INVESTIGATION OF PERFLUOROPENTACENE THIN FILMS ON SUBSTRATES WITH DIFFERENT CHEMICAL STRUCTURES

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES OF MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN MICRO AND NANOTECHNOLOGY

Approval of the thesis:

INVESTIGATION OF PERFLUOROPENTACENE THIN FILMS ON SUBSTRATES WITH DIFFERENT CHEMICAL STRUCTURES

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ABSTRACT

INVESTIGATION OF PERFLUOROPENTACENE THIN FILMS ON SUBSTRATES WITH DIFFERENT CHEMICAL STRUCTURES

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July 2020, 206 pages

Due to their promising properties in electronic device applications, organic semiconductors (OSs) are being studied heavily. In this study, we aimed to investigate the structural properties of PerFluoroPentacene (PFP) thin films on flat and vicinal Au(111), and Ag(111) surfaces grown by the Supersonic Beam Deposition(SMBD) technique as a function of film thickness, metal surface step density, the effect of chemical and electronic properties of substrate, molecular flux (deposition rate), and energy during film growth which will enable us to determine the growth parameters that yield the highest quality PFP films. This study consists of two stages. In the first stage, we used conventional techniques such as Atomic Force Microscopy (AFM), Contact Angle measurements (CAs) and X-Ray Photoelectron Spectroscopy (XPS) for PFP film characterization. In the second stage, we aimed to present the design and construction of a new He diffraction system and the investigation of crystallographic properties of PFP films with this setup. The results indicate that PFP molecules arrange in standing-up orientation in the first layer and upper layers on all surfaces. The first layer of PFP thin films tends to wet the substrate surfaces, and after the first layer is almost completely covered, the second and other layers start to grow with needle-like grains which indicate a layer plus island (Stranski-Krastanow) growth mode. Substrate surface hydrophobicity and deposition rate directly affect the mean grain size and dendriticy of the first layer grains. The film formation is observed to be faster when the PFP molecules were seeded in lighter carrier gas resulting in higher kinetic energy PFP molecules. Construction of the new helium diffraction system was completed, and the performance of all parts of the system was tested. After a final optimization and minor modifications, the system is ready to collect diffraction data.

Keywords: Perfluoropentacene, SMBD, Deposition Rate, Thin Film, Film Growth

PERFLOROPENTASEN İNCE FİLMLERİN FARKLI KİMYASAL YAPILARA SAHİP ALTTAŞLAR ÜZERİNDE İNCELENMESİ

Yavuz, Adem Doktora, Mikro ve Nanoteknoloji Tez Yöneticisi: Doç. Dr. M. Fatih Danışman Ortak Tez Yöneticisi: Doç. Dr. Selçuk Yerci

Temmuz 2020, 206 sayfa

Organik yarı-iletkenler (OYİler) hakkındaki çalışmalar, bu maddelerin farklı elektronik aygıt uygulamalarındaki üstün/ümit vaat eden özellikleri nedeni ile artan bir hızda/yoğunlukta devam etmektedir. Bu çalışmada, düz ve basamaklı (vicinal) Au(111) ve Ag(111) yüzeyler üzerindeki perfloropentasen (PFP,C22F14) ince filmlerin, film kalınlığına, alttaşların fiziksel ve kimyasal yapılarının etkisi, film büyütme esnasındaki molekül akısı ve enerjisine ve metal yüzeyin basamak yoğunluğuna bağlı yapılarının aydınlatılması ve dolayısıyla en yüksek kaliteli filmi veren parametrelerin ortaya çıkarılması amacıyla, Süpersonik Moleküler Demet Kaplama (SMDK) tekniği ile elde edilen PFP ince filmlerin yapısal özelliklerini araştırmak amaçlanmıştır. Bu çalışma iki aşamadan oluşmaktadır, ilk aşamada PFP ince filmlerin karakterizasyonu için, Atomik Kuvvet Mikroskobu (AKM), Temas Açısı ölçümleri (CA) ve X-Işını Fotoelektron spektroskopisi (XPS) gibi geleneksel teknikler kullanılmıştır. İkinci aşamada ise, yeni bir helyum kırınım sisteminin dizaynı ve kurulumu, ve bu kurulumla PFP filmlerinin kristalografik özelliklerinin araştırılması amaçlanmıştır. Elde edilen sonuçlar PFP moleküllerinin, hem ilk hem de üst katmanlarda dik oryantasyon ile dizilidiğini göstermektedir. İlk katman yüzeyi

tamamen ıslatmaya eğilimli iken, ilk katman neredeyse yüzeyi tamamen kapladıktan sonra, ikinci ve diğer üst katmanlar bu ilk katman üzerinde, katman-artı-adacık (Stranski-Krastanow) büyüme modunda iğnemsi adacıklar oluşturmaktadırlar. Alttaş yüzey hidrofobikliği ve kaplama hızı (DR), ilk katman adacıklarının ortalama adacık boyutunu (MGS) ve adacık dendiritikliğini doğrudan etkilemektedir. Film oluşumu, yüksek kinetik enerjili demet durumunda daha hızlıdır. Yeni helyum kırınımı sisteminin kurulumu tamamlanmış ve sistemin tüm parçalarının performansı test edilmiştir. Son optimizasyon ve küçük bazı değişikliklerin ardından, sistem kırınım verilerini toplamaya hazırdır.

Anahtar Kelimeler: Perfluropentasen, SMDK, Kaplama Hızı, İnce Film, Film Büyütme To my dear wife, PİA

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my supervisor, Assoc. Prof. Dr. M. Fatih Danışman for his guidance, advice, criticism, encouragement, endless supports and insight throughout the research. I would also like to thank Dr. Gianangelo Bracco for his helps, suggestions and comments on construction of the new He atom diffraction system. I would also like to thank Ferenc Borondics for his helps and being my mentor for RAIRS studies in SOLEIL Synchrotron.

My special thanks go to thesis monitoring committee members Assoc. Prof. Emrah Özensoy, Prof. Dr. Okan Esentürk and Prof. Dr. Mürvet Volkan for their valuable contribution to each part of this dissertation and for their endless patience to me. I would like to thank all jury members not only for their time and patience, but also helping me improve this thesis significantly with their valuable comments.

I would like to thank Dr. Tomas Base for providing the carboxyl functionalized carboranethiols.

I would like to express my sincere thanks to Saliha Görgülü for her assistance in the laboratory. I would like to thank my all family for their love and support during my whole life.

I thank The Center for Solar Energy Research and Applications (GÜNAM) and Prof. Dr. Levent Toppare for letting us use their thermal evaporator for gold film growth and Mertcan Erer for helping us using the evaporator.

This work is partially funded by the Scientific and Technological Research Council of Turkey under grant number TUBİTAK 113F022 and partially supported by Middle East Technical University BAP grant no. DKT-103-2018-3683.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

a	Ambipolar
ABL	Average Boundary Length
a-CA	advancing Contact Angle
AFM	Atomic Force Microscopy
AR-XPS	Angle-Resolved Photoelectron Spectroscopy
ATR	Attenuated Total Reflection
BTBT	Benzothienobenzothiophene
C60	Buckminsterfullerene
CA	Contact Angle
CCG	Cold Cathode Gauge
CEM	Multi-Channel Continuous Dynode Electron Multiplier
CSC	Chopper Stage Collimator
СТ	Carboranethiol
DC	Drop-Casting
DFT	Density Functional Theory
DIP	Diindenoperylene
DR	Deposition Rate
DRC	Detector Box Collimator
EA	Electron Affinity
EC	Edge Cast

EF	Fermi Level
Eg or Egap	Bandgap Energy
EI	Ionization Energy
F16CuPc	Fluorinated copper-phthalocyanine
FC	Faraday Cup
FET	Field-Effect Transistor
FOTS	Perfluorooctyltrichlorosilane
FTIR	Fourier-Transform Infrared Spectroscopy
GIXD	Grazing X-ray Diffraction
HAD	He Atom Diffraction
HAS	He Atom Scattering
HMDS	Hexamethyldisilazane
HOD	11-hydroxyundecyl octadecyl disulfide
НОМО	Highest Occupied Molecular Orbital
HS	Helium Source
HV	High Vacuum
If	Filament Current
IG	Ion Gauge
IGC	Ion Gauge of Chopper Stage
IGH	Ion Gauge of He Source
IGK	Ion Gauge of Diffraction Chamber
IR	Infrared

LED	Light Emitting Diode
LEED	Low Energy Electron Diffraction
LUMO	Lowest Unoccupied Molecular Orbital
m	Meta
M1	m-1-carboranethiol
M9	m-9-carboranethiol
MAOPTS	3-methacryloxypropyltrichlorosilane
MGA	Mean Grain Area
MGS	Mean Grain Size
MUD	Mercaptoundecanol
NEXAFS	Near Edge X-ray Absorption Fine Structure
<u>.</u>	Ortho
0	ortito
0	o-1-carboranethiol
0 O1 OBS	o-1-carboranethiol Organic Beam Source
0 01 0BS 0DT	o-1-carboranethiol Organic Beam Source Octadecanethiol
0 01 0BS 0DT 0FET	o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor
0 01 0BS 0DT 0FET 0MBD	o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor Organic Molecular Beam Deposition
01 OBS ODT OFET OMBD OSC	o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor Organic Molecular Beam Deposition Organic Semiconductor
01 OBS ODT OFET OMBD OSC OTS	o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor Organic Molecular Beam Deposition Organic Semiconductor Octyltrichlorosilane
0 01 0BS 0DT 0FET 0MBD 0SC 0TS P	o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor Organic Molecular Beam Deposition Organic Semiconductor Octyltrichlorosilane Para
0 01 0BS 0DT 0FET 0MBD 0SC 0TS 0TS P PAH	 o-1-carboranethiol Organic Beam Source Octadecanethiol Organic Field-Effect Transistor Organic Molecular Beam Deposition Organic Semiconductor Octyltrichlorosilane Para Polycyclic Aromatic Hydrocarbon

PFP	Perfluoropentacene
РН	Differential Pumping Line Connection Flange
PM	Parabolic Mirror
P _{ss}	Pressure of SMBD
PTCDA	Perylenetetracarboxylic dianhydride
QCM	Quartz Crystal Microbalance
QMS	Quadrupol Mass Spectrometer
RAIRS	Reflection-Absorption Infrared Spectroscopy
r-CA	receding Contact Angle
RF	Radio Frequency
RFL	Reflected Focal Length
RHEED	Reflection High Energy Electron Diffraction
RP	Rotary Platform
S_C	Spin-Coating
SAM	Self-Assembled Monolayer
SC	Semiconductor
s-CA	static Contact Angle
SD	Worm Gear
SE	Spectroscopic Ellipsometer
SH	Sample Holder
SMBD	Supersonic Molecular Beam Deposition
SRI	Specular Reflection Intensity

s-SNOM	Scattering-type Scanning Near-Field Optical Microscopy
STM	Scanning Tunnelling Microscopy
TCG	Thermocouple Gauge
ТЕ	Thermal Evaporation
TFT	Thin Film Transistor
TIPS-pentacene	6,13-bis[(triisopropylsilyl)Ethinyl)] pentacene
TOF	Time of Flight
TPD	Temperature-Programmed Desorption
ТРОС	Thiophene-phenylene co-oligomer
TSAu	Template Stripped Gold
UHV	Ultra High Vacuum
UPS	Ultraviolet Photoelectron Spectroscopy
V	Vacuum
$\mathbf{V}_{\mathbf{f}}$	Filament Voltage
VS	Vacuum Sublimination
WF	Work Function
XAFS	X-ray Absorbtion Fine Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRR	X-ray Reflectivity

"God made the bulk, but the surface was invented by the devil."

-Wolfgang Pauli

CHAPTER 1

INTRODUCTION

Due to their promising properties in electronic device applications like thin-film transistors (TFTs), light-emitting diodes (LEDs), organic field-effect transistors (OFET), and solar cells, organic semiconductors (OSCs) are being studied widely. [1,2] Studies have shown that electronic and crystal structure of interfaces between the metal electrode-OSC layer and OSC layer-dielectric, directly or indirectly, affect the performance of organic TFTs. [3,4] Both in the former and the latter, most of the charge carriers are produced in the first few OSC layers. [5–8] The irregularities in these interfaces affect the charge transfer and exciton dynamics negatively and cause the devices to lose their efficiency. [9,10] For the fabrication of different types of electronic devices from organic components, two kinds of semiconductors (SCs) are necessary. These are n-type SCs, in which the charge carriers are electrons, and p-type SCs, in which the charge carriers are holes. Primary considerations that should be taken into account when designing an organic electronic device (in particular organic TFTs) and that may directly or indirectly affect device performance are:

1) The isolated electronic and crystal structure of the OSCs

2) Electronic and crystal structure of the films formed by the OSCs on the dielectric layer (usually SiO_2) in the device

3) The electronic and crystal structure of the film formed on the metal electrodes (typically gold) in the device (see Figure 1.1).

Therefore, defining the OSC used for the development of high performance organic electronic devices under different conditions is crucial. Obviously, to improve the understanding of the OSCs on these interfaces, better insight into their nucleation

and growth mechanisms on both metal and different dielectric surfaces should be developed. [11]



Figure 1.1. Schematic description of the crystal structure of organic semiconductors in bulk and thin-film phase (top) and some common organic TFT types.

The flow of this introduction will be as follows; firstly, the basic features and the growth mechanism of crystals for OSCs will be introduced. Later, the electronic and crystal structures of OSCs will be discussed. Finally, a review of recent studies on the perfluoropentacene (PFP) molecule that intended to study in this thesis will be given.

1.1 Fundamentals of Organic Semiconductors

1.1.1 Properties of Organic Semiconductors

OSCs can be classified into two groups: small-molecules and polymers. The lower molecular weight of small molecules constitutes an advantage over polymers. As a result, small molecules can be thermally evaporated and have better crystallinity than
polymers. Table 1.1 shows a detailed comparison of properties for polymers and small molecules. Small molecules have an extra advantage over polymers, which are difficult to obtain in crystalline films due to their long chains. Hence, polymers form amorphous structures, which cause relatively low mobilities.

Table 1.1. Comparison of polymers and small molecules

Type of OSC	Polymers	Small Molecules
Length (nm)	≈ 100	≈ 1
Weight (g.mol ⁻¹)	> 1000	< 1000
Charge Mobility (cm ² .V ⁻¹ . s ⁻¹)	$\approx 1-600$	$\approx 10^{-6}$ -1
Degree of crystallinity	low	high
Degree of disordering thin film	large	small
Process for thin film	easy (solution based via	hard (generally thermal

n spin coating, e.g.) evaporation based)

Some small molecules commonly used in electronic applications are given in Figure 1.2. In the selection of small molecules for electronic device studies, some properties are to be considered, such as excellent charge carrier properties, high emission properties, and perfect single crystal arrangement. For instance, rubrene molecule comprises the combination of these properties in a single crystal and shows maximum hole mobility of up to $\sim 43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a field-effect transistor (FET) device configuration. [12] Thiophene-phenylene co-oligomers (TPCOs) are small molecules with different molecular configurations, which can easily be synthesized by simply changing the total number and arrangements of thiophenes and phenylenes (benzenes) at the molecular level. In TPCOs, molecules possess a great transition dipole moment along the long molecular axis. [13] This causes the strongest light to be emitted in the direction perpendicular to the long molecular axis. The dipole moment of TPCO crystals is parallel to the crystal plane because the molecules are aligned nearly upright against that plane, contrary to many other OSCs. For instance, BP3T is a type of TPCO that has hole mobility up to 1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. [14] Diindenoperylene (DIP, $C_{32}H_{16}$) is a perylene molecule fused to a benzene moiety at each end. It is a p-type organic semiconductor and shows high hole mobility in thin films up to $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Flat-lying DIP molecules in a herringbone arrangement improve the adsorption properties, which can increase the organic device efficiency. [15–17] Fluorinated copper–phthalocyanine (F16CuPc) is an n-type semiconductor, and it exhibits air-stable behavior and high electron mobility under ambient conditions. It differs owing to its excellent electrical and optical properties, such as relatively high mobility of 0.6 cm²V⁻¹s⁻¹ and broad optical absorption spectrum compared to other organic semiconductors. [15,18–20]



Figure 1.2. Some examples for small molecules, details about these molecules are given in the text.

Buckminsterfullerene (C_{60}) is a type of fullerene, represents an unusual case of a plastic crystal phase at room temperature. Its bandgap energy is about 1.9 eV. Transistors made with C_{60} show acceptable performance, which they are coated with a sputtering technique, and their electron mobility reaches up to 11 cm²V⁻¹s⁻¹. [21] Benzothienobenzothiophene (BTBT) is a liquid-crystalline semiconductor that arises

with high-charge carrier transport (between $1.8 - 43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and long-range order crystallinity properties. Molecular semiconductors tend to form plate-like crystals, and they have herringbone packing motifs. [22] Perylenetetracarboxylic dianhydride (PTCDA), an n-type organic semiconducting molecule, has received widespread attention in electronic and optoelectronic devices. The electron mobility of PTCDA nanoparticles is 0.08 cm²V⁻¹s⁻¹ at 300 K and 0.5 cm²V⁻¹s⁻¹ at 80 K, while single-crystal electron mobility is very low. [23,24] One of the most intensively studied p-type molecules is pentacene (PEN). Pentacene is a polyaromatic hydrocarbon that consists of five linearly fused aromatic rings. PEN can be deposited only through thermal evaporation, whereas 6.13bis[(triisopropylsilyl)Ethinyl)] pentacene (TIPS-pentacene) features side chains that improve its solubility and simplify its processing while maintaining high crystallinity. TIPS-pentacene is a p-type semiconductor and widely used for organic FET applications, with mobility above 1 cm²V⁻¹s⁻¹. [22] It has excellent solubility in organic solvents, and this makes it easy to process into devices.

The processing and preparing conditions can have a great impact on the performance of FETs. In FET design, OSC and dielectric layer selection, deposition techniques for these layers, and electrode type directly affect the charge transport state. [25] A comprehensive literature review to get an understanding of the relationship between small molecules, dielectric materials, preparation methods, and FET performances is summarized in Table 1.2, where SiO₂ surfaces were coated with silane-based and phosphonate derivative-based SAM molecules to improve hole mobility in FET.

	osc	OSC Film	•	average mobility		osc	OSC Film	•	average mobility
type	material	deposition*	electrode	(cm ² V ⁻¹ s ⁻¹)	type	material	deposition*	electrode	(cm ² V ⁻¹ s ⁻¹)
4	pentacene	OMBD	TC Au	1.2	u	C60	TE	TC Au	0.2 (0.27)
Ч	pentacene	sc	BC Au	~0.3 (0.36)	u	C60	TE	TC Au	4.1 (5.3)
4	rubrene	sc	BC Au	$0.6 \pm 0.5 \ (2.4)$	ď	PTAA	s_c	BC Au	$5.2 (\pm 1.3) \times 10^{-4}$
п	C60	sc	BC Au	0.03	đ	PTAA	s_c	BC Au	5.2 (±1.5) × 10 ⁻⁴
a	TCNQ	sc	BC Au	10-4	ď	PTAA	s_c	BC Au	$1.4 (\pm 0.7) \times 10^{-4}$
ď	MEH-PPV	sc	TC Au	1.2×10^{-4}	đ	PTAA	s_c	BC Au	$2.0 (\pm 0.1) \times 10^{-4}$
Р	MEH-PPV	sc	TC Au	1.3×10^{-3}	ď	pentacene	TE	TC Au	2.8 ± 0.2
Р	OCICI0-PPV	sc	TC Au	1.6×10^{-4}	ď	pentacene	TE	TC Au	0.52 ± 0.04
Р	OCIC10-PPV	sc	TC Au	1.3×10^{-3}	u	C60	TE	TC Au	4.7 ± 0.41
d	pentacene	OMBD	TC Au	~0.6	u	C60	TE	TC Au	0.27 ± 0.15
Р	pentacene	OMBD	TC Au	~0.3	u	PTCDI-C4F7	TE	TC Au	1.4
đ	pentacene	NS	BC Au	0.1-0.6	u	PTCDI-C4F7	TE	TC Au	0.72
Р	pentacene	Λ	TC Cu	0.4	đ	pentacene	TE	TC Au	0.8 (0.9)
Р	8QT8	DC	TC Au	0.014	ď	pentacene	TE	TC Au	1.6 (2.4)
đ	8QT8	DC	TC Au	0.17	đ	pentacene	TE	TC Au	1.8 (3.6)
Р	pBTCT	sc	чч	0.021	đ	pentacene	TE	TC Au	2.5 (4.7)
Р	pBTCT	s_c	ηų	0.018	ď	P-BTDT	TE	TC Au	0.22(0.250)
Р	pBTCT	s_c	чΑ	0.005	ď	P-BTDT	TE	TC Au	0.085(0.090)
Р	pBTCT	sc	чч	1.6×10^{-3}	đ	pentacene	TE	TC Au	0.517 ± 0.015
Ч	pBTCT	sc	чΑ	5 × 10 ⁻⁵	đ	pentacene	TE	TC Au	0.449 ± 0.002
Р	PB16TTT	sc	BC Au	0.24 (0.25)	ď	C10-DNF-VV	EC	TC Au	1.3
Р	PB16TTT	sc	BC Au	0.28 (0.30)	đ	C10-DNF-VW	EC	TC Au	1.0
Р	PB16TTT	sc	BC Au	0.48 (0.51)	đ	C10-DNF-VW	EC	TC Au	1.1
Р	PB16TTT	sc	BC Au	0.56 (0.74)	ď	pentacene	OMBD	TC Au	0.46 (0.61)
Р	PB16TTT	sc	TC Au	0.35 (0.38)	ď	pentacene	OMBD	TC Au	0.31
Р	PB16TTT	sc	TC Au	0.41 (0.46)	ď	pentacene	OMBD	TC Au	0.19
Р	PB16TTT	s_c	TC Au	0.59 (0.65)	ď	P3HT	sc	BC Au	0.156 ± 0.010
Р	PB16TTT	sc	TC Au	0.84 (1.0)	**	PNDTI-BT-DT	s_c	TC Au	0.2 (p)/0.28(n)
Р	pentacene	TE	TC Au	0.6 (0.9)	a ⁺	PNDTI-BT-DT	s_c	TC Au	0.43(p)
Р	pentacene	TE	TC Au	2.1 (2.3)	* ₽	PNDTI-BT-DT	s_c	TC Au	0.24(n)

Table 1.2. Summaries of the devices with SAM-Modified SiO₂ Dielectrics. Table retrieved from ref [25].

(*Abbreviation of OSC film deposititon techniques: OMBD - organic molecular-beam deposition SC-single crystals, S_C-spin-coating (from ultrasonicated solution for 4 min), EC - edge-cast, V - vacuum, VS - vacuum sublimation, DC - drop-casting, TE - thermal evaporation,+: a- ambipolar)

The most critical group of conjugated small organic molecules are polycyclic aromatic hydrocarbons (PAHs), which consist of aromatic molecules containing laterally fused benzene rings. The molecules investigated in this work are perfluoropentacene (which belongs to a group of acene molecules), and the terms OSC and thin-film are exclusively used to refer to them. In the following section, the bulk crystal structures of OSCs will be discussed.

1.1.2 Organic Molecular Packing Motifs

Similar to other crystal systems, OSC crystals are formed in a perfectly ordered point lattice and a basis by the molecular assembly. In OSC crystals, the basis is formed by organic molecules. This crystal arrangement leads to a molecular packing motif. Within this molecular packing, conjugated molecules bond by Van der Waals forces, which are weak and long-ranged compared to covalent and ionic bonds. The molecular packing is associated with electronic, optoelectronic, and energetic properties. Therefore, this arrangement determines the mechanical, thermodynamic, optical, and also charge transport properties. The weak Van der Waals force causes sufficient separation between adjacent molecules, which leads to the low melting point of the crystal. π -conjugation leads to effective charge delocalization and results in excellent charge transport. Charge carriers (electron or hole) that provide charge transport reside in HOMO or LUMO energy states. Charge transport occurs via continuous hopping transport from one localized state to the next within adjacent molecules. The optimal electronic performance of OSC requires strong electronic coupling between adjacent molecules and charge transport modulated by molecular packing. [26–28]

There exist three stacking geometries between two aromatic rings, which are cofacial, parallel-displaced, and edge-to-face (see Figure 1.3-a). [29] Stoichiometrically, between two neighboring aromatic rings, C-C, C-H, and H-H interactions modulate the different packing structures. The strong overlap in PAHs is achieved via two typical crystal packing structures: Herringbone and π -stacked (see Figure 1.3-b). Herringbone is characterized by tilted molecules (edge-to-face; C-H interactions), and π -stacked is characterized by parallel molecules (face-to-face; C-C interactions). In the thin-film phase, molecule-molecule and molecule-substrate interactions lead to the formation of one of these two packings. In the herringbone, intermolecular interactions are very strong and push molecules to arrange on the surface in standing-up geometries; on the contrary, when substrate-molecule interactions become dominant, these interactions give rise to π -stacked packing with lying-down geometries. The π -stacked arrangement has a significant overlap of π -orbitals between faces of adjacent molecules, which leads to smaller intermolecular distance, which enhances the charge carrier mobility. [26–31] As mentioned above, molecule-molecule interactions are dominant in the formation of molecular packing motifs in bulk structures. However, in the case of thin-films, molecular packing motifs, and the growth mechanism of the film are affected by molecule-substrate interactions. To improve the understanding of interactions between molecule-substrate, in the next part, thin-film growth modes will briefly be mentioned.



Figure 1.3. Molecular packing motifs in acene crystals. Examples of three possible stacking geometries between two aromatic rings (a), herringbone and π -stacked arrangement side view (b), and herringbone arrangement top view (c). Figure adapted from [29].

1.2 Thin Film Growth

In general, OSC thin-film formation onto substrates occurs either in the vapor phase under vacuum conditions or from solution (in the case the molecules are solvable in an appropriate solvent), depending on the desired application, one of these techniques is utilized. In this part, firstly, film growth in vacuum via molecular beam deposition will be discussed, and it will be followed by a discussion of solutionbased growth techniques.

Organic molecules deposited by a molecular beam deposition technique reach the surface with a specific flux (rate of arrival on the surface). The growth of a thin organic film is a dynamic and non-equilibrium that involves many kinetic processes. These are: adsorption, desorption (re-evaporation into the vacuum), nucleation or dissociation of molecular clusters, and adsorbate flux, the formation of molecular assemblies, and diffusion in the layer (intra-layer) and/or between layers (inter-layer) of thin-film (see in Figure 1.4). [27,28,32–34]

Interpretation of molecule-substrate interactions is simple with the wetting phenomena described in the Young's equation $[\cos(\theta)=(\gamma_{s}-\gamma_{sa})/\gamma_{a}]$. Here, the relation between substrate surface tension (γ_{s}) , film surface tension (γ_{a}) , and substrate-film interface surface tension (γ_{sa}) give rise to different growth modes. Lattice mismatch at the film-substrate interface and the film thickness affect the surface tension.

- In the extreme cases of Young's equation, the wetting angle could be zero(θ=0). Young's equation turns into [y_{sa}=y_s+ y_a] so that the "drop" spreads out completely (a layered thin film).
- In the case of θ>0, the equation changes to [y_{sa}<y_s+ y_a], which means the interface tension becomes smaller than the substrate tension, and the drop reduces contact area on the surface and island type films occurs. [34,35]

Three types of growth modes occur depending on adsorbate-adsorbate and adsorbate-substrate interactions, which affect the thin-film morphology. If the interactions between the adsorbates are stronger than the substrate-adsorbate interactions, molecules form rigid islands that grow steeply in the vertical direction resulting in separated 3D islands. This growth mode is called Volmer-Weber or island growth mode. If the substrate-adsorbates interactions are stronger than the interactions among adsorbates, the substrate is wetted fully with the adsorbates. The growth process follows after the first layer is coated completely, and then the upper layers start to grow on these layers. This is called Frank-van der Merwe or layer-by-layer growth mode. In this growth mode, smooth 2D films occur. When the first few monolayers coat the surface entirely, adsorbate-substrate interaction is shielded by these wetting layers and growth type changes into the island formation. This mode is called as Stranski-Krastanov or layer-plus-island growth mode (see in Figure 1.4). As we mentioned above, small molecules are usually covered by thermal evaporation techniques, and these techniques generally operate under high vacuum (HV) or ultrahigh vacuum (UHV) conditions. So "why do we need vacuum?" this question will be answered in the next part.



Figure 1.4. (a) Schematic diagram of processes on a molecular scale in nucleation and film growth on surfaces. (b) Schematic illustration of different crystal growth modes. The figure adapted from [27].

1.2.1 Why Need Vacuum?

As stated in Section 1.2, OSC thin-films obtained with small molecules are generally deposited by evaporating under vacuum conditions. In the case a film is formed in atmospheric pressures or low vacuum, undesirable particles may block evaporated molecules from moving toward the targeted substrate. Thus, molecules rarely reach the substrate and cannot form high-quality films. Even if the molecules reach the substrate, several problems arise; for instance, the adsorption of the molecules becomes weak or molecules bond with other substrates in the air. The vacuum environment serves to:

- increase the mean free path by reducing particle density in the medium
- provide vapor flow control in the evaporation process
- preserve the surfaces and the chamber volume from unwanted molecules or atoms (contaminants)

The average distance, a molecule will move before colliding with another molecule is called the mean free path, which is shown with the symbol λ . Mean free path (MFP) is inversely proportional to chamber pressure ($\lambda \approx 1/p$) and increases as chamber pressure decreases (vacuum increases). However, when the MFP reaches the chamber diameter, no matter how low the chamber pressure is, the movement of molecules is limited, and MFP remains constant since the molecules in the chamber will collide with the chamber walls. As the pressure decreases, the average distance within the collisions between two molecules becomes longer, and Table 1.3 shows the λ values corresponding to given system pressure. Knudsen number (K_n) introduces an explicit way to characterize gas flow in a chamber (or pipe); it is defined as the ratio of λ to a characteristic dimension of the chamber (D) through which the gas flow can be explained via K_n = λ/D (unitless).

Pressure 1×10^{2} 1×10^{-3} 1x10⁻⁴ 1×10^{-5} 1x10⁻⁶ 760 1 (Torr) Mean Free 6x10⁻⁶ 5×10^{-4} 5×10^{-1} $5 \text{ x} 10^1$ $5 \text{ x} 10^2$ $5 \text{ x} 10^3$ $5 \text{ x} 10^4$ Path (mm)

Table 1.3. Mean free path at different pressures

The kinetic gas theory explains that molecules in vapor move at high speed and frequently collide with other molecules or chamber surfaces. The flow mechanism of molecules depending on K_n can be classified into three types, which are given in Figure 1.5. In the case λ is very low at high pressure, K_n is about lower than 0.01, collisions between molecules are much more dominant than collisions between molecules and chamber walls. The characteristics of gas flow are then necessarily determined by the intermolecular collisions. Consequently, gas can be considered to be a viscous fluid. At low pressure (λ is very high), and K_n is bigger than 1, here the gas flow is limited by molecular collisions with the walls of the chamber. Intermolecular collisions are now almost non-existing; thus, this type of flow is known as molecular flow. In the molecular flow, flow determinations and characterization face with a geometric problem of the restrictive effects of walls on the motion of a molecule. Between the regions of viscous and molecular flow, we can expect some transitional behavior that will exhibit the properties of both regions to some extent since both types of collisions are involved. This type of flow is known as transitional flow. [36,37] As we mentioned in this part, the flow of molecules is essential in the production of thin films under vacuum conditions. In vacuum conditions, the molecular beam is needed for this molecule vapor to reach the substrate surface. In the next part, a brief introduction about molecular beam production techniques will be given.



Figure 1.5. Types for the flow of molecules in a pipe wall. The figure is retrieved from ref [38].

1.2.2 Molecular Beam Production for Thin Film Growth

OSC thin-films obtained with small molecules are generally deposited by organic evaporation techniques; in this part, a brief introduction to molecular beam production systems will be given. A molecular beam is defined by molecules that are collision-free and flow in the same direction. The thermal evaporation systems generally consist of three main parts: molecular source reservoir (Knudsen cell or nozzle), a beam collimator, and the sample volume. Both sources (nozzle and Knudsen cell), are made of a reservoir in which the small molecules can be evaporated to create a molecular beam. Evaporated molecules with a certain temperature and pressure are expanded from a reservoir through a hole into a vacuum chamber (pressure is usually $\sim 10^{-6}$ Torr). The kinetic energy of a molecular beam is not more than a few eV, which means that the molecules constituting the beam are physically unable to penetrate the substrate bulk, and are attached to the substrate surface. Generated molecular beam shows Maxwellian (or gaussian) distribution from sources. The basic parameters needed to describe both types of sources are the pressure in the source (the Knudsen cell or nozzle) stagnation chamber ($P_{\text{stagnation}}$), the diameter of the hole through which the gas flows (d), the pressure in the vacuum chamber (P), and the mean free path of the molecules into the source (λ). The two different regimes are obtained, depending on how large λ is in comparison with d, it means that Effusive (Knudsen) and supersonic molecular beams are distinguished depending on the Knudsen number describing the expansion through the source orifice/nozzle. Figure 1.6 shows the two primary techniques to produce high-quality thin-films. [36,37]



Figure 1.6. Schematic views of Knudsen and supersonic source (figure adapted from [37])

The Knudsen source consists of a gas chamber and effusion orifice (hole). In a Knudsen cell, the vapor formed will effuse in a molecular regime. The source works at low gas pressure in the gas chamber ($P_{\text{stagnation}} \sim P$ at the source exit), Knudsen number in the source orifice is large: λ is bigger than *d*, and molecules leaving the source will not experience any more collisions as the gas expands. The velocity and internal energy distributions of the molecules follow a Maxwell–Boltzmann distribution function, whereas the angular distribution is typically cosine-like.

The main idea in the nozzle source is the translation of the thermal gas energy into the ordered motion of the supersonic flow. As the effusion source, it has the same pumped sections but added by a high-pressure nozzle [by seeding the molecular species in a lighter inert carrier gas (He, Ar, or Kr)] with a supersonic nozzle. The central core of the supersonic flow is screened out by a sharp edge skimmer. During the supersonic operation, $\lambda < d$ ($P_{stagnation} > P$), the free-jet regime occurs; consequently, the Knudsen number is small, and gas with relatively high pressure (several atm) reaches the speed of sound at the nozzle. In a nozzle source, there is net transport through the nozzle, and this involves the conversion of the total enthalpy into beam transitional energy, allowing higher beam energies. As a result of this operation, the beam is cooled by adiabatic expansion through the nozzle, and the velocity distribution of molecules stay unchanged along the beam axis. In other words, rotational, vibrational, and some translational (degrees of freedom) are frozen out and converted into translational motion along the beam axis. By seeding the molecular vapor in a carrier gas (He, Ar, or Kr), a supersonic expansion allows controlling the kinetic internal energy and momentum of the molecules. In contrast with the Knudson source, since the nozzle source is operated at a Knudsen number less than unity, the gas expands isoentropically through the nozzle from high pressure to the vacuum chamber. As the vapor expands into the vacuum region, lower molecule densities result in increasing distance from the nozzle. The result is that free-molecule flow eventually takes over from the continuum flow in the nozzle, as the collision frequency decreases; the beam becomes supersonic in the process and is characterized by Mach number. Mach number is a rate which is;

$$M = \frac{v_{beam}}{v_s} \qquad eqn.\,1.1$$

where v_{beam} is the average speed of the molecules in the beam, v_s is the speed of sound in air, which is about 330 ms⁻¹. The ratio of the speed of the beam to the speed of sound characterizes the beam velocity. Subsonic conditions occur for M < 1 ($v_{beam} < v_{sound}$). As the speed of the beam is higher than the speed of sound, Mach numbers greater than one, M > 1 ($v_{beam} > v_{sound}$), beam velocities reach the supersonic velocities. [39–41] The production of thin-films with small molecules is carried out under vacuum conditions as well as by dissolving in a suitable solvent in the solution. Self-assembled monolayers (SAMs) are one of these solution-based techniques. Since we also examined carbonranetiol SAMs in this dissertation, a brief explanation will be given about the SAM film growth mechanism in the next part.

1.2.3 Self-Assembled Monolayers

In order to control the physical, chemical, and electronic properties of OSs, sacrificial layers are added between the substrate and organic semiconductors. Self-assembled monolayers (SAMs) can be given as an example of these sacrificial layers.

In this dissertation, during the production of PFP thin films, besides templatestripped gold (TSAu) surfaces, carboranethiol self-assembled monolayer (SAM) coated TSAu surfaces were also used as a substrate. The substrate preparation processes will be explained in detail in Section 2.1. Investigations show that utilizing the SAMs as a sacrificial layer on the substrate to vary the surface electronic and chemical structure is advantageous. [42,43] The content of this part will consist of the description of SAMs and the formation mechanism of these films.

SAMs are molecular assemblies formed by the adsorption of an active surfactant on a solid surface. SAMs are composed of molecules that have three parts in their structure, which are headgroup, molecular backbone, and end group, as shown in Figure 1.7. The headgroup is the part of the molecule called a thiol group and is generally formed with organosulfur groups (R-SH). The headgroup usually binds to the substrate surface through highly strong molecule-substrate interactions that exceed the energy barrier to break down the S-H bond, and reactive R-S binds to the surface through a covalent bond, known as chemisorption. [44] The molecular backbone group, which consists of an aliphatic or aromatic structure, connects the headgroup to the endgroup. In SAMs, molecular rearrangement depends on both intermolecular interactions, such as van der Waals, dipole-dipole, or π - π interactions, and endgroup-endgroup interactions. [45] The backbone group and headgroup govern the strength of intermolecular interactions. [46,47] The endgroup (terminal group) is the end part of molecules forming the SAM that is responsible for functionalizing the SAMs. The terminal group is responsible for successive adsorption or chemical reaction on top of SAMs. [48–52] Endgroup can be modified to add different groups leads to a change in the physical and chemical properties of SAMs. [53,54] By adding different terminal groups, surfaces gain hydrophobic or hydrophilic properties. [55,56] Studies on mixing different end-group thiols SAMs show that surface properties (such as wetting and reactivity) can be varied by using the different ratios of these different end-group thiols. [57]



Figure 1.7. A schematic diagram showing the constituents of a SAM-molecule.

In addition to growing by thermal evaporation techniques, preferentially substrates are coated with SAMs by immersing them in the thiol solution. In the solution, the adsorption process of thiol SAMs on TSAu consists of two-steps. The first one is the formation of the monolayer in which 80-90% of the monolayer is formed within the time scale of seconds to a few minutes. The second step is a reorganization step with a time scale of hours or even days during which molecules in the monolayer undergo orientation ordering, resulting in complete film formation in which the molecules form the highest density packing arrangement (the surface is saturated), and is referred to as the full-coverage phase. [44,58] In the monolayer formation, the cleanliness of both the thiol source material and the solution is essential, so any kind of contamination will affect the adsorption mechanism. The monolayer formation is directly affected by the existence of contamination. [59,60]

SAM formation mechanism on Au(111) surface is shown in Figure 1.8, and the formation mechanism could be summarized as follows [44]:

- I. The molecular axis is parallel to the Au (111) surface with the lyingdown position, and molecule-substrate interaction is dominated by physisorption.
- II. In this process, molecules on the surface have higher mobility. They tend to nucleate grains (lying nucleates), as shown in Figure 1.8.
- III. As the amount of molecules on the surface increases, the rate of intermolecular interaction (through Van-der-Waals forces and endgroup/end-group interaction among the molecules) increases. As the intermolecular interactions increase, the molecules begin to stand up.

IV. While the standing-up orientation proceeds thanks to the intermolecular interaction, head group-substrate interactions become dominant and cause very densely packed domains via chemisorption (see Figure 1.8). At the end of this stage, molecules are oriented with their molecular axis nearly perpendicular to the surface.

Coating thin films alter the electronic structure of substrates. To obtain the desired electronic structure of the substrate, the necessary information on how thin films have changed the substrate's electronic structure and the electronic structure of thin films, will be given in the next part.



Figure 1.8. Scheme of the different steps taking place during the self-assembly of alkanethiol on Au (111): (i) physisorption, (ii) lying down phase formation, (iii) nucleation of the standing up phase, (iv) completion of the standing up phase. Adapted from ref [44].

1.3 Electronic Structure of Organic Semiconductors

The electronic structure of a conjugated OSCs is defined by choice of a molecular repeat of units (and also the number of repeat units), for instance, Polyacenes'

absorption characteristics directly depend on the number of repeat benzene rings. [27,61–63] Characteristic absorption phenomena arise from the excitation of the π -electron system, and the required energy value to excite these electrons is in the order of eV. For instance, optical transition wavelengths of PFP and its nonfluorinated counterpart PEN in thin films are around 576 nm (2.15 eV) and 670 nm (1.85 eV), which are in the green and red region of the visible spectrum, respectively.[64–66] These energy values correspond to their bandgap energies (E_{gap}). This molecular excitation is defined as the π -electron transition from the HOMO energy level to the LUMO energy level. [63]

Electron affinity (EA) is the gained energy when an electron is added to the LUMO energy level. Ionization energy (EI) is the energy to extract an electron from the HOMO level. When an electron is removed from the HOMO level, the OSC reoptimizes the bond structure and creates a hole. In organic electronic devices, thin films are used instead of single molecules, and Egap of thin films is smaller with respect to an individual molecule. Figure 1.9 shows the energy levels of a single molecule and thin films. EVAC is the vacuum level, EI is ionization energy (required energy to remove an electron from an atom/molecule), EA is the electron affinity (required energy to attach an electron into an atom/molecule), (g) and (f) denote the single-molecule and thin film, respectively. When a thin film absorbs energy in the order of $E_{gap}(f)$, electron-hole pairs, called excitons, are generated. The energy value of the optical transition origin is the optical gap (E_{gap}^{Opt}) and is usually lower than the $E_{gap}(f)$ due to exciton binding energy ($E_{ex}^{Bind} = E_{gap}(f) - E_{gap}^{Opt}$). [67–69] When an electron is removed from the HOMO, the molecule's electron density is reorganized, and the neighbor molecule's electron density is slightly modified because the excited molecule is polarized since other molecules surround it. This polarization energy (E(P)) is calculated by $E(P_+) = EA(f) - EA(g)$ and $E(P_-) = EI(g) - EI(f).[27,70]$



Figure 1.9. Schematic representation of the electronic structure of a molecule in the gas phase and film phase

1.3.1 Interfaces between Organic Thin Film and Metal Substrate

Thin film-metal interface studies are essential in many research fields such as organic electronics, molecular electronics, and surface photochemistry. Film-metal contact results in an energy level alignment at the interface, and by equalizing the chemical potential on both sides, charge flow within the interface is achieved. [27,71–73] Metal is chosen as a substrate due to its properties of work function (ϕ) and electron or hole injection. In the case of physiosorbed films on metals, the electronic structure of molecules remains undisturbed upon adsorption, unlike chemisorption. In the interface dipole (Δ) between molecule and metal that shifts the molecular levels relative to metal Fermi energy (E_F). [1, 71,74–76]

Figure 1.10 shows energy level alignments of circumstances where Δ is available and not. In the case of Δ is zero, known as the Schottky–Mott limit, interaction between interfaces are expected to be weak. The energy level differences of HOMO and LUMO with respect to E_F of the metal are represented by E_{HOMO} (also called hole injection barrier) and E_{LUMO} (also called electron injection barrier), respectively. E_{HOMO} and E_{LUMO} are simply derived from EI, EA and ϕ via $E_{HOMO} = EI - \phi$ and $E_{LUMO} = \phi - EA$. When the adsorption of the organic molecules on metal substrates leads to the formation of Δ , energy levels align, and E_{HOMO} increases. Where $\Delta =$ ϕ + E_{HOMO} – EI. The formation phenomena of Δ is not fully explained, and may arise from many factors or their combination, such as chemical reactions, ion formation, surface electronic rearrangement, etc. ϕ is the sum of the bulk chemical potential of the metal and surface dipoles due to electron flow from the metal surface into the vacuum. [27,77–81] The main idea of the analysis of the energy level alignment in the film–metal interfaces are: a smaller energy gap between HOMO and LUMO results in smaller energy difference corresponding to the E_F, which determines the charge transport across the metal-film interface and leads to higher conductivity. [82]



Figure 1.10. Sketch for the energy level alignments of SC films on a metal substrate in the absence (left) or presence (right) of dipole

During designing an electronic device using metal and OSCs, the energetic relationship at the interfaces should be considered. In short, the relation between the Fermi level of metal and HOMO-LUMO levels of OSCs is the key point during the selection of the materials, because HOMO (LUMO) levels define the hole (electron) injection contacts. Fermi levels of metals and HOMO-LUMO levels of several OSC materials are given in Figure 1.11, so the relation between the electrode and SC material magnitudes can be seen readily. [13]



Figure 1.11. Energy level diagram of OSCs and metals. The diagram represents the HOMO and LUMO levels of the organic semiconductors and Fermi levels of the metals. Figure retrieved from ref [13].

Takenobu et al.'s studies [13] on the rubrene molecule will be considered here as an example system to discuss several concepts. In this study, the effects of source and drain electrode metals on the OSC devices were investigated. In the electronic device obtained with rubrene crystals, when Ca electrodes were used, they observed high electron mobility up to $0.81 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, when using Au instead of Ca, they could not observe a good electron transport from Au to a rubrene crystal. Considering Figure 1.11, the LUMO level of rubrene is very close to the Fermi level of Ca rather than Au. [83] However, while having poor electron transport from Au to rubrene crystal, hole transport reaches up to $2.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is understandable when considering the energy barrier between the fermi levels of both electrodes and the LUMO (with Ca) and HOMO (with Au) in rubrene crystal. This barrier is 0.28 eV with Ca (the difference between the LUMO level) and 0.26 eV with Au (the difference between the HOMO level). [84]



Figure 1.12. The device structure of the field-effect transistor based on an organic heterostructure. Figure retrieved from ref [85].

Ambipolar organic field-effect transistors (OFETs) are used to obtain devices with both electron and hole mobility, and different metal electrodes are used as source and drain electrodes to increase the performance of these devices. Rost et al. (2004) studied Pentacene/PTCDI-C₁₃H₂₇ ambipolar OFETs (Figure 1.12 gives the heterostructure device). HOMO and LUMO levels for PTCDI-C₁₃H₂₇ are 5.4 eV and 3.4 eV, respectively, pentacene values are given in Figure 1.11. In this device, Au and Mg electrodes are used to increase the hole and electron injection, respectively. Depending on the applied bias, either an accumulation layer of holes (negative gate bias) or an accumulation layer of electrons (positive gate bias) is formed in the pentacene and in the PTCDI-C₁₃H₂₇ layer, respectively. In this device, electron and hole mobilities reach $3x 10^{-3}$ and $1x 10^{-4}$ cm²V⁻¹s⁻¹, respectively. [85] In the next part, a literature summary of the studies in the literature on carboranethiol SAMs will be given since they were utilized as sacrificial layers in this thesis.

1.3.2 Carboranethiol SAMs

A summary of the literature for carboranethiol SAMs will be given in this section. Well-ordered monolayer films of alkanethiols form on Au (111) surface through the Au-S bond, and the weak intermolecular interaction of alkyl chains also plays a crucial role during film formation. [86] However, weak interaction of alkyl chains results in the flexibility of monolayer, the formation of tilt domains, and lying down phases producing various defects on the surface. [87–90] For instance, Allara and co-workers reported that when the gold surface is coated with asymmetric dialkyl disulfides, the long alkane chains bend over shorter ones, which results in further defects. [91] These defects reduce the quality of films from the application point of view.

In order to tailor the WF of metal interfaces by n-alkanethiols, the metal surface can be co-deposited with two or more alkanethiols with distinct dipole moments. [92] For example, Campbell et al. have demonstrated that n-alkanethiol SAMs decrease and fluorinated thiol SAMs increase the WF of the SAM coated metal. [93] Also, Evans et al. were able to show that fluorinated alkanethiols have opposite dipole moment direction relative to un-functionalized alkanethiols, which explains the effect of these SAMs on the metal WF. [86] The surface coverage ratio can be controlled and varied by using mixed SAMs. Controlling the surface coverage ratio helps to change the work function of the interface such that it allows estimating the WF of the coated surface. [94,95] However, the co-deposition of alkanethiols results in changing morphology and/or crystal structure of SAMs, in addition, to increase defect density as discussed above when compared with pure SAMs. In order to eliminate these problems, a superior solution can be a new promising SAMs of dicarba-dodecaboranethiols or carboranethiols (CTs). [42,96–103]

Dicarba-closo-dodecaboranes (C₂B₁₀H₁₂), or carborane, has three isomers depending on the position of carbons in the cluster. The carbons separated by one or two boron atoms are referred to as Meta (m) and Para (p), respectively, and adjacent carbons in cage denoted as Ortho (o). Electron deficiency and bond delocalization in carborane lead to pseudoaromaticity of the borane cage, which has typical aromatic reactivity. [104] In addition, CTs are highly stable towards chemical, oxidation, and thermal degradation. [105–107] Advanced synthetic approaches in the preparation of this compound offer substitution on both boron and carbon. [108,109] These pathways propose thiolation of the cluster at different positions for the three isomers, which make it an auspicious compound for surface modification. By altering positions of carbon atoms in the cage, dipole moment and its direction (also its magnitude) can be manipulated without changing the geometry of the molecule. [105,110]

Utilizing this fact, Lübben and co-workers were able to tune the surface potential of Ag surfaces by preparing mixed SAMs of two CT derivatives with oppositely oriented dipoles. [99] Weiss group, on the other hand, studied two meta isomers, m-1-carboranethiol (M1) and m-9-carboranethiol (M9), with different dipole moments and were able to tune the work-function of gold surfaces in a range of 0.8 eV by preparing mixed SAMs of these isomers with varying ratios of mixing (see in Figure 1.13). [96] In addition, they were able to show that M1 has a higher affinity to the gold surface (when compared with M9) due to the parallel direction of its dipole moment to the gold surface that enables a head-to-tail dipole-dipole interaction, which increases the SAM's stability. [110] Such an intermolecular interaction is absent for M9 molecules, which have a dipole moment almost perpendicular to the surface. For instance, even when the SAMs were grown from a solution with 1:3, M1 to M9 ratio, M1 surface coverage was still higher than that of M9, as evidenced by contact angle and XPS measurements. All of these results indicate that CT isomers have intrinsic molecular dipoles which enable them to tune surface properties of metals by co-deposing them without altering the crystal structure and/or morphology of the SAM.



Figure 1.13. UPS spectra of Au surfaces decorated with pure or mixed SAMs and calculated work function of the gold surface covered by carboranethiols with respect to M1 mole fraction. Retrieved from ref [96].

Nevertheless, to reach a safe conclusion regarding the effect of dipole moment on the CT SAM structure and further stability, studies should systematically change the dipole moment with appropriate CT isomers. In our previous study, we studied the mixed SAMs of three CT isomers on TSAu, and Au/Mica surfaces with dipole moment vectors parallel to the surface (M1 isomer), pointing away from the surface (M9 isomer) and pointing towards the surface (o-1-carboranethiol, O1 isomer), with magnitudes of 1.76, 3.87, and 3.66 D in the gas phase, respectively as shown in Figure 1.14. [42,111] Since the direction and magnitude of these isomers are distinct, co-deposited SAMs are expected to have different properties relative to their pure SAMs. Carboranethiol coated TSAu surfaces showed the distinct wetting properties by altering the surface chemical properties from hydrophobic to hydrophilic, using M1, M9, and O1, respectively (see in Figure 1.14). As mentioned in detail above, when the M1 molecule is used, it adheres to the surface better than the other isomers and provides high-quality SAM surfaces.

For this reason, in this study, M1 / TSAu surfaces were used as an alternative substrate for TSAu surfaces, and the properties of PFP films on these surfaces were compared. One of the most important factors affecting the electronic, chemical, and physical properties of OSC thin films is the crystal structure of the thin-film. In the

next part, the techniques used to detect the crystal structure of thin films will be discussed.



Figure 1.14. Molecular sketch and dipole moment directions of M1, M9, and O1. Hydrogen atoms are omitted for clarity. The arrows point in the direction of a positive charge (top row). Contact angles for pure carboranethiol SAMs on TSAu surfaces (bottom row).

1.4 Crystal Structure of Surfaces

Now within this part, the techniques used to obtain the crystal structure of surfaces will be summarized. Thin-films are made of molecules, so knowledge of how molecules are arranged in the surface crystal structures informs us of the growth, structure, and properties of films. Most of the information about surfaces can be extracted from the crystal structure, which affects thermal, optical, electrical, and mechanical properties. Diffraction techniques are used to find the crystallinity and quality of organic thin films. Crystallographic orientations of small crystallites

within the surface of the films can be learned by comparing the known single crystal structures and their simulated diffraction patterns. Table 1.4 gives the classification and descriptions of different diffraction methods.

Table 1.4. Type of Di	ffraction Techniques
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Туре	Description	Information depth (# of layers)	The energy resolution (meV)	Sample
Atom	Interacts with the atoms through long-range interactions (e.g., van der Waals forces)	1	0.2	Single crystal
Electron	Interacts with the atoms	3-5	3	Single crystal
Neutron	Interacts mainly with the nuclei	>>1	0.0001	Powder
X-Ray	Interacts mainly with the electrons with weak interactions	>>1	>8	Single crystal or powder

Since the characterization of thin films will be discussed intensively in this thesis, surface-sensitive diffraction techniques will be briefly explained below. Techniques used to obtain the surface crystallographic structure include low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), grazing-incidence X-ray diffraction (GIXD), and He atom diffraction (HAD). A comparison of these surface sensitive techniques is given in Table 1.5.

LEED is a surface-sensitive technique because energies of incident electrons are between 20-200 eV corresponding to wavelengths comparable to the atomic spacing. In LEED, the beam of incident electrons comes to the normal of the sample surface at a constant angle and with variable wavelengths. Low energy electrons are elastically scattered by surface atoms in the first few layers of the sample. The crystallographic structure of the surface can be determined as spots formed by scattered electrons on a phosphorescent screen. The relative position of these spots shows the surface crystallographic structure. LEED spot pattern defines 2D lattice and shows long-range order exists on the surface. LEED may be used to determine the symmetry of the unit cell (qualitatively) and the position of the atoms in the crystal surface (quantitatively).

RHEED is an alternative technique to obtain the surface crystallographic structure when using high energy electrons (> 1 keV). Taking into account the high energy electrons, these electrons are directed to surface at grazing incidence to keep the penetration depth very small, which increases the surface sensitivity. Elastically scattered electrons, which are at the origin of the diffraction pattern, will only be scattered by the surface atoms. The sample in RHEED must be turned azimuthally to establish the full two-dimensional periodicity. By using RHEED, it is possible to measure and control atomic layer growth rates and the evolution of the growth in real-time.

X-ray diffraction is the technique for determining the three-dimensional structure of bulk in the absence of surface sensitivity. GIXD is the most valuable experimental technique for assessing thin-film structures. The grazing incidence geometry for XRD is surface selective at a lower angle, which minimizes penetration depth and enhances surface signal so that diffraction can be made more surface sensitive. With the grazing configuration, the penetration depth of x-rays inside the surface is reduced from 1-10 μ m to 1-10 nm. [112–114]

	LEED	RHEED	GIXD	HAD
Incident Beam	Normal to	Grazing	Grazing	Variable
	Surface	Incidence	Incidence	
Probe Energy	10-200 eV	5-100 keV	4-30 keV	5-100 meV
Penetration Depth	10 Å	10 Å at 1°	10 nm at 5°	Scatter from the
				topmost layer
Scattering Type	Dynamical		Kinematical	

Table 1.5. Comparison of surface sensitive diffraction techniques

HAD is another surface specific diffraction technique which is also heavily employed in our research group. One of the aims of this thesis work was to update the HAD system in our laboratory in order to study organic thin films. For this reason, now, the significance of He atom diffraction (or He atom scattering, HAS) technique will briefly be mentioned. Updates and details of the construction of the new He atom diffraction system will be explained in the relevant chapter (Chapter 6). After giving information about the kinematic expressions of the He atom diffraction technique, the concept of reciprocal space will be briefly mentioned, and the theory and applications of the He atom diffraction technique will be discussed.

A schematic representation of the scattering of He atoms sent from the surface as a supersonic beam is given in Figure 1.15-a. Figure 1.15-b shows the quantum mechanical representation of the scattering intensity obtained as a result of this scattering, with the incident He beams reaching and scattering from the surface. The HAS technique has the unique advantage of perfect surface sensitivity. It uses light He atoms at low energies (10-300 meV), and the de Broglie wavelengths are at the order of a few angstroms. The low energy of helium atoms, which are not accessible by other techniques, have the advantage over other probe particles, such as electrons and photons, in that they do not penetrate the surface but, instead, turn away 3-4 Å from the surface where the electron density is low. This electron density attracts the incident He atoms, and the incident atoms probe the topmost layer of the substrate surface in a non-destructive manner (see Figure 1.15-a). The scattered He atoms are measured with a detector. The highly intense peak shown in Figure 1.15-b represents the intensity of the specular peak, which has the same momentum with the incident beam, while the other periodic peaks are present having lower momentum than incident beam momentum. By analyzing the locations, intensities, and widths of the peaks obtained as a result of this scattering, information about the structure of the surface is obtained. The diffraction spectrum of the surface can be obtained without any damage to the surface, and unit cell structure and symmetry of the surfaces can be obtained by analyzing HAS data. [115–117]



Figure 1.15. a) Scattering of the Supersonic He beam from a surface b) quantum mechanical representation of the scattering.

When the temperature of a crystal is increased by annealing, the amplitude of motion for atoms on the surface increases. Accordingly, if this crystal is annealed without covering the surface of a crystal with any substance, the specular intensity of the He beam will decrease as the mobility of the atoms on the surface increases. The decrease in the intensity of the diffraction peaks by increasing the temperature without any change in the shape of the peak is called the Debye-Waller effect. Another undesired effect of temperature is the infrared radiation inside the He beam, which scatters from the surface and reaches the detector, reducing the sensitivity of the detector. In order to prevent both this Debye-Waller effect and the decrease of detector sensitivity with temperature and the error in the measurements, the obtained He beam intensity is normalized depending on the temperature change data. With temperature, the negative aspects of the decrease of specular intensity are eliminated by normalization, TPD measurements can be made using the point where the specular reflection intensity is maximum in the annealing curves of SAM thin films. There are many studies carried out with the old He atom diffraction system in our laboratory. [90,118–122] One of them is 11-hydroxyundecyl octadecyl disulfide (HOD) SAMs on Au (111). As can be seen in the Figure 1.16-top, the specular intensities from the films on Au (111) surface decrease as the temperature increases, which is an example of the temperature effect on the diffraction intensity. At the

same time, this figure shows the TPD measurements and the points where the molecules start to break off from the surface at the points where while the intensity decreases and suddenly it starts to rise, thus, it enables to detect the thermal desorption energies of the molecules.



Figure 1.16. Annealing curves for MLs of MUD, ODT and HOD on Au(111) surface (top) and diffraction scans of MLs of MUD, ODT and HOD (bottom).Figure retrieved from ref [120].

In Figure 1.16-bottom, the results of HOD SAMs were compared with old diffraction scans of mercaptoundecanol (MUD) and octadecanethiol (ODT). Because the

molecular size of HOD molecules very large, resulting films were more disordered compared to MUD and ODT SAMs. Helium scattering results for HOD SAMs were very poor with low signal/noise ratio. For this reason, the results obtained at 200K for ODT and MUD were compared with the data after HOD SAMs were annealed at 400K.

He atoms have low adsorption energy and are chemically inert, so they do not depend on surface conductivity, and are equally applicable to insulators, semiconductors, and metals. HAS is also a powerful tool for investigating structural disorder on surfaces. The beam of He atoms is generated with very narrow velocity distributions using supersonic expansion, permitting resolutions in the low sub-meV range. This resolution is combined with the large cross-section for scattering from molecules. In the case of existence adatoms (or admolecules), they give rise to the attenuation of the specular intensity and scattered through larger angles, so this situation yields geometrical information on the surface defect. Thanks to the high sensitivity of He atom specular reflection measurements (by the attractive long-range interactions like surface diffusion), film growth can be studied in real-time again without inducing any damage on the surface during the specular reflection measurements. [123–125]



Figure 1.17. a) He specular reflection intensity (SRI) (black trace) and QRFS (red trace) as a function of pentacene deposition time on the gold surface of a quartz oscillator. The deposition was performed with the helium carrier gas. b) He SRI as a function of coverage for pentacene deposition on single-crystal Au(1 1 1) surface with different carrier gasses. Figure retrieved from ref [122].

A good example of this situation is the He specular reflection measurement experiment taken in the previous configuration of our He diffraction system (see in Figure 1.17). Figure 1.17-a shows the specular reflection results during the supersonic pentacene beam hitting to gold-coated quartz microbalance crystal, while Figure 1.17-b shows the results obtained during the film growth of pentacene on Au(111) single crystal. As seen in both figures, specular reflection intensities (SRI) are exposed to attenuation. Considering Figure 1.17-b, in both He and Kr carrier gas situation, He SRI decreases up to 0.5 ML. Then these diffusing PEN molecules start to form grains, and the intensity starts to increase. SRI then reaches a maximum when the 1st layer (1 ML) is completely covered on Au (111) surface. Then PEN molecules that come onto these fully coated 1st ML also cause attenuation in SRI. As can be seen from this example, the surface sensitivity of the He diffraction technique is superior. Updates and detailed operations of construction of a new He atom diffraction system will be explained in Chapter 6.

1.5 Review of PFP thin films

This section briefly summarizes previous studies regarding the growth of PFP thin films on different substrates to give an overview of the current status of PFP thinfilm studies.

Perfluoropentacene (PFP) is composed of five linearly arranged benzene rings. It is the perfluorinated version of pentacene (PEN) and has a chemical formula of C₂₂F₁₄. Moreover, due to the similarity of molecular dimensions of PEN and PFP, the molecular skeleton of PEN remains unchanged after the fluorination. However, its electronic, physical, and chemical structure change completely. Figure 1.18 illustrates the sketch of PEN and PFP molecules and the stages of PFP synthesis. PFP synthesis is carried out by gradually repeating the Friedel-Craft reaction. [126,127] This synthesis is described in detail in the work of Sakamoto Y. and coworkers. [127] Since fluorine atoms have the highest electronegativity, the fluorination process gives rise to negative charge affinity. Due to variation in the charge distribution in the molecule, the charge carrier type in this compound changes compared to PEN. While PEN (acting as an acceptor) is a p-type OSC, PFP (acting as a donor) is an n-type OSC with electron mobility. Table 1.6 presents the comparison of the structural and physical properties of PFP and PEN molecules.



Figure 1.18. Pentacene and PerFluoroPentacene molecule sketches and synthesis process of PerFluoroPentacene. Figure adapted from [127].

Table	1.6	Com	parative	pro	perties	of PEN	and	PFP	molec	cules

					Mob	oility		
		(0				$V^{-1}.s^{-1}$)		
		Lonoth	Weight	Donaity			Vapor	Flash
	Formula	ormula	weight		Electron	Hole	Pressure	Point
		(nm)	$(g.mol^{-1})$	(g.cm ⁻³)			(mmHg	(°C)
							at 25°C)	
PEN	C ₂₂ H ₁₄	1.44	278.3	1.3	0.04	5.5	0.0 ± 0.7	264.5
PFP	$C_{22}F_{14}$	1.51	530.2	1.9	0.22	-	$0.0{\pm}1.4$	195.9

Hinderhofer et al. (2007) studied PEN and PFP thin films on SiO₂ surfaces by using X-ray reflectivity and AFM. They found out that both PEN and PFP follow the same motif (herringbone) with slightly different d(001) lattice spacing (15.4 and 15.7 Å in PEN and PFP thin films, respectively). PEN and PFP molecules arranged in the films almost parallel to the surface normal of SiO₂. [64] Koch et al. (2012) studied the PFP thin films and showed that molecules form two different molecular motifs with herringbone and π -stacking on SiO₂ and graphene surface, respectively, via grazing incidence x-ray diffraction method. [128] Comparison of the crystal structures in single crystal, and thin films of PFP, and comparison of unit-cell parameters each are given in Figure 1.19. The crystal structures are monoclinic with two molecules in both the PFP single-crystal (bulk) and PFP thin-film on SiO₂. These data show that crystal structure in thin-film on SiO_x and single crystal of PFP are different from each other. The two structures have the herringbone packing with angles between the plane normals of the unequal molecules of 74.35° and 75.31° for the thin film and single crystal, respectively. Salzman et al. (2008) studied the crystal structure of PEN and PFP by using specular XRD and GIXD for thin films on SiO₂ and published the crystal structure of PFP, and the results are consistent with the results given in Figure 1.19-c. [129]



Figure 1.19. Comparison of the crystal structures in single crystal and the thin-films of PFP **a**) Herringbone arrangement of PFP single-crystal **b**) Herringbone arrangement of the thin film PFP on SiO_x viewed along the long molecular axes, **c**) illustrated within the unit cell (middle), and **d**) as a top view on the (100) texture plane (*i.e.*, along a^* axis), **e**) π -Stacked arrangement of the PFP on graphene viewed along the long molecular axes, **f**) within the unit cell, and **g**) as a top view on the (001) texture plane parallel to graphene (*i.e.*, along c^* axis). Similar π -stacked motifs are shaded in red; π -stacking distances are indicated. **h**) Comparison of unit-cell parameters for single crystal and thin films. Figure adapted from ref [26,128].
Although PFP thin films are used in organic thin-film transistors, the number of paper is limited in literature on the formation mechanisms and structural properties of these films on metal surfaces. Götzen et al. (2011) studied PFP thin films on Ag(111) surfaces with AFM, STM, LEED, and XPS. They showed that the growth mode for the first two layers on Ag (111) is layer by layer, as full coverage of the first monolayer is observed before any formation of second layer islands. [130–132] The first layer behaves as a seed layer for PFP films grown on Ag superficially, while the multilayers form separate islands and exhibit a new polymorph crystalline phase. [130] Based on the STM data, the unit cell constants of the first layer was found to be $b_1 = 17.3$ Å and $b_2 = 8.6$ Å (see in Figure 1.20-a). As the PFP thin film thickness increases, the initial stage of bilayer growth is seen. Molecules adopt the same orientation as that in the first layer with slightly larger unit cell constants of $b_3 = 18.3$ ± 1 Å and $b_4 = 9.4 \pm 0.5$ Å (see in Figure 1.20-b). Right after completion of the bilayer wetting layer with π -stacked motif, upper layers start to grow on this bilayer. Where molecules adopt new polymorphism in which the molecules are oriented with their long axis parallel and the short molecular axis tilted to the substrate in multilayer films, which is most likely in the herringbone arrangement (see in Figure 1.20-c). This data indicates that a new polymorphism occurs because moleculemolecule interactions start to be dominant on substrate-molecule interactions.



Figure 1.20. Schematically representation of PFP monolayer (first layer), bi-layer formation on Ag (111) (a, b), and formation of the disjointed island in which π -stacking arrangement turns to herringbone packing in the multilayers (c). (Figure retrieved from ref [130]).

Lo et al. (2013) [131] showed a similar result for Au(111). There is a remarkable consensus on coinage metals that PFP molecules in the wetting layer (first layer) are arranged on the surface with lying down structures with π -stacked packing. As the thickness of the film increases (usually after the second layer), PFP molecules start to arrange with lying down geometries in herringbone packing on the surface. [26, 34, 130,133] As a summary, these molecules assemble with π -stacking in monolayer and herringbone in multilayer on metal surfaces. [9, 131,134–138] Multilayer films have the shape anisotropy of molecular entities with herringbone packing. [26, 133,139,140] Both in monolayer and multilayer, the structure of PFP grains are rigid and compact. The stability of PFP molecules on Ag and Cu metal surfaces are shallow. Still, on Au surfaces, these molecules remain without being destroyed even at high temperatures, unlike PEN. [134,135,141]



Figure 1.21. Comparison fo UPS spectra results of (a) PEN for a lying monolayer on Au(111), and standing molecules on SiO_x and (b) PFP for a lying monolayer(bottom) and inclined multilayer (center) on Au(111), and standing molecules on SiO_x (top). On metals, the Fermi level is marked with E_F . Figure retrieved from ref [142].

Figure 1.21 can be seen as a short summary of the effect of molecular orientation on electronic devices. The vacuum level of an electronic device fabricated with OSCs depends on the orientation of the molecules on the surface.[143] As seen in Figure

1.21-a, when PEN molecules arranged with lying on the surface (molecular plane parallel to the surface), IE is around 5.45 eV. In contrast, when molecules arrange in standing geometries (molecular plane perpendicular to the surface), this value is about 4.8 eV, and depending on this, the vacuum level decreases. In the case of PFP (Figure 1.21-b), molecules are arranged with lying (pi-stacked), and tilted lying (herringbone) geometries in the first layer and the upper layers on Au surface, respectively. Similar to PEN, on the SiO₂ surface, molecules are arranged in standing geometry. In contrast to PEN, when looking at the UPS spectrum of PFP, IE value is changing through 5.8, 6.0, and 6.65 eV, in the arrangement of molecules while lying, tilted lying, and standing, respectively. These results show that, while the orientation of molecules changes from lying to standing on the surface, the IE (therefore vacuum level) value of the electronic device increases. Consequently, for the desired performance of an electronic device designed with OSCs, molecular orientation control in OSC thin films is critical.

Breuer et al. (2015) studied PEN and PFP heterostructures and observed the molecular orientations by using NEXAFS and AFM techniques. Results are given in Figure 1.22, these results could be good examples for the studies on controlling the molecular orientation studies of molecules within films. This process is done by coating PFP thin films on surfaces with different chemical structures, and the molecules adopt either lying or standing orientation in each layer.



Figure 1.22. AFM images of pure PEN and PFP films (left) and PEN / PFP stacks (right) of 30 nm thickness grown on SiO₂, graphite, KCl(100) (a), Schemes of all observed mutual configurations between PEN and PFP(b), effective molecular orientations from NEXAFS dichroism for interface layers deposited on multilayer films (inset table). Figure retrieved from ref [132].

Contrary to what is seen on metal surfaces, the molecules are arranged with the same orientation in the wetting layer and the top layer. For example, these molecules adopt lying geometry on KCl, ZnO, and graphite, while they are arranged with standing geometry on SiO₂ and NaF. [9,144–146] While PFP molecules are in standing orientation, they show herringbone molecular packing, but in the lying orientation, this packing could be herringbone or pi-stacking. By using NEXAFs, XRD, and AFM, Witte et al. [9] showed that on KCl and graphite, PFP molecules are oriented with lying geometries, but molecular packings are herringbone and π -stacking, respectively.

The common stake of the studies mentioned above is that PFP films were grown by conventional organic molecular beam coating systems. The effect of the deposition rate, the kinetic energies of the molecules in the beam, and the substrate type have not been studied based on the nucleation and growth mechanisms. The PFP thin films on different substrates and with varying rates of deposition using the SMBD technique were studied by Schreiber et al. [147], which is unique in this regard. Within this study, they used several sacrificial layers beneath PFP thin films, namely octyltrichlorosilane (OTS), perfluorooctyltrichlorosilane (FOTS), 3-methacryloxypropyltrichlorosilane (MAOPTS), hexamethyldisilazane (HMDS), and SiO₂ surfaces. The results obtained with the help of different complementary techniques (such as AFM, XRR, and contact angle) are summarized below:

- 1. As the deposition rate increases in the obtained 0.63nm thick PFP films, the average grain size decreases, and average grain density on the surface (total grain number) increases, but the shape of the grains remains unchanged. (see Figure 1.23-a)
- 2. The second study is the analysis of films obtained with different deposition rates on various substrates. The morphology change due to film thickness was investigated by growing thin and thick films on SiO₂. Although the first layer tends to wet the surface entirely with spherical grains, the other layers growing on this layer form needle-like fibers and have a very different morphology from the first layer. Multilayers grow on this first layer in a layer-by-layer fashion. (see Figure 1.23-b)
- 3. In the study conducted by considering the substrate effect, the nucleation was observed to be homogeneous, and the absolute densities of the grains strongly depend on the surface termination. When surface termination is considered, as hydrophobicity decreases for substrates, grain density decreases while the average grain area increases (Hydrophobicity character of surfaces is in order of FOTS>HDMS>OTS>SiO₂>MAOPTS). (see Figure 1.23-b)



Figure 1.23.AFM images, 3 x 3 μ m², Deposition rate (a), and substrate (b) effect on the PFP film growth mechanism. Figure retrieved from ref [139].

When the vibrational properties of PFP films are examined, it can be seen that the characteristic C-F in-plane stretching modes of the PFP molecule arise at 920 and 980 cm⁻¹. However, both peaks split into two resulting in four peaks due to Davydov splitting. [129,144] The most comprehensive study in this regard was performed by Breuer et al. (2012) [144]; in this study, PFP films were grown on KCl (100) and NaF (100) substrates, in which PFP molecules were oriented with standing up and lying down configuration, respectively (see in Figure 1.24). While the peaks remain unsplit on NaF surfaces, Davydov splitting seen on KCl surfaces.



Figure 1.24. Absorption spectra of PFP molecules: (a) isotropic orientation in KBr pellet, (b) lying orientation in thin films on KCl(100), and (c) upright orientation in thin films on NaF(100). Solid, dotted, and dashed lines indicate modes that appear in both orientations, only active in PFP/KCl, and only appear in PFP/NaF, respectively. Figure retrieved from ref [144].

All these studies described above form the framework for the understanding of nucleation and growth mechanism of PFP thin films, and the effect of both substrate chemical structure, and also kinetic energy of molecular beam on the PFP thin-film formation. Thus, PFP molecules would be an ideal case for understanding the nucleation and growth mechanism of thin films on surfaces with different chemical properties. PFP thin films have not been investigated on mica and carboranethiol (CT) self-assembled monolayers (SAMs) at all. Also, though there are few studies regarding the electronic structure of PFP on Au(111), there is a lack of characterization of the film morphology and growth mechanism. [131, 136,148] In this dissertation, the effects of substrates and kinetic energy of beams on the nucleation and growth mechanism of PFP films were studied using a combination of surface-sensitive techniques. Within this thesis, three types of substrates having different chemical surface structures with similar morphologies with low roughness were considered. These are mica, template-stripped gold (TSAu), and m-carborane-

1-thiol self-assembled monolayers on template-stripped gold (M1). In terms of their chemical properties, these substrates follow the order from hydrophilic to hydrophobic character as mica, TSAu, and M1. PFP thin films were deposited by using the supersonic molecular beam deposition (SMBD) technique, which was shown to produce higher quality OS films when compared with conventional thermal evaporation techniques. [119,120, 122,125] AFM measurements were taken immediately after film growth in order to focus on film (grain) evolution on different substrates. XPS measurements were also employed to probe the evolution of chemical and electronic properties of each molecular layer. Contact angle measurements and scattering-type scanning near-field optical microscopy (s-SNOM) were performed to observe the wetting and vibrational properties of the films with respect to their thickness on different substrates, respectively.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 Substrate Preparation

The aim of this dissertation is to clarify the nucleation and growth mechanism of PFP thin films on ultra-flat surfaces depending on the film thickness, molecular flux and energy, and substrate surface chemical structure. To this end template-stripped gold (TSAu) and Mica on TSAu (Mica) and m-carborane-1-thiol self-assembled monolayers on TSAu (M1) were used as substrates to understand the nature of PFP thin films. Substrates were produced using the template stripping method, and each stage of this method, as well as the preparation of SAMs, is schematically described in Figure 2.1 and will be explained below:

(1) Muscovite mica (0.2 nm of roughness) with grade V1-V2 was purchased from S and J Trading Company and freshly cleaved before use, and Au (99.99 % pure) films of 100 nm thickness were prepared by thermal evaporation on freshly cleaved mica wafers (15 x 15 cm²) at room temperature with a rate of ≈ 0.4 Ås⁻¹. Evaporation was carried out in a deposition chamber pumped with an oil-free pump at a pressure of a 1×10^{-6} mbar. (2) Next, freshly prepared gold-coated mica wafers were cut into strips of 15 x 2 cm². Approximately 50 µL drops of UV-activated Norland Optical Adhesive - 61 epoxy was dripped over them. 2 x 2 cm² glass wafers were placed on top of these epoxy droplets. (3) The sandwiches prepared in the 2nd stage were left under UV-light all day long for curing. After the curing is complete, Mica/Au/epoxy/glass sandwiches were stored under a nitrogen atmosphere. (4) The films (attached to glass wafers) can be stripped mechanically immediately before the PFP film growth process. (5) Mica surfaces consist of mica layers remaining on the TSAu surface after mechanical striping of TSAu films. (6) M1 coated TSAu substrates were produced by immersing TSAu films into 1 mM ethanolic solution of

m-carborane-1-thiol (Purchased from Katchem spol. s r.o., Czech Republic and used as received, the molecular structure is shown in Figure 2.2) for 24 h. at room temperature. After taking out the slides from solutions, they were rinsed with ethanol (absolute, \geq 99.8% Sigma-Aldrich or absolute for analysis, \geq 99.8%, Merck) and then dried with N₂ stream.



Figure 2.1. Substrate preparation processes. Atomic force micrographs, $1.25 \times 1.25 \mu m^2$, of surfaces that were used as substrates with the roughness values of 0.43, 0.24 and 0.4 nm for Mica, TSAu and CT/TSAu, respectively.

Figure 2.1 shows the AFM images of resulting substrate surfaces, and these substrates have an average roughness of 0.2, 0.4, and 0.4 nm for TSAu, Mica, and M1, respectively. Because the roughness values are very low, these substrates are the ideal choices to understand the nucleation and growth mechanism of PFP thin films. Contact mode AFM images of these substrates are shown in Figure 2.2. We should also note that, since the freshly stripped TSAu surfaces were exposed to ambient air, before placing them in the PFP evaporation chamber or thiol solution, some level of oxidation and carbon contamination was inevitable. In fact in the exsitu XPS spectrum, shown in Figure 2.2, oxygen and carbon peaks can be observed

with relative ratios of 2.4% and 14.9% (gold being 82.8%) for freshly stripped TSAu, 5.2% and 22.8% for freshly prepared M1 and 14.9% and 34.5% for freshly stripped Mica. Due to the chemical structure of Mica [KAl₃Si₃O₁₀(OH)₂], the amount of oxygen and carbon is higher than the others.



Figure 2.2. Contact mode AFM images, $1.25 \times 1.25 \mu m^2$, of substrate surfaces. Roughness values are 0.4, 0.2 and 0.4nm for mica, TSAu, and M1 respectively (top). XPS survey spectrums for freshly stripped TSAu, Mica, and freshly prepared M1 surfaces.

2.2 PFP Thin Film Growth by SMBD

PFP was purchased from Konta Denka Kogyo Co. Ltd. (Japan) and was used without further purification. Supersonic Molecular Beam Deposition (SMBD) system has notable advantages over conventional molecular evaporation techniques in producing PFP thin films, as well as in understanding the mechanism of nucleation and growth. The SMBD system consists of two main vacuum chambers seperated by the shutter in front of the skimmer. These are organic beam source (OBS) chamber in which PFP molecules are evaporated, and the sample holder chamber (SH) in which substrates and quartz crystal microbalance reside. High-capacity diffusion pumps pump each vacuum chamber and their operation pressures are P_{SH} : 5 x 10⁻⁶ Torr and P_{OBS} : 1 x 10⁻⁵ Torr. A schematic representation of the SMBD system used in this study is given in Figure 2.3.



Figure 2.3. Schematic views of SMBD system (left), organic beam source used to produce the organic beam (middle-top), sample holder with QCM (middle-bottom) and film profile on the surface obtained by AFM image analysis (right).

The source chamber consists of a Pyrex tube with a hundreds of microns diameter hole, and in this pyrex tube a quartz spoon (which will be referred to as source) containing the organic molecule is enclosed. The spiral heater causes the organic material placed in the source to evaporate in the flow of a carrier gas (usually helium, argon, or krypton). Evaporated molecules in the quartz tube mix with the carrier gas and the resulting mixture expands supersonically into vacuum. During the production of supersonic organic beam, the source and nozzle temperatures are controlled. Substrates and QCM on a moving mechanism can be inserted into and removed from the beam path. In the first step, the QCM is taken to the beam path and the flux of the material (deposition rate) to be grown in the beam is measured. Then the sample (substrate) is inserted into the beam path, and the film growth process continues until the desired thickness film is obtained (by monitoring deposition time). By varying the source temperature and/or the pressure of the carrier gas, the flux and kinetic energy of the organic matter in the beam can be controlled. In addition, the speed (kinetic energy) of the organic matter in the beam can be increased by raising the temperature of the micro-nozzle and/or reducing the mass of the carrier gas (for example using helium instead of argon). Time of flight (TOF) measurements are performed to determine the kinetic energy of the molecular beam. On the other hand, kinetic energy due to the supersonic expansion of the molecules in the lighter carrier gas can be estimated by with a emprical equation:

$$E_{kin} = \frac{5}{2} \frac{m_{organic}}{m_{average}} RT_{Nozzle} \qquad eqn. 2.1$$

where E_{kin} is the kinetic energy (eV); *R* is the gas constant (eV K⁻¹ mol⁻¹); T_{nozzle} is the nozzle temperature (K); and $m_{organic}$ and $m_{average}$ are the organic molecule molar mass and average (organic molecule and carrier gas) molar mass (g mol⁻¹), respectively. In previous studies with pentacene in the He atom diffraction system in our laboratory, under the standard SMBD working conditions pentacene kinetic energies were determined before[118,122] by time of flight measurements both for He and Kr gases (2.2 eV and 0.2 eV for He and Kr, respectively) and these results were very close to this empiric equation results (5 eV and 0.4 eV for He and Kr, respectively). [122] The SMBD source parameters during the film growth of PFP molecules and estimated kinetic energies are summarized in Table 2.1. Beam kinetic energy was changed by keeping the deposition rate constant and only by changing the carrier gas without changing other parameters, therefore parameters (Stagnation pressure, Nozzle Temperature, etc.) were kept constant, only adjusting the evaporation temperature. By changing the distance between the sample holder and the skimmer, the size of the film profile (film diameter on substrate), which has a Gaussian shape, growing on the substrate can be changed. For the films reported in this study, skimmer-sample holder distance was 3 cm, the film diameter was about 12 mm and the homogenous region (center of the film) was about 5 mm, as shown Figure 2.3. Figure 2.3. Schematic views of SMBD system (left), organic beam source used to produce the organic beam (middle-top), sample holder with QCM (middle-bottom) and film profile on the surface obtained by AFM image analysis (right). The film profiles shown in Figure 2.3 were obtained from AFM measurements performed on 2.5 um x 2.5um regions located at different positions from the film center and thicknesses presented are the *effective (local) thicknesses* obtained from AFM image analysis. The effective thicknesses at the center of the films are also in agreement with the nominal thicknesses determined by QCM.

Carrier Gase	He	Ar	Kr
Estimated Kinetic Energies (eV)	11.26	0.65	0.25
Nozzle Diameter (µm)	150		
Stagnation Pressure (bar)	0.25		
Evaporation Temperature (°C)	320±10		
Nozzle Temperature (°C)	175±10		
Vacuum Pressure (Torr)	$2x10^{-5}$		

Table 2.1. SMBD source working parameters during PFP film growth

The advantage of this technique is that by growing a single film with a certain nominal thickness and nominal DR one can obtain film regions with different effective thicknesses and effective DRs reproducibly and in a precisely controlled way. In this study, all the films were grown with a nominal DR of 0.05 Å/s, but by examining different regions (distances from the center) of the films different effective DRs could be studied. The given DRs in the results part correspond to the effective deposition rates and the given thicknesses correspond to the effective thicknesses otherwise is explicitly mentioned. At least 3 parallel samples for

each set of growth parameters were prepared and data (contact angle, AFM, etc.) were collected from at least 3 different points on each sample.

2.3 Characterization Techniques

2.3.1 Contact Angle Measurements

Contact angle measurement is an important technique to identify the wetting properties of solid surfaces based on the surface tension properties. These wetting properties are surface chemical characteristics such as hydrophobicity or hydrophilicity. This measurement technique provides micro-scale characterization of surfaces by using a liquid as a probe. In the contact angle measurement, an optical tensiometer is usually employed to record the image of a droplet on the surface. The contact angle (θ) extracted from the recorded image can be fitted by Young's equation (eqn.2.2), which describes the mechanical equilibrium of droplet under interfacial tensions of liquid, air, and solid.

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \qquad eqn. 2.2$$

Where V_{LV} , V_{SV} , and V_{SL} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and θ is Young's contact angle (also shown as θ_{Y}) which are schematically described in Figure 2.4. Young's equation is valid for an ideal surface. Since real surfaces are not ideal, several models were developed to describe the contact angles on real surfaces. Two such models are the Wenzel model and the Cassie-Baxter model. [149,150] Wenzel equation is:

$$\cos \theta_{observed} = r \cos \theta_{ideal} \qquad eqn. 2.3$$

where r represents the surface roughness, θ_{ideal} is the contact angle of the ideal surface, and $\theta_{observed}$ is the measured angle. According to this model, for a hydrophobic surface (θ > 90°) as roughness decreases, the observed contact angle decreases whereas for a hydrophilic surface as roughness decreases, contact angle increases.

In practice, there are metastable states of a liquid droplet on the surface; hence, the measured contact angle is not exactly equal to Young's contact angle. Therefore, measuring the static contact angle is not adequate to characterize the surface wetting properties. One approach to investigate detailed surface wettability is dynamic contact angles. In other words, the contact angles that are formed during contracting and expanding the liquid (by increasing/decreasing the volume of liquid which causes the edges of the droplet to advance or recede) is measured and interpreted. Advancing and receding angles are the maximum value and the minimum value that the angle reaches, respectively. Figure 2.4 shows water droplets during advancing and receding angle measurements. The difference between the receding and advancing angle is defined as hysteresis (Δ) and is formulated as:

$$\Delta = \theta_A - \theta_R \qquad eqn. 2.4$$

Here, θ_A is the advancing, and θ_R is the receding contact angle. The interpretation of surface heterogeneity and roughness can be performed based on hysteresis values.



Figure 2.4. Illustration of static contact angle with Young's construction of the force balance at a three-phase contact line between a droplet, its vapor, and a solid surface for hyrdophilic, hydrophobic and superhydrophobic surfaces, and dynamic contact angle measurements with a sketch of advancing and receding angle. Adapted from ref [151].

In this dissertation, static contact angles (sCAs) of water were measured at room temperature on an Attension Theta Lite optical tensiometer. Approximately 2 μ l drop of water was formed at the end of a needle attached to a 50 μ l syringe. The needle was lowered until the drop touched the surface and then raised, detaching the drop. An average of ten measurements of stable static drops was made for each surface. Dynamic contact angle measurements were done using a dynamic sessile drop method, where a sample is placed near the tip of the needle. A drop of deionized water (2 μ L) is deposited on the surface of the sample, and the needle is carefully positioned in the center of the drop without changing its shape. The advancing contact angle (aCAs) was determined by increasing the volume of drop on the

surface constantly to a size of 4 μ L. The receding contact angle was determined at the same speed of volume reduction to a size of 2 μ L. All these measurements were collected on an automated system with photographs collected at 20 frames per second for three cycles. The drop images were processed with an image analysis system, which calculated both left and right contact angles from the shape of the drop with an accuracy of $\pm 0.1^{\circ}$.

2.3.2 Spectroscopic Ellipsometer

Spectroscopic ellipsometry (SE) is a very powerful optical technique for the characterization of thin films. It offers to extract the optical constants [like refractive index (n) and extinction coefficient (k)] and determine of the thickness of the thin films. In this study, SE was used to optimize and control the QCM used during the growth of PFP films and to determine the thickness and homogeneity of the M1 surfaces used as substrate. The basic working principle of SE can be briefly described as follows:

- 1. a linear-polarized light is directed onto the thin film
- 2. due to the interaction of the incident light with the surface, the polarization of the reflected light changes (usually elliptical-polarized),
- 3. the reflected light is collected through the detector located at the angle of specular reflection
- 4. the polarization states of the incident and reflected lights are analyzed comparatively
- 5. the reflected light is monitored and analyzed in terms of the complex reflectance ratio (ρ) which is a function of ψ and Δ
- 6. Finally, a model fit to these data is utilized to calculate thickness or desired properties

Electromagnetic waves have two components, which are s and p. The p component is parallel, and the s component is perpendicular to the plane of incidence. These components are shown in Figure 2.5. When linearly polarized light is reflected from a surface (interface) its polarization changes which can be expressed by two factors, ψ , and Δ , where ψ is the ratio of the amplitude of the p polarized component of the light to s polarized component and formulated as follows:

$$tan(\psi) = \left|\frac{r_p}{r_s}\right| \qquad eqn. 2.5$$

Where r_p and r_s are Fresnel reflection coefficients. Δ is the phase difference between the p and s polarized light and denoted as:

$$\Delta = \delta p - \delta s \qquad \text{eqn. 2.6}$$

Where δ_p is a phase change in p polarized light, and δ_s is the phase change in s polarized component upon reflection from the sample surface. If the sample is made up of several different layers, each with different optical properties than at each interface (between the neighboring layers) reflection and transmission will take place. Then the total amplitude of light reflected from the top layer's surface with p and s polarization will be given by total reflection coefficients R_p and R_s [these coefficients are analogs to r_p and r_s that are relevant for a single layer (interface) system]. As discussed earlier, these two parameters R_p and R_s (or r_p and r_s for a single layer system) can be correlated to reflectance ratio as follows:

$$\rho = \frac{R_p}{R_s} = \tan(\psi) e^{i\Delta} \qquad \text{eqn. 2.7}$$

Reflectance ratio, ρ , is a complex function which depends on the incidence angle (ϕ_0) and the wavelength (λ) of the light and complex refractive indices ($N_j=n_j+ik_j$, where j labels the layers. It should be noted that N, which is also named as optical constant, further depends on λ) and thicknesses (d_i) of all the layers (labeled by j) in the sample (in addition to N_{air}).

In spectroscopic ellipsometry, ψ and Δ are measured as a function of wavelength (λ) at a fixed incidence angle (ϕ_0). Hence by fitting the experimentally measured ψ vs. λ and/or Δ vs. λ curves to a function (based on Fresnel equations) which parametrically depends on d_j and N_j, the thickness and the refractive indices of all the layers could be determined. Additionary, the reliability of the results obtained strongly depends on the fit function used. If, on the other hand, some of the parameters (d_j and/or N_j) are already known from previous measurements

(literature), the number of fit parameters can be reduced, which increases the reliability of the results significantly. The quality of the fit is judged by using the mean square error (MSE) of the data produced by the fit function compared to the experimentally measured data. For the best fit, MSE is expected to be minimum (as close to zero as possible).



Figure 2.5. The working principle of spectroscopic ellipsometry. Retrieved from ref [152].

To construct the fit function, a model is used, which describes the number and nature (optical constants, N) of the layers that make up the sample. There are different dielectric function models to obtain N as a function of wavelength. For semi-transparent and transparent films, Cauchy or Sellemeier (dielectric function) models are used commonly, whereas, for absorbing or opaque films, Drude-Lorenz and Lorentz (dielectric function) models can be used.

For modeling SAMs and PFP films studied here, we used a three-phase model in which the samples are assumed to be made up of three layers as gold/SAM/air for SAMs and gold/PFP/air for PFP thin films. For the PFP thin films on M1 surfaces, this operation is done by using a four-phase model in which the samples are assumed to be made up of four layers as gold/SAM/PFP/air.

The layer beneath the gold film (which is epoxy in case of TSAu) need not be considered because the thickness of the gold film is very high (about 100nm) through which light is incapable of passing and reaching the layer beneath. For modeling dielectric properties of the gold film, however, either the Drude-Lorenz model or the N values (as a function of wavelength) reported in the literature can be used both of which yield equally good fits. The dielectric properties of the SAMs and PFP, on the other hand, is modeled by using the Cauchy model and refractive index values determined for visible light (by using Abbe Refractometer).

Before the SAM film is grown, measurement on bare TSAu is made first and experimentally observed Δ data is fit to a gold/air two-phase model (with the dielectric properties modeled as discussed above) and all the parameters for the gold film are determined and stored as reference (Figure 2.6 – A). Then, films are grown on the previously measured TSAu, and the resulting sample is modeled by using the three-phase model described above. Since the reference parameters for TSAu is already known, the thickness of the PFP and SAMs is obtained after the fit with an MSE value of 0.05-0.3 (unitless) (Figure 2.6 – B).



Figure 2.6. Experimentally measured data fitted with models A) Fitted template stripped gold film by using Drude-Lorenz dielectric function and gold/air two-phase model. B) Fitted carboranethiol film by using the reference gold parameters, Cauchy dielectric function for SAM and gold/SAM/air three-phase model.

The ellipsometric measurements were performed on a Phe-102 Variable Angle Spectroscopic Ellipsometer (VASE) equipped with a 75W Xe lamp from 250 nm to 1100nm at an incident angle of 65°. Measurements were taken with a spot size of 1.5mm. Samples were rinsed with ethanol and blown dry in a stream of nitrogen before characterization. The film thickness calculations were based on a three-phase ambient-film-gold model in which the film was assumed to have a refractive index of 1.45.

2.3.3 Atomic Force Microscopy

AFM is one type of scanning probe microscopy. The working principle of the AFM is based on measuring the interaction of sample surface and a sharp tip (which originates from various forces such as van der Waals forces, electrostatic or magnetic). AFM consists of three major components, which are cantilever with a sharp tip as probe, piezo-electric scanner to move the sample and/or tip, and the split photodiode to measure the deflection of the cantilever. The deflection of the cantilever is measured by means of a laser. The laser is focused on the reflective backside of the cantilever. The reflected laser beam from cantilever then is focused on the center of quadrupole photodiode. Therefore, as cantilever deflects due to interaction with the surface, the laser will be deflected too, and the quadrupole photodetector measures this deflection. The working principle of AFM is depicted in Figure 2.7.



Figure 2.7. Schematic illustration of the AFM working principle. Retrieved from [153].

The force versus distance curve between the surface and the tip of the cantilever is presented in Figure 2.8. As can be seen, at a larger distance, there is a very weak attraction between the tip and the surface. By approaching the surface, this attraction increases until a specific distance (about several angstroms). By means of choosing a certain interaction regime, AFM can be operated in contact mode, non-contact mode, and tapping mode. In contact mode, tip and sample surface has physical

contact; hence, short-range repulsive force is the tool to imaging topography of the sample. This regime of operation usually enables high-resolution topographic images. However, due to the nature of the force, the sample may be damaged. In non-contact mode, the tip and surface are separated from 1 nm to 10 nm, which results in weak attractive forces between tip and sample surface. A piezoelectric is used to oscillate cantilever at its resonance frequency. Then amplitude, phase, and frequency of oscillations are measured. In the tapping mode, the cantilever is oscillated at a constant amplitude in a way that the tip touches the surface gently at the bottom of the oscillation. Bringing the tip intermittently in contact with the sample, the reduction in the oscillation of cantilever is inevitable due to energy lost by touching the surface. Hence, the amplitude of oscillation changes which is detected and used to identify surface features. This mode is commonly used to image rough surfaces.



Figure 2.8. Illustrative force vs. distance curve between the scanning tip and the sample.

The system used in the AFM study was a commercially available Ambient AFM/MFM (Nanomagnetics instruments, Ankara). All images $(2.5x2.5 \ \mu m^2)$ were collected in air at room temperature, after PFP film growth process completed

immediately. Tapping mode measurements were performed by the use of a Silicon cantilever (rectangular with 225 μ m long) with force constant of 48 N/m. Contact mode measurements were performed by the use of a soft silicon cantilever (rectangular with 350 μ m long and 35 μ m width) with force constant of 0.03 N/m. Both type of tips had a reported curvature (by the manufacturer) of less than 10 nm. The images were taken at a scan rate of 0.5 μ m/s, and WSXM software was used to plane-fit for the images (after auto height correction, auto line correction, and horizontal scar correction). All image analysis processes were performed by using Gwyddion software. The height-scale of all the reported AFM images were kept between 12nm and 15 nm and are not shown explicitly to allow for a clear review of images and the results are reported as average of three samples for each film.

2.3.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique that uses the photoelectric effect to get quantitative and qualitative information such as elemental composition, chemical, and electronic state information, of the surfaces. The working principle of XPS can be briefly explained with steps such that: surface is illuminated with an X-ray beam, and due to the interaction between X-ray and surface, photoelectrons are generated, which are escaping from a depth of up to about 10 nm. On the other hand, the number and kinetic energies of the generated photoelectrons are measured simultaneously. A schematic illustration of the XPS system is given in Figure 2.9. XPS systems are operated in high (or ultra-high) vacuum environment. Measuring the kinetic energy of photoelectrons allows us to determine the binding energies of the electrons which in turn yields the elemental composition and chemical state of surface.

The energy of the incident radiation used in XPS is usually more than 1000 eV. The most extensively used sources to generate X-rays in XPS are Al K α and MgK α lines with the energies of 1486.6 eV and 1253.6 eV, respectively. Under UHV, when a sample is bombarded with X-rays of characteristic energy, photoelectrons are

emitted from the surface. By using a proper electron energy analyzer, the kinetic energy (KE) of the emitted photoelectrons and then the binding energy of the electrons (BE) can be measured. In the context of XPS, "binding energy" refers to the energy required to remove an electron from an atom. Binding energy depends on the type of atom from which the electron is emitted, the orbital from which the electron is ejected, the oxidation state of the atom, and the chemical environment of the atom. According to Koopman's approximation, binding energy can be calculated by using the below equation.

$$BE = h\vartheta - E_{Kin} - \phi \qquad eqn. 2.8$$

Where ϕ is the work function of the spectrometer, E_{Kin} is the kinetic energy of emitted photoelectron, BE is the binding energy of a core level in the sample, and finally, hv is the energy of the exciting X-ray radiation. The XPS spectrum can be converted to a plot of photoelectron intensity, number of electrons per unit time, as a function of binding energy with known values of ϕ and hv. The peaks appear in an XPS spectrum at distinct values of BE; hence the spectrum provides a "fingerprint" of the elements in the material and their chemical environment. [100] XPS is a quantitative chemical spectroscopy technique since the area of a photoemission peak is proportional to the number of emitters in the analysis volume.



Figure 2.9. Schematic illustration of the XPS system, retrieved from [154]

Angle-resolved XPS (ARXPS) is capable of giving depth profile information without removing the top surface layers. [155] In these systems, the depth information of thin films is derived from correlating the signal from the upper layer of the film surface and signals from the substrate. In ARXPS, changing the angle of the sample with respect to the direction probed by the detector, the so-called takeoff angle, one can vary the effective sampling depth. [156,157]

The probability of photoelectrons to reach the surface is calculated by,

$$P(d) = e^{-d/\lambda\cos\theta} \qquad eqn. 2.9$$

where d approximate escaping depth, λ is the inelastic mean free path of the photoelectron, and θ is the take-off angle. Take-off angle means that the angle at which photoelectrons emitted from the surface are received with a detector, describes the angle between surface and detector. This probability is proportional to the detected kinetic energy of the photoelectrons. This quantitative analysis enables us to calculate the inter-layer depth and to detect the elemental transition between the interfaces. By varying the take-off angle at which the photoelectrons are detected, thereby enabling photoelectron detection from different depths (see Figure 2.10).



Figure 2.10. Change in escaping depth from the surface as a function of take-off angles. Figure retrieved from [156].

For instance, analysis of a thin oxide film on metal at near-normal and near-grazing collection angles could produce spectra with a larger relative intensity of the oxide peak at the near-grazing emission angle (see Figure 2.11). [157]



Figure 2.11. Relative intensities of an oxide layer on metal surfaces at different takeoff angles. Figure retrieved from [157].

For the XPS measurement report in this thesis ex-situ X-ray Photoelectron Spectra were measured by using a Thermo Scientific K-Alpa (ThermoFisher) spectrometer. Monochromatic Al source used for electron excitation and hemispherical electron analyzer was fixed at 45° with respect to the surface normal, and spot size was 400 μ m. For the ARXPS measurements, a PHI Versaprobe 5000 Scanning X-ray Photoelectron Spectrometer (XPS) with Al K α as an X-ray source was used. 24.9 W X-ray power was used for analysis with 100 μ m X-ray spot size. Take-off angles of 10°, 30°, 45°, 60°, and 75° were utilized in the acquisition of high energy resolution spectra. For both ordinary and angle-resolved measurements, X-Ray Spectrometers were calibrated with Au 4f_{7/2} peak at 84.0 eV. The photoelectrons of Au 4f, C 1s, F 1s, B 1s, O 1s, and S 2p were detected at room temperature. High-resolution spectra of S and B were recorded with 30 scans. The operating pressure of the analyzer chamber was about 2x10⁻⁹ mbar. Curve fitting was carried out with XPSPeak analysis software with a Gaussian: Lorentzian ratio of 70:30%, and the results are reported as average of three samples for each thickness.

2.3.5 Infrared Scattering Nearfield Optical Microscopy (s-SNOM)

The s-SNOM analysis is a convenient method for obtaining the IR absorption spectra of different regions on the surface locally. The s-SNOM technique combines AFM with optical imaging and IR spectroscopy at the nanoscale, by using standard metal-coated AFM tips (T) illuminated by a focused IR laser (L). Illuminated tips generate a nano-focused area (N), used as an ultra-small light source to probe the sample locally. The tip curvature determines the size of the nano-focused area, and absorption spectra and optical imaging can be obtained by detecting the elastically backscattered (S) light interferometrically (optical amplitude and phase are collected simultaneously).



Figure 2.12. (a) Schematic view of the s-SNOM measurement system. (b)Schematic representation of the IR laser, AFM tip, and surface interaction. In the figure, AFM tip, incident laser, scattered light, and illuminated area shown with T, L, S, and N, respectively. Figure adapted from ref [158].

Since absorption spectra are very sensitive to environmental changes in the films, thin films were studied by the s-SNOM technique that provides an opportunity to compare and assess the vibrational properties depending on the morphological changes. Witte's group showed that, in the IR spectrum of Pentacene, only a few vibrational modes are seen in the 750-1400 cm⁻¹ range since the characteristic C-H stretching region is around 3050 cm⁻¹. In contrast to Pentacene, it's perfluorinated analog, perfluoropentacene (PFP), presents highly intense vibrational modes in this region. [144] These results help us to determine which region of spectra we need to focus on and study for the vibrational characterization of PFP thin films. In our latest study, we showed that the thicker PFP films (>15 nm) behave as a bulk crystal. This bulk phase will be our reference to investigate the thinner films. In our measurements, absorption amplitude images were taken from 3 parallel samples, and absorption spectra were extracted from 10 different points from these images. In the 4th section, "PFP films on TSAu and M1", absorption amplitude images are given for 1 and 15 nm films on each surface. In these images, dark regions indicate the IR active regions by using the AFM tip as an antenna. These absorption signal changes give the absorption amplitude images, and these images are very similar to the phase images of the tapping mode. In Figure 2.13, a comparison for s-SNOM results between agglomerated PFP region and needle-like grain region is given. As seen in these figures, the agglomerated region and the ordinary grain result have different absorption spectrum, because the agglomerated region has different oriented PFP molecules inside it and behaves as PFP pellet.



Figure 2.13. Comparison for s-SNOM results between agglomerated (lower spectra) and the grain (top spectra) regions of 15 nm PFP on M1. In the middle row, absorption amplitude image (left) and AFM height image(right) are given. The dark region (2^{nd} point) on the absorption image refers to the agglomerated region.

Infrared Scattering Scanning Nearfield Optical Microscopy (s-SNOM) measurements were performed at TARLA Experimental Stations in Ankara University, Institute of Accelerator Technologies. A Nano-FTIR setup (Neaspec Gmbh, Germany) equipped with mid-IR DFG laser (average output power of about 600 μ W) with wavelengths 5-15 μ m was used in this work. Measurements were performed in tapping mode using a Pt coated AFM probe (NanoWorld *Arrow* NCPt) with a tapping frequency of ~250 kHz and a tapping amplitude 60 nm. An AFM test

grating (Si wafer) was used to obtain a reference spectrum before the chemical characterization of samples. Infrared near-field imaging and obtaining hyperspectral spectroscopy with chemical identification was performed by asymmetric Michelson interferometer. Full spectra were recorded for 2.5 μ m x 2.5 μ m at 10.6 ms per pixel with a 2 cm⁻¹ spectral resolution. Resulting interferograms were detected by a Mercury-Cadmium-Telluride (MCT) detector in the spectral range of 800-1700 cm⁻¹ (Channel-B) with a spot size of approximately 50 nm (commercial value is about 20 nm and this value is directly depending on the tip curvature and sharpness). The s-SNOM setup is illustrated in Figure 2.12.

2.3.6 **Reflection-Absorption InfraRed Spectroscopy (RAIRS)**

IR radiation can be classified by dividing into three regions, near-IR $(12800 - 4000 \text{ cm}^{-1})$, mid-IR $(4000 - 200 \text{ cm}^{-1})$, and far-IR $(200 - 33 \text{ cm}^{-1})$. Organic molecular vibration arises in the mid-IR region. RAIRS is a powerful tool for characterizing thin films on metal surfaces, allows for identifying molecules and their chemical interaction with the substrates. IR absorption spectra make it possible to determine molecules' interactions with their surroundings by comparing the rotational and vibrational energy values for molecules, both thin films and in the gas phase. Studying IR radiation at grazing angles maximizes the surface sensitivity, so it permits the determination of the structure and the orientation of molecular adsorbates on metal surfaces. Since metal surfaces have highly high reflectivity properties, they are generally preferred as substrate, so intensity losses are avoided.

In a typical RAIRS system, a broadband IR source is directed from the source through a series of highly reflective metal-coated mirrors towards the surface. After the interaction between IR source and surface, the IR source is reflected by the substrate. Then reflected light is detected at an angle equal to incidence angle and focused on the detector through another series of mirrors. The raw signal is then Fourier transformed into the familiar frequency domain. In the studies of thin films at grazing incidence, their interaction with the incident IR laser depends on the polarization of the light.



Figure 2.14. Schematic representation of the p- and s-polarized incident and reflected electric vectors, Ep, Ep', Es and Es'. Primed and unprimed vectors refer to reflected and incident radiation, respectively. Figure is adapted from ref [159].

Linearly polarized incident light has two different components, s, and p. The spolarized is parallel to the surface and perpendicular to the plane of incidence. The p-polarized is perpendicular to the s-component; that is, it is parallel to the plane of incidence and perpendicular to the surface. As shown in Figure 2.14, at the interaction light with the surface, the s-polarized light undergoes a 180° phase shift which results in net amplitude is zero (destructive interference between the incident and the reflected rays), and p-polarized light undergoes a 90° phase shift which results in net amplitude almost twice that of the incident radiation (constructive interference between the incident and the reflected rays). Therefore, *p*-polarized IR light may result in a finite interaction with the film surface. For a vibrational mode to absorb IR light, a change in the molecule's dipole moment should occur during the vibration; that is, transition dipole moment must satisfy *eqn.2.10* (IR active). In such a case the absorption intensity will be given by *eqn.2.11*, which, in the *case* of RAIRS, implies that only molecular vibrational modes giving rise to a dynamic dipole moment perpendicular to the surface will be observed in the vibrational spectrum; this is referred to as the so-called "surface selection rule";

$$M \propto \frac{d\mu}{dR} \neq 0$$
 eqn. 2.10

$$I = |\vec{M}.\vec{E}|^{2} = |\vec{M}|^{2} |\vec{E}|^{2} .\cos^{2} \phi_{(\vec{E},\vec{M})}$$
 eqn. 2.11

where M is the transition dipole moment, μ is the dipole moment in the infrared active bond, \vec{E} is the electric field vector (*Since the s-polarized component of* \vec{E} *causes destructive interference, here is* \vec{E} *express the p-polarized component* $\vec{E_p}$), *R* is the vibrational coordinate and $\phi_{(\vec{E},\vec{M})}$ is the angle between the transition dipole moment and electric field vectors. This rule states that only absorption modes that have a component of their transition dipole moment perpendicular to the surface will be excited. Modes that are completely parallel to the surface normal do not interact with p-polarized light and are not vibrationally excited. [159–161] Greenler [162] developed the mathematical basis of RAIRS and studied both the effects of the light's polarization and the angle of incidence at which the light strikes the surface. Greenler also found that by using Maxwell's equations, the amplitude of the p-polarized light reaches a maximum (amplitude of \vec{E} in eqn.2.11) at a grazing angle of incidence (θ). In parallel with that, the absorption intensity increases at grazing incidence.

In Chapter 5, the construction stages of RAIRS system in SOLEIL Synchrotron and the RAIRS results of CT-SAMs will be described in detail.

CHAPTER 3

STUDY on THE EFFECT of CHEMICALLY DIFFERENT SUBSTRATES on NUCLEATION and GROWTH MECHANISM

We studied the effect of chemical properties of substrates on the structural properties of perfluoropentacene (PFP) thin films grown by supersonic molecular beam deposition (SMBD) technique. To this end, we have used template-stripped gold (TSAu), m-carborane-1-thiol (M1) coated TSAu, and mica substrate surfaces and investigated the PFP film properties as a function of film thickness and molecular flux (deposition rate). On all three substrates, the PFP molecules adsorb in standing up orientation in the first and over layers. However, with increasing hydrophobicity of the substrate, mean grain size in the first layer increases. Bulk like PFP films with needle-shaped grains grows on top of the first (wetting) layer on all the substrates with smaller and taller grains on gold and larger and wider grains on mica surfaces.

3.1 Result and Discussion

3.1.1 Contact Angle (CA) Measurements:

CA values as a function of nominal film thickness are shown in Figure 3.1, for PFP films on different substrates. Clean substrates have static contact angles of 0, $45.1 \pm 2.1^{\circ}$ and $85.4 \pm 1.8^{\circ}$ for Mica, TSAu, and M1, respectively, indicating Mica to be least hydrophobic and M1 to be the most hydrophobic surface. On all surfaces, static and dynamic CAs increase gradually with thickness up to 3 nm. After this thickness, the advancing CAs, which are very sensitive to surface composition [42,163,164],

converge to about 110° on all substrates which indicate that after 3 nm thickness all three substrates are completely covered with PFP films. However, the behavior of static and receding CAs on mica with more than 3 nm PFP film thickness is much different than that on M1 and TSAu. Receding CAs which are sensitive to surface roughness converge to 90° on M1 and TSAu, with the thickness more than 3 nm, whereas on mica it only increases up to 70°. This results in an average hysteresis of $23.7 \pm 3.5^{\circ}$, 18.5 ± 2.1 , and $48.9 \pm 14.6^{\circ}$ for M1, TSAu, and mica surfaces, respectively. On the basis of these observations, it can be concluded that all three substrates up to 3 nm PFP film thickness are not covered completely and that the growth mechanism is not much different. For thicker films, however, the morphology on mica is significantly different than that on M1 and Au.



Figure 3.1. Contact angle values of PFP films grown on mica, M1 and TSAu surfaces with a nominal deposition rate of 0.05Å/s vs. nominal film thickness measured by QCM. Static (black-square), advancing (red-circle) and receding (green-triangle) and hysteresis (blue-open square) are plotted.

3.1.2 Atomic Force Microscopy:

AFM images recorded as a function of distance from the film center for PFP films, with a nominal thickness of 2.5 nm, grown with a nominal DR of 0.05 Å/s are shown in Figure 3.2 (top row). As mentioned in the **Section 2.2**, the effective thicknesses and the corresponding effective DRs, which vary as a function of distance from the film center for fixed nominal thickness, were obtained from AFM grain analysis. By performing such AFM grain analysis on films with different nominal thicknesses (1, 2.5, and 4 nm) and using the resulting coverage values, the coverage versus thickness
plots shown in Figure 3.2 were obtained. As can be seen from the film analysis, for all three substrates, the first layer tends to wet the substrate surfaces, and after the first layer is almost completely covered, the second and other layers start to grow with needle-like grains. A similar behavior was observed earlier for PFP on other surfaces. [10, 139, 143,165]



Figure 3.2. Atomic force micrographs, $2.5x2.5 \ \mu m^2$, of 2.5 nm nominal thickness PFP thin films recorded at different distances from the film center (top). Coverage vs. thickness plots obtained by combining effective thicknesses data extracted from different nominal thickness films.

Nevertheless, some small but significant coverage of the second layer can be observed even before the completion of the first layer. The fact that this behavior is slightly more pronounced for mica surfaces (see, for instance, the AFM images in Figure 3.2 at 3 and 4 mm from the center) - which is expected as PFP is hydrophobic and mica is the most hydrophilic one of the three substrates—can be the cause of the difference between the CA behaviors of PFP films on mica and on the other two substrates. Coverage-thickness plots evolve quite similarly for all three substrates after the completion of the first layer as well and indicate a layer-plus-island (Stranski-Krastanov) growth mode (see Figure 3.2 bottom row for comparison). The only significant difference between the three substrates is the slightly higher coverage of the third and fourth PFP layers on M1 when compared with mica and TSAu. The overall coverage-thickness dependence discussed above for the three different substrates is significantly different from the behavior of PFP films on SiO₂ reported by Kowarik et al. who observed a nonlinear coverage increase for the first layer and an earlier onset of growth of the second layer compared with what is reported here. [166]

The coverage–thickness plots given in Figure 3.2 (middle row) also contain information regarding the effect of DR on the growth mechanism. In these plots, open data points correspond to a DR of 0.01-0.03 Å/s, whereas the solid data points correspond to a DR of 0.03-0.05 Å/s. As can be seen, regardless of the DR, the data points follow the same coverage/thickness curves for all the three substrates, which indicate that in the DR range investigated in this study (0.01-0.05 Å/s) growth mechanism does not change with DR.

The results of a more detailed grain size analysis for 1 nm thick films as a function of DR are provided in Figure 3.3 along with the representative AFM images used for the analysis. As can be seen in this figure, the mean grain size (MGS) increases with decreasing DR and with increasing hydrophobicity of the substrate. Grain density, on the other hand, does not change with the DR and hydrophobicity of the substrates, significantly for DRs less than or equal to 0.03 Å/s and is about 2 grains/ μ m². For DR of 0.05 Å/s, however, grain densities on all three substrates increase significantly

and decrease with increasing hydrophobicity. As discussed above, the grain shape for the first layer is almost circular on all three substrates. However, with increasing hydrophobicity of the substrate, the shape becomes more dendritic. This observation is more pronounced for lower coverage films shown in Figure 3.4. The average boundary length (ABL) of grains increases with increasing surface hydrophobicity.



Figure 3.3. AFM images (left) and grain size analysis (right) results for 1 nm PFP films. Contact mode AFM images, $2.5x2.5\mu m^2$, with DRs of 0.05Å/s, 0.03Å/s and 0.015Å/s (top-left). AFM cross section along the green lines shown in contact mode AFM images (middle-left). Tapping mode AFM images, $2.5x2.5\mu m^2$, with a DR of 0.05Å/s (bottom-left). MGS (black solid) and grain density (blue open) vs. different substrates with DRs of 0.05Å/s (bottom right). ABL (black solid) and dendriticy order (blue open) vs. different substrates with DRs of 0.03Å/s (circle) and 0.015Å/s (triangle) (top-right).

To quantify the change in the dendriticy of grains, first, we calculated the circumference for hypothetical perfectly circular grains whose radii were determined by using the actual MGSs reported in Figure 3.3 and Figure 3.4. The ratio of ABL to the circumference of these perfect circular grains gives the deviation from the perfect circularity of grains (this deviation will be referred to as dendriticy order). The dendriticy of grains increases with both increasing surface hydrophobicity and decreasing DR. Grain height is also similar for all three substrates and is about 1.5 nm, which is equal to the length of PFP molecules and indicates that the molecules are standing up along their long axis on all three substrates. To check if lying-down PFP regions were present under the standing-up grains, tapping-mode AFM images were recorded and are shown in Figure 3.3. The clear difference in the phase signal of the standing-up grains and the regions between them indicates that the regions between the standing-up grains are not made up of PFP molecules and that the molecules are standing up directly on the substrates. On mica and M1, this is expected based on previous studies in the literature; however, on gold and other metal surfaces, PFP was reported to adsorb in a lying-down geometry (long molecular axis parallel to the surface) in the first layer. [131, 141,148] In some other studies, even in bilayer films [133,135] and multilayer films [130] on metal surfaces PFP was reported to adsorb with the long axis parallel to surface. The perpendicular orientation observed in our study may either be due to the high kinetic energy of the PFP molecules during deposition by SMBD or the presence of oxides or carbon contamination on the gold surface before PFP deposition. In fact, on SiO₂ surfaces, PFP is well known to adsorb perpendicularly. [147,167] However, this issue deserves further investigation by using gold substrates cleaned in vacuum immediately before SMBD of PFP, which was not possible in the setup we used.



Figure 3.4. AFM images (top) and grain size analysis (bottom) results for 0.3 nm (DR: 0.015Å/s) and 0.15 nm (DR: 0.007Å/s) PFP films.



Figure 3.5. Contact mode AFM images $(2.5x2.5\mu m2)$ and grain size analysis results for 2.5 nm PFP films grown with DR of 0.05Å/s on different substrates.

Figure 3.5 shows the AFM images of 2.5 nm thick PFP films grown with a DR of 0.05 Å/s and the corresponding grain size analysis for the second and third layers. Though the difference of the MGSs on different substrates is minimal, the largest grain size is observed on the mica surface. This behavior is the opposite of what is observed for the first layer and indicates that the effect of the substrate's chemical nature is mostly blocked by the first layer. The grain shapes are also completely different from the shapes observed in the first layer, as discussed before. Though on all surfaces, the grains are elongated, they are more rectangular on mica, more needle-like on M1, and have an intermediate shape on TSAu.



Figure 3.6. Contact mode atomic force micrographs of 15 nm nominal thickness PFP films grown on different substrates, $2.5x2.5\mu$ m2, with a nominal DR of 0.05Å/s (top-left); line profile (bottom-left); Height histograms (right).

In Figure 3.6, AFM results of PFP films of 15 nm nominal thickness grown with a nominal DR of 0.05 Å/s are shown along with the corresponding height histograms. On all three surfaces, needle-like grains can be observed, which was also reported for PFP films on SiO₂ surfaces. [129, 147, 165,168] The grains become more pyramidal and larger with decreasing hydrophobicity of the substrate, that is, the sidewalls of the grains rise more sharply for the films on M1, but they rise more slowly on mica, in agreement with the grain shapes observed in the second and third layers. This is also in agreement with the coverage-thickness curves shown in Figure 3.2 and indicate that though on all surfaces, there is a layer-plus-island growth, on M1, the growth mode is more Volmer–Weber-like and on mica more layer-by-layerlike. The height distributions of PFP films on mica and M1 have similar widths of 5.1 and 6.0 nm, respectively, whereas the width for films on TSAu is 7.4 nm. In addition, the height distribution for mica peaks at a much lower height value than those of M1 and TSAu. This is most probably caused by films growing more layerby-layer-like on mica, which may result in the formation of pyramidal islands on top of fully covered first few layers. This hypothesis is explained schematically in Figure 3.7 with the corresponding three-dimensional (3D) AFM images. This mechanism is also compatible with the analysis provided in Figure 3.5, which shows larger MGS

for the second and third layers on mica when compared with the other two substrates. Finally, as can clearly be seen in the cross-sectional plots, on all three substrates, the height of each layer is about 1.5 nm, indicating that the films grow with the PFP molecules oriented with their long axis perpendicular to the substrate surface.



Figure 3.7. Schematic description of proposed PFP thin film growth mechanism on different substrates and corresponding 3D AFM images.

Grain orientation analysis on AFM images was also performed by using MatLab program. During this process, grains were detected by using the RegionPross and Height Threshold commands on AFM images, then the grains at the image boundary was removed from the calculation. Each grain was fitted with an ellipse, and then minor axis length, major axis length, and the angle between these ellips and x-axis of AFM image were detected. According to grain orientation analysis, all grains were oriented in a different direction and were not found in a specific direction. The grain shapes are also similar for all three substrates, with circular grains in the first layer and more elongated/rectangular grains in the over layers. Relative orientation analysis of the grains (angles between the long axes of the grains in the second and third layers) did not result in any preferred direction for the grains; grain orientations are given in the angle vs. frequency charts given in Figure 3.8.



Figure 3.8. Grain orientation analysis of PFP thin films with 1, 2.5 and 15 nm thickness on all surfaces

3.1.3 X-Ray Photoelectron Spectroscopy:

We used ex situ XPS to examine the electronic structures of PFP/M1, PFP/TSAu, and PFP/mica interfaces and to investigate the energy shift of C 1s and F 1s core levels versus the nominal thickness of PFP thin films. The XPS spectra of C 1s and F 1s core levels with various thicknesses of PFP on different substrates are shown in Figure 3.9. On M1 and TSAu, binding energies have been referenced to Au 4f (84 eV), and on mica surfaces, they have been referenced to Al 2p (74.6 eV). When the C 1s core-level spectra are examined, three distinctive peaks can be seen for 1 nm PFP thin films on all three substrates (although the third peak on the mica surface is not well resolved). When the F 1s core-level spectra are examined for 1 nm PFP

films, only a single peak can be observed on all three substrates. The positions and widths of these peaks are shown in Table 3.1. As the film thickness increases, C 1s peaks shift to lower energies, and the third peak disappears, whereas no significant shift in the position of F 1s peak takes place. Because of its molecular structure, the PFP molecule has two types of carbon atoms: the ones which are bonded to fluorine atoms [will be denoted as C(F)] and the ones bonded only to other carbons atoms [will be denoted as C(C)]. XPS peaks corresponding to these two types of carbons atoms separated by ~ 1.5 eV have been reported in the literature for PFP films on different metal surfaces. [130,131, 133, 135, 141, 148,169] Hence, the first C 1s peak can be attributed to C(F) atoms, whereas the second peak can be attributed to C(C)atoms. In Figure 3.10, the separation of these two peaks is plotted as a function of film thickness and can be seen to approach ~ 1.5 eV with increasing thickness. Since in a PFP molecule, there are 14 C(F) atoms and 8 C(C) atoms, the ratio of the intensities of these two peaks $(I_{C(F)}/I_{C(C)})$ is expected to be 1.75. As can be seen in Figure 3.10, $I_{C(F)}/I_{C(C)}$ increases as the thickness increases, and at 4 nm, it reaches to about 1.6. The third C 1s peak [will be referred to as C(3)] has also been observed in the previous studies in the literature and reported to be because of either carbon contamination or reaction of PFP molecules in the first layer with the substrate surface. [131, 135, 141, 148]



Figure 3.9. XPS spectra of C1s and F1s core levels for various nominal thickness PFP films grown with nominal DR of 0.05 Å/s.

Though we cannot rule out the presence of carbon contamination in our samples, we believe, in our case, the third C 1s peak is due to the existence of a third type of carbon atom in the PFP molecules in the first layer because of the interaction of PFP with the substrate. An increase of $I_{C(F)}/I_{C(C)}$ with increasing film thickness can also be a consequence of this hypothesis: if there were only two types of carbon atoms [C(F) and C(C)] in all the PFP film layers, then $I_{C(F)}/I_{C(C)}$ should have been constant at about 1.75 regardless of the film thickness.

	Thick	Cls					F1s		
		C(F)		C(C)		C(3)		115	
	ness (nm)	BE (eV)	fwhm (eV)	BE (eV)	fwhm (eV)	BE (eV)	fwhm (eV)	BE (eV)	fwhm (eV)
M1	1	288.2	1.10	286.5	0.95	284.8	1.24	688.0	1.50
	15	288.0	0.90	286.4	0.68			688.0	1.32
TSAu	1	288.2	1.25	286.6	0.98	284.7	1.45	688.2	1.47
	15	279.9	0.88	286.4	0.65			688.0	1.26
Mica	1	288.6	1.31	286.9	1.19	285.7	1.54	688.1	1.67
	15	288.2	0.97	286.7	0.77			688.5	1.44

Table 3.1. C1s and F1s XPS peak positions for 1 nm and 15 nm films.

In addition, this ratio should not depend on the presence of other carbon species (because of contamination). However, in our case, this ratio is significantly less than 1.75 for thin films and converges to a constant value only at 4 nm. Hence, we believe some of the C(F)-type carbon atoms in the first layer have a slightly different chemical environment resulting in a shift in their binding energies, which decreases $I_{C(F)}/I_{C(C)}$ for the first layer. As on all three substrates, PFP adsorbs in a standing-up orientation (long molecular axis perpendicular to the surface) in the first layer, the C(F) carbons closest to the substrate surfaces (carbon atoms bonded to fluorine atoms which are in direct contact with the substrate surface) may be expected to experience larger core-hole screening and hence shift to lower binding

energies, resulting in the third C 1s peak. Similarly, the first and second C 1s peaks may be expected to shift to higher binding energies with increasing film thickness because of decreased screening. This was actually observed for PFP on Ag(111) by several different research groups. [130, 133,169] Interestingly in our case, the first and second C 1s peaks shift to lower energies, on all three surfaces, with increasing thickness. Though this may be because of slight changes in the orientation (crystal structure) of the molecules with increasing thickness, further studies are necessary for a better investigation of the reasons for this behavior.



Figure 3.10. Evolution of positions and intensities of C(F) and C(C) peaks as a function of nominal film thickness.

As we mentioned above, we cannot exactly determine either the presence of carbon contamination under the wetting layer or the existence of lying molecules in the wetting layer via ordinary XPS measurements. When PFP molecules adsorb on the TSAu surface, we can talk about four different adsorption scenarios. These are; TSAu surface either clean or contaminated, and on these surfaces, PFP molecules adsorb in a standing-up or lying down geometries (see Figure 3.11). To further study the nature of the third C 1s peak, we have performed angle-resolved XPS measurements on 2 nm nominal thickness PFP films on TSAu and M1. A schematic illustration of these measurements are shown in Figure 3.12, and the results of which are summarized in Figure 3.13.



Figure 3.11. Illustration of possible interactions among PFP molecules, contamination, and TSAu



Figure 3.12. Illustration of AR-XPS measurement scenario for PFP films on TSAu surfaces

With an increasing take-off angle (angle from the surface plane), the ratio of C(3) peak intensity to the sum of the intensities of C(F) and C(C) increases for both surfaces. This is in agreement with a model where C(3) is due to a layer at the substrate–PFP film interface (below the PFP film). If the source of C(3) peak was at the top of the PFP film, the intensity ratio should have decreased, which is not the case. The results of the simulated XPS peak intensities, also shown in Figure 3.13, for two different models where a 1 nm organic layer exists below and above the PFP

film, respectively, are in agreement with this conclusion. The ratio of the sum of the intensities of C(F) and C(C) to F 1s peak intensity also decreases with an increasing take-off angle, again, in agreement with a model with a carbon layer below the PFP film. However, the same model also predicts the ratio of C(3) to F 1s peak intensities to increase with the take-off angle, which is not in agreement with the constant ratio observed experimentally. On the basis of these observations, the source of the C(3) peak can be concluded to be below the PFP film. Though this is in agreement with the presence of a third type of carbon atom in the PFP molecules at the substrate–film interface, we can still not rule out the presence of carbon contamination below the PFP film based on the angle-resolved XPS results.



Figure 3.13. Angle-resolved XPS peak intensity ratios as a function of take-off angle. Top row: Experimental results. Bottom row: Simulated intensities for PFP films on TSAu with a 1 nm thick carbon layer below (left) and on top (right) of the PFP film.

3.2 Conclusion:

In summary, we have compared the PFP films on mica, TSAu, and M1 surfaces to understand their growth mechanism. It was observed that, with more than 3 nm thickness, all three substrates are completely covered with PFP films. On all three substrates, the first layer tends to wet the substrate surfaces, and after the first layer is almost completely covered, the second and other layers start to grow with needlelike grains. MGS and dendriticy of the first layer increase with decreasing DR and increasing hydrophobicity of the substrate. As opposed to previous results regarding metal surfaces in the literature, the PFP molecules were found to be standing up even in the first layer on the gold surface, which may either be because of the high kinetic energy of the PFP molecules during deposition by SMBD or the presence of oxides or carbon contamination on the gold substrate. On all three surfaces, needle-like grains, formed by standing-up PFP molecules, can be observed, which become more pyramidal and larger with decreasing hydrophobicity of the substrate.

CHAPTER 4

VIBRATIONAL PROPERTIES and THE EFFECT of BEAM KINETIC ENERGY on PFP THIN FILMS

4.1 Kinetic Energy Effect on PFP thin-film Growth

4.1.1 SMBD system Kinetic Energy Manipulation on PFP films

PFP thin films on different surfaces were grown by using the Supersonic Molecular Beam Deposition (SMBD) system. In the supersonic molecular beam source chamber, the organic source material is evaporated in the presence of an inert carrier gas (He, Ar, etc.) in a quartz tube and the organic molecule/carrier gas mixture is expanded with supersonic expansion into the vacuum. A detailed explanation of the system was given in **Section 2.2**. The SMBD source parameters, during film growth for this study, are summarized in Table 4.1.

The kinetic energy of PFP molecules in the beam can be approximately calculated after the supersonic expansion via a semi-theoretical approximation as

$$E \approx \frac{5}{2} \frac{m_{pfp}}{m_{avg}} RT_{Nozzle} \qquad eqn. 4.1$$

where m_{pfp} is the perfluoropentacene molar mass and m_{avg} is the average molar mass of carrier gad PFP mixture beam. In our system, in the existence of Ar as carrier gas, stagnation pressure was kept at 0.25 bar (187.5 Torr) in order to achieve reasonable PFP flux at temperatures low enough to prevent decomposition of PFP. By assuming the vapor pressure of PFP to be close to PEN and equal to about $3x10^{-3}$ Torr at the source temperature (320 - 340 °C), the kinetic energy of PFP molecules can be calculated to vary from 11.26 eV to 0.65 eV by changing the carrier gas from He to Ar, respectively.

Carrier Gas	Не	Ar		
Nozzle Diameter (µm)	150			
Stagnation Pressure (bar)	0.25			
Evaporation Temperature (°C)	320±10	340±10		
Nozzle Temperature (°C)	175±10			
Vacuum Pressure (Torr)	2x10 ⁻⁵	4x10 ⁻⁴		
Kinetic Energy (eV)	11.26	0.65		

Table 4.1. SMBD source working parameters during film growth

4.1.2 Contact Angle (CA) Measurements:

CA values as a function of nominal film thickness are shown in Figure 4.1, for PFP films with different carrier gases. Clean TSAu substrates have static contact angles of $45.1\pm2.1^{\circ}$. With each carrier gas, static and dynamic CAs increase gradually with thickness. After the thickness of 2.5 nm, the advancing CAs converge to about 110° with each carrier gas, which indicates that after 2.5 nm thickness, TSAu surfaces are completely covered with PFP films. The reason for the high standard deviation in each CA value is that three samples were prepared for each thickness, and CA measurements were made at three points on each sample. For both carrier gases, regardless of film thickness, the hysteresis of the contact angles was very close to each other and was about 22° degrees. Based on these results, it can be concluded that up to 2.5 nm thickness TSAu surfaces are not covered with PFP film completely. In addition, the CA values are relatively higher for He carrier gas compared to Ar.



Figure 4.1. Contact angle values of PFP films grown with He and Ar carrier gas with a nominal deposition rate of 0.025 Å/s vs. nominal film thickness measured by QCM. Static (black-square), advancing (red-circle) and receding (green-triangle) and hysteresis (blue and black triangle) are plotted.

4.1.3 Grain Analysis of Kinetic Energy Effects on PFP films:

In Figure 4.2, AFM images and coverage vs. thickness plots for PFP films on TSAu grown by using He and Ar carrier gases are shown. The height-scale of all the reported AFM images were kept between 12 nm and 15 nm and are not shown explicitly to allow for a clear review of images. In this study, all the films were grown with a nominal DR of 0.025 Å/s and the given thicknesses correspond to effective thicknesses (determined as discussed in the previous chapter) unless otherwise is explicitly mentioned. At least 3 parallel samples for each set of growth parameters were prepared/analyzed.

AFM images were recorded as a function of distance from the film center for 2.5 nm nominal thickness PFP films are shown in Figure 4.2 - top row. By performing AFM grain analysis on films with different nominal thicknesses (1 nm, 2.5 nm, and 4 nm) and using the resulting coverage values, the coverage vs. thickness plots shown in Figure 4.2 was obtained. Similar to what was observed in **Chapter 3**, the PFP growth follows a layer+island mechanism with different carrier gases as well, where the first layer completely wets substrate surface and second and other layers start to form needle-like grains on this first layer immediately.



Figure 4.2. Atomic force micrographs, $2.5 \times 2.5 \ \mu m^2$, of 2.5 nm nominal thickness PFP thin films recorded at different distances from the film center (top), Coverage vs. Thickness plots obtained by combining effective thicknesses data extracted from different nominal thickness films.

Similar behavior was observed before for PFP on other surfaces. [1, 11, 147, 165,170] In each situation, the 2nd layer can be observed even before the completion of the 1st layer. Coverage-thickness plots evolve quite similarly for each carrier gas after the completion of the 1st layer as well and indicate a layer plus island (Stranski–Krastanow) growth mode (see Figure 4.2 bottom row for comparison). The grain shapes are also similar, with circular grains in the first layer and more elongated/rectangular grains in the over-layers. Coverage-thickness plots show that each layer follows the same growth mechanism with changing kinetic energy. In the

case of Ar gas, the 2^{nd} and 3^{rd} layer start to grow on the TSAu surface sooner than those of He.



Figure 4.3. AFM images (top) and grain size analysis (bottom) results for 0.5 nm (DR: 0.015 and lower than 0.01 Å/s) PFP films with carrier gases He (solid square), and Ar (open square)

Results of a more detailed grain size analysis for 0.5 nm thick films as a function of DR is provided in Figure 4.3 along with representative AFM images used for the analysis. As expected, as the deposition rate decreases, mean grain size increases and accordingly grain density decreases. [11, 147,171–173] Grain density changes from 1.5 grains/ μ m² to 0.5 grains/ μ m², as DR decreases from 0.015 to <0.01 Å/s for both gases which implies that carrier gas type does not affect grain density significantly. On the other hand, mean grain size (MGS), dendriticy and average boundary length (ABL) are significantly different for He and Ar when the DR is less than 0.01 Å/s. Such a difference, however, is not present for the DR of 0.015 A/s. This finding implies that changing the kinetic energy of the PFP molecules results in a difference in the film properties only for low deposition rates. ABL, MGS, and the dendriticy of grains increase as DR decreases for both gases. However, the amount of increase is significantly larger for He: MGS values increased by 2.1 and 1.4 times, ABL values increased by 2.2 and 1.5 times and dendriticy increased by 1.3 and 1.1 times

for He and Ar, respectively. This observation indicates that film growth is effected by the DR more significantly when the carrier gas is lighter (kinetic energy is higher). Another difference that needs to be noted here is that although film formation mechanism is similar in both gases with respect to DR, it is clear that ABL, dendriticy, MGS (and grain density inversely proportional to MGS) values are much higher for He carrier gas compared to Ar. Considering that the films obtained with both carrier gases are grown on the same substrate, this result shows us that varying the carrier gas (hence beam kinetic energy) affect the film formation. Grain heights are also similar for each carrier gas and are about 1.5 nm, which is equal to the length of PFP molecules, and indicate that the molecules are standing up along their long axis on the substrate.



Figure 4.4. AFM images (top) and grain size analysis (bottom) results for 1 nm (DR: 0.025, 0.015 and lower than 0.01Å/s) PFP films with carrier gases He (square), and Ar (open square)

Grain size analysis and comparisons for 1 nm thick films as a function of DR and carrier gas are provided in Figure 4.4 along with representative AFM images used for the analysis. As can be seen in this figure, mean grain size (MGS) increases with decreasing DR. Though carrier gas type does not affect grain density significantly, in the case of Ar, grain density remains a little higher than its He counterpart. As

discussed above, grain shapes for the 1st layer are almost circular in each situation. As expected, dendriticy order increases, while DR decrease from 0.025 to <0.01 Å/s. Besides, this value is dramatically lower than the 0.5 nm films, which means that deviation from perfect circular grain decreases. As DR decreases, ABL and MGS values increase similarly for both He and Ar gases, and similar results have been seen in 0.5 nm films. However, for the same DRs, ABL and MGS values are higher for He than those for Ar. This could be directly related to the kinetic energy of the PFP molecular beam. [174] Because in the case of high kinetic energy, PFP molecules impinging the surface may have higher diffusion length on the surface, so they will have higher probability to encounter nucleated clusters on the surface, and tend to combine with those clusters to create larger grains more quickly. In contrast, PFP molecules impinging the surface with the low-energy state will form smaller grains on the substrate as the diffusion on the surface may be limited. For this reason, grain densities are higher (inversely MGSs are lower) in the low-energy state. In addition, the fact that static contact angle results for 0.5 and 1 nm (see Figure 4.1) are slightly higher in the case of high kinetic energy than in the case of low kinetic energy also indicates that the film formation is faster in the high energy state. Grain heights are also similar for both carrier gases and are about 1.5 nm, which is equal to the length of PFP molecules, and indicate that the molecules are standing up along their long axis on the substrate.



Figure 4.5. AFM images (top) and grain size analysis (bottom) results for 2.5 nm (DR: 0.025, 0.015 Å/s) PFP films with carrier gases He (square), and Ar (open square) for 2nd and 3rd layers

Figure 4.5 shows the AFM images of 2.5 nm thick PFP films grown with different DRs and the corresponding grain size analysis for the 2nd and 3rd layers. In 2.5 nm thickness films, the 1st layer has completely coated the substrate for both carrier gases, and the 2nd, 3rd, and other upper-layers form needle-like grains on this 1st layer. The difference in the MGS, ABL and dendriticy order values for different carrier gases is minimal in the 2nd layer. The grain shapes are also completely different from the shapes observed in the first layer. Unlike in the 1st layer, in 2nd layers; MGS and ABL values decrease as DR decreases. This is because grain shape is circular in the 1st layer, and grain shape in the 2nd layer is due to the transition phase from circular to needle-like shape (neither circular nor needle-like). Based on these results,

overlayer grains are elongated and needle-like on the wetting layer, indicating that the effect of the substrate's chemical nature is mostly blocked in the wetting layer.

4.2 ATR and s-SNOM Results:

4.2.1 Attenuated Total Reflection (ATR) result of PFP powder

Figure 4.6 shows ATR spectra recorded for PFP powder. The wavenumber range was set between 400 and 4000 cm⁻¹ with a scan number of 128 per run at resolution of 2 cm⁻¹. PFP exhibits only very few intense vibrational modes between 4000 and 1750 cm⁻¹ that means no modes occur above 1700 cm⁻¹ due to perfluorinated pentacene. In the ATR spectrum, PFP molecules exhibit very strong vibrational modes between 1750 and 650 cm⁻¹, indicating which region we need to focus on to determine the vibrational properties of PFP molecules These ATR measurements were performed to have reference IR data for s-SNOM measurements and were used to identify the region where PFP molecules have strong vibration modes. It can be clearly seen from the results of the ATR that the strong absorption modes in the spectra are seen at around 1600 cm⁻¹, 1300-1500 cm⁻¹, 1250 cm⁻¹, 1100 cm⁻¹ and 1000-850 cm⁻¹. Between 1000-850 cm⁻¹, PFP's characteristic C-F in-plane stretching modes can be seen. At 1250 cm⁻¹ and 1100 cm⁻¹, PFP has C-F asymmetric and symmetric stretching modes, respectively. At around 1500 cm⁻¹, PFP has C = Cstretching modes, but in addition, in the spectra, there exists a very broad peak between $1500-1250 \text{ cm}^{-1}$, which is due to the existence of water.



Figure 4.6. ATR absorption spectra of PFP powder

4.2.2 Scattering Infrared Scanning Nearfield Optical Microscopy (s-SNOM) results of PFP thin-films

AFM/SNOM images and total absorption spectra of 1 nm and 15 nm PFP thin films grown on TSAu and M1 by using helium carrier gas with deposition rate of 0.05 Å/s, are given in Figure 4.7-Figure 4.10. In the spectra highly intense absorption peaks are highlighted in the given inset tables with green font. For comparison, ATR results of PFP powder are shown as well in total absorption spectra. In the ATR spectrum, there are strong absorption peaks in this region, and the intensity of the s-SNOM peaks appear to be weaker compared to the ATR results. As can be seen from Figure 4.7-10, the absorption peaks in the s-SNOM spectra have shifted to higher energies than those in the ATR. In the thin-film phase, such shifts are understandable compared to pellet and substrate-molecule interactions also may contribute to this shift to higher energies. [144] Each peak intensity is given in tables in figures along with relative intensity with respect to total spectra intensity.



Figure 4.7. Frequencies (v in cm⁻¹), Intensities (I, the area under each peak), I_{Rel} (normalized to the most intense mode at 1504 cm⁻¹) of all experimentally observed absorption peaks (Left); Absorption spectra recorded between 1650-860 cm⁻¹ (Right-top), and Absorption amplitude and AFM image, with roughness of 2 nm (Right-bottom row) for 15 nm PFP on TSAu



Figure 4.8. Frequencies (v in cm⁻¹), Intensities (I, the area under each peak), I_{Rel} (normalized to the most intense mode at 1104 cm⁻¹) of all experimentally observed absorption peaks(Left), Absorption spectra recorded between 1650-860 cm⁻¹(Right-top), and Absorption amplitude and AFM image of 1 nm PFP on TSAu, with roughness of 0.7 nm (Right-middle row) for 1 nm PFP on TSAu



Figure 4.9. Frequencies (v in cm⁻¹), Intensities (I, the area under each peak), I_{Rel} (normalized to the most intense mode at 1504 cm⁻¹) of all experimentally observed absorption peaks (Left), Absorption spectra recorded between 1650-860 cm⁻¹(Right-top), and Absorption amplitude and AFM images, with roughness of 1.8 nm (Right-middle row) for 15 nm PFP on M1



Figure 4.10. Frequencies (v in cm⁻¹), Intensities (I, the area under each peak), I_{Rel} (normalized to the most intense mode at 1501 cm⁻¹) of all experimentally observed absorption peaks (Left), Absorption spectra recorded between 1650-860 cm⁻¹ (Right-top), and AFM and Absorption amplitude images, with the roughness of 0.8 nm (Right-middle row) for 1 nm PFP on M1

4.2.3 Comparison of s-SNOM:

A comparison of characteristic C-F in-plane stretching modes on TSAu and M1 is given in Figure 4.11. According to the theoretical calculations of PFP molecules, characteristic C-F in-plane stretching modes were reported to be at 920 (1st peak), 933 (2nd peak), 974 (3rd peak), and 980 (4th peak) cm⁻¹, in the literature. [144,175,176] Corresponding peak positions in our SNOM measurement are given in Table 4.2. Since the 15 nm film behaves as bulk crystal, the difference between the crystal structure of the thin-film phase (1 nm) and bulk phase (15 nm) can cause the peak shifts in the spectrum, but this shift is very small. Also, the peak profiles (shapes) are very similar to each other. The small shifts in 1 nm films from the 15 nm ones,

points to a different molecular environment of PFP molecules on TSAu, also clearly seen on M1, which could be attributed to strong intermolecular interactions.

Table 4.2. s-SNOM results for peak positions in modes between 1000-890 cm⁻¹ of PFP films on TSAu and M1 for 1 and 15 nm PFP films on TSAu and M1 surfaces.

Surface	Thickness	Peak Positions (cm ⁻¹)					
Surrace		1 st	2 nd	3 rd	4 th		
TSAu	1 nm	914	928	962	982		
	15 nm	914	930	965	981		
M1	1 nm	923	933	976	989		
	15 nm	922	930	968	986		



Figure 4.11. s-SNOM results for comparison of characteristic C-F in-plane stretching modes between 1000-890 cm⁻¹: for same thicknesses on TSAu and M1 (top) and comparison of 15 nm and 1 nm PFP films on same substrates (bottom).

For both 15 nm and 1 nm on the M1 surface, 1st and 2nd peaks are overlapped with enveloping, and these peaks were separated and determined by peak fitting. Breuer

et al. (2012) showed that for PFP molecules adsorbed in lying flat configuration, with π -stacking, there are only two peaks arising between 1000 and 900 cm⁻¹; these results were confirmed by both experimental measurements and theoretical calculations. [144] The single-molecule DFT calculation results and π -stacking (PFP molecules absorb in lying geometries) experimental results are compatible with each other, and peaks arise at 933 and 980 cm⁻¹ (DFT results are given in Figure 4.12). In the case there exist second oriented species within the unit cell (as in herringbone packing), characteristic vibrational modes are split. This situation is known as Davydov splitting. In the study of Breuer et al. (2012), when the PFP molecules absorb in standing up geometries, these two characteristic peaks split and were observed at 920 (1st peak), 933 (2nd peak), 974 (3rd peak), and 980 (4th peak) cm⁻¹. This observation was explained to be a result of herringbone stacking arrangement in the crystal structure of PFP films.



Figure 4.12. Vibrational modes of characteristic C-F in-plane stretching modes. Figure retrieved from [144].

Our results show that the crystal arrangement in PFP films is very similar for both phases (thin film and bulk phase) with the herringbone arrangements. As can be seen in Figure 4.11, for the bulk phase films, characteristic C-F peaks are seen nearly at the same energies, with very low shifting to higher energies on M1 with regard to TSAu. However, the intensity of the 1st peak on M1 (0.4) is higher with respect to TSAu (0.18). In addition, at 950 cm⁻¹ in 1 nm film on M1, an additional peak arose, and this peak is also seen in spectra of 15 nm on M1 with a too low intensity nearly at the same energy. Also, at 902 cm⁻¹, another new peak arose on PFP film on M1. In the literature these peaks were assigned to C-H out-of-plane stretching and

bending modes in pentacene. [175] These new peaks can be caused from M1 SAMs on TSAu due to the C-H bond in carboranethiol molecules. These extra peaks and the peak shifting to higher energies on M1 surfaces can be easily explained by the environmental changes due to M1 SAMs on TSAu.

Table 4.3. s-SNOM results for peak positions in the region around 1264 cm⁻¹ of PFP films on TSAu and M1 for 1 and 15 nm PFP films on TSAu and M1 surfaces

Surface	Thickness	Peak Positions (cm ⁻¹)				
Surrace	T memess	1 st	2 nd	3 rd		
TSAu	1 nm	1480	1499	1515		
Torra	15 nm	1483	1504	1518		
M1	1 nm	1475	1501	1524		
	15 nm	1481	1504	1520		

A comparison of vibrational modes between 1540-1465 cm⁻¹ on both TSAu and M1 is given in Figure 4.13, and peak positions are tabulated in Table 4.3. This region is where aromatic C=C stretching modes occur. [130,177–182] The 1st peak is assigned as C-F in-plane stretching mode, and 2nd and 3rd peaks are assigned to C=C in-plane stretching modes in the literature. [183] These three peaks occur on the spectra together in both phases. As is seen in these results, in the thin-film phase (1 nm) these vibrational modes occur at lower binding energies compared to their bulk phase (15 nm) counterparts, and the variations in the energies are less than 5 cm⁻¹. Interactions between the substrate and PFP thin films could be the reason for this small variation.



Figure 4.13. s-SNOM results for comparison of vibrational modes in the region around 1500 cm⁻¹ of PFP films on TSAu and M1.



Figure 4.14. Vibrational modes around 1500 cm⁻¹. Figure retrieved from [144].

C-F asymmetric stretching vibrational modes around 1264 cm⁻¹ is given in Figure 4.15. [181] For both 15 nm and 1 nm on TSAu, the peak is at 1264 cm⁻¹. For both 15 nm and 1 nm on M1, the peak is at 1279 cm⁻¹. As can be seen in the above figure, peak profiles for 15 nm and 1 nm on TSAu and M1, are very similar to each other. On M1 surfaces, this asymmetric stretching peak constitutes a very broad peak at 1279 cm⁻¹ and is shifted to higher energies up to 10 cm⁻¹ with respect to its TSAu

counterpart. This result can be explained with the effect of the environmental difference between TSAu and M1 surfaces.



Figure 4.15. s-SNOM results for comparison of vibrational modes in the region between 1300 -1240 cm⁻¹ of PFP films on TSAu and M1.



Figure 4.16. Vibrational modes around 1280 cm⁻¹. Figure retrieved from [144].

C-F very strong symmetric stretching vibrational modes around 1100 cm⁻¹ are shown in Figure 4.17. [181] For both 15 nm and 1 nm on both TSAu and M1, the peak is nearly at 1107 cm⁻¹. It seems that this mode is not affected by the effect of the environmental difference between TSAu and M1 surfaces.



Figure 4.17. s-SNOM results for comparison of C-F symmetric streching modes between 1125-1045 cm⁻¹: for same thicknesses on TSAu and M1 (top) and comparison of 15 nm and 1 nm PFP films on same substrates (bottom).



Figure 4.18. Vibrational modes around 1100 cm⁻¹. Figure retrieved from [144].

4.3 Conclusions

It was observed in both carrier gas situations; the first layer coats the substrate surface completely. After completion of the first layer, the second and other upper layers start to grow on this layer with needle-like grains immediately. Coveragethickness plots evolve quite similarly for both carrier gases after the completion of
the 1st layer and indicate a layer plus island (Stranski–Krastanow) growth mode. In the case of Ar gas, the 2nd and 3rd layer starts to grow on the TSAu surface sooner than those of He. Considering the contact angle measurement results, it can be concluded that TSAu substrates, up to 2.5 nm PFP film thickness, are not covered completely and the CA values are relatively higher in the case of high kinetic energy (carrier gas He), which shows that the film formation is faster in the high kinetic energy state. Although film formation mechanism seems similar for both gases with respect to DR, it is clear that ABL, dendricity, MGS (and grain density inversely proportional to MGS) values are much higher for He when compared with Ar. As DR decreases, ABL and MGS values increase similarly for both He and Ar gases. Grain heights are also similar for both carrier gases and are about 1.5 nm, which is equal to the length of PFP molecules, and indicate that the molecules are standing up along their long axis on the substrate. In the s-SNOM results, the difference between the crystal structure of the thin-film phase (1 nm) and bulk phase (15 nm) can cause the peak shifts in the spectrum, but this shift is very small. The small shifts in 1 nm films from the 15 nm one, points to a different molecular environment of PFP molecules on TSAu and M1 surfaces, which could be attributed to strong intermolecular interactions between PFP molecules and substrates. Our results show that molecular arrangement (packing) in PFP films is very similar for both phases (thin film and bulk phase) with the herringbone arrangements.

CHAPTER 5

REFLECTION-ABSORPTION INFRARED SPECTROSCOPY (RAIRS) SETUP and RESULTS

This part of the dissertation was performed at the SMIS beamline in SOLEIL Synchrotron Paris/France. In the scope of the OPEN SESAME Training Program, our project titled "IR and XAFS Studies of PFP films on TSAu surface grown by Supersonic Molecular Beam Deposition at Grazing Incidence" was accepted by the OPEN SESAME Training Committee. The aim was to characterize (a) TSAu and CT coated TSAu substrates and (b) PFP films on these substrates by means of RAIRS and XAFS measurements. Within the scope of this program, our project was supported for two months. Because the training period was too short and due to some technical problems, some parts of the project remained uncompleted. Specifically, the construction of the SMBD system and preparation of TSAu films could not be finished in time. Hence PFP films could not be studied at all, and CT films could only be prepared on annealed Au films on silicon. In this chapter, RAIRS studies of CT SAMs on Au/Si will be described.

5.1 **Designing the RAIRS Setup:**

For designing the Reflection-Absorption Infrared Spectroscopy (RAIRS) setup, we have used three 90° Off-Axis Gold coated Parabolic Mirrors (MPD249-M03), RFL=4" (101.6 mm). In addition to these mirrors, RAIRS system consists of an FTIR source (Nicolet 6700 FT-IR Spectrometer), MCT detector (Preamp 410-025500) and the sample holder. A schematic view of the RAIRS system is given in Figure 5.1



Figure 5.1. Schematic and real images of the RAIRS system (a) top - view without sample, (b) top - view schematic and real image of the RAIRS system with the sample, and (c) side view schematic and real image of the RAIRS system with the sample.

1st PM and IR source are fixed on the bench where the system is fixed. 2nd and 3rd PMs, and the detector (The detector was attached to the system in the last step of the set-up, that is why detector is not seen in figures) is fixed to a movable plate, and it can move in one direction (X-direction) on the bench. The 1st and 2nd PMs are placed parallel to each other, and the 3rd PM is placed right across the 2nd PM, and sends the laser reflected from the 2nd PM to the detector. MTC Detector is located right across the 3rd PM at the RFL distance of the 3rd PM. The sample holder is placed in the middle of the 1st and 2nd PMs and can move in the X-direction and the Y-direction

(which is perpendicular to the plane of these mirrors). The centers of the movable plate and 2^{nd} PM are overlapped, that is, the position of 2^{nd} PM also expresses the location of the movable plate. The distance between 1^{st} PM and sample holder and the distance between the sample holder and 2^{nd} PM is equal to X. Figure 5.1 gives the schematic and real views of the RAIRS system and the location of the PMs and sample holder. The height of the sample from the plane of the 1^{st} and 2^{nd} PM is indicated by Y in Figure 5.1 – c. Sample can move along two directions (X and Y) to change the incidence angle of IR light, and movable plate (also 2^{nd} PM) moves only along X direction. The X and Y values dictated by RFL of PMs and the desired incidence angle, θ , were calculated for different incidence angles by using the following simple relations:

$$Y = RFL * sin(\theta)$$
 and $X = RFL * cos(\theta)$ eqn. 5.1

For four different grazing angle values, all distances and angles were calculated and are given in Table 5.1.

θ(°) X (mm)	Y (mm)	1st PM (°)	2nd PM (°)	3rd PM (°)	2nd PM Position (mm)
90) 101.6	0	66	276	316	203.2
85	5 101.2	8.85	71	271	316	202.4
80) 100.5	17.64	76	266	316	201
75	5 98.1	26.3	81	261	316	196.2
70) 95.4	34.7	86	256	316	190.8

 Table 5.1. RAIRS System distances and angles

By taking into consideration these calculations, the RAIRS system setup and alignment procedures were carried out. For alignment, a green diode laser was used. The path that the laser beam follows is shown by the green arrows in Figure 5.2-a. The alignment procedure was carried out with a cube prism and a silver-coated mirror placed with a separation of 203.2 mm (8 inches), which corresponds to twice the RFL of PMs. In the first step of the alignment procedure, 1st and 2nd PMs were placed at 180 degrees relative to each other (looking at each other), which results in a grazing angle of 90° to sample normal (view of this setup is given in Figure 5.2-

b). When the green laser comes to cube prism, the laser is divided into two paths, forming the green path-1 and green path-2, which are perpendicular to each other. The cube prism and silver-coated mirror are located right across the 1st and 2nd PMs, respectively. Since cube prism is placed at a distance of 2xRFL with silver-coated mirror, as in Figure 5.1-a, if 1st and 2nd PMs are placed in 2xRFL, green path-1 and green path-2 must overlap exactly on 2nd PM (in the alignment stage of 1st and 2nd PMs, 3rd PM was removed from the movable table). After this process is completed successfully, the alignment process of the 1st and 2nd PM is completed. For the 3rd PM alignment, 3rd PM is inserted into the green path -2 path and placed right across the 2nd PM. In the next step, a gold mirror was added to the system as a sample between 1st and 2nd PMs' angles, sample holder and 2nd PM position, and sample holder height (Y) values were determined. These values are given in Table 5.1.



Figure 5.2. (a) Left image: The picture of the alignment process of the RAIRS system, the green arrows indicate the laser path. (The green laser source is out of the image. Right image: The location of each PMs and Sample Holder in the RAIRS system (movable plate borders highlighted with red lines for clarity). (b) The picture of the stage of determining the position and angles of the PMs by using the green laser in the RAIRS system, by using a gold mirror as a sample.

5.2 Connection RAIRS Setup to FTIR System and Measurements:

The RAIRS system was mounted on the IR beam path, and the focal width falling on the detector was measured using white light. Since the MCT detector size (laser inlet window) was about 1mm, the width of the beam had to be reduced to this size. With MPD249-M03 (RFL=4") PM, the focal width is about 2 mm, which was measured by keeping a squared paper (each square line 5 mm) in front of the 3^{rd} PM (which was used to focus the incident beam from 2^{nd} PM into the detector) as shown in Figure 5.3. By changing the 3^{rd} PM with another PM having lower RFL (2"), this focal width could be changed to about 1 mm.



Figure 5.3. Beam focal width measurement for the detector beam hole

Calculation of the illuminated length of the sample was made by considering the beam diameter falling on the sample, which was about 2 mm. Calculated values are given as a table inset in Figure 5.4, where θ is the grazing incidence angle, *L* is the incident beam diameter, and *P* is the illuminated length of the sample.



Figure 5.4. Illuminated length of the sample with respect to the incident angle

Considering *P* according to grazing angles, the maximum sample length we need to get the measurements was found to be 25 mm. After these procedures, RAIRS setup was ready for measurements. The first measurements were performed without any sample with the configurations shown in Figure 5.2 (Left) ($\theta = 90^\circ$). As seen in IR spectra in Figure 5.5, between 4000-3000 cm⁻¹, there is a very broad peak (because of icing in detector). In order to check whether the water vapor has decreased after a while, we prepared a macro to take measurements with 5 min intervals. After waiting for about 15 hours, the water vapor level remained unchanged.



Figure 5.5. The first signal from the RAIRS system

The detector was pumped for 30 hours with Alcatel 5150 to overcome the icing problem in the detector, and its pressure decreased to $3x10^{-7}$ mbar. The detector was then mounted into the system again, and measurements were repeated with the same configuration.



Figure 5.6. First signal after pumping detector for 30 hours

As seen in Figure 5.6, the broad ice peak between 4000-3000 cm⁻¹ disappeared, and with this result, the system was ready for the measurements. The sample holder was placed in the system, and an Au/Si film was attached to the sample holder to take measurements with different grazing incidence angles and detect the problems that would be faced in the measurement process. In order to stabilize the amount of H₂O and CO₂ in the IR signal and to stabilize the signal, a purge box was prepared, and continuous dry airflow was provided. Figure 5.7 shows the design and view of the purge box. The FTIR system is not directly connected to RAIRS; IR light is first sent to an ellipsometer system (big box behind the RAIRS in Figure 5.7) on the same bench, where IR light is then directed to the ellipsometer system, so even though we had made purge boxes for both systems, H₂O and CO₂ were still constantly flowing into the RAIRS system. By continuously circulating dry air in the system, the amount of CO₂ and H₂O has been tried to be reduced and kept stable. After the construction of the purge box, the signal was analyzed by taking absorption measurements for 1 hour

in order to determine how long time is needed for signal stabilization. As a result, it appears that the signal became stable after 30 min after the cover of the purge box was closed. Based on these observations, in order to be able to take measurements from each sample, it was necessary to wait for 30 minutes after the sample is placed on the sample holder.



Figure 5.7. Inside and outside view of the purge box built to stabilize the amount of H_2O and CO_2 within the RAIRS system. The RAIRS system is connected to an ellipsometer system, so IR light is first sent to the ellipsometer and then directed to the RAIRS system with a mirror.

After determining the effect of purging on the signal, measurements were taken in order to determine the number of scans and resolution needed to obtain high-quality spectra. These measurements which were taken on M1 coated Au / Si film at the angle of incidence 80° are summarized in Figure 5.8. As a result of this optimization procedure, the number of scans with the highest signal-to-noise ratio was determined to be 1024 and 2048, with a resolution of 4 cm⁻¹. In the light of these results, 1024

scans and 4 cm⁻¹ resolution was preferred for measurements because the measurements took a shorter time (15 min for each sample) with more manageable noise levels. In the literature, RAIRS experiments of CT films on metal surfaces have been performed only by Weiss et al. by using 1024 scans and 2 cm⁻¹ resolution. [184]



Figure 5.8. RAIRS results of M1 coated Au / Si film at an incidence angle of 80° for determining the number of scans and resolution.

5.3 **Results of Carborane-thiol surfaces:**

CT SAMs films have been extensively studied on metal surfaces. [42, 97,185] However, grazing incidence absorption measurements of the SAMs on these metal surfaces have almost never been carried out except for a single study by Weiss et al.. [184] Hence, the Weiss group's work is a reference for us to test how well our RAIRS system works. As can be seen in Figure 5.9, the peak profiles of the M1 and M9 molecules are consistent with the results obtained by Weiss et al.. In the B-H stretching region between 2500 – 2700 cm⁻¹, two peaks for both isomers were observed at 2586 cm⁻¹ and 2608 cm⁻¹ for M1 and at 2604 cm⁻¹ and 2629 cm⁻¹ for M9. Peaks at 2586 cm⁻¹ and 2629 cm⁻¹ will be referred to as *the characteristic peaks* of M1 and M9, respectively. The peaks in the range 2600-2615 cm⁻¹ are originating from the *carborane cluster* [186,187] and will be referred to as the main peaks of M1 and M9 (in our results carborane cluster originated peaks are observed at 2604 and 2608 cm⁻¹ for M9 and M1, respectively).



Figure 5.9. Grazing incidence absorption measurement of M1and M9 CT SAM films on gold surface (a) literature results taken with the angle of incidence at 82°, and (b) our RAIRS results taken with the angle of incidence at 80°.

For M1 and M9 SAMs, measurements were also taken at 70° and 75°, and no peaks were observed between 2500 - 2700 cm⁻¹. Because of these results, measurements were taken at 80° and 85°. The carboxylic attached derivatives of M1 and M9 (M1-COOH and M9-COOH) were also prepared, and their absorption spectra taken at both 80° and 85° are shown in Figure 5.10. As can be seen from Figure 5.10, strong absorption peaks of M1 and M9 are around 2600 cm⁻¹, which correspond to B-H stretching modes. Also, it can be easily seen from absorption peaks, as the angle of incidence increases, very low shifting (1cm⁻¹) to higher energies occur. The peaks of M1-COOH arises at the same energies with M1; however, the peaks of M9-COOH shifts to higher energies (2635 cm⁻¹) when compared with those of M9. When the M1-COOH absorption signal is carefully examined, two peaks are clearly visible at 2586 and 2611 cm⁻¹. Also, between these two peaks, a shoulder around 2600 cm⁻¹ clearly appears both at 80° and 85°. When carborane clusters form interactions with cations and neutral molecules containing NH, CH, OH groups, these interactions lead to the splitting of the BH stretching bond into several components indicating the change of the initial state of the BH bonds in carborane clusters. [187] Based on this explanation, it can be said that by attaching -COOH group to M1 leads to the splitting of the BH stretching band and arises the shoulder around 2600cm⁻¹, which originates from -COOH group. This shoulder can be referred to as the characteristic peak of the M1-COOH. Furthermore, when the RAIRS spectrum of M9-COOH films are considered, it is easy to see that it presents a broad and irregular peak compared to other carboranethiols. Absorption spectra of disordered films could give a broad and irregular spectrum. [186] The contact angle results of mixed SAMs of these molecules showed that the bonding strength of these molecules on gold surfaces decreases in the order of M1, M9, M1-COOH, and M9-COOH. [188] Based on these results, we can say that, compared to M9-COOH thin films, M1-COOH molecules are more regularly and homogeneously arranged on the gold surface. The absorption spectrum of M9-COOH is very broad, and its interpretation is very difficult. This may be due to the fact that M9-COOH molecules are very irregular on the gold surface compared to other carboranethiol molecules, and molecules are arranged in different orientations, and different phases (there are molecules in the film that could not hold onto the surface), or M9-COOH may not have completely covered the surface. In addition to the compatibility of the results of M1 and M9 films with the literature results, the vibrational properties of carboxylated carborane-thiol films, which have not been studied at all in the literature, have been obtained within this project by RAIRS system.



Figure 5.10. B-H streching results of carboranethiol SAMs on Au/Si surfaces at 80° and 85° and schematic sketches of these molecules.

5.4 Conclusions

As a result of these construction and optimization procedures, RAIRS measurements were done at 1024 scans with a resolution of 4 cm⁻¹. RAIRS measurements for carboranethiol SAMs on Au/Si were done at 70°, 75°, 80°, and 85°, and it is observed that BH stretching modes seen in just at 80 and 85 degrees between 2500 - 2700 cm⁻¹. In the B-H stretching region, the main peak originating from the carborane cluster arises around 2600-2615 cm⁻¹. The characteristic peaks of M1, M9, and M1-COOH were found at 2586, 2629, and 2600 cm⁻¹, respectively. As the angle of incidence increases, very low shifting in BH stretching band (1cm⁻¹) to higher energies occurs. The absorption spectrum of M9-COOH was irregular, so interpreting was very hard. Irregularity in the spectrum of M9-COOH may be due to the irregularity of the molecules in film.

CHAPTER 6

CONSTRUCTION OF A NEW He ATOM DIFFRACTION SYSTEM

One of the main purposes of this thesis work was to construct a new helium atom diffraction system (HADs) with extended capabilities that would enable us to study organic films in a way that was not possible before. With this system, we were hoping, initially, to study PFP thin films for demonstrating the capabilities of the setup. To this end, our design goal was to construct a helium diffraction system with the following capabilities and components

- High precision 6-axis sample holder/manipulator that can work in temperature 60 K- 1000 K via liquid N₂ and/or liquid He cooling.
- 2) He diffraction detection via quadrupole mass spectrometer detector with the possibility of time of flight measurements.
- Main vacuum chamber with extension ports for Low Energy Electron Diffraction, X-Ray Photoelectron Spectroscopy, and Reflection Absorption Infrared Spectroscopy.
- Supersonic molecular beam deposition with time of flight measurement for beam energy detection.

Since the design was very ambitious and the project budget was limited, unfortunately, we were not able to study PFP thin films. Nevertheless, the initial construction and the first tests of the system were completed. After final optimization and fine adjustments/tuning, the system can be used for thin-film and surface characterization. In this chapter of the thesis, we will describe the construction process and the initial tests of the system. The design and a picture of the new HADs are shown in Figure 1. The HADs consists of 3 main vacuum chambers. These are He Source (HS) chamber where the monoenergetic supersonic He beam is produced (1), chopper stage where the continuous beam is modulated by a mechanical chopper that converts it to a pulsed beam whose diameter is determined by a collimator (3), and the diffraction chamber where the diffraction event occurs and is detected (2). The Supersonic Molecular Beam Deposition (SMBD) chamber, which can be used both independently and with HADs, is the fourth vacuum chamber that forms HADs. The HS chamber and the SMBD system were parts of the old HAD system in our laboratory and have been adapted to the new HADs with minor modifications. [119,120, 125,189] The diffraction chamber and the chopper stage were designed and built from scratch for this study. The chopper stage is constructed adjacent to the diffraction chamber and is differentially pumped (Figure 6.1). The chopper stage is connected to the HS chamber with a flexible bellow. In this way, the HS chamber and chopper stage (and thus the diffraction chamber) can be moved relative to each other under vacuum, enabling a full alignment of the He beam axis. He-beam can be fully aligned with collimators on the chopper stage and diffraction chamber. The diffraction chamber is a large UHV chamber with ports at which different analyzers can be connected to extend the possibility of performing measurements with techniques complementary to HAD (Figure 6.1). At the top of the chamber, a port allows the mounting of a 6axis manipulator whose sample holder can work in a 100 K - 1200 K temperature range (Figure 6.1). In this chamber, there is a second vacuum chamber (detector box) that contains a rotatable detector, which is used for the measurement of the helium beam scattered from the sample surface (Figure 6.2). A modified quadrupole mass spectrometer (SRS RGA100) is used as the detector. This quadrupole mass spectrometer (QMS) is optimized for He, although it can operate in the mass range of 1-100 amu. "Rotatable QMS" or "detector" terms will be used to refer to this QMS. The rotating movement of the detector box is provided by a gear mechanism (rotary platform, RP), which is located in the diffraction chamber and is differentially pumped. Thanks to this mechanism, the detector box can rotate 360° continuously (unless one of the other system components interferes with the rotation path). The diffraction chamber also has a second QMS (Hiden HAL / 3F RC 501 PIC, 1-500 amu mass range) mounted just opposite the SMBD chamber with its axis at a fixed angle with respect to the incident He beam but with a degree of freedom so it can be translated for approaching to and moving away from the sample surface.





Figure 6.1. Schematic representation of the HADs from the top (top) and a current picture (bottom). In the schematic representation, the 6-axis sample holder, ion gun, and fixed QMS are not shown. In the picture, the SMBD chamber and the diffraction chamber are in separate configurations. In the top view schematic representation of the diffraction chamber, the top cover is added open for easy viewing of the rotary platform and detector reservoir.

With this QMS, it is possible to perform temperature-programmed desorption (TPD) and time of flight (TOF) measurements, as well as to measure helium scattering at a constant angle (this QMS will be referred to as "fixed QMS"). In summary, the diffraction chamber contains two QMSs, one of which is rotatable (and optimized for helium), and the other is fixed. Finally, an argon ion gun system completes the system for cleaning the sample surfaces in a vacuum. The new HADs (diffraction chamber) is designed to be expandable by adding different components (such as RAIRS, XPS, and LEED) in the future.

The SMBD chamber is placed perpendicular to the HS, and the organic molecular beam and the helium beam axes coincide vertically on the sample (crystal) surface (see Figure 6.2). In this way, while the organic film is grown on the substrate surface, helium diffraction data can be collected simultaneously (using rotatable QMS). Other alternative measurement configurations are described below in Figure 6.2. Since the SMBD chamber and the HS are connected to the diffraction chamber by means of sliding valves, both can be separated from the diffraction chamber without breaking the vacuum of the diffraction chamber, if necessary. The existing components of the system, the diffraction chamber, and the different measurement configurations will be discussed in more detail under separate titles in the following sections. The pumping scheme of the system is shown in Figure 6.3. As different pre-vacuum line connections are used during individual tests of system components, the pre-vacuum line valve diagram and pressure gauge positions are also shown in Figure 6.4. In this study, for the pressure control, hot filament gauges, cold cathode gauge, and thermocouple gauges were used. In hot filament gauges, bare ion gauges are used in the chopper stage (IGC), diffraction chamber (IGK), and the rotary platform (IGD). Tube ion gauges were used in HS (IGH) and SMBD chamber (P_{ss}). Cold cathode gauge (CCG) was used as a control gauge between pre-vacuum lines. Thermocouple gauges (TCGs) were used to measure pre-vacuum lines, and their positions are shown in Figure 6.4.



Figure 6.2. Schematic drawing showing the detectors in HADs. The illustration is shown from the top of the diffraction chamber. The horizontal plane containing the helium beam axis coming to the surface with the Θ_i angle and the surface normal indicated by the blue plane is scattering plane. The detector axis is in this plane, and atoms are collected with a scattering angle Θ_f . In the figure also, the horizontal directions x-y are indicated while the z-axis is the vertical axis.

The rotatable QMS is rotated around the vertical z-axis, and the helium scattering intensity is measured as a function of Θ_f for fixed Θ_i . Measurements of He diffraction can be carried out by measuring the helium scattering intensity with both the rotatable QMS and the fixed QMS depending on the position of the sample normal (sample configuration 1 or 2 in Figure 6.2). When the sample is facing the organic beam, the scattering intensity can be recorded by only rotatable QMS; however, in real-time while the film is growing. When the sample is facing fixed QMS, helium scattering intensity can be measured with both the rotatable QMS and the fixed QMS. The sample can be removed from the helium (and also organic) beam path by moving it upward in the z-axis. In this case, the organic beam directly goes into the fixed QMS, which allows the TOF measurements, and the energies of the molecules in the organic beam can be measured. Without the need for a helium beam using only fixed





Figure 6.3. HADs pumping scheme. Dashed lines indicate alternative mechanical pump lines (pre-vacuum line). In this drawing, the valves on the front vacuum line (fore-line) are not shown.



Figure 6.4. Schematic drawing showing the pressure gauges and valve positions of HADs. The orange boxes show the pre-vacuum line traps (fore-line trap).

6.1 Setup and Test Operations of Completed Parts

In this section, each of the components of the HADs will be discussed under separate headings, and information about manufacturing and the test/optimization processes will be given.

6.1.1 He Source Chamber

He beam source chamber is pumped by a diffusion pump with a pumping capacity of 8000 liters per second (VHS400). The source consists of a 20 μ m hole (nozzle), which can be cooled down to 40 K. The source is located in a position in front of a 0.29 mm skimmer, located in the intermediate zone that separates the bellows adapter from the He beam source chamber, and can be moved in three directions via electric motors. This ensures that the helium beam is exactly in front of the skimmer. The

source is cooled by means of a flexible copper rod connected to a closed-cycle helium compressor. The source temperature is controlled by a nickel-chromium alloy heater resistor and a Lakeshore temperature controller with a silicon diode temperature sensor. For helium diffraction experiments, helium gas, typically at a pressure of 70-90 psig at 70 K, is expanded from the micro nozzle to vacuum and a supersonic helium beam with about 5 Å⁻¹ wave vector is formed. The source chamber, which has a base pressure of 10^{-7} Torr, increases its pressure (70 psig He pressure, 70 K source temperature) to 10^{-5} Torr during He source operation. In this study, all the components of the He source chamber, which was taken from the old HADs system, were checked and confirmed to work normally. The base pressure is 10^{-7} Torr, and the pressure in the source operating conditions is 10^{-5} Torr. The source temperature could be kept constant at 70 K. At the end of these tests, testing of other components of HADs was continued.



Figure 6.5. Schematic view of He Source used in the new He Atom Diffraction system. Figure adapted from ref [189].

6.1.2 Chopper Stage

The chopper stage is shown in Figure 6.6 (region 3 in Figure 6.1). The beam chopper chamber is pumped through a diffusion pump, and there is also a -80 °C ethanol trap attached to this chamber. The supersonic helium beam passes through a skimmer

firstly, and then through a bellows region (Figure 6.1 and Figure 6.6) into the chopper stage. In this region, the helium beam is first pulsed between 300-500 Hz and with a 50% duty cycle. The pulsed helium beam then enters the diffraction chamber through the collimator on the CF 40 flange on the outer wall of the diffraction chamber between the chopper stage and the diffraction chamber (Figure 6.9.a and Figure 6.6). On the sliding valve, there are two collimators with a diameter of 0.7 mm and the other with a diameter of 1.5 mm. By sliding the valve, one of these two collimators can be inserted into the beam path. When the valve is shifted to the end, it closes, and the chopper stage can be isolated from the diffraction chamber. A photodiodephototransistor pair in the chopper generates a signal at the chopping frequency; this signal is used as the reference signal in the lock-in-amplifier. Chopper stage's tests were started by first measuring the vacuum level. In the situation isolated from the diffraction chamber, and in the absence of a helium beam, using the ethanol trap, it was found that the base vacuum (pressure) in this chamber descended to 10^{-8} Torr. This value is the best value available with the pumping system (diffusion pump + ethanol trap). After this stage, tests of the specially designed sliding valve and the movable motor housing, shown in Figure 6.6, were carried out. The chopper motor and sensor electronics have been tested. As a result of the tests, it has been seen that the chopper can be rotated smoothly up to 500 Hz, and the rotation frequency can be measured by the sensor without any noise. At this point, chopper stage tests were completed, and tests of other components were continued.



Figure 6.6. Technical drawing of chopper stage and connected chambers (top) and chopper parts inside the stage (bottom).

6.1.3 Supersonic Molecular Beam Deposition System (SMBDs)

The SMBDs is a high vacuum device (the base pressure is 10^{-7} Torr), which houses the SMBD source and is pumped by a high-capacity diffusion pump. This system can be connected to HADs or can be operated independently. The SMBD source consists of a Pyrex tube with a micro-sized hole. The organic material placed in the source is vaporized by heating during the passage of carrier gas (usually helium or krypton) through the source and allowed to be introduced into the carrier gas. The resulting mixture is expanded supersonically through a nozzle of about 100 µm in diameter to obtain a supersonic molecular beam. When used independently, the flange shown in Figure 6.7.a is closed by a cap which accommodates a moveable sample holder and a quartz crystal microbalance (QCM). Substrates and QCM can thus be introduced into the organic beam path. In this way, the flow of the organic matter in the beam is measured by first taking the QCM into the beam path, then the sample is inserted into the beam path, and the film growth process is continued until the desired thickness film is obtained. By varying the source temperature and/or the pressure of the carrier gas, the flux and kinetic energy of the organic matter in the beam can be controlled. In addition, the speed (kinetic energy) of the organic matter in the beam can be increased by increasing the temperature of the micro-nozzle and/or reducing the mass of the carrier gas (for example, using helium instead of krypton).



Figure 6.7. A photograph of the SMBD chamber (a), top view of the organic source of SBMD (b) the schematic drawing of the SMBD source (c).

6.1.4 Diffraction Chamber

Technical drawings of the diffraction chamber and intended use of the flanges are given in Figure 6.8. Inner view of the diffraction chamber and the detector box/rotary platform is shown in Figure 6.9. The helium detector (rotatable QMS) in the detector box, shown in Figure 6.9 and Figure 6.10, which is one of the most important components of the system, can be rotated perpendicular to the sample surface and around the sample (fixed distance to the sample). This box is fixed to the bottom of the diffraction chamber via a gearbox, which is differentially pumped. A detailed description of the detector and the rotary platform will be made further in the following sections. The other important component of the diffraction chamber is the fixed QMS. This QMS is connected to the chamber by a unidirectional translator and can be approached to/retracted from the sample surface. Using this QMS, scattered helium atoms from the sample surface can be measured at a fixed angle. Since the distance between QMS and sample surface can be adjusted, it is also in a very convenient configuration for TPD measurements since the mass spectra of desorbed materials from the surface can be measured without the need for He beam. However, it is also possible to use the fixed QMS simultaneously with the rotatable QMS (provided that it is not in the field of view) or independently as a helium detector. Therefore, these two QMS form a very useful system by complementing each other. The last important component in the diffraction chamber is the 6-axis manipulator (or sample holder). This sample holder can rotate in three directions and is capable of translational movement in all three orthogonal directions. For helium diffraction measurements, it is of great importance that the rotation movement is very controlled and error-free. A detailed discussion on this component will be made in the following sections. The chopper stage (shown in blue in Figure 6.8) and the He beam forming elements (such as beam chopper and collimators), which are adjacent to but not part of the diffraction chamber, was discussed in section 6.1.2.

In addition to the components mentioned above, the diffraction chamber is designed so that different analyses and/or film preparation components can be installed in the future. The most important of these components are the reflection-absorption IR spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS), which impose restrictions on the geometry/structure of the diffraction chamber. In fact, in accordance with the RAIRS measurements, the necessary mirrors and IR spectrometer must be placed in the appropriate positions outside the diffraction chamber and the necessary ports were positioned to take the IR beam into and out of diffraction chamber at the same plane/height as the helium scattering plane (see Figure 6.8). In this way, it will be possible to collect He diffraction and RAIRS data from a sample simultaneously. A system with this capacity is not available in the world as far as we know and will allow for valuable work if, in the future, a suitable IR spectrometer may be acquired. For XPS measurements, two flanges are placed for X-ray source and X-ray analyzer connections to a level above the helium scattering plane. The positions and angles of these flanges and the distance of the XPS analyzer to the sample (determined by the analyzer) have imposed severe restrictions on the design of the chamber and the sample holder. In order to bring the XPS analyzer closer to the sample, the sample holder had to be designed very compact. In addition, the design and manufacture of the sample holder, which must be able to rotate very precisely in three directions and be cooled to at least 100 K, has taken quite a long time due to these requirements. However, if an X-ray source and analyzer can be connected to the system in the future, it will be possible to collect both He diffraction and XPS data from the same sample (although not simultaneously). It is possible to install a LEED device on the flange designed for the XPS analyzer. When designing the chamber, different X-ray analyzers and LEED devices have been examined (dimensions and specifications are determined), and the X-ray analyzer / LEED flange is designed accordingly. In addition, a flange suitable for connection to a load-lock vacuum chamber is added to the chamber to be able to transfer the sample without breaking the vacuum for future use. The possible intended use of the other flanges is given in Figure 6.8. This section will provide information on the manufacturing and testing processes of the diffraction chamber. The 6-axis sample holder and the He detector (and the rotary platform) will be

discussed separately under separate headings. As mentioned above, the diffraction chamber was designed to be multi-functional. For this reason, the construction of the chamber took a long time and it was necessary to work with more than one company. In the final state of the chamber, after baking (at 200°C for three days), chamber pressure could be reduced to 1.1×10^{-9} Torr. The mass spectra (measured by SRS QMS) indicating the amount of gases in the chamber at this level are given in Figure 6.11. Since the turbo-molecular pumps (Edwards/nEXT400 pumps, pumps speeds for nitrogen is 400 l/s, ultimate pressure < 1×10^{-10} mbar) used have a 5×10^5 compression ratio for H₂ and the rough vacuum level at the rear of the turbopumps (obtained by using a mechanical pump) is 10^{-3} mbar, H₂ level in the chamber is acceptable. An old Ti sublimation pump in our laboratory was connected to the chamber to lower the amount of H₂. This final condition of the diffraction chamber was considered sufficient and the construction of other parts of the He diffraction system began.



Figure 6.8. A technical drawing showing the intended use of the flanges in the diffraction chamber.



Figure 6.9. a) A cross-sectional view of the diffraction chamber. The red line shows the incoming helium beam. The green line shows the organic molecular beam from the SMBD chamber. The location of the samples to be analyzed (the center of the chamber) is indicated by a black star. The detector box can be rotated around the center in the plane containing the helium beam and the surface normal (the scattering plane is shown in green) thanks to the RP on which it is mounted. In the drawing, no detector is shown in the detector box. b) Detector chamber and rotary platform (RP) on the base of the diffraction chamber are shown in detail.


Figure 6.10. Top panel: Inside view of the diffraction chamber from the flange marked with a star in Figure 6.8. This picture shows the fixed QMS, the rotatable QMS, and the sample holder. Bottom panel: External view of the chamber from the same angle (the direction in Figure 6.8).



Figure 6.11. SRS Quadrupole electron multiplier (CEM) signal acquired during the heating process (a) and thereafter (b).

6.1.4.1 Rotary Platform

The technical drawings of the rotary platform (RP) and the connections within the diffraction chamber are shown in Figure 6.12 and Figure 6.13. This part is one of the most critical components of HADs. The detector box is rotated around the sample by RP. Therefore, in order to measure the angle-dependent variation of the helium scattering intensity with as few errors as possible, the collimator on the detector box

(Figure 6.9.b) during the rotation of the RP (and thus the detector) should always stay in the scattering plane shown in Figure 6.2 and Figure 6.9.a. In order to achieve this, the construction of this part requires high precision to avoid tilting of the detector box. Again, for accurate measurement of the angles, the RP center and the vertical axis of rotation of the sample holder must be exactly coincident. Moreover, it is also necessary that the rotation is smooth, the vacuum in the RP remains high at the time of rotation, and there is no gas leak from the diffraction chamber to RP, excluding the flow through the collimators. For all these reasons, RP is designed, as shown in Figure 6.12, and needed to be manufactured with very low fault tolerance. After the delivery of the RP, it was first subjected to rough vacuum and mechanical tests. In the first tests, it was observed that the Viton seals used for sealing were too tight (black round parts in Figure 6.12). Some parts also were not exactly the desired size, so that the rotational movement did not occur easily (the parts were stuck due to friction during the rotation). Thereupon, very small/delicate changes were made to the dimensions of the gaskets and some parts. In the subsequent tests, the vacuum level in the RP was 10⁻³ Torr, the gears were rotated with a torque wrench to test how smooth the rotation was, and whether a leak occurred during the rotation. At the 10⁻ ³ Torr level, after confirming that the RP is operating smoothly, the vacuum tests were continued by connecting the RP to a high vacuum pump. In these tests, it was seen that the vacuum inside the RP decreased to a 10^{-5} Torr level. After this step, the RP was tested in a high vacuum (10^{-5} Torr), and the worm gear was rotated by the stepping motor and tested to see whether the motor was stuck during the rotation movement. During these tests, it was found that, at some rotations (angles), the movement became more difficult, and leakage occurred. A reason for the compression and leakage problem during these operations was that the rotation wheel (the orange ring in Figure 6.12) could not sit parallel to the wheel housing since the compression screws (shown in Figure 6.12 with red arrows) were not sufficiently homogenously tightened. In order to minimize this problem, the design of the rotation wheel has been changed. Also, in this process, a UHV compatible special lubricant having a very low vapor pressure and could be heated to high

temperature was provided (Krytox-LVP). Following these changes, the rotation movement became very smooth, and the leak was reduced to an acceptable level. However, the leak could not be eliminated completely because it is not possible to tighten the compression screws fully. However, only a few small zones during the rotation movement cause leaking. At this stage, RP was mounted into the diffraction chamber, and the vacuum and mechanical tests were repeated by connecting the detector box on to the RP. In the first tests, a leak was detected on the RP differential pumping line flange (Figure 6.13 red arrow). In addition, because the bellow pipe used for this line is not soft enough, it has been realized that it is challenging to fix the RP to the bottom of the diffraction chamber. The differential pumping connection line was then renewed, and the tests restarted. During these tests, as seen in Figure 6.4, the diffraction chamber and the detector box were pumped by two separate turbopumps, and their pressures were measured with different ion gauges. During the tests, the chopper stage was isolated from the diffraction chamber (with the sliding valve), and the RP was pumped through the chopper stage. Also, in order to complete the tests quickly, the diffraction chamber was not baked. In this configuration and the RP at stationary state, the pressure inside the diffraction chamber (IGK) was measured as 7.2×10^{-9} Torr, the pressure inside the detector box (IGD) was 1.1x10⁻⁸ Torr, and the internal pressure of RP (CCG) was 1.2x10⁻⁶ Torr. These base pressures were evaluated as normal since the diffraction chamber was not pre-heat-treated. Then the RP was rotated, the pressure of the diffraction chamber and the detector box were monitored, and it was observed whether there was a leak between them. During the rotational movement, the pressure of the diffraction chamber increased to 7.2×10^{-9} Torr and the pressure of the detector box to 1.2×10^{-8} Torr. In the light of these final test results, it was concluded that the RP was leaking at a level of about 10⁻⁹ Torr from both the diffraction chamber and the detector box, and RP was mechanically working without any problem.



Figure 6.12. Views and sections of the rotary platform from different angles. The directions shown in this drawing are not the same as those shown in Figure 6.9 (the x, y, z directions of the diffraction chamber and the x, y, z directions in the drawing of the rotary platform are not the same). PH: Differential pumping line connection flange, SD: Worm gear.



Figure 6.13. A photo of a rotary platform's differential pumping line in the diffraction chamber and rotary feedthrough connections.

6.1.4.2 Quadrupole Mass Spectrometers

6.1.4.2.1 Rotatable Quadrupole Mass Spectrometer

SRS RGA100 QMS was used as a rotatable helium detector in this system. The rotatable helium detector operates in the range of 1-100 amu with better than 1 amu resolution and includes both Faraday Cup (FC) and Macro Multi-Channel Continuous Dynode Electron Multiplier (CEM) ion detectors, and with in this detector, for the electron emission, dual thoria coated iridium (ThO₂/Ir) filament is used. The technical drawings and pictures of this QMS are given in Figure 6.14, together with explanations. In order for this commercial QMS to be adapted to HADs, it was necessary to make changes to the hardware: the FC and CEM systems were disconnected from the commercial flange, and proper support was designed with electrical connections. In this way, the QMS body can work independently from the original QMS controller. Moreover, we also needed the flexibility to send the detected signal to a different data acquisition/analysis device. Changes made in the QMS I/V converter card made in this context are shown in Figure 6.15. At the output of the circuit shown in Figure 6.15 added an Op-amp circuit (will be referred to as analog output), so the FC and CEM signals can be measured directly in different ways (with oscilloscope, data acquisition card, the QMS own software). Next, the ionization zone of the QMS was modified to reduce the background signal (see Figure 6.16 for a more detailed description). In this way, the control electronics and the ionization zone modified QMS was connected and tested in a small chamber pumped by one of the turbopumps. Figure 6.17 shows the CEM signal simultaneously acquired by the QMS proprietary software and analog output signal recorded by an oscilloscope and a data acquisition card (by using Labview interface). As can be seen, the signal with the oscilloscope and data acquisition card is compatible with the signal collected by QMS's software (provided by SRS).



Figure 6.14. a) Technical drawing of the SRS RGA-100 QMS system. The filter and detector section is located in a steel tube, which is indicated by a dashed line in regular use. b) Picture of the part which is formed by ionization region, filter, and detector in a vacuum and the connection flange and CEM has been removed. c) A technical drawing is showing the positions of the FC and CEM detectors (indicated as CDEM in the illustration) on the CF 40 connection flange. d) Images of the inside and outside of the vacuum of the CF 40 connection flange. On the inside of the vacuum, FC and CEM anode can be seen.





Figure 6.15. Top: Company-supplied drawing of the I/V converter board of the SRS electronic control unit. Bottom: Op-amp circuit added to the I/V converter board by us (shown in the dashed line in the top figure) proving analog output. This circuit is connected to the output of the I/V converter, the U211A "logarithmic amplifier (1 kHz) which is fast enough for our measurements (the red point in the top figure). FC and CEM signals both can be measured directly at the output of the circuit.



Figure 6.16. The original state of the ionization zone of the SRS-QMS (a,b). In the helium atom diffraction (HAD) measurement apparatus, the helium atoms scattered through the sample will follow a path perpendicular to the ionization zone (cross beam). However, the original filament of the ionization zone is designed as a ring parallel to this path, and this design is not suitable for the ionization of helium atoms with the highest efficiency. Therefore, the filament is reshaped in the geometry shown in (c). In addition, the QMS is designed as a residual gas analyzer, and the ion collection volume was made large by the SRS company to increase sensitivity. However, since we will use this QMS as a helium detector, such a large ionization zone will increase the background signal since regions not crossed by the He beam will contribute to the detected signal. Therefore, the anode grid volume is reduced to a smaller size in which the helium beam can pass, as shown in (c). Also, holes were opened to allow the helium beam to pass through the repeller grating, but the anode

was not drilled (because it was made of fragile wires) initially. Images are showing the anode grid and repeller after the process (d).



Figure 6.17. The CEM signal received with the proprietary software (top), the signal recorded with the oscilloscope (middle), and the signal received with a Labview interface and data acquisition card (bottom). While the signal is collected against the

time with the oscilloscope and data acquisition card, the QMS own software gives the signal based on the mass number

Following the modification discussed above the next step was to mount the QMS head in the detector box. To this end the vacuum side of the QMS head (including the detector, quadrupole, and ionization zone (see Figure 6.14.b.)) was disconnected from the CF40 adapter and connected to a specially designed adapter in the detector box (see Figure 6.18). The original connecting adapter of the QMS was connected to the appropriate CF40 flange on the diffraction chamber (shown in Figure 6.18.a). For this purpose, the adapter was firstly tested with the Kapton-coated coaxial cable for radio frequency (RF), FC, and CEM high-voltage connections; normal (non-coaxial) Kapton coated cable was used for filament, anode grid, CEM anode, and focus plate connections.



Figure 6.18. Drawings/illustrations of the QMS adapter in the detector box and the cable connections (first iteration). a) Illustration showing the connection configuration of extension cables. b) A technical drawing is showing the QMS in the detector box. c) Picture of the QMS connection adapter with extension cables on it. d) and e) Images showing the connecting adapter in the detector box. These images (d, e) show FC (the cylindrical part in the center of the adapter), but the QMS is not yet attached to the adapter.

In the second iteration of the detector system, a coil of eight 0.25 mm cables were used for CEM anode and filament connections (Figure 6.19). In this way, when the QMS was re-tested, the filament worked smoothly up to an emission current of 1.0

mA. After this stage due to the capacitance of the extension cables, the resonance frequency of the QMS changed and the original RF frequency supplied by the SRS controller was not able to modify the frequency to be tuned at the new conditions; hence, the commercial electronic was modified to enable the injection of an external 5 MHz square wave to the RF card in the control unit. In this way, it was possible to test the QMS inside the diffraction chamber in high vacuum with RP in a stationary state, and the CEM signal could be obtained in the range of 1-100 amu. However, it was not possible to receive signals with FC. In the third iteration, a separate ground line has been connected to FC, due to the fact that failure to receive signals from FC was because of a missing ground connection. This final version of the system is shown in Figure 6.21. After this change, the detector box was connected to RP again, and placed into the diffraction chamber. In the tests conducted with RF-fed externally, data could be collected using both CEM and FC and SRS software (Figure 6.22). However, due to the changes made on the QMS, the peaks were enlarged, and the mass calibration was slightly distorted. However, due to the fact that this detector will primarily be used for He detection, it is sufficient to measure only the He peak correctly. At this stage, the FC and CEM signal were monitored simultaneously while the RP was rotated, and no change/problem was observed in the signals (due to the movement of the extension cables) originating from the rotational movement.



Figure 6.19. Images are showing the QMS adapter and cable connections for the detector box (second iteration). In this picture, QMS is attached to the adapter, and CEM can be seen.



Figure 6.20. Changes made to the external signal input on the QMS controller electronic unit RF card. The JP 103 1 and 2 are connected to each other, and the J100 input has a 4.6 V amplitude and a 5.21 MHZ square wave.



Figure 6.21. QMS adapter for detector box and illustrations of cable connections (third iteration). In this picture, QMS is attached to the adapter, and CEM can be seen.



Figure 6.22. Mass spectra were taken by CEM and FC (with helium in the chamber) by external RF feed. H (1), H₂ (2), He (4), H₂O (18), N₂/CO mix (28) peaks are seen.

6.1.4.2.2 Fixed Quadrupole Mass Spectrometer

Hiden HAL / 3F RC 501 QMS was used as a fixed helium detector in this system. The fixed helium detector operates in the range of 1-500 amu and contains twin oxide coated iridium filament for electron emission and a pulse ion counting Channeltron electron multiplier detector. Maximum operating pressure of fixed QMS is $5x10^{-6}$ Torr, and minimum detectable partial pressure is $5x10^{-15}$ Torr. A schematic drawing of this QMS is given in Figure 6.23, together with explanations. Fixed QMS was mounted just opposite the SMBD chamber and sample holder and this configuration makes it possible to use as TPD, and TOF spectrometer with its translational degree of freedom (so it can be translated for approaching to and moving away from the sample surface).



Figure 6.23. Picture of fixed QMS in the diffraction chamber (top) and schematic representation (bottom). Figure retrieved from ref [190]

6.1.4.3 6-Axis Sample Holder

For helium diffraction experiments, samples should be rotated in three directions. The polar angle (θ) determines, for example, the angle between the incoming helium beam and the sample surface, and must be changed in a very fine manner so as to be able to conduct experiments at different incidence angles. The tilt angle (χ) should be very precisely adjusted to ensure that the sample surface is precisely perpendicular to the incident helium beam. Finally, in order to perform diffraction measurements in different directions in the plane of the sample surface, the azimuthal angle (ϕ) must be changed very precisely. For this reason, the sample holder is designed to move 360° degrees in the θ direction, \pm 90° in the ϕ direction and \pm 10° in the χ direction. It is necessary to move the XY plane of the sample holder very precisely so that the center of rotation of the sample holder can be precisely matched with the center of rotation of the moving QMS detector (or RP). If this alignment is not done correctly, the moving QMS detector angle will be determined incorrectly, which will cause the angle-dependent helium diffraction data to be inaccurate. For this reason, the sample holder is designed to move in X and Y direction by ± 12.5 mm. Finally, the sample holder is designed to vertically move 100 mm in the Z direction in order to be able to carry the samples to different levels of Z (see Figure 6.9.a) in the diffraction chamber. In order to cool the samples to 100 K, the holder is designed to be cooled with both liquid nitrogen and liquid helium. The copper cable connections required for heat transfer have added additional mechanical constraints to the design. The technical drawings and cross-sectional area of the sample holder/manipulator designed in accordance with all these requirements are given in Figure 6.24, and a photograph is shown in Figure 6.25.



Figure 6.24. Technical drawings showing the top-left of the 6-axis manipulator and the sample holder section closely



Figure 6.25. View of the sample holder part of the 6-axis manipulator. There are two separate thermocouples on the sample holder (SH) and the sample holder retainer (R).

The mechanical tests of the 6-axis manipulator were completed first. There were no problems with X, Y, Z, and θ movements. However, some problems were observed in the direction of ϕ and γ . Since these problems were not at the level to affect helium diffraction measurements significantly, and it was considered that it would be neglectable, and the sample holder vacuum tests were started. After the sample holder was connected to the diffraction chamber, all the motors were moved and checked for any leakage during movement. Also, the leak test was performed on all flanges of the manipulator. No problems were identified in these stages. Finally, the sample holder, heating, and cooling performance (with liquid nitrogen) have been tested. The heater was working smoothly. The cooling and heating performance is shown in Figure 6.26 and Figure 6.27 below. These initial tests were performed in an HV environment. During the tests, the diffraction chamber vacuum was at 10^{-8} Torr level, and during the cooling, the sample holder acts as a cold trap to pump water vapor in the environment. It is hoped that the diffraction chamber will be baked before the beginning of the helium diffraction experiments, and with the help of the sublimation pump a base pressure 10^{-10} Torr will be achieved. In this case (under 10^{-10} ¹⁰Torr pressure), it is thought that the water vapor concentration on the sample holder during cooling will not be as much a problem (which will contaminate the samples). Of course, this can only be done by operating the system at ideal base pressure $(10^{-1})^{-1}$ ¹⁰ Torr) and by measuring the helium diffraction on real samples. [In the event of such a problem, flanges to mount liquid nitrogen cold traps and/or to mount a cold head (cryopump) cooled by the helium compressor were placed in the appropriate positions on the diffraction chamber (Figure 6.8)]. At this stage, the heating and cooling performance of the system was found to be sufficient.



Figure 6.26. Cooling performance of the sample holder, graphs are temperature of the sample holder (a) and the pressure of the diffraction chamber (b) versus time during cooling of the sample holder with liquid hydrogen.



Figure 6.27. Heating performance when the e-beam heater is switched on while cooling with liquid nitrogen is in progress. During this test, the electrons were not accelerated (e acceleration voltage = 0) in the e-beam heater. Heating was performed only by controlling the filament voltage (Vf) and filament current (If).

6.2 He Atom Diffraction System First Tests

The components of the HAD system discussed above were individually tested/optimized, and all components were tested comprehensively by connecting them to the diffraction chamber. The first study at this stage was to take the helium beam produced in the He source chamber into the diffraction chamber after being

pulsed in the chopper stage and to measure the intensity of the incoming helium beam with the rotatable detector. In this respect, first of all, the studies were started by aligning the rotation center of the RP with the diffraction chamber (or rather the sample holder rotation center). For this purpose, firstly, using a caliper, RP was roughly shifted to the center of the diffraction chamber. By using the screws shown in Figure 6.28 in the red ring, the RP can be moved parallel to the diffraction chamber base. However, although the centers can be largely overlapped with this method, an excellent result cannot be obtained due to the resistance of the RP differential pumping line to RP motion (see Figure 6.28). As a result of this rough centering, the remaining center-deflection can be compensated by moving the sample holder rotation center (thanks to the 6-axis manipulator XY movement). In addition, the angle of the He source relative to the diffraction chamber (thanks to the bellows adapter) can be altered so that the helium beam path passes through the RP center of rotation. These stages will be discussed in the future.





Figure 6.28. Plot showing the alignment of the RP center of rotation with the center of the diffraction chamber.

After this step, the detector was placed in the box and RP, diffraction chamber, chopper stage, and He source chamber were pumped. During these tests, turbopumps and RP's differentially pumping lines were pumped through the chopper stage (see

Figure 6.3 and Figure 6.4 for pumping connections). Under these conditions, the vacuum levels of the system were as follows:

- IGK (diffraction chamber): 5,8x10⁻⁸ Torr
- IGD (detector box): 8,5x10⁻⁸ Torr
- IGH (He source):5,5x10⁻⁶ Torr
- IGC (chopper stage):5,2x10⁻⁶ Torr

CCG (RP):1,5x10⁻⁶ Torr



Figure 6.29. Illustration showing the method of alignment with a telescope. The illustration also shows the telescope view line (blue dashed line) which is also indicated in the picture above.

Collimator

While the entire system is under vacuum, the detector box is placed in front of the collimator (called CSC) in the chopper stage. Next, using a telescope, the collimators on the detector box (called DRC) are aligned with the CSC and the CF 16 view-port. After this stage, the intensity and width of the helium beam were measured by

rotating the detector (during these measurements, the sample holder was removed from the beam path, and only the incoming helium beam was measured). This measurement was carried out in two ways: In the first method, a continuous (not chopped) He beam was used, and CEM signal of the detector was recorded, while rotating the detector continuously, with the SRS company's computer software and plotted against detector angle (known rotation speed is used as a conversion constant). The resulting graph is shown in Figure 6.30.a. In the second method, the signal of the helium beam was measured while chopping the beam at 300 Hz and using the lock-in amplifier and the analog output circuit shown in Figure 6.15. In this measurement, the detector angle is changed in steps, and the average signal is recorded by waiting for a certain time in each position. The resulting graph is shown in Figure 30.b. In the first graph, it can be seen that the incoming helium peak is symmetrical, but consists of a combination of 5 peaks. This peak shape is thought to originate from the anode grid in the ionization zone of the detector. As mentioned in section 3.2.3, it was thought that the grid wires of the anode grid would not affect the shape of the helium beam because they were too thin. However, the resulting peak shape shows that the anode grid wires divide the helium beam. This division did not appear in the signal received with the lock-in, but the symmetry of the peak was lost. After these measurements, the detector box was rotated 180° to check the alignment of the system.

In the case of perfect alignment, after the 180° rotation, the center of the peak must be reached. However, as shown in Figure 6.31, there is a deficiency of 1,1°. One of two things may have been the cause of this deficiency. The first of these, the collimators on the detector box, were not fully face to face (shown in red and orange in Figure 6.31). The second reason may be, RP, could not be fully aligned to the center of the base of the diffraction chamber. In light of these results, in order to eliminate the problems described above and to reduce the peak width, some changes were made by removing the detector box and QMS from the system. In this context, firstly, a hole was drilled on the anode grid, which the helium beam can pass, and the filament was re-shaped so as not to block the helium beam. Besides, the alignment of the collimators on the detector box was checked, and the collimators have been replaced with smaller ones to provide better alignment and reduce peak width. The changes are summarized in Figure 6.32.

As a result, it can be said that in the light of the information given above, the construction of the HAD system is over and the HAD tests can be started after the system is re-aligned. The most important task at this stage is to write a computer code (Labview) for data collection.



Figure 6.30. The intensity of the incoming helium beam measured by the CEM detector. Top: Recorded against time by the SRS firmware. Bottom: Recorded signal with the lock-in amplifier. The detector moves continuously when data is collected with the SRS software. When the signal was collected with the lock-in, the detector was moved differentially, and the signal was collected for a certain period of time at each angle position



Figure 6.31 The angle corresponds to the angle of the CEM signal recorded in counter clockwise direction by the SRS software while the detector is rotated continuously for 180 degrees. At the bottom, the measurement is summarized schematically (top view of the diffraction chamber is shown) Center of rotation is indicated by the star symbol.



Figure 6.32. Pictures, showing the changes made in DRC and QMS anode grid.

CONCLUSION

In summary, in this study, two main objectives were aimed. The first of these was to investigate the effects of DR, thickness, molecular beam kinetic energy, substrate chemistry on the nucleation and growth mechanism of PFP thin films. For this purpose, PFP films were grown on chemically different substrates (mica, TSAu, and M1) with different thicknesses and DR by means of SMBD technique. Then AFM, SE, contact angle, XPS, s-SNOM measurements were performed to characterize these films. In addition, RAIRS measurements were conducted to characterize M1 SAMs used as substrate. The conclusions can be summarized as follows:

- Substrates are not completely covered with PFP films up to 2.5 nm thickness. The first layer of PFP thin films tends to wet the substrate surfaces, and after the first layer is almost completely covered, the second and other layers start to grow with needle-like grains which indicate a layer plus island (Stranski– Krastanow) growth mode.
- Surface hydrophobicity and DR directly affect the MGS and dendriticy of the first layer grains in a way that as the DR decreases (or hydrophobicity of substrate increase) MGS and dendriticy order increase.
- iii. The grains in the first layer of PFP thin films were circular. As the film thickness increases, substrate-molecule interactions are shielded by the first layer, and upper layers grow with needle-like grains. Grain heights are similar in the first and upper layers and are about 1.5 nm, which is equal to the length of PFP molecules. This result shows that the molecules are standing up along their long axis on the substrate with herringbone arrangement (see s-SNOM results). As opposed to previous results regarding metal surfaces in the literature, the PFP molecules were found to be standing up even in the first layer on the gold surface.

- iv. The film formation is faster in the high kinetic energy beam state, however n the low energy case, the 2nd and 3rd layers of films starts to grow on the 1st layer surface sooner than those of high kinetic energy state.
- v. The difference between the crystal structure of the thin-film phase (1 nm) and bulk phase (15 nm) can cause the very small peak shifts to higher energies in the absorption spectrum. The small shifts points to a different molecular environment of PFP molecules which could be attributed to strong intermolecular interactions between PFP molecules.
- vi. The characteristic peaks of M1, M9, and M1-COOH SAMs were found at 2586, 2629, and 2600 cm⁻¹, respectively, thanks to RAIRS measurements.

The second purpose of this thesis was to update the existing HAD system in our laboratory to make it more compact and with extended capabilities that would enable us to study organic films. Though, due to the very ambitious and technically challenging design of the new system and budget limitations, the construction of the system could not be finalized, initial vacuum, mechanical and electronic tests are completed and after a final optimization and control software implementation the system is ready to gather data.

REFERENCES

- Koch N. Electronic structure of interfaces with conjugated organic materials
 // Physica Status Solidi Rapid Research Letters. 2012. Vol. 6, № 7. P. 277–293.
- Klauk H. Organic thin-film transistors // Chemical Society Reviews. 2010.
 Vol. 39, № 7. P. 2643–2666.
- Fraxedas J. Perspectives on Thin Molecular Organic Films // Adv. Mater.
 2002. Vol. 14, № 22. P. 1603–1614.
- 4. Veres J., Ogier S., Lloyd G., de Leeuw D. Gate Insulators in Organic Field-Effect Transistors // Chem. Mater. 2004. Vol. 16, № 23. P. 4543–4555.
- Ruiz R., Papadimitratos A., Mayer A.C., Malliaras G.G. Thickness dependence of mobility in pentacene thin-film transistors // Adv. Mater. 2005. Vol. 17, № 14. P. 1795–1798.
- Dinelli F., Murgia M., Levy P., Cavallini M., Biscarini F., De Leeuw D.M. Spatially Correlated Charge Transport in Organic Thin Film Transistors // Phys. Rev. Lett. 2004. Vol. 92, № 11. P. 90–93.
- Muck T., Wagner V., Bass U., Leufgen M., Geurts J., Molenkamp L.W. In situ electrical characterization of DH4T field-effect transistors // Synth. Met. 2004. Vol. 146, № 3. P. 317–320.
- Ueki H., Yano H., Cai L., Ohuchi H., Takayanagi Y., Duan Z.F., Nishioka Y. Influence of oxygen exposure on instabilities of perfluoropentacene transistor characteristics with different gate insulators // Prog. Nat. Sci. Mater. Int. Chinese Materials Research Society, 2011. Vol. 21, № 1. P. 12– 16.
- Breuer T., Witte G. Controlling nanostructures by templated templates: Inheriting molecular orientation in binary heterostructures // ACS Appl.

Mater. Interfaces. 2015. Vol. 7, № 36. P. 20485–20492.

- Breuer T., Witte G. Thermally activated intermixture in pentaceneperfluoropentacene heterostructures // J. Chem. Phys. American Institute of Physics, 2013. Vol. 138, № 11. P. 114901.
- Yavuz A., Danlşman M.F. Study on the Effect of Chemically Different Substrates on Nucleation and Growth Mechanism of Perfluoropentacene Thin Films // J. Phys. Chem. C. 2019. Vol. 123, № 32. P. 19610–19618.
- Yamagishi M., Takeya J., Tominari Y., Nakazawa Y., Kuroda T., Ikehata S., Uno M., Nishikawa T., Kawase T. High-mobility double-gate organic single-crystal transistors with organic crystal gate insulators // Appl. Phys. Lett. American Institute of Physics, 2007. Vol. 90, № 18. P. 182117.
- Hotta S., Yamao T., Bisri S.Z., Takenobu T., Iwasa Y. Organic singlecrystal light-emitting field-effect transistors // J. Mater. Chem. C. 2014. Vol. 2, № 6. P. 965–980.
- 14. Anni M., Lattante S. Organic Lasers // Organic Lasers. 2018. Vol. 1. 338 p.
- De Oteyza D.G., Barrena E., Dosch H., Ortega J.E., Wakayama Y. Tunable symmetry and periodicity in binary supramolecular nanostructures // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2011. Vol. 13, № 10. P. 4220–4223.
- Huang H., Sun J.T., Feng Y.P., Chen W., Wee A.T.S. Epitaxial growth of diindenoperylene ultrathin films on Ag(111) investigated by LT-STM and LEED // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2011. Vol. 13, № 47. P. 20933–20938.
- Schuster B.E., Casu M.B., Biswas I., Hinderhofer A., Gerlach A., Schreiber F., Chassé T. Role of the substrate in electronic structure, molecular orientation, and morphology of organic thin films: Diindenoperylene on rutile TiO 2(110) // Phys. Chem. Chem. Phys. Royal Society of Chemistry,

2009. Vol. 11, № 40. P. 9000–9004.

- Zou T., Wang X., Ju H., Wu Q., Guo T., Wu W., Wang H. Crystal structure tuning in organic nanomaterials for fast response and high sensitivity visible-NIR photo-detector // J. Mater. Chem. C. Royal Society of Chemistry, 2018. Vol. 6, № 6. P. 1495–1503.
- Yang J.L., Schumann S., Jones T.S. Nanowire-array films of copper hexadecafluorophthalocyanine (F 16CuPc) fabricated by templated growth // J. Mater. Chem. Royal Society of Chemistry, 2011. Vol. 21, № 15. P. 5812– 5816.
- 20. Wu F.C., Cheng H.L., Yen C.H., Lin J.W., Liu S.J., Chou W.Y., Tang F.C. Electron transport properties in fluorinated copper-phthalocyanine films: Importance of vibrational reorganization energy and molecular microstructure // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2010. Vol. 12, № 9. P. 2098–2106.
- Schweicher G., Olivier Y., Lemaur V., Geerts Y.H. What currently limits charge carrier mobility in crystals of molecular semiconductors? // Isr. J. Chem. 2014. Vol. 54, № 5–6. P. 595–620.
- Schweicher G., Olivier Y., Lemaur V., Geerts Y.H. What currently limits charge carrier mobility in crystals of molecular semiconductors? // Isr. J. Chem. 2014. Vol. 54, № 5–6. P. 595–620.
- Huang H., Chen S., Gao X., Chen W., Wee A.T.S. Structural and electronic properties of PTCDA thin films on epitaxial graphene // ACS Nano. American Chemical Society, 2009. Vol. 3, № 11. P. 3431–3436.
- Nguyen L.N., Kumar Pradhan S., Yen C.N., Lin M.C., Chen C.H., Wu C.S., Chang-Liao K.S., Lin M.T., Chen C.D. High performance phototransistors based on single crystalline perylene-tetracarboxylic-dianhydride nanoparticle // Appl. Phys. Lett. American Institute of Physics, 2013. Vol. 103, № 18. P. 183301.

- Chen H., Zhang W., Li M., He G., Guo X. Interface Engineering in Organic Field-Effect Transistors: Principles, Applications, and Perspectives // Chem. Rev. American Chemical Society, 2020. Vol. 120, № 5. P. 2879–2949.
- Rocio F. Electron Microscopy Characterization of Pentacene and Perfluoropentacene Grown on Different Substrates. Philipps-Universitat Marburg, 2017.
- 27. Salzmann I. Structural and energetic properties of pentacene derivatives and heterostructures. 2008.
- 28. Frank C.H. Real-time x-ray scattering studies on organic thin films. 2014.
- Yao Z.F., Wang J.Y., Pei J. Control of π-π Stacking via Crystal Engineering in Organic Conjugated Small Molecule Crystals // Crystal Growth and Design. American Chemical Society, 2018. Vol. 18, № 1. P. 7–15.
- Fujikawa T., Mitoma N., Wakamiya A., Saeki A., Segawa Y., Itami K. Synthesis, properties, and crystal structures of π-extended double
 [6]helicenes: Contorted multi-dimensional stacking lattice // Org. Biomol. Chem. Royal Society of Chemistry, 2017. Vol. 15, № 21. P. 4697–4703.
- Campbell J.E., Yang J., Day G.M. Predicted energy-structure-function maps for the evaluation of small molecule organic semiconductors // J. Mater. Chem. C. Royal Society of Chemistry, 2017. Vol. 5, № 30. P. 7574–7584.
- 32. Venables J.A., Spiller G.D.T., Hanbucken M. Nucleation and growth of thin films // Reports on Progress in Physics. IOP Publishing, 1984. Vol. 47, № 4. P. 399–459.
- Kowarik S., Gerlach A., Schreiber F. Organic molecular beam deposition: Fundamentals, growth dynamics, and in situ studies // J. Phys. Condens. Matter. 2008. Vol. 20, № 18.
- Schreiber F. Organic molecular beam deposition: Growth studies beyond the first monolayer // Phys. Status Solidi Appl. Res. 2004. Vol. 201, № 6. P.
1037-1054.

- Khairnar A. Chapter 2 Thin Film Deposition and Characterization Techniques // Thin Film Growth Charact. Tech. 2010. № 2014. P. 1–36.
- Venables J.A. Introduction to Surface and Thin Film Processes // Introduction to Surface and Thin Film Processes. Cambridge University Press, 2000.
- Steckelmacher W. Vacuum physics and techniques // Vacuum. Chapman & Hall, 1994. Vol. 45, № 12. P. 1229.
- Gas Molecules and Gas Flow [Electronic resource]. URL: https://vacaero.com/information-resources/vacuum-pump-technologyeducation-and-training/9364-gas-molecules-and-gas-flow.html (accessed: 02.05.2020).
- Halwidl D. Development of an Effusive Molecular Beam Apparatus // Development of an Effusive Molecular Beam Apparatus. 2016.
- Iannotta S., Toccoli T. Supersonic molecular beam growth of thin films of organic materials: A novel approach to controlling the structure, morphology, and functional properties // J. Polym. Sci. Part B Polym. Phys. John Wiley & Sons, Ltd, 2003. Vol. 41, № 21. P. 2501–2521.
- Hudson J.B., Diehl R.D. Surface Science: An Introduction // Am. J. Phys. J.
 Wiley & Sons, 1992. Vol. 60, № 12. P. 1155–1156.
- Yavuz A., Sohrabnia N., Yilmaz A., Danışman M.F. Mixed carboranethiol self-assembled monolayers on gold surfaces // Appl. Surf. Sci. 2017. Vol. 413. P. 233–241.
- Nuzzo R.G., Allara D.L. Adsorption of Bifunctional Organic Disulfides on Gold Surfaces // Journal of the American Chemical Society. American Chemical Society, 1983. Vol. 105, № 13. P. 4481–4483.

- Schreiber F. Structure and growth of self-assembling monolayers // Prog.
 Surf. Sci. Elsevier Science Ltd, 2000. Vol. 65, № 5–8. P. 151–257.
- Langmuir I. Oil lenses on water and the nature of monomolecular expanded films // J. Chem. Phys. American Institute of Physics, 1933. Vol. 1, № 11. P. 756–776.
- 46. Safran S.A., Robbins M.O., Garoff S. Tilt and splay of surfactants on surfaces // Phys. Rev. A. American Physical Society, 1986. Vol. 33, № 3. P. 2186–2189.
- Ulman A., Eilers J.E., Tillman N. Packing and Molecular Orientation of Alkanethiol Monolayers on Gold Surfaces // Langmuir. American Chemical Society, 1989. Vol. 5, № 5. P. 1147–1152.
- 48. Rajalingam K., Bashir A., Badin M., Schröder F., Hardman N., Strunskus T., Fischer R.A., Wöll C. Chemistry in Confined Geometries: Reactions at an Organic Surface // ChemPhysChem. Wiley-VCH Verlag, 2007. Vol. 8, № 5. P. 657–660.
- 49. Ulman A. Formation and structure of self-assembled monolayers // Chem.
 Rev. American Chemical Society, 1996. Vol. 96, № 4. P. 1533–1554.
- Wesch A., Dannenberger O., Woll C., Wolff J.J., Buck M. Structural investigation of a self-assembled monolayer of a p-nitroanilino-terminated thiol // Langmuir. American Chemical Society, 1996. Vol. 12, № 22. P. 5330–5337.
- Käfer D., Bashir A., Witte G. Interplay of anchoring and ordering in aromatic self-assembled monolayers // J. Phys. Chem. C. American Chemical Society, 2007. Vol. 111, № 28. P. 10546–10551.
- Reed M.A., Zhou C., Muller C.J., Burgin T.P., Tour J.M. Conductance of a molecular junction // Science (80-.). American Assoc for the Advancement of Science, 1997. Vol. 278, № 5336. P. 252–254.

- 53. Pflaum J., Bracco G., Schreiber F., Colorado R., Shmakova O.E., Lee T.R., Scoles G., Kahn A. Structure and electronic properties of CH3- and CF3terminated alkanethiol monolayers on Au(1 1 1): A scanning tunneling microscopy, surface X-ray and helium scattering study // Surf. Sci. North-Holland, 2002. Vol. 498, № 1–2. P. 89–104.
- Bain C.D., Troughton E.B., Tao Y.-T., Evall J., Whitesides G.M., Nuzzo R.G. Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold // J. Am. Chem. Soc. 1989. Vol. 111.
- 55. Love J.C., Estroff L.A., Kriebel J.K., Nuzzo R.G., Whitesides G.M. Selfassembled monolayers of thiolates on metals as a form of nanotechnology // Chemical Reviews. 2005. Vol. 105, № 4. P. 1103–1169.
- 56. Gittins D.I., Bethell D., Schiffrin D.J., Nichols R.J. A nanometre-scale electronic switch consisting of a metal cluster and redox-addressable groups // Nature. 2000. Vol. 408, № 6808. P. 67–69.
- 57. Blomberg E., Claesson P.M., Konradsson P., Liedberg B. Globotriose- and oligo(ethylene glycol)-terminated self-assembled monolayers: surface forces, wetting, and surfactant adsorption // Langmuir. 2006. Vol. 22, № 24. P. 10038–10046.
- 58. Vericat C., Vela M.E., Benitez G., Carro P., Salvarezza R.C. Self-assembled monolayers of thiols and dithiols on gold: New challenges for a well-known system // Chemical Society Reviews. 2010. Vol. 39, № 5. P. 1805–1834.
- 59. Biebuyck H.A., Whitesides G.M. Interchange between Monolayers on Gold Formed from Unsymmetrical Disulfides and Solutions of Thiols: Evidence for Sulfur-Sulfur Bond Cleavage by Gold Metal // Langmuir. American Chemical Society, 1993. Vol. 9, № 7. P. 1766–1770.
- 60. Gottschalck J., Hammer B. A density functional theory study of the adsorption of sulfur, mercapto, and methylthiolate on Au(111) // J. Chem.

Phys. American Institute of Physics, 2002. Vol. 116, № 2. P. 784–790.

- Karl N. Organic semiconductors. In: Queisser H.J. (eds) Festkörperprobleme
 // Organic semiconductors. In: Queisser H.J. (eds) Festkörperprobleme.
 Springer Berlin Heidelberg, 1974. P. 261–290.
- Schwoerer M., Wolf H.C. Organic Molecular Solids // Organic Molecular Solids. Wiley-VCH, 2008. 1–427 p.
- Bao Q., Braun S., Wang C., Liu X., Fahlman M. Interfaces of (Ultra)thin Polymer Films in Organic Electronics // Adv. Mater. Interfaces. 2019. Vol. 6, № 1. P. 1–15.
- 64. Hinderhofer A., Heinemeyer U., Gerlach A., Kowarik S., Jacobs R.M.J., Sakamoto Y., Suzuki T., Schreiber F. Optical properties of pentacene and perfluoropentacene thin films // J. Chem. Phys. 2007. Vol. 127, № 19. P. 1–6.
- Broch K., Heinemeyer U., Hinderhofer A., Anger F., Scholz R., Gerlach A., Schreiber F. Optical evidence for intermolecular coupling in mixed films of pentacene and perfluoropentacene // Phys. Rev. B - Condens. Matter Mater. Phys. 2011. Vol. 83, № 24.
- 66. Jariwala D., Howell S.L., Chen K.S., Kang J., Sangwan V.K., Filippone S.A., Turrisi R., Marks T.J., Lauhon L.J., Hersam M.C. Hybrid, Gate-Tunable, van der Waals p-n Heterojunctions from Pentacene and MoS2 // Nano Lett. American Chemical Society, 2016. Vol. 16, № 1. P. 497–503.
- 67. Hill I.G., Kahn A., Soos Z.G., Pascal R.A. Charge-separation energy in films of π -conjugated organic molecules // Chem. Phys. Lett. Elsevier, 2000. Vol. 327, № 3–4. P. 181–188.
- Soos Z.G., Tsiper E. V., Painelli A. Polarization in organic molecular crystals and charge-transfer salts // J. Lumin. 2004. Vol. 110, № 4 SPEC. ISS. P. 332–341.

- Peumans P., Yakimov A., Forrest S.R. Small molecular weight organic thinfilm photodetectors and solar cells // Journal of Applied Physics. American Institute of Physics, 2003. Vol. 93, № 7. P. 3693–3723.
- Salaneck W.R. Intermolecular relaxation energies in anthracene // Phys.
 Rev. Lett. American Physical Society, 1978. Vol. 40, № 1. P. 60–63.
- Knupfer M., Peisert H. Electronic properties of interfaces between model organic semiconductors and metals // Phys. Status Solidi Appl. Res. John Wiley & Sons, Ltd, 2004. Vol. 201, № 6. P. 1055–1074.
- Koch N., Ueno N., Wee A.T.S. The Molecule-Metal Interface // The Molecule-Metal Interface / ed. Koch N., Ueno N., Wee A.T.S. Weinheim, Germany: Wiley-VCH, 2013.
- Hill I.G., Rajagopal A., Kahn A., Hu Y. Molecular level alignment at organic semiconductor-metal interfaces // Applied Physics Letters. 1998.
 Vol. 73, № 5. 662–664 p.
- Tsiper E. V., Soos Z.G., Gao W., Kahn A. Eletronic polarization at surfaces and thin films of organic molecular crystals: PTCDA // Chem. Phys. Lett. 2002. Vol. 360, № 1–2. P. 47–52.
- 75. Sze S.M., Ng K.K. Frontmatter // Phys. Semicond. Devices. 2006. P. i–x.
- 76. Schreiber F. Organic molecular beam deposition: Growth studies beyond the first monolayer // Phys. Status Solidi Appl. Res. 2004. Vol. 201, № 6. P. 1037–1054.
- 77. Kahn A., Koch N., Gao W. Electronic structure and electrical properties of interfaces between metals and π-conjugated molecular films // J. Polym. Sci. Part B Polym. Phys. John Wiley and Sons Inc., 2003. Vol. 41, № 21. P. 2529–2548.
- Koch N., Kahn A., Ghijsen J., Pireaux J.J., Schwartz J., Johnson R.L., Elschner A. Conjugated organic molecules on metal versus polymer

electrodes: Demonstration of a key energy level alignment mechanism // Appl. Phys. Lett. American Institute of Physics, 2003. Vol. 82, № 1. P. 70– 72.

- 79. Cahen D., Kahn A. Electron energetics at surfaces and interfaces: Concepts and experiments // Adv. Mater. John Wiley & Sons, Ltd, 2003. Vol. 15, № 4. P. 271–277.
- Knupfer M., Peisert H. Electronic properties of interfaces between model organic semiconductors and metals // Phys. Status Solidi Appl. Res. John Wiley & Sons, Ltd, 2004. Vol. 201, № 6. P. 1055–1074.
- Kaneko S. Design and Control of Highly Conductive Single-Molecule Junctions. 2017.
- Koch N., Ueno N., Wee A.T.S. The Molecule-Metal Interface // The Molecule-Metal Interface / ed. Koch N. Singapore: Wiley-VCH, 2013.
- Bisri S.Z., Takenobu T., Takahashi T., Iwasa Y. Electron transport in rubrene single-crystal transistors // Appl. Phys. Lett. American Institute of Physics, 2010. Vol. 96, № 18. P. 183304.
- Takenobu T., Takahashi T., Takeya J., Iwasa Y. Effect of metal electrodes on rubrene single-crystal transistors // Appl. Phys. Lett. American Institute of Physics, 2007. Vol. 90, № 1. P. 013507.
- Rost C., Gundlach D.J., Karg S., Rieß W. Ambipolar organic field-effect transistor based on an organic heterostructure // J. Appl. Phys. 2004. Vol. 95, № 10. P. 5782–5787.
- 86. Evans S.D., Urankar E., Ulman A., Ferris N. Self-Assembled Monolayers of Alkanethiols Containing a Polar Aromatic Group: Effects of the Dipole Position on Molecular Packing, Orientation, and Surface Wetting Properties // J. Am. Chem. Soc. 1991. Vol. 113, № 11. P. 4121–4131.
- 87. Poirier G.E. Characterization of organosulfur molecular monolayers on

Au(111) using scanning tunneling microscopy // Chem. Rev. 1997. Vol. 97, № 4. P. 1117–1127.

- 88. Weiss P.S. Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements // Acc. Chem. Res. 2008. Vol. 41, № 12. P. 1772–1781.
- Albayrak E., Karabuga S., Bracco G., Danisman M.F. Study of the helium cross-section of unsymmetric disulfide self-assembled monolayers on Au(111) // Appl. Surf. Sci. 2016. Vol. 390. P. 283–288.
- 90. Albayrak E., Karabuga S., Bracco G., Danisman M.F. Investigation of the deposition and thermal behavior of striped phases of unsymmetric disulfide self-assembled monolayers on Au(111): The case of 11-hydroxyundecyl decyl disulfide // J. Chem. Phys. 2015. Vol. 142, № 1.
- 91. Heister K., Allara D.L., Bahnck K., Frey S., Zharnikov M., Grunze M. Deviations from 1 : 1 compositions in self-assembled monolayers formed from adsorption of asymmetric dialkyl disulfides on gold // Langmuir. 1999. Vol. 15, № 17. P. 5440–5443.
- 92. Watcharinyanon S., Moons E., Johansson L.S.O. Mixed Self-Assembled Monolayers of Ferrocene-Terminated and Unsubstituted Alkanethiols on Gold: Surface Structure and Work Function // J. Phys. Chem. C. 2009. Vol. 113, № 5. P. 1972–1979.
- 93. Campbell I.H., Rubin S., Zawodzinski T.A., Kress J.D., Martin R.L., Smith D.L., Barashkov N.N., Ferraris J.P. Controlling Schottky energy barriers in organic electronic devices using self-assembled monolayers // Phys. Rev. B. 1996. Vol. 54, № 20. P. 14321–14324.
- 94. Witte G., Lukas S., Bagus P.S., Woll C. Vacuum level alignment at organic/metal junctions: "Cushion" effect and the interface dipole // Appl. Phys. Lett. 2005. Vol. 87, № 26. P. 3.

- 95. Chen C.-Y., Wu K.-Y., Chao Y.-C., Zan H.-W., Meng H.-F., Tao Y.-T. Concomitant tuning of metal work function and wetting property with mixed self-assembled monolayers // Org. Electron. 2011. Vol. 12, № 1. P. 148– 153.
- 96. Kim J., Rim Y.S., Liu Y., Serino A.C., Thomas J.C., Chen H., Yang Y., Weiss P.S. Interface control in organic electronics using mixed monolayers of carboranethiol isomers // Nano Lett. 2014. Vol. 14, № 5. P. 2946–2951.
- 97. Hohman J.N., Zhang P., Morin E.I., Han P., Kim M., Kurland A.R., McClanahan P.D., Balema V.P., Weiss P.S. Self-Assembly of carboranethiol isomers on Au{111}: Intermolecular interactions determined by molecular dipole orientations // ACS Nano. UTC, 2009. Vol. 3, № 3. P. 527–536.
- 98. Hohman J.N., Claridge S.A., Kim M., Weiss P.S. Cage molecules for self-assembly // Mater. Sci. Eng. R Reports. Elsevier B.V., 2010. Vol. 70, № 3–6. P. 188–208.
- 99. Lubben J.F., Base T., Rupper P., Kunniger T., Machacek J., Guimond S. Tuning the surface potential of Ag surfaces by chemisorption of oppositely-oriented thiolated carborane dipoles // J. Colloid Interface Sci. 2011. Vol. 354, № 1. P. 168–174.
- 100. Base T., Bastl Z., Plzak Z., Grygar T., Plesek J., Carr M.J., Malina V., Subrt J., Bohacek J., Vecernikova E., Kriz O. Carboranethiol-modified gold surfaces. A study and comparison of modified cluster and flat surfaces // Langmuir. 2005. Vol. 21, № 17. P. 7776–7785.
- Schwartz J.J., Mendoza A.M., Wattanatorn N., Zhao Y., Nguyen V.T., Spokoyny A.M., Mirkin C.A., Baše T., Weiss P.S. Surface dipole control of liquid crystal alignment // J. Am. Chem. Soc. 2016. Vol. 138, № 18. P. 5957–5967.
- Thomas J.C., Boldog I., Auluck H.S., Bereciartua P.J., Dusek M., Machacek
 J., Bastl Z., Weiss P.S., Base T. Self-Assembled p-Carborane Analogue of p-

Mercaptobenzoic Acid on Au{111} // Chem. Mater. 2015. Vol. 27, № 15. P. 5425–5435.

- 103. von Wrochem F., Scholz F., Gao D.Q., Nothofer H.G., Yasuda A., Wessels J.M., Roy S., Chen X.D., Michl J. High-Band-Gap Polycrystalline Monolayers of a 12-Vertex p-Carborane on Au(111) // J. Phys. Chem. Lett. 2010. Vol. 1, № 24. P. 3471–3477.
- Bregadze V.I. Dicarba-closo-dodecaboranes C2B10H12 and Their Derivatives // Chem. Rev. 1992. Vol. 92, № 2. P. 209–223.
- 105. Base T., Bastl Z., Plzak Z., Grygar T., Plesek J., Carr M.J., Malina V., Subrt J., Bohacek J., Vecernikova E., Kriz O. Carboranethiol-modified gold surfaces. A study and comparison of modified cluster and flat surfaces // Langmuir. 2005. Vol. 21, № 17. P. 7776–7785.
- Plesek J. Potential Applications of the Boron Cluster Compounds // Chem. Rev. 1992. Vol. 92, № 2. P. 269–278.
- 107. Yoshizaki T., Shiro M., Nakagawa Y., Watanabe H. Amine-catalyzed hydrolysis of bromomethylcarboranes // Inorg. Chem. 1969. Vol. 8, № 3. P. 698–699.
- 108. Frank R., Boehnke S., Aliev A., Hey-Hawkins E. From ortho-carbaborane-9-thiol towards new building blocks // Polyhedron. 2012. Vol. 39, № 1. P. 9–13.
- 109. Langecker J., Fejfarova K., Dusek M., Rentsch D., Base T. Carbonsubstituted 9,12-dimercapto-1,2-dicarba-closo-dodecaboranes via a 9,12bis(methoxy-methylthio)-1,2-dicarba-closo-dodecaborane precursor // Polyhedron. 2012. Vol. 45, № 1. P. 144–151.
- 110. Hohman J.N., Zhang P., Morin E.I., Han P., Kim M., Kurland A.R., McClanahan P.D., Balema V.P., Weiss P.S. Self-Assembly of Carboranethiol Isomers on Au{111}: Intermolecular Interactions

Determined by Molecular Dipole Orientations // ACS Nano. 2009. Vol. 3, № 3. P. 527–536.

- 111. Mete E., Yilmaz A., Danisman M.F. A van der Waals density functional investigation of carboranethiol self-assembled monolayers on Au(111) // Phys. Chem. Chem. Phys. 2016. Vol. 18, № 18. P. 12920–12927.
- Simbrunner J., Hofer S., Schrode B., Garmshausen Y., Hecht S., Resel R., Salzmann I. Indexing grazing-incidence X-ray diffraction patterns of thin films: Lattices of higher symmetry // J. Appl. Crystallogr. Wiley-Blackwell, 2019. Vol. 52, № 2. P. 428–439.
- 113. Resel R., Bainschab M., Pichler A., DIngemans T., Simbrunner C., Stangl J., Salzmann I. Multiple scattering in grazing-incidence X-ray diffraction: Impact on lattice-constant determination in thin films // J. Synchrotron Radiat. International Union of Crystallography, 2016. Vol. 23, № 3. P. 729–734.
- 114. Dutta P. SPECIAL SECTION: SURFACE CHARACTERIZATION
 Grazing incidence X-ray diffraction // Curr. Sci. 2000. Vol. 78, № 12. P.
 1474–1483.
- 115. Farías D., Rieder K.H. Atomic beam diffraction from solid surfaces // Reports Prog. Phys. IOP Publishing, 1998. Vol. 61, № 12. P. 1575–1664.
- Kraus P., Tamtögl A., Mayrhofer-Reinhartshuber M., Apolloner F.,
 Gösweiner C., Miret-Artés S., Ernst W.E. Surface Structure of Bi(111) from Helium Atom Scattering Measurements. Inelastic Close-Coupling Formalism // J. Phys. Chem. C. American Chemical Society, 2015. Vol. 119, № 30. P. 17235–17242.
- Ernst W.E. Atomic Scale Dynamics at Surfaces: Theory and Experimental Studies with Helium Atom Scattering Giorgio Benedek and J. Peter Toennies, Springer, New York, NY, 2018. 652 pp. ISBN: 3662564416. // Microsc. Microanal. Cambridge University Press (CUP), 2020. Vol. 26, №

1. P. 182–182.

- Mete E., Demiroğlu I., Albayrak E., Bracco G., Ellialtioğlu Ş., Danişman M.F. Influence of steps on the tilting and adsorption dynamics of ordered pentacene films on vicinal Ag(111) surfaces // J. Phys. Chem. C. 2012. Vol. 116, № 36. P. 19429–19433.
- 119. Albayrak E., Danişman M.F. Helium diffraction study of low coverage phases of mercaptoundecanol and octadecanethiol self-assembled monolayers on Au(111) prepared by supersonic molecular beam deposition // J. Phys. Chem. C. 2013. Vol. 117, № 19. P. 9801–9811.
- 120. Albayrak E., Karabuga S., Bracco G., Danişman M.F. 11-Hydroxyundecyl octadecyl disulfide self-assembled monolayers on Au(1 1 1) // Appl. Surf. Sci. 2014. Vol. 311. P. 643–647.
- 121. Albayrak E., Karabuga S., Bracco G., Danışman M.F. Study of the helium cross-section of unsymmetric disulfide self-assembled monolayers on Au(111) // Appl. Surf. Sci. Elsevier B.V., 2016. Vol. 390. P. 283–288.
- Albayrak E., Danişman M.F. Helium diffraction study of pentacene films on Au(1 1 1) // Appl. Surf. Sci. 2014. Vol. 295. P. 54–58.
- 123. Hofmann F., Toennies J.P. High-resolution helium atom time-of-flight spectroscopy of low-frequency vibrations of adsorbates // Chem. Rev. American Chemical Society, 1996. Vol. 96, № 4. P. 1307–1326.
- 124. Graham A.P. The low energy dynamics of adsorbates on metal surfaces investigated with helium atom scattering // Surface Science Reports. North-Holland, 2003. Vol. 49, № 4–5. P. 115–168.
- 125. Albayrak E., Karabuga S., Bracco G., Danışman M.F. Study of the helium cross-section of unsymmetric disulfide self-assembled monolayers on Au(111) // Appl. Surf. Sci. 2016. Vol. 390. P. 283–288.
- 126. Cossy J. et al. Friedel–Crafts Acylation [Electronic resource] // Ketones.

2005. P. 1. URL: https://www.organic-

chemistry.org/namedreactions/friedel-crafts-acylation.shtm (accessed: 28.03.2020).

- 127. Sakamoto Y., Suzuki T., Kobayashi M., Gao Y., Fukai Y., Inoue Y., Sato F., Tokito S. Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene. 2004.
- 128. Salzmann I. et al. Terms of Use Epitaxial Growth of π Stacked Per fl uoropentacene on Graphene-Coated Quartz // ACS Nano. 2012. Vol. 6, № 12. P. 10874–10883.
- 129. Salzmann I., Duhm S., Heimel G., Rabe J.P., Koch N., Oehzelt M., Sakamoto Y., Suzuki T. Structural order in perfluoropentacene thin films and heterostructures with pentacene // Langmuir. 2008. Vol. 24, № 14. P. 7294–7298.
- 130. Götzen J., Schwalb C.H., Schmidt C., Mette G., Marks M., Höfer U., Witte G. Structural evolution of perfluoro-pentacene films on Ag(111): Transition from 2D to 3D growth // Langmuir. 2011. Vol. 27, № 3. P. 993–999.
- 131. Lo Y.-Y., Chang J., Hoffmann G., Su W.-B., A C.W., Chang C.-S. A Comparative Study on the Adsorption Behavior of Pentacene and Perfluoropentacene Molecules on Au (111) Surfaces // Jpn. J. Appl. Phys. IOP Publishing, 2013. Vol. 52, № 10R. P. 1–6.
- Breuer T., Witte G. Controlling nanostructures by templated templates: Inheriting molecular orientation in binary heterostructures // ACS Appl. Mater. Interfaces. 2015. Vol. 7, № 36. P. 20485–20492.
- 133. Wong S.L., Huang H., Huang Y.L., Wang Y.Z., Gao X.Y., Suzuki T., Chen W., Wee A.T.S. Effect of fluorination on the molecular packing of perfluoropentacene and pentacene ultrathin films on Ag (111) // J. Phys. Chem. C. American Chemical Society, 2010. Vol. 114, № 20. P. 9356–9361.

- 134. Schmidt C., Breuer T., Wippermann S., Schmidt W.G., Witte G. Substrate induced thermal decomposition of perfluoro-pentacene thin films on the coinage metals // J. Phys. Chem. C. American Chemical Society, 2012. Vol. 116, № 45. P. 24098–24106.
- 135. Glowatzki H., Heimel G., Vollmer A., Wong S.L., Huang H., Chen W., Wee A.T.S., Rabe J.P., Koch N. Impact of fluorination on initial growth and stability of pentacene on Cu(111) // J. Phys. Chem. C. American Chemical Society, 2012. Vol. 116, № 14. P. 7726–7734.
- 136. Koch N., Vollmer A., Duhm S., Sakamoto Y., Suzuki T. The effect of fluorination on pentacene/gold interface energetics and charge reorganization energy // Advanced Materials. Wiley-Blackwell, 2007. Vol. 19, № 1. P. 112–116.
- 137. Yang H., Shin T.J., Ling M.M., Cho K., Ryu C.Y., Bao Z. Conducting AFM and 2D GIXD studies on pentacene thin films // J. Am. Chem. Soc. American Chemical Society, 2005. Vol. 127, № 33. P. 11542–11543.
- 138. Duhm S., Hosoumi S., Salzmann I., Gerlach A., Oehzelt M., Wedl B., Lee T.L., Schreiber F., Koch N., Ueno N., Kera S. Influence of intramolecular polar bonds on interface energetics in perfluoro-pentacene on Ag(111) // Phys. Rev. B - Condens. Matter Mater. Phys. 2010. Vol. 81, № 4.
- 139. Desai T. V., Woll A.R., Schreiber F., Engstrom J.R. Nucleation and growth of perfluoropentacene on self-assembled monolayers: Significant changes in island density and shape with surface termination // J. Phys. Chem. C. 2010. Vol. 114, № 47. P. 20120–20129.
- Breuer T., Witte G. Controlling nanostructures by templated templates: Inheriting molecular orientation in binary heterostructures // ACS Appl. Mater. Interfaces. 2015. Vol. 7, № 36. P. 20485–20492.
- 141. Koch N., Gerlach A., Duhm S., Glowatzki H., Heimel G., Vollmer A., Sakamoto Y., Suzuki T., Zegenhagen J., Rabe J.P., Schreiber F. Adsorption-

induced intramolecular dipole: Correlating molecular conformation and interface electronic structure // J. Am. Chem. Soc. American Chemical Society, 2008. Vol. 130, № 23. P. 7300–7304.

- 142. Heimel G., Salzmann I., Duhm S., Koch N. Design of organic semiconductors from molecular electrostatics // Chem. Mater. American Chemical Society, 2011. Vol. 23, № 3. P. 359–377.
- 143. Koch N. Electronic structure of interfaces with conjugated organic materials
 // Phys. Status Solidi Rapid Res. Lett. 2012. Vol. 6, № 7. P. 277–293.
- 144. Breuer T., Celik M.A., Jakob P., Tonner R., Witte G. Vibrational Davydov splittings and collective mode polarizations in oriented organic semiconductor crystals // J. Phys. Chem. C. 2012. Vol. 116, № 27. P. 14491–14503.
- 145. Wang X., Broch K., Schreiber F., Meixner A.J., Zhang D. Revealing nanoscale optical properties and morphology in perfluoropentacene films by confocal and tip-enhanced near-field optical microscopy and spectroscopy // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2016. Vol. 18, № 23. P. 15919–15926.
- 146. von Helden L., Breuer T., Witte G. Anisotropic thermal expansion in pentacene and perfluoropentacene: Effects of molecular packing motif and fixation at the interface // Appl. Phys. Lett. AIP Publishing LLC, 2017. Vol. 110, № 14. P. 141904.
- 147. Desai T. V., Woll A.R., Schreiber F., Engstrom J.R. Nucleation and growth of perfluoropentacene on self-assembled monolayers: Significant changes in island density and shape with surface termination // J. Phys. Chem. C. American Chemical Society, 2010. Vol. 114, № 47. P. 20120–20129.
- 148. Schmidt C., Breuer T., Wippermann S., Schmidt W.G., Witte G. Substrate induced thermal decomposition of perfluoro-pentacene thin films on the coinage metals // J. Phys. Chem. C. 2012. Vol. 116, № 45. P. 24098–24106.

- 149. Gu Y., Zhang W., Mou J., Zheng S., Jiang L., Sun Z., Wang E. Research progress of biomimetic superhydrophobic surface characteristics, fabrication, and application // Adv. Mech. Eng. SAGE Publications Inc., 2017. Vol. 9, № 12. P. 168781401774685.
- Kamaraj A.B., Shaw V., Sundaram M.M. Novel Fabrication of Un-coated Super-hydrophobic Aluminum via Pulsed Electrochemical Surface Modification // Procedia Manufacturing. Elsevier B.V., 2015. Vol. 1. P. 892–903.
- 151. Gundersen H., Leinaas H.P., Thaulow C. Surface structure and wetting characteristics of Collembola cuticles // PLoS One. Public Library of Science, 2014. Vol. 9, № 2. P. e86783.
- 152. Rosenberg A., Hu D., Chouaib H., Tan Z., Malkova N. Tracking the defects of ultra-thin HfO2 using a Cody-Lorentz multiple oscillator model // Metrology, Inspection, and Process Control for Microlithography XXXII / ed. Adan O., Ukraintsev V.A. SPIE, 2018. Vol. 10585. P. 102.
- 153. Acrylonitrile- A.B.S.S., See A.F.P. 原子力顯微術 Atomic Force Microscopy // 報告. № Cmc. P. 311–317.
- 154. New Industry Reports: Global X-ray Photoelectron Spectroscopy (XPS) Market Top Manufacturers Analysis till 2024 [Electronic resource]. URL: http://newindustryreport.blogspot.com/2019/03/global-x-ray-photoelectronspectroscopy.html (accessed: 16.04.2020).
- 155. Matthew J. Surface analysis by Auger and x-ray photoelectron spectroscopy.
 D. Briggs and J. T. Grant (eds). IMPublications, Chichester, UK and SurfaceSpectra, Manchester, UK, 2003. 900 pp., ISBN 1-901019-04-7, 900 pp // Surf. Interface Anal. Wiley, 2004. Vol. 36, № 13. P. 1647–1647.
- 156. Tod Schneider †, Kateryna Artyushkova ‡, Julia E. Fulghum ‡, Laurie Broadwater §, Ashley Smith †,∥ and, Oleg D. Lavrentovich* †. Oriented

Monolayers Prepared from Lyotropic Chromonic Liquid Crystal. American Chemical Society, 2005.

- 157. ThermoScientific. Angle Resolved XPS (ARXPS) [Electronic resource] // Angle Resolved XPS (ARXPS). 2014. URL: https://xpssimplified.com/angle_resolve_xps.php (accessed: 16.04.2020).
- 158. Technology neaspec GmbH [Electronic resource]. URL: https://www.neaspec.com/technology/ (accessed: 09.05.2020).
- Watcharinyanon S. Structure of Self-Assembled Monolayers on Gold Studied by NEXAFS and Photoelectron Spectroscopy. 2008. 69 p.
- 160. Uzarski J.R. Reflection Absorption Infrared Spectroscopic Studies of Surface Chemistry Relevant to Chemical and Biological Warfare Agent Defense // ProQuest Dissertations and Theses. 2009. 270 p.
- 161. Hosseinpour S. Molecular studies of initial atmospheric corrosion of copper: Exploration of ultra-sensitive techniques for the inhibiting effect of self assembled monolayers, and the effect of gamma radiation. 2013.
- 162. Greenler R.G. Infraredc study of adsorbed molecules on metal surfaces by reflection tehniques // J. Chem. Phys. 1966. Vol. 44, № 1. P. 310–315.
- Wang X., Wang L. Dynamic Contact Angle on a Surface with Gradient in Wettability. 2016.
- 164. Jafari M., Jung J., Jafari M., Jung J. Direct Measurement of Static and Dynamic Contact Angles Using a Random Micromodel Considering Geological CO2 Sequestration // Sustainability. Multidisciplinary Digital Publishing Institute, 2017. Vol. 9, № 12. P. 2352.
- 165. Haas B., Beyer A., Witte W., Breuer T., Witte G., Volz K. Application of transmission electron microscopy for microstructural characterization of perfluoropentacene thin films // J. Appl. Phys. 2011. Vol. 110, № 7.

- 166. Kowarik S., Gerlach A., Hinderhofer A., Milita S., Borgatti F., Zontone F., Suzuki T., Biscarini F., Schreiber F. Structure, morphology, and growth dynamics of perfluoro-pentacene thin films // Phys. Status Solidi - Rapid Res. Lett. 2008. Vol. 2, № 3. P. 120–122.
- 167. Frank C., Novák J., Gerlach A., Ligorio G., Broch K., Hinderhofer A., Aufderheide A., Banerjee R., Nervo R., Schreiber F. Real-time X-ray scattering studies on temperature dependence of perfluoropentacene thin film growth // J. Appl. Phys. 2013. Vol. 114, № 4.
- 168. Frank C., Novák J., Gerlach A., Ligorio G., Broch K., Hinderhofer A., Aufderheide A., Banerjee R., Nervo R., Schreiber F. Real-time X-ray scattering studies on temperature dependence of perfluoropentacene thin film growth // J. Appl. Phys. 2013. Vol. 114, № 4.
- 169. Cabellos J.L., El-Sayed A., Foreano L., Goiri E., Mowbray D.J., Ortega J.E., Rogero C., Rubio A., de Oteyza D.G. Understanding Charge Transfer in Donor-Acceptor/Metal Systems: A Combined Theoretical and Experimental Study // J. Phys. Chem. C. 2012.
- 170. Breuer T., Witte G. Thermally activated intermixture in pentaceneperfluoropentacene heterostructures // J. Chem. Phys. 2013. Vol. 138, № 11.
- 171. Meyer Zu Heringdorf F.J., Reuter M.C., Tromp R.M. The nucleation of pentacene thin films // Appl. Phys. A Mater. Sci. Process. 2004. Vol. 78, № 6. P. 787–791.
- Winkler A. On the nucleation and initial film growth of rod-like organic molecules // Surf. Sci. 2016. Vol. 652. P. 367–377.
- 173. Pratontep S., Brinkmann M., Nüesch F., Zuppiroli L. Nucleation and growth of ultrathin pentacene films on silicon dioxide: Effect of deposition rate and substrate temperature // Synth. Met. 2004. Vol. 146, № 3. P. 387–391.
- 174. Libuda J., Freund H.J. Molecular beam experiments on model catalysts //

Surface Science Reports. 2005. Vol. 57, № 7-8. P. 157-298.

- 175. Salzmann I., Duhm S., Heimel G., Rabe J.P., Koch N., Oehzelt M., Sakamoto Y., Suzuki T. Structural order in perfluoropentacene thin films and heterostructures with pentacene // Langmuir. 2008. Vol. 24, № 14. P. 7294–7298.
- 176. Salzmann I., Duhm S., Heimel G., Oehzelt M., Kniprath R., Johnson R.L., Rabe J.P., Koch N. Tuning the ionization energy of organic semiconductor films: The role of intramolecular polar bonds // J. Am. Chem. Soc. 2008. Vol. 130, № 39. P. 12870–12871.
- 177. Tkachenko I.M., Shekera O. V., Shevchenko V. V. Allyl-containing polyaryl ethers with perfluorinated mono- and biphenylene fragments // Polym. Sci. -Ser. B. 2013. Vol. 55, № 5–6. P. 336–343.
- 178. Kobzar Y.L., Tkachenko I.M., Bliznyuk V.N., Shekera O. V., Turiv T.M., Soroka P. V., Nazarenko V.G., Shevchenko V. V. Synthesis and characterization of fluorinated poly(azomethine ether)s from new corefluorinated azomethine-containing monomers // Des. Monomers Polym. 2016. Vol. 19, № 1. P. 1–11.
- Andersen M.P.S., Nielsen O.J. Atmospheric chemistry of a cyclic hydro-fluoro-carbon: Kinetics and mechanisms of gas-phase reactions of 1-trifluoromethyl-1,2,2-trifluorocyclobutane with Cl atoms, OH radicals, and O 3 // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2019. Vol. 21, № 3. P. 1497–1505.
- 180. Mondal R., Tönshoff C., Khon D., Neckers D.C., Bettinger H.F. Synthesis, stability, and photochemistry of pentacene, hexacene, and heptacene: A matrix isolation study // J. Am. Chem. Soc. 2009. Vol. 131, № 40. P. 14281– 14289.
- 181. Kreienborg N.M., Merten C. How to treat C-F stretching vibrations? A vibrational CD study on chiral fluorinated molecules // Phys. Chem. Chem.

Phys. Royal Society of Chemistry, 2019. Vol. 21, № 7. P. 3506–3511.

- 182. Fujii K., Himcinschi C., Toader M., Kera S., Zahn D.R.T., Ueno N. Vibrational properties of perfluoropentacene thin film // J. Electron Spectros. Relat. Phenomena. 2009. Vol. 174, № 1–3. P. 65–69.
- 183. Rao P.V.R., Srishailam K., Ravindranath L., Reddy B.V., Rao G.R. Structural and vibrational properties of pentabromophenol and pentafluorophenol: A spectroscopic investigation using density functional theory // J. Mol. Struct. Elsevier B.V, 2019. Vol. 1180. P. 665–675.
- 184. Hohman J.N., Zhang P., Morin E.I., Han P., Kim M., Kurland A.R., McClanahan P.D., Balema V.P., Weiss P.S. Self-Assembly of carboranethiol isomers on Au{111}: Intermolecular interactions determined by molecular dipole orientations // ACS Nano. 2009. Vol. 3, № 3. P. 527–536.
- 185. Schwartz J.J., Mendoza A.M., Wattanatorn N., Zhao Y., Nguyen V.T., Spokoyny A.M., Mirkin C.A., Baše T., Weiss P.S. Surface dipole control of liquid crystal alignment // J. Am. Chem. Soc. 2016. Vol. 138, № 18. P. 5957–5967.
- 186. Leites L.A. Vibrational Spectroscopy of Carboranes and Parent Boranes and Its Capabilities in Carborane Chemistry // Chem. Rev. 1992. Vol. 92, № 2.
 P. 279–323.
- 187. Avdeeva V. V., Vologzhanina A. V., Malinina E.A., Kuznetsov N.T. Dihydrogen Bonds in Salts of Boron Cluster Anions [BnHn]2– with Protonated Heterocyclic Organic Bases // Crystals. 2019. Vol. 9, № 7. P. 330.
- 188. Görgülü S. Investigation of Carboxyl-Functionalized Self-Assembled Monolayers on Gold Surfaces. Middle East Technical University, 2020. № January.
- 189. Albayrak E. Bazi kendiliğinden düzenlenmiş organik ince filmlerin helyum

kirinim metoduyla incelenmesi. Sakarya Üniversitesi, 2012.

190. 3f Series Mass Spectrometers | Triple Filter & Quadrupole | Hiden Inc.
[Electronic resource]. URL: https://www.hidenanalytical.com/products/for-residual-gas-analysis/3f-series-1000-series-rga/ (accessed: 21.05.2020).

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Ph.D. – Micro and NanoTechnology (MNT) (2014-Current), Middle East Technical University, Ankara, Turkey.

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M.S. – Physics (2011-2012), Bosphorus University, Istanbul, Turkey.

M.S. – Physics (2011-2013), Selcuk University, Konya, Turkey.

B.S. – Physics (2007-2011), Selcuk University, Konya, Turkey.

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SKILLS:

- Fabrication of MOS capacitors
- Fabrication of Organic Field-Effect Transistors (OFETs)
- Experience in oxide film growth by Chemical Vapor Deposition (CVD) technique
- Experience in Metal (Au, Al, and Cu) film growth by Physical Vapor Deposition (PVD) technique
- Setup a new Ultra-High Vacuum (UHV) system
- Setup and design a new He Diffraction System
- Experience in Supersonic Molecular Beam Deposition
- Current-Voltage Measurements and Analysis of MOS capacitors
- Experience on X-Ray Photoelectron Spectroscopy (XPS)
- Experience on Atomic Force Microscopy (AFM)
- Experience on Variable Wavelength/Angle Spectroscopic Ellipsometer (VWSE/VASE)
- Experience on Fourier Transform Infrared Spectroscopy (FTIR)
- Experience on Reflection-Absorption Infrared Spectroscopy (RAIRS) (in SOLEIL)
- Experience on NanoIR
- Experience on Contact Angle Measurements (CAs)
- Experience on the production of Template Stripped Metal Film

TRAINING:

AFM, SEM, TEM, Energy Dispersive X-ray Microanalysis Spectroscopy(EDX), FTIR (with synchrotron radiation), RAIRS (with synchrotron radiation), NanoIR, ATR-FTIR, UV-VIS, Raman Spectroscopy, XPS, NMR, Spectrometric Ellipsometer, Refractometer, Micro Electro Mechanical System Design (MEMS), Lytography, Hydrofluoric Acid Based Etching, Chemical Etching, Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD)

INTERNATIONAL CONFERENCES / MEETINGS ATTENDED:

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- 9th International Physics Conference of the Balkan Physical Union, 24-27 August 2015, Istanbul University, Istanbul, Turkey (Poster Presentation).
- 1st Conference of Solar Energy in Turkey / Energy and Renewables, 29-30 April 2010, Middle East Technical University (METU), Ankara, Turkey.

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A. Yavuz, M.F. Danisman "<u>Study on the Effect of Chemically Different Substrates</u> <u>on Nucleation and Growth Mechanism of Perfluoropentacene Thin Films</u>" J. Phys. Chem. C 2019, 123,32, 19610-19618, DOI: 10.1021/acs.jpcc.9b04850.

A. Yavuz, N. Sohrabnia, A. Yılmaz, M. F. Danisman "<u>Mixed carboranethiol self-assembled monolayers on gold surfaces</u>" Appl. Surf. Sci. 413, 233 (2017), DOI: 10.1016/j.apsusc.2017.03.294.

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