Taken from compound specification.



Figure 4.18: (a) Typical AFM image of the scratch made on PEDOT:PSS/photo-resist structure with the line denoted as A. (b) Height profile along the line A from (a).

Standard processing protocol of PEDOT:PSS consist of heating the samples on a hotplate after spin-coating, in order to evaporate the solvent. For the application of PEDOT:PSS in large-area molecular junction this is not advisable as SAM could be damaged at increased temperatures. Instead, long time of spin-coating (110 s) was employed as well as drying in the vacuum chamber. Slow pumping during this step decreases the probability of holes formation. The final PEDOT:PSS thickness (ca. 100 nm) has been established using AFM, similarly to the procedure mentioned in the section 4.2 The Fig. 4.18 shows AFM image of the scratch made on PEDOT:PSS/photo-resist structure.

The final step in the junction fabrication is the oxygen RIE etching of residues of PEDOT:PSS, in order to eliminate additional current paths. In this case, top golden electrode act as a selfaligning shadow mask and protects the PEDOT:PSS layer underneath. For optimization of the RIE etching a layer of PEDOT:PSS was spin-coated on silicon substrate and its thickness was measured using AFM. Then, RIE was performed with different parameters and afterwards the thickness was measured roughly in the same spot once again. This experiment showed that a very aggressive RIE treatment (power: 100 W, pressure: 0.2 mbar, time: 3 min) is needed to etch PEDOT:PSS layer. Those parameters should also be chosen carefully and may depend on technical details of a plasma cleaner. Too aggressive treatment can lead to a significant heating of the samples which in turn, can damage the SAM. Moreover, occasional top electrode damage has been observed.

4.5 SAM conduction measurements

Current-voltage characteristics of the large-area molecular junctions has been measured using the Keithley 2400 source meter under ambient conditions. Spring-loaded probes with a typical resistance of ca. 10 m Ω (5099-D, Phoenix Mecano Company) was used for connecting the source meter with a junction. Resistivity of PEDOT:PSS was measured by fabrication of junctions by the procedure listed in section 4.1, but without formation of SAM. Obtained results are shown



Figure 4.19: (a) Typical *I-V* characteristics for junctions Au-Au and Au-PEDOT:PSS-Au. (b) Absolute value of the current density versus voltage for junctions Au-Au and Au-PEDOT:PSS-Au. Estimated area of the junctions was ca. $6.4 \cdot 10^{-12}$ m².

in the Fig. 4.19. This measurements confirmed that resistivity of PEDOT:PSS layer is negligible only for long molecules. For highly-conductive SAMs this parasitic resistivity should be taken into account.

In order to verify performance of large-area junctions alkanethiol has been chosen to study. Those molecules has been used as a model system in almost every electronic transport across SAM experiments. For SAM formation, the samples were immersed in 1 mM solutions of $CH_3(CH_2)_{10}CH_2SH$ (C12), $CH_3(CH_2)_{14}CH_2SH$ (C16) or $CH_3(CH_2)_{20}CH_2SH$ (C22) in ethanol and incubated for at least 20 h. The obtained yield of working devices was ca. 60%. Exemplary current-voltage curves for C12, C16 and C22 are shown in the Fig. 4.20, Fig. 4.21 and Fig. 4.21, respectively.

The insets presented in the Fig. 4.20a, Fig. 4.21a and Fig. 4.22a clearly show linear I-V relation in the range of small voltages which stays in agreement with theoretical predictions presented in the section 2.3. The shape of I-V characteristics as well as estimated values of current density match the results presented in [11].

Electrical measurements of SAMs in fabricated junctions varies greatly for different junctions (see Fig. 4.23a). This effect was also observed in previous reports [11, 65, 81, 84, 85, 87]. One of the proposed explanations was the influence of the defects in SAM [90], which is directly connected to the substrate's roughness. In fabricated junctions the Au substrate roughness was estimated to be ca. 2.9 nm (for $1 \ \mu m^2$) which is quite high, but this is a typical value of evaporated Au. One of the methods of obtaining a better quality Au substrates is the template stripping method [90] which could be a further improvement for the large-area molecular junction approach.

Due to large spread of obtained data, numerous measurements are needed for a statistical analysis. However, the observed differences of averaged (from 10 mesurements) current density for C12 and C16 in a small voltage region (see Fig. 4.23b) seems to be consistent with the results obtained elsewhere [11].

Another important parameter which is frequently used for comparison of electrical conductance of aliphatic SAMs is the coefficient of tunnel current decay per carbon atom β_n . The current density



Figure 4.20: (a) *I-V* characteristic for C12 large-area molecular junction. Inset shows the linear region. (b) Absolute value of the current density versus voltage for C12 large-area molecular junction. Estimated area of the junctions was ca. $6.4 \cdot 10^{-12} \text{ m}^2$.



Figure 4.21: (a) *I-V* characteristic for C16 large-area molecular junction. Inset shows the linear region. (b) Absolute value of the current density versus voltage for C16 large-area molecular junction. Estimated area of the junctions was ca. $6.4 \cdot 10^{-12}$ m².



Figure 4.22: (a) *I-V* characteristic for C22 large-area molecular junction. Inset shows the linear region. (b) Absolute value of the current density versus voltage for C22 large-area molecular junction. Estimated area of the junctions was ca. $6.4 \cdot 10^{-12} \text{ m}^2$.



Figure 4.23: Comparison of J-V characteristics of C12, C16 and C22. (a) Spread of observed J-V characteristics for both C12 (red line) and C16 (black line) for 10 measurements for each SAM. (b) Averaged (from 10 measurements) J-V characteristics for C12, C16 and C22. Error bars correspond to standards deviation of each point. Inset shows dependence of averaged log (|J|) versus the number of carbon atoms in the SAM measured at voltages 0.5 V (black), 0.3 V (red), 0.1 V (green).

J in a small voltage regime can be expressed in terms of β_n and the number of carbon atoms in the aliphatic chain n as:

$$J = J_0 \exp\left(-\beta_n n\right) \tag{4.6}$$

From the averaged current- voltage characteristics of C12, C16 and C22 in the small voltage region $(\pm 0.5 \text{ V})$ the value of β_n was estimated as a slope parameter of fitted relation $\ln J$ versus the number of carbon atoms in the SAM (see the inset in the Fig. 4.23b). Obtained value of $\beta_n = 0.22(0.14)$ for 0.5 V seems to be smaller than reported values (0.51-1.13) [87] for alkanethiols on gold substrate using various techniques. This could be a result of small amount of data taken into analysis. In case of those measurements, a large spread of data is unavoidable. Only statistical analysis of a large quantity of data can be a source of convincing argumentation about electrical transport properties of SAM. Nevertheless, the aim of this project was to build a testbench for measuring the electrical conductance of SAMs and verify its operation. This task, in author's opinion, has been fulfilled as described in details in this chapter of thesis.

Chapter 5

Summary

Presented thesis documents author's experimental work on design and optimization of the largearea molecular junction for charge transport measurements of self-assembled monolayers (SAMs). SAM's molecules has been implanted on bottom golden electrode inside vertical tunnels (diameter ca. 100 μ m) made photo-lithographically in the insulating layer of photo-resist. Additional layer of a highly-conductive polymer PEDOT:PSS has been introduced in order to prevent shorts formation during evaporation of the top golden electrode.

The whole process of device fabrication is presented together with a detailed junction's characterization by means of several experimental techniques (AFM, IRRAS, contact angle measurements). Verification of a proper operation of the junction has been performed by measuring the current-voltage characteristics of 1-dodecanethiol (C12), 1-hexadecanethiol (C16) and 1-docosanethiol (C22). Obtained results stays in good agreement with the previously reported values [11].

This project proved the robustness of a large-area molecular junction approach for measuring electric transport properties of SAMs. To the best of author's knowledge only three scientific groups has managed to construct such a junction. The obtained in this project yield of working devices ca. 60% is lower than in the previous reports. However, the fabrication process during presented project has been performed outside clean-room environment and without specialized photo-lithographical equipment such as mask-aligner.

References

[1] Chiang C K, Fincher C R, Jr., Park Y W, Heeger A J, Shirakawa H, Louis E J, Gau S C and MacDiarmid A G 1977 *Physical Review Letters* **39** 1098-101

[2] Di Ventra M and Zwolak M 2004 Encyclopedia of Nanoscience and Nanotechnology, ed H S Nalwa American Scientific Publishers 475-93

[3] Murphy C J, Arkin M R, Jenkins Y, Ghatlia N D, Bossmann S H, Turro N J and Barton J K 1993 Science 262 1025-9

[4] Kasumov A Y, Kociak M, Guéron S, Reulet B, Volkov V T, Klinov D V and Bouchiat H 2001 Science **291** 280-2

[5] Slowinski K, Fong H K Y and Majda M 1999 Journal of the American Chemical Society 121 7257-61

[6] Mantooth B A and Weiss P S 2003 Proceedings of the IEEE 91 1785-802

[7] Love J C, Estroff L A, Kriebel J K, Nuzzo R G and Whitesides G M 2005 Chem Rev 105 1103-69

[8] Xia Y, Sun K and Ouyang J 2012 Advanced Materials 24 2436-40

[9] Ortmann F, Bechstedt F and Hannewald K 2010 New Journal of Physics 12 023011

[10] Woll C 2009 Physical and chemical aspects of organic electronics Wiley VCH

[11] Park S, Wang G, Cho B, Kim Y, Song S, Ji Y, Yoon M H and Lee T 2012 Nat Nanotechnol **7** 438-42

[12] Hamadani B H, Corley D A, Ciszek J W, Tour J M and Natelson D 2006 Nano Letters 6 1303-6

[13] Blum A S, Kushmerick J G, Long D P, Patterson C H, Yang J C, Henderson J C, Yao Y, Tour J M, Shashidhar R and Ratna B R 2005 Nat Mater 4 167-72

[14] Nakanishi H, Walker D A, Bishop K J, Wesson P J, Yan Y, Soh S, Swaminathan S and Grzybowski B A 2011 Nature Nanotechnology **6** 740-6

[15] Lane P A, deMello J C, Fletcher R B and Bernius M 2003 Applied Physics Letters 83 3611-3

[16] Mathijssen S G J, van Hal P A, van den Biggelaar T J M, Smits E C P, de Boer B, Kemerink M, Janssen R A J and de Leeuw D M 2008 Advanced Materials **20** 2703-6

[17] Park T H, Kim Y M, Park Y W, Choi J H, Jeong J-W, Choi K C and Ju B-K 2009 Applied Physics Letters **95** 113310-3

[18] McGehee M D and Topinka M A 2006 Nat Mater 5 675-6

[19] Nelson J 2002 Current Opinion in Solid State and Materials Science 6 87-95

[20] Dou L, You J, Yang J, Chen C-C, He Y, Murase S, Moriarty T, Emery K, Li G and Yang Y 2012 Nature Photonics **6** 180-5

[21] de Boer B, Hadipour A, Mandoc M M, van Woudenbergh T and Blom P W M 2005 Advanced Materials 17 625

[22] Yip H-L, Hau S K, Baek N S and Jen A K Y 2008 Applied Physics Letters 92 193313-3

[23] Imahori H, Norieda H, Yamada H, Nishimura Y, Yamazaki I, Sakata Y and Fukuzumi S 2000 Journal of the American Chemical Society **123** 100-10

[24] Lam K B, Liwei L, Irwin E F and Healy K E 2005 Solid-State Sensors, Actuators and Microsystems, 2005. Digest of Technical Papers 2 1772-5

[25] Koezuka H, Tsumura A and Ando T 1987 Synthetic Metals 18 699-704

[26] Veres J, Ogier S, Lloyd G and de Leeuw D 2004 Chemistry of Materials 16 4543-55

[27] Trung T Q, Tien N T, Seol Y G and Lee N-E 2012 Organic Electronics 13 533-40

[28] Baeg K-J, Khim D, Kim J, Yang B-D, Kang M, Jung S-W, You I-K, Kim D-Y and Noh Y-Y 2012 Advanced Functional Materials **22** 2915-26

[29] Tinivella R, Camarchia V, Pirola M, Shen S and Ghione G 2011 Organic Electronics 12 1328-35

[30] Murmann B and Wei X 2010 Computer-Aided Design (ICCAD), 2010 IEEE/ACM International Conference on Communication, Networking & Broadcasting, 504-7

[31] Malenfant P R L, Dimitrakopoulos C D, Gelorme J D, Kosbar L L, Graham T O, Curioni A and Andreoni W 2002 Applied Physics Letters 80 2517-9

[32] Salleo A, Chabinyc M L, Yang M S and Street R A 2002 Applied Physics Letters 81 4383-5

[33] Marmont P, Battaglini N, Lang P, Horowitz G, Hwang J, Kahn A, Amato C and Calas P 2008 Organic Electronics **9** 419-24

[34] Kim D-S, Park H-J, Jung H-M, Shin J-K, Choi P, Lee J-H and Lim G 2004 Japanese Journal of Applied Physics 43 3855

[35] Arya S K, Solanki P R, Datta M and Malhotra B D 2009 Biosensors and Bioelectronics 24 2810-7

- [36] Schreiber F 2000 Prog. Surf. Sci. 65 151-256
- [37] Schreiber F 2004 J. Phys.: Condens. Matter 16 R881-R900

[38] Ulman A 1996 Chem. Rev. 96 1533-54

[39] Szelagowska-Kunstman K, Cyganik P, Szüpbach B and Terfort A 2010 Phys. Chem. Chem. Phys. **12** 4400-6

- [40] Bhushan B 2004 Springer Handbook of Nanotechnology Springer
- [41] Protsalio L V and Fawcett W R 2002 Langmuir 18 9342-9
- [42] Cyganik P 2009 Optymalizacja struktury krystalicznej samoorganizujacych sie monowarstw organicznych opartych na molekulach aromatycznych, habilitation thesis UJ
- [43] Liao S, Shnidman Y and Ulman A 2000 J. Am. Chem. Soc. 122 3688-94
- [44] Poirier G E 1997 Chem Rev 97 1117-27
- [45] Leung T Y B, Schwartz P, Scoles G, Schreiber F and Ulman A 2000 Surf. Sci. 458 34-52
- [46] Azzam W, Fuxen C, Birkner A, Rong H T, Buck M and Wöll C 2003 Langmuir **19** 4958-68
- [47] Hautman J and Klein M L 1989 Journal of Chemical Physics 91 4994-5001
- [48] Siepmann J I and MCDonald I R 1993 Langmuir 9 2351-5
- [49] Chang S C, Chao I and Tao Y T 1994 J. Am. Chem. Soc. 116 6792-805
- [50] Alexiadis O, Daoulas K C and Mavrantzas V G 2008 J. Phys. Chem. B 112 1198-211
- [51] Dendzik M, Terfort A and Cyganik P 2012 The Journal of Physical Chemistry C 116 19535-42
- [52] Smith R K, Lewis P A and Weiss P S 2004 Prog. Surf. Sci. 75 1-68
- [53] Piner R D, Zhu J, Xu F, Hong S and Mirkin C A 1999 Science 283 661-3
- [54] Xia Y N and Whitesides G M 1998 Angew. Chem.-Int. Edit. 37 551-75
- [55] Liao W-S, Cheunkar S, Cao H H, Bednar H R, Weiss P S and Andrews A M 2012 Science **337** 1517-21
- [56] Lahann J, Mitragotri S, Tran T-N, Kaido H, Sundaram J, Choi I S, Hoffer S, Somorjai G A and Langer R 2003 *Science* **299** 371-4
- [57] Pranzetti A, Mieszkin S, Iqbal P, Rawson F J, Callow M E, Callow J A, Koelsch P, Preece J A and Mendes P M 2013 Advanced Materials **25** 2181-5
- [58] Holmlin R E, Haag R, Chabinyc M L, Ismagilov R F, Cohen A E, Terfort A, Rampi M A and Whitesides G M 2001 J. Am. Chem. Soc. **123** 5075
- [59] Chen F, Li X, Hihath J, Huang Z F and Tao N J 2006 J. Am. Chem. Soc. **128** 15874
- [60] Beebe J M, Engelkes V B, Miller L L and Frisbie C D 2002 J. Am. Chem. Soc. 124 11268
- [61] Stein N, Korobko R, Yaffe O, Lavan R H, Shpaisman H, Tirosh E, Vilan A and Cahen D 2010 J. Phys. Chem. C 114 12769
- [62] Thuo M M, Reus W F, Nijhuis C A, Barber J R, Kim C, Schulz M D and Whitesides G M 2011 J. Am. Chem. Soc. **133** 2962

[63] Akkerman H B, Kronemeijer A J, Harkema J, van Hal P A, Smits E C P, de Leeuw D M and Blom P W M 2010 Org. Electron. **11** 146

[64] Nijhuis C A, Reus W F, Barber J R and Whitesides G M 2012 The Journal of Physical Chemistry C 116 14139-50

[65] Simmons J G 1963 J. Appl. Phys. 34 1793

[66] Akkerman H B, Naber R C G, Jungbloed B, van Hal P A, Blom P W M, de Leeuw D M and de Boer B 2007 *Proc. Natl. Acad. Sci.* **104** 11161-6

[67] Tomfohr J K and Sankey O F 2002 Phys. Rev. B 65 245105

[68] Galperin M, Ratner M, Nitzan A and Troisi A 2008 Science **319** 1056-60

[69] Okabayashi N, Konda Y and Komeda T 2008 Phys. Rev. Lett. 100 217801

[70] Beebe J M, Moore H J, Lee R and Kushmerick J G 2007 Nano Lett. 7 1364-8

[71] Reichert J, Beckmann D, Weber H B, Mayor M and Löhneysen H 2002 *Phys. Rev. Lett.* 88 176804

[72] Cuevas J C, Heurich J, Martín-Rodero A, Levy Yeyati A and Schön G 2002 *Physical Review Letters* 88 157001

[73] Yegeneh S, Galperin M and Ratner M 2007 J. Am. Chem. Soc. **129** 13313-20

[74] Li C, Zhang D H, Liu X L, Han S, Tang T, Zhou C W, Fan W, Koehne J, Han J, Meyyappan M, Rawlett A M, Price D W and Tour J M 2003 *Appl. Phys. Lett.* **82** 645-7

[75] Li J C 2010 Organic Nanostructured Thin Film Devices and Coatings for Clean Energy, ed S Zhang Taylor & Francis 189-236

[76] Cygan M T, Dunbar T D, Arnold J J, Bumm L A, Shedlock N F, Burgin T P, Jones L, Allara D L, Tour J M and Weiss P S 1998 Journal of the American Chemical Society **120** 2721-32

[77] Cui X D, Primak A, Zarate X, Tomfohr J, Sankey O F, Moore A L, Moore T A, Gust D, Harris G and Lindsay S M 2001 *Science* **294** 571-4

[78] Tao N J 2006 Nat Nanotechnol 1 173-81

[79] Chiechi R C, Weiss E A, Dickey M D and Whitesides G M 2008 Angewandte Chemie International Edition 47 142-4

[80] Thuo M M, Reus W F, Nijhuis C A, Barber J R, Kim C, Schulz M D and Whitesides G M 2011 Journal of the American Chemical Society 133 2962-75

[81] Nijhuis C A, Reus W F, Barber J R, Dickey M D and Whitesides G M 2010 Nano Lett. **10** 3611

[82] Nijhuis C A, Reus W F and Whitesides G M 2009 J. Am. Chem. Soc. 131 17814

[83] Akkerman H B, Blom P W M, de Leeuw D M and de Boer B 2006 Nature 441 69-72

[84] Akkerman H B, Kronemeijer A J, Harkema J, van Hal P A, Smits E C P, de Leeuw D M and Blom P W M 2010 Organic Electronics **11** 146-9

[85] Wang G, Na S-I, Kim T-W, Kim Y, Park S and Lee T 2012 Organic Electronics 13 771-7

[86] Wang G, Kim Y, Choe M, Kim T-W and Lee T 2011 Advanced Materials 23 755-60

[87] Neuhausen A B, Hosseini A, Sulpizio J A, Chidsey C E and Goldhaber-Gordon D 2012 ACS Nano 6 9920-31

[88] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colchero J, Gómez-Herrero J and Baro A M 2007 *Review of Scientific Instruments* **78** 013705

[89] Weiss E A, Chiechi R C, Kaufman G K, Kriebel J K, Li Z, Duati M, Rampi M A and Whitesides G M 2007 J. Am. Chem. Soc. **129** 4336

[90] Laibinis P E, Nuzzo R G and Whitesides G M 1992 The Journal of Physical Chemistry **96** 5097-105

[91] Laibinis P E, Whitesides G M, Allara D L, Tao Y T, Parikh A N and Nuzzo R G 1991 J. Am. Chem. Sci. 113 7152-67

Odd-Even Effect in the Polymorphism of Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Au(111)

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ABSTRACT: Self-assembled monolayers (SAMs) of ω -(4'-methylbiphenyl-4-yl) alkaneselenolates CH₃(C₆H₄)₂(CH₂)_nSe⁻ (BPnSe, n = 2-6) on Au(111) substrates, prepared in solution at elevated temperature (333 K), were studied using scanning tunneling microscopy (STM). Molecularly resolved images reveal that even-numbered BPnSe SAMs form two or three different coexisting phases, including the one observed at room temperature. In contrast, odd-numbered species exhibit only a single phase, which is the same as the one observed at room temperature, i.e. close to a commensurate oblique $(2\sqrt{3}\times\sqrt{3})$ R30° structure with two molecules per unit cell. Importantly, one of the phases observed for even-numbered BPnSe/



Au(111) at room temperature (α -phase) has a well-defined periodicity only in 1D, whereas the new additional phases observed at elevated temperature are fundamentally different and have 2D periodic character, exhibiting a commensurate rectangular $5\times 2\sqrt{3}$ lattice with four molecules per unit cell (β -phase) and an incommensurate oblique $2\sqrt{3}\times1.2\sqrt{3}$ lattice with two molecules per unit cell (γ -phase). For all systems, partial reorientation of the Au(111) step edges was observed upon SAM formation, indicating significant mobility of the topmost gold atoms induced by the adsorbates. To elucidate the effect of the S \rightarrow Se substitution on the SAMs structure on Au(111), present results for BPnSe/Au(111) systems are discussed in view of the previously reported microscopic, spectroscopic, and desorption data obtained for these SAMs and for their thiol analogs, i.e. for BPnS/Au(111).

I. INTRODUCTION

The broad range of applications of self-assembled monolayers (SAMs) on Au(111) in nanotechnology qualifies them as a prototype system for surface design.¹ Despite the huge popularity of SAMs on Au(111), which is mainly driven by the ease of formation and modification, their detailed structure remains controversial due to the complicated interplay of molecule–molecule and molecule–substrate interactions in these systems.^{2,3} Considering the present difficulties in calculating the structures for even the simplest SAMs on Au(111),^{2,3} the rational design of technologically attractive, and thus more complicated, SAMs relies on systematic experimental approaches.

Following this general argumentation and the potential application of aromatic SAMs in molecular electronics,^{4,S} systematic studies on the homologous series of the aromatic/ aliphatic hybrid system $CH_3-(C_6H_4)_2-(CH_2)_n-S/Au(111)$ (BPnS, n = 1-6) have been undertaken.⁶⁻¹⁰ For purely aromatic thiolate SAMs on Au(111), the defect density is high, due to the relaxation of stress resulting from the misfit between the lattice preferred by the aromatic moieties and the one of the Au(111) substrate.^{11,12} Our study demonstrated that introduction of the aliphatic chain in BPnS/Au(111) can solve this stress problem, since insertion of a flexible aliphatic chain gives additional degrees of freedom, providing other pathways to reduce stress without breaking up the structure preferred by the

aromatic moieties.¹³ However, insertion of an aliphatic chain, the length of which is described by the parameter n, has deeper consequences for the BPnS/Au(111) SAMs. As demonstrated by previous detailed microscopic^{9,10} and spectroscopic^{7,8} measurements, the structure of the BPnS/Au(111) SAMs depends strictly on the parity of this parameter and results in a higher density of more upright oriented molecules for the oddnumbered members of this series. This odd–even structural effect influences also the stability of these SAMs toward electrochemical desorption,^{14,15} ion-induced desorption,¹⁶ exchange by other thiols,^{17,18} and electron irradiation.¹⁹ In all these odd–even effects, related to different aspects of film stability, the odd-numbered BPnS/Au(111) SAMs turn out to be the more stable ones.

In parallel, as another route toward optimization of the quality of aromatic SAMs, we have proposed substitution of the anchoring atom which binds molecules to the Au(111) substrate. Experiments performed for BP0Se/Au(111) demonstrated that substitution of the anchoring S atom by Se permits the formation of SAMs of high structural quality.²⁰ This observation was also reproduced later by investigations of anthraceneselenolate²¹ and anthracenethiolate¹² SAMs on

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Figure 1. STM data for BP2Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a–d) STM images taken with different resolutions. In parts e and f, heights profiles A and B are taken along the lines depicted in part c. In parts g and h, height profiles C and D are taken along the lines depicted in part d. In part a, the red arrow indicates kinks at step edges. In parts a–d, the α and β symbols mark different phases (see text for details). In part d, the rectangular box marks the rectangular $5 \times 2\sqrt{3}$ unit cell of the β -phase with dimensions marked in the height profiles presented in parts g and h, respectively.

Au(111). To understand the impact of this substitution on SAMs structure, we have performed systematic microscopic²² and spectroscopic^{23,24} studies of the selenol analogs of BPnS/Au(111) SAMs vs the $CH_3-(C_6H_4)_2-(CH_2)_n$ -Se/Au(111) (BPnSe, n = 1-6) series. These experiments demonstrated that BPnSe/Au(111) SAMs exhibit very similar odd–even structural effects as observed for their thiolate analogs. As a next step to investigate the influence of the S \rightarrow Se substitution on SAM stability, we have performed recently exchange¹⁸ and ion-desorption experiments^{16,25} which demonstrated the odd–even effect in Se–Au and S–Au bond stability as well as higher stability of the Se–Au bond as compared to the S–Au in BPnSe/Au(111) and BPnS/Au(111) SAMs, respectively.

To further elucidate the impact of the S \rightarrow Se substitution on SAMs structure and stability, in the present experiments, we investigate the influence of the formation temperature on the structure of BPnSe/Au(111) SAMs and compare the results with the corresponding data obtained by us earlier for their thiol analogs.

II. EXPERIMENTAL SECTION

The precursor molecules for BPnSe SAM fabrication were d is e l e n i d e c o m p o u n d s (B P n S e – S e B P n : $CH_3(C_6H_4)_2(CH_2)_nSe-Se(CH_2)_n(C_6H_4)_2CH_3)$. The synthesis of these molecules has been described elsewhere.²⁶ The gold films were prepared at a base pressure of $\sim 10^{-7}$ mbar by evaporating (rate 2 nm/s) 150 nm of gold onto mica substrates at 610 K. Before deposition, the freshly cleaved mica sheets had been heated at the evaporation temperature for about 24 h under vacuum conditions to remove residual water. After deposition, the gold/mica substrates were flame-annealed in a butane/oxygen flame. This procedure yielded high-quality Aufilms with flat terraces of several 100 nm exhibiting a (111) surface orientation and steps faceting along the $\langle 1\overline{10} \rangle$

directions. The BPnSe SAMs have been prepared by immersion of Au(111) substrates into a 0.1 mM solution of the respective BPn diselenide (BPnSe–SeBPn) in ethanol at 333 K for 24 h. The incubation temperature was selected to be well below the boiling point of ethanol (352 K). This is the same temperature as in our previous studies^{9,10} with the thiol analogs (BPnS), making a comparison of the behavior of both types of SAMs possible. After immersion, samples were rinsed with pure ethanol and blown dry with nitrogen.

All STM measurements were carried out in air at room temperature using a MultiMode IIIa Digital Instruments microscope. In all cases, tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. The data were collected in constant current mode using tunnelling currents in the range of 20-50 pA and a sample bias between 0.7 and 1.2 V (tip positive). No tip-induced changes were observed under these imaging conditions.

III. RESULTS

The STM data obtained in this study are summarized in Figures 1-4 for even-numbered BPnSe/Au(111) SAMs and in Figures 5 and 6 for odd-numbered BPnSe/Au(111) SAMs. All analyzed samples were prepared by 24 h incubation in ethanolic solution (0.1 mM) of the respective molecules at an elevated temperature of 333 K. The STM analysis was performed in air at room temperature.

Even BPnSe/Au(111) SAMs (n = 2, 4, 6**).** Results obtained for the BP2Se/Au(111) system are presented in Figure 1. Data obtained at large scale are shown in Figure 1a and reveal two interesting features, i.e. characteristic kinks at step edges (indicated by red arrow) and sample areas showing clearly different contrast labeled by α and β letters. These areas labeled by α and β correspond to two different molecular structures, as is more clearly visible in Figure 1b. High resolution data are



Figure 2. STM data for BP4Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a–d) STM images taken with different resolutions. In parts e and f, height profiles A and B are taken along the lines depicted in part c. In parts g and h, heights profiles C and D are taken along the lines depicted in part d. In parts a–d, the α , β , and γ symbols mark different phases (see text for details). In part c, the rectangular box marks the commensurate rectangular $5 \times 2\sqrt{3}$ unit cell of the β -phase with dimensions marked in the height profiles presented in parts e and f, respectively. In part d the oblique box marks the incommensurate oblique $2\sqrt{3} \times 1.2\sqrt{3}$ unit cell of the γ -phase with dimensions marked in the height profiles presented in parts g and h, respectively.

presented in Figure 1c for the α -phase and Figure 1d for the β phase. Cross section B taken in Figure 1c and presented in Figure 1f indicates that the distance between molecules is welldefined along one of the $\langle 11\overline{2} \rangle$ substrate directions and amounts to ca. 0.5 nm (the average taken from five images give 0.52 ± 0.04 nm) with additional intensity modulation at every second row of molecules. In contrast, cross section A taken in Figure 1c along another equivalent $\langle 11\overline{2} \rangle$ substrate direction (i.e., at the angle of 120° with respect to the direction along cross section B) shows irregular distances between molecules (between ca. 0.5 and 0.8 nm; see Figure 1e) which coincidence with the irregular contrast variation in Figure 1c. The average distance between the molecules along this direction amounts to ca. 0.64 ± 0.04 nm (averaged from five different cross sections). High-resolution data presented in Figure 1d show that the β phase forms a rectangular structure. The unit cell dimensions of this structure could be determined by the cross sections C and D (see Figure 1g and h) and correspond to about 1.0 nm along one of the $\langle 11\overline{2} \rangle$ substrate directions and 1.5 nm along one of the perpendicular $\langle 1\overline{10} \rangle$ directions, respectively.

Data obtained for the BP4Se/Au(111) system are presented in Figure 2. Similarly as for the BP2Se/Au(111) system, large scale data shown in Figure 2a indicate kink formation at step edges and areas corresponding to different STM contrast variation. In this case, however, not two but three different types of contrast patterns could be identified, which are labeled in Figure 2a as α , β , and γ . Higher resolution data presented in Figure 2b clearly show that these three types of contrast patterns correspond to three different structural phases. High resolution data presented in Figure 2c show details of two phases. Cross sections A and B taken in Figure 2c and presented in Figure 2e and f, respectively, clearly indicate that the respective phase structure is identical with the one of the β - phase identified above for BP2Se/Au(111). A similar analysis of the other region visible in Figure 2c (data not shown) revealed that this type of structure is identical with the α -phase identified above for BP2Se/Au(111). High resolution data in Figure 2d enabled identification of a third phase, denoted as the γ -phase, which was not observed for BP2Se/Au(111) and consisted of molecular rows running along one of the $\langle 11\overline{2} \rangle$ substrate directions with alternating contrast of every second row of molecules. The cross section D taken across these molecular rows exhibits intermolecular distances of about 0.5 nm with characteristic contrast variation of every second row of molecules (see Figure 2h), similarly as is observed in the α phase. This row structure is intersected by regularly spaced contrast lines running along another equivalent $\langle 11\overline{2} \rangle$ substrate direction at the angle of 120°. Cross section C taken in Figure 2d along one of these molecular rows shows a well-defined intermolecular distance of about 0.6 nm (see Figure 2g), in contrast to the irregular distance variation observed in the α phase along the same substrate direction. This rather regular structure of characteristic contrast variation lines along one of the $\langle 11\overline{2} \rangle$ substrate directions could, at first sight, indicate that the γ -phase consists of molecules arranged in elongated unit cells with the long side determined by the distance between the contrast variation lines. However, a more detailed analysis of the data in Figure 3a (for better contrast, the error signal image is shown) indicates that the observed contrast variation lines (marked in yellow) are in fact regularly spaced translational domain boundaries which separate narrow domain stripes of about 3.5-3.6 nm. These domains are shifted parallel to the direction of the domain boundaries, which in turn run along one of $\langle 11\overline{2} \rangle$ substrate directions, by a small fraction of the total unit cell length (1.0 nm, as marked in the image). As pointed out by the net of white lines in Figure 3a, which mark every



Figure 3. STM data (error signal) for BP4Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. In parts a and b, yellow lines in the γ -phase mark the very regular boundaries of the translational domains with their separation distances of ca. 3.5–3.6 nm depicted in part a and measured along one of the $\langle 11\overline{2} \rangle$ directions. To enable tracking the relative shift of the γ -phase structure between subsequent translational domains in parts a and b, short white lines mark every second molecular row with a separation distance of 1.0 nm (indicated in white) measured along one of the $\langle 11\overline{2} \rangle$ directions. Red lines in parts a and b are shown to track the effect of the periodic cancellation of the relative translational shift after every fourth domain boundary (numbered I–IV; see text for details).

second molecular row in the γ -phase, one can observe that neighboring translational domains numbered I to IV exhibit a systematic shift in the same direction. Interestingly, after crossing four such translational domain boundaries, the structure is back in phase with the domain from which counting was started (assigned by number I). This effect is indicated by two parallel red lines in Figure 3a. Figure 3b shows a larger area scan (error signal image) taken at the same location as data in Figure 3a. Here it can be seen that the effect of periodic cancellation of the translation after every fourth domain boundary is of general character inside any given rotational γ -phase domain.

Data shown in Figure 4 summarize results obtained for the BP6Se/Au(111) system. Similarly as for the two other evennumbered BPnSe/Au(111) SAMs, also in this case, large scale data reveal kink formation at step edges and areas exhibiting different STM contrast (Figure 4a). For BP6Se/Au(111), as in the case of the BP2Se/Au(111) system, only two phases assigned as α and β were observed, which are identified in Figure 4a and b. High resolution data for the α -phase region (Figure 4c) exhibit exactly the same structure as reported above for BP2Se/Au(111) and BP4Se/Au(111). High-resolution data obtained for the β -phase are shown in Figure 4d. The cross sections A and B taken in this image are shown in Figure 4e and f, respectively. The distances which define the dimensions of the β -phase unit cell along one of $\langle 11\overline{2} \rangle$ and $\langle 1\overline{10} \rangle$ substrate directions are ca. 1.0 and 1.5 nm, respectively. Thus, the β -phase for BP6Se/Au(111) is identical with that identified above for BP2Se/Au(111) and BP4Se/Au(111).

Odd-Numbered BPnSe/Au(111) SAMs (n = 3, 5). Figure 5 summarizes data obtained for BP3Se/Au(111) SAMs. Large scale images (Figure 5a) show similar kinks at step edges as reported above for even-numbered members of the BPnSe/ Au(111) series. In this case, however, no regions corresponding to different contrast could be observed. Higher resolution data shown in Figure 5b show different rotational domains of the same structure which are characterized by molecular rows running along one of the $\langle 11\overline{2} \rangle$ substrate directions with alternating contrast of every second row of molecules. The data presented in Figure 5c show additional stripes of contrast modulation within each rotational domain. However, as documented by the cross sections A and B taken in Figure 5d along two of the $\langle 11\overline{2} \rangle$ substrate directions and presented in Figure 5e and f, respectively, these contrast modulation stripes have no influence on the measured intermolecular distances, which are constant and amount to 0.5 nm. The orientation of these stripes is quite regular and ca. 15° off from the closest high symmetry substrate direction, which is one of the $\langle 11\overline{2} \rangle$ directions.

Data obtained for BP5Se/Au(111) are show in Figure 6. Similarly as for BP3Se/Au(111), also in this case a single phase was observed with kink formation at the step edges (Figure 6a). As documented by the high resolution data in Figure 6b and c and the corresponding cross sections presented in Figure 6d and e, this phase is identical with the one observed for the BP3Se/Au(111) system considering both the characteristic stripes of contrast variation within the rotational domains (Figure 6b) and the distances between molecules.

IV. DISCUSSION

Our experiments show clear and systematic differences in the structure of BPnSe/Au(111) SAMs with odd and even numbers of *n* prepared from solutions at elevated temperature (333 K). However, before a detailed discussion of these differences, we would like to briefly comment on a feature which is common to all measured BPnSe/Au(111) samples, i.e. kink formation at step edges. This effect was also reported in our previous investigations of BPnSe/Au(111) SAMs prepared at room temperature and results from partial change of the substrate step orientation from the $\langle 1\overline{10} \rangle$ directions, which is characteristic for the bare Au(111) substrate, into the $\langle 11\overline{2} \rangle$ directions after SAM formation.²² Importantly, such reorientation of substrate step edges was not observed for the thiol analogs (BPnS/Au(111)) prepared in solution at room or elevated temperatures¹⁰ and, thus, indicates higher mobility of gold atoms at the top layer of the substrate upon selenol adsorption as compared to the thiol case. It is well-known that increased strength of the chemical bonding between adsorbate and the metal surface may increase mobility of surface metal atoms.^{27,28} Considering this general observation, we have speculated in our previous publication that reorientation of step edges observed for BPnSe/Au(111) SAMs and not for their



Figure 4. STM data for BP6Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a–d) STM images taken with different resolutions. In parts e and f, height profiles A and B are taken along the lines depicted in part d. In parts a–d, the α and β symbols mark different phases (see text for details). In part d, the rectangular box marks the commensurate rectangular $5 \times 2\sqrt{3}$ unit cell of β -phase with dimensions marked in the height profiles presented in parts e and f, respectively.



Figure 5. STM data for BP3Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a–d) STM images taken with different resolutions. In parts e and f, height profiles A and B are taken along the lines depicted in part d. In part b, yellow arrows mark three different rotational domains following the $\langle 11\overline{2} \rangle$ directions of the substrate. In part d the oblique box marks the commensurate oblique $(2\sqrt{3}\times\sqrt{3})R30^{\circ}$ structure, the dimensions of which are marked in the height profiles presented in parts e and f, respectively.



Figure 6. STM data for BP5Se SAMs on Au(111) prepared in 0.1 mM ethanolic solution at 333 K. (a-c) STM images taken with different resolutions. In parts d and e, height profiles A and B are taken along the lines depicted in part c. In part b yellow arrows mark different rotational domains following the $\langle 11\overline{2} \rangle$ directions of the substrate. In part c the oblique box marks the commensurate oblique ($2\sqrt{3}\times\sqrt{3}$)R30° structure, the dimensions of which are marked in the height profiles presented in parts d and e, respectively.

thiol analogs indicates higher strength of the Se–Au bonding as compared to the S–Au bond(ing).²² Importantly, this initial prediction has been fully confirmed by our recent exchange experiments¹⁸ and ion desorption data²⁵ demonstrating the higher strength of the Se–Au bonds as compared to S–Au in these SAMs.

Turning back to structural differences between odd- and even-numbered BPnSe/Au(111) SAMs prepared at elevated temperatures, we start with a structure common to all evennumbered BPnSe/Au(111) SAMs. As documented by the data in Figures 1, 2, and 4, this is the α -phase, the structure of which is schematically presented in Figure 7. This structure is formed by evenly separated rows of molecules running along one of the $\langle 11\overline{2} \rangle$ substrate directions with characteristic contrast variation of every second row. This contrast variation is typically ascribed to a herringbone arrangement of the biphenyl moieties, as it is found in the solid state structure of biphenyl²⁹ and is also assumed for most aromatic SAMs.^{10,12,21,22,30–34} Interestingly,



Figure 7. Schematic illustration of the different structures observed at elevated deposition temperature (333 K) for BPnSe SAMs on Au(111) with n = odd (upper panel) and n = even (lower panel). Figures in the right and left columns show schematically the top view and the side view of the structures, respectively. For all structures, herringbone arrangement of phenyl rings was assumed. Open circles in the top view correspond to gold atoms at the Au(111) surface; light and dark gray filled circles correspond to Se atoms with the exact adsorption sites taken to be arbitrary. In the upper panel (n = odd), the commensurate oblique $(2\sqrt{3}\times\sqrt{3})R30^{\circ}$ unit cell is marked by the a and b basis vectors (~0.216 nm²/molecule). In lower panel (n =even), three different phases are shown with (1) α -phase, for which only the b basis vector is defined whereas the distance a is irregular (shown by different values of *a*: $a_1 \approx 0.63$ nm, $a_2 \approx 0.73$ nm, and $a_3 \approx$ 0.53 nm, ~0.260-0.275 nm²/molecule); (2) commensurate β -phase described by a rectangular $5 \times 2\sqrt{3}$ unit cell (~0.375 nm²/molecule); and (3) incommensurate (in a vector direction) γ -phase described by the oblique $2\sqrt{3} \times 1.2\sqrt{3}$ lattice (~0.26 nm²/molecule).

despite the regular separation between these molecular rows, which allows us to define the respective unit cell vector, the intermolecular distances along these molecular rows are irregular, so that a respective lattice vector cannot be defined. Considering the average distances between the molecules in this structure, the area per molecule is in the range 0.260-0.275nm²/molecule. The same structure, having well-defined periodicity only in 1D, was reported previously by us for even-numbered BPnSe/Au(111) prepared at room temperature.²² However, in contrast to our previous experiments, after preparation at an elevated temperature of 333 K, this 1D ordered structure coexists with one or two other phases which are ordered in 2D. The first 2D ordered structure, assigned as the β -phase, was observed for all even-numbered BPnSe/ Au(111) SAMs after deposition at elevated temperature. This structure can be described, as schematically presented in Figure 7, by a commensurate rectangular $5 \times 2\sqrt{3}$ lattice with four molecules per unit cell. The area per molecule in the β -phase structure is about 0.375 $nm^2/molecule$, which means a 36–44% lower packing density as compared to the α -phase. The second 2D ordered phase, the γ -phase, was observed exclusively for the BP4Se/Au(111) system. Similarly to the α -phase, this structure is formed by evenly separated rows of molecules running along one of the $\langle 11\overline{2} \rangle$ substrate directions. However, in contrast to the α -phase, the distance between molecules along these rows is constant. Thus, an oblique unit cell can be defined in this case as schematically presented in Figure 7. This structure is, however, incommensurate with the substrate along the direction of the molecular rows due to an increased molecular separation of ca. 0.6 nm instead of 0.5 nm. It thus needs to be described by an oblique $2\sqrt{3} \times 1.2\sqrt{3}$ lattice with two molecules per unit cell and the area per molecule of about 0.26 nm²/molecule, which is similar as for the α -phase. This significant misfit of about 20% between the Au(111) substrate lattice and the γ -phase along one of the $\langle 11\overline{2} \rangle$ substrate directions must generate significant stress. This stress is apparently released by a dense network of translational domain boundaries crossing this structure perpendicular to the misfit direction, i.e. along one of the $\langle 1\overline{1}0 \rangle$ directions. Interestingly, the pattern formed by the translational domain boundary is extremely regular regarding both their separation and translation sequence. The distance between these translational domain boundaries typically amounts to 3.5 nm, i.e. the distance which is commensurate with the Au(111) substrate lattice along the $\langle 11\overline{2} \rangle$ directions. Since the system is in phase again after four transitions, the shift in between each translational phase is 1/4 of the *b* vector of the unit cell, i.e. about 0.25 nm.

In summary of this part we would like to underline that the formation of even-numbered BPnSe/Au(111) SAMs at higher temperatures fundamentally changes the way the molecules are arranged on the surface. Whereas the room temperature α -phase structure is ordered only along one surface direction, the β -phase and γ -phase show ordering along two surface directions and thus form fully ordered 2D structures.

Considering now results obtained for odd-numbered BPnSe/Au(111), we point out that for both BP3Se/Au(111) and BP5Se/Au(111) only one common structure was observed. This structure consists of evenly separated rows of molecules along one of the $\langle 11\overline{2} \rangle$ directions exhibiting alternating contrast variation every second row, which presumably can be ascribed to a herringbone arrangement of the biphenyl moieties, similarly as for the α and γ phases in even BPnSe/Au(111)

SAMs. However, in contrast to the α and γ phases, in this case the separation between molecules along these rows is constant and commensurate (or close to commensurate-see text below) with the Au(111) substrate lattice. As schematically shown in Figure 7, this structure could be described by an oblique $(2\sqrt{3}\times\sqrt{3})R30^{\circ}$ lattice with two molecules per unit cell and a packing density of about 0.216 nm²/molecule. This structure is the same as observed previously for these SAMs prepared at room temperature.²² Similarly as for the room temperature preparation,²² also in this case, characteristic stripes with contrast variation are observed which run in a direction off-axis from the high symmetry substrate directions. Importantly, the periodicity of the $(2\sqrt{3}\times\sqrt{3})R30^{\circ}$ lattice as observed by STM is not affected by these additional contrast variations. Following the argumentation proposed in our previous works,^{13,22} we believe that this effect results from domain boundaries (solitons) at the molecule-substrate interface and thus indicates that the $(2\sqrt{3}\times\sqrt{3})R30^{\circ}$ lattice can be considered only as an approximation of a not fully commensurate molecular lattice formed by the BP3Se and BP5Se adsorbates.

Taking into consideration all results of the present studies, a clear odd-even effect in polymorphism of BPnSe/Au(111) SAMs is observed with even-numbered systems exhibiting two or three different phases, while the odd-numbered systems are characterized by a single phase. We note here that such polymorphism of BPnSe/Au(111) SAMs was not observed for samples prepared at room temperature, and only preparation at elevated temperature revealed the new phases of the evennumbered members of this homologous series. This indicates lower thermal stability of room temperature phase for evennumbered BPnSe/Au(111) SAMs, which upon annealing start to coexist with other phases. To address the possible mechanism responsible for this odd-even effect in BPnSe/ Au(111) SAMs stability, we point out that similar odd-even effects in polymorphism were observed previously by us for thiol analogs of these SAMs, i.e. for the BPnS/Au(111) series. $^{35-37}\ {}^{}$ Importantly, this odd–even polymorphism of BPnSe/Au(111) and BPnS/Au(111) SAMs is following other related similarities between these systems, i.e. a very similar odd-even effect in their structure^{22,23} (when prepared at room temperature) as well as odd-even effects regarding their stability toward exchange by aliphatic SAMs (alkanethiols and alkaneselenols, respectively)¹⁸ and ion-induced desorption.^{16,25} Considering all these similarities, we believe that the simple phenomenological model proposed by us previously³⁶ to explain different stabilities in the BPnS/Au(111) systems could also be applied for BPnSe/Au(111) SAMs. Following our previous argumentation, the difference in stability of oddand even-numbered BPnSe/Au(111) SAMs could be explained by the way in which factors, such as coverage, intermolecular interactions, and bonding configuration at the moleculesubstrate interface (defined by the C-Se-Au angle), work together to determine the energy balance of a SAM (see Figure 11 in ref 36). In this model, the bonding configuration at the molecule-substrate interface contributes significantly to the energetics of the SAM, and its stability depends on whether this factor can be optimized along with the other two factors (cooperatively) or at the expense of these factors (competitively). The cooperative way leading to a stable system is realized in odd-numbered BPnSe/Au(111) SAMs in which high coverage structure and optimized intermolecular interactions can be achieved simultaneously with the optimized C-Se-Au

bonding configuration defined by the C–Se–Au bond angle and the Se adsorption sites on the Au(111) substrate. The opposite situation applies for the even-numbered BPnSe/ Au(111) SAMs where competition between optimization of the C–Se–Au bonding configuration and the other two factors leads to the formation of structures with lower stability.

Present experiments indicate also clear differences between the stability of BPnSe/Au(111) SAMs and their thiols analogs, i.e. BPnS/Au(111). An interesting difference regards the formation of the β -phase, which has a significantly lower packing density (36–44%) than the room temperature α -phase, which in turn has very similar packing density for BPnSe/ Au(111) and BPnS/Au(111) SAMs. Since under the present experimental conditions a full transition into the β -structure was not achieved, we could not probe the stability of this new phase. Importantly, preparing BPnS/Au(111) SAMs at a solution temperature of 333 K did not result in any phases with a lower packing density.¹⁰ New phases for even-numbered BPnS/Au(111) SAMs were only observed when samples prepared at room temperature were annealed at much higher temperatures (starting from 373 K).³⁵⁻³⁷ This observation could lead to the conclusion that the BPnSe molecules are much more weakly bound to the Au(111) substrate than their thiol analogs. This, however, contradicts our present observation regarding the reorientation of the substrate steps as well as previous exchange¹⁸ and desorption experiments²⁵ which clearly indicated higher stability of the Au-Se bonding as compared to the Au-S in these SAMs. However, these experiments indicated that the higher strength of the Au-Se bonding results in weakening of the Au_{surface}-Au_{bulk} bonds (substrate steps reorientation in the present experiments) as well as the Se-C bonds (desorption experiments²⁵). Thus, reorganization of the BPnSe/Au(111) structure at higher incubation temperature and lack of such an effect for BPnS/ Au(111) results from complex changes at the SAM-substrate interface induced by the S \rightarrow Se substitution. These changes are not only limited to the Au-S(Se) bond stability but also to the related mobility of the surface gold atoms and stability of the S(Se)-C bond. As is documented by the present experiments, all these processes have a profound impact on the molecule-substrate interface and, thus, on the resulting film structure.

Since the observed transition to the β - and γ -phase is only partial, it remains impossible at the moment to decide whether formation of these phases is thermodynamically or kinetically controlled. It should be noted, however, that for the thiol analogs (BPS/Au(111)) similar transitions to lower density structures such as the β -phase³⁶ led to much more stable structures than the respective room temperature phase. Thus, lowering the packing density (to some extend) in the SAMs investigated here does not ultimately mean a reduction of the film stability. As discussed in our former paper,³⁶ surface stress arising from the misfit between the lattices of aromatic SAMs and the Au(111) substrate¹³ is an important contribution to the overall film stability and may be compensated by lowering the film density.

It seems that surface stress reduction could also be an origin for γ -phase formation. In this case, the surface coverage remains virtually unchanged, since the BPnSe lattice on the Au(111) surface simply undergoes a transition along the $\langle 11\overline{2} \rangle$ surface direction. As a result, the disorder along this direction of the α phase is transferred into the ordered but incommensurate structure of the γ -phase. The surface stress induced by the

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structural misfit in the γ -phase is reduced in a very specific way by the formation of an extremely regular network of translation domains. In addition, the distance between the boundaries of these translation domains is commensurate with the Au(111) substrate lattice. Such an "elegant" solution for surface stressrelaxation was observed, under our experimental conditions, exclusively for the BP4Se/Au(111) system. Since the intermolecular interactions in BPnSe SAMs are mainly governed by the interactions between phenyl rings (π stacking), observation of the γ -phase for only one certain length of evennumbered alkyl spacer indicates a very high sensitivity of the detailed course of the phase transition depending on the interplay of the factors governing the energetics and kinetics of these SAMs.

V. SUMMARY

In summary, the data obtained from BPnSe/Au(111) SAMs prepared at elevated solution temperatures revealed several important features related to the $S \rightarrow Se$ substitution in SAMs. First we observed an odd-even effect in the polymorphism of BPnSe/Au(111) SAMs that is similar to the one for their thiol analogs. This information is important since it allows us to propose a model in which the bonding configuration at the molecule-substrate interface contributes dominantly to the energetics of the SAM. In this model, the stability of a certain SAM structure depends on whether the bonding configuration at the molecule-substrate interface can be optimized *along with* (cooperatively) or at the expense of (competitively) two other factors (surface coverage and intermolecular interactions), resulting in a stable or unstable film, respectively. Furthermore, the appearance of new phases in the BPnSe/Au(111) SAMs at much lower temperatures than for BPnS/Au(111) indicates that $S \rightarrow Se$ substitution has a complex influence on the SAMsubstrate interface. This influence is not only limited to the increased strength of the Au-Se bond as compared to Au-S bond but also to the reduced, as a consequence of this increase, strength of the Au_{surface}-Au_{bulk} and Se-C bonding.

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Notes

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REFERENCES

(1) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Chem. Rev. 2005, 105, 1103–1170.

- (2) Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. Chem. Soc. Rev. 2010, 39, 1805–1834.
- (3) Maksymovych, P.; Voznyy, O.; Dougherty, D. B.; Sorescu, D. C.; Yates, J. T. Prog. Surf. Sci. 2010, 85, 206–240.
- (4) Song, H.; Reed, M. A.; Lee, T. Adv. Mater. 2011, 23, 1583-1608.
- (5) McCreery, R. L.; Bergren, A. J. Adv. Mater. 2009, 21, 4303-4322.

- (6) Zharnikov, M.; Frey, S.; Rong, H. T.; Yang, Y. J.; Heister, K.; Buck, M.; Grunze, M. Phys. Chem. Chem. Phys. 2000, 2, 3359–3362.
- (7) Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.;
 Wühn, M.; Wöll, C.; Helmchen, G. *Langmuir* 2001, *17*, 1582–1593.
- (8) Heister, K.; Rong, H. T.; Buck, M.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O. J. Phys. Chem. B 2001, 105, 6888–6894.
- (9) Azzam, W.; Cyganik, P.; Witte, G.; Buck, M.; Wöll, C. Langmuir 2003, 19, 8262-8270.
- (10) Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. J. Phys. Chem. B 2004, 108, 4989-4969.
- (11) Azzam, W.; Fuxen, C.; Birkner, A.; Rong, H. T.; Buck, M.; Wöll, C. *Langmuir* **2003**, *19*, 4958–4968.
- (12) Käfer, D.; Witte, G.; Cyganik, P.; Terfort, A.; Wöll, C. J. Am. Chem. Soc. 2006, 128, 1723-1732.
- (13) Cyganik, P.; Buck, M.; Wilton-Ely, J. D.; Wöll, C. J. Phys. Chem. B 2005, 109, 10902–10908.
- (14) Long, Y. T.; Rong, H. T.; Buck, M.; Grunze, M. J. Electroanal. Chem. 2002, 524, 62–67.
- (15) Thom, I.; Buck, M. Surf. Sci. 2005, 581, 33-46.
- (16) Vervaecke, F.; Wyczawska, S.; Cyganik, P.; Bastiaansen, J.; Postawa, Z.; Silverans, R. E.; Vandeweert, E.; Lievens, P. *ChemPhysChem* **2011**, *12*, 140–144.
- (17) Felgenhauer, T.; Rong, H. T.; Buck, M. J. Electroanal. Chem. 2003, 550, 309-319.
- (18) Szelagowska-Kunstman, K.; Cyganik, P.; Schüpbach, B.; Terfort, A. Phys. Chem. Chem. Phys. **2010**, *12*, 4400–4406.
- (19) Frey, S.; Rong, H. T.; Heister, K.; Yang, Y. J.; Buck, M.; Zharnikov, M. *Langmuir* **2002**, *18*, 3142–3150.

(20) Shaporenko, A.; Cyganik, P.; Buck, M.; Terfort, A.; Zharnikov, M. J. Phys. Chem. B 2005, 109, 13630–13638.

(21) Bashir, A.; Käfer, D.; Müller, J.; Wöll, C.; Terfort, A.; Witte, G. Angew. Chem., Int. Ed. 2008, 47, 5250–5253.

(22) Cyganik, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov, M. J. Phys. Chem. C 2008, 112, 15466–15473.

- (23) Weidner, T.; Shaporenko, A.; Müller, J.; Schmid, T.; Cyganik, P.; Terfort, A.; Zharnikov, M. J. Phys. Chem. C 2008, 112, 12495–12506.
- (24) Shaporenko, A.; Müller, J.; Weidner, T.; Terfort, A.; Zharnikov, M. J. Am. Chem. Soc. 2007, 129, 2232–2233.
- (25) Wyczawska, S.; Cyganik, P.; Terfort, A.; Lievens, P. ChemPhysChem 2011, 12, 2554–2557.
- (26) Müller, J.; Terfort, A. Inorg. Chim. Acta 2006, 359, 4821–4827.
 (27) Sette, F.; Hashizume, T.; Comin, F.; MacDowell, A. A.; Citrin,
- P. H. Phys. Rev. Lett. 1988, 61, 1384-1387.
- (28) Trevor, D. J.; Chidsey, C. E. D.; Loiacono, D. N. Phys. Rev. Lett. 1989, 62, 926–932.
- (29) Trotter, J. Acta Crystallogr. 1961, 14, 1135-1140.
- (30) Käfer, D.; Bashir, A.; Witte, G. J. Phys. Chem. C 2007, 111, 10546–10551.
- (31) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R.; Yang, G. H.; Liu, G. Y. Langmuir **2001**, *17*, 95–106.
- (32) Yang, G. H.; Liu, G. Y. J. Phys. Chem. B 2003, 107, 8746-8759.
- (33) Chesneau, F.; Schüpbach, B.; Szelagowska-Kunstman, K.; Ballav, N.; Cyganik, P.; Terfort, A.; Zharnikov, M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12123–12137.
- (34) Azzam, W.; Bashir, A.; Terfort, A.; Strunskus, T.; Wöll, C. Langmuir 2006, 22, 3647–3655.
- (35) Cyganik, P.; Buck, M. J. Am. Chem. Soc. 2004, 126, 5960-5961.
- (36) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. J. Am. Chem. Soc. **2006**, 128, 13868–13878.
- (37) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Witte, G.; Zharnikov, M.; Wöll, C. J. Phys. Chem. C 2007, 111, 16909–16911.