



UNIVERSITÀ DEGLI STUDI DI TRIESTE
XXIX CICLO DEL DOTTORATO DI RICERCA IN
NANOTECNOLOGIE

ORGANIC SEMICONDUCTING SINGLE CRYSTAL
GROWTH ON NANOSTRUCTURED MATRICES

Settore scientifico-disciplinare: **ING-IND/22**

PhD STUDENT
Mirta Sibia

COORDINATOR
PROF. Lucia Pasquato

SUPERVISOR
PROF. Alessandro Fraleoni Morgera

ACCADEMIC YEAR 2015/2016

Al mio Pigmalione e a tutti coloro i quali,

davanti alla propria Coscienza,

dimostrano Coraggio Altruismo e Fantasia.

Stat rosa pristina nomine,

nomina nuda tenemus

ABSTRACT

In recent years, the development of the *organic electronics* has led to the employment of organic materials as the basis for many electronic devices, such as organic light emitting diodes, organic field effect transistors, organic solar cells and radiation sensors. As regards radiation sensors, the studies reported in literature mainly refer to devices based on thin film organic semiconductors, which, however, present problems due to instability, degradation and low reproducibility. Organic single crystals overcame most of the major limitations inherent to thin film-based detectors.

In this experimental work, a starting plethora of commercially available compounds has been crystallized and evaluated in terms of both overall crystallizability and applicability as direct X-ray detectors. This first step of work allow to select only those structures capable to provide single-crystals with good morphological properties and electronic properties suitable for X-ray detections.

A careful screening of some thermodynamic variables affecting the growth has been carried out and the obtained results suggest applicability of the present approach to achieve the control of size, quality and crystal habit. Indeed, single crystals with dimensional and morphological properties suitable to the application as X-ray detector have been prepared.

Single-crystals have been physically attached to Au electrodes deposited on a thin film of polyethylenaphthalate – via the functionalization of the electrode with different self-assembled monolayers (SAMs), chemically and structurally similar to the molecule constituting the selected crystal. In particular, two of the explored SAMs showed very promising results in the first qualitative adhesion tests.

INDEX

ABSTRACT	I
----------	---

ABBR.	II
-------	----

CHAPTER 1 INTRODUCTION

1.1	Organic electronics.....	1
1.2	Semiconductor.....	6
1.2.1.	Inorganic semiconductor.....	6
1.2.2.	Organic semiconductor.....	10
1.2.2.1.	Polymers.....	15
1.2.2.2.	Organic Semiconducting Single Crystals...	17
1.3	OSSCs growth techniques.....	19
1.4	Aims of the work.....	29
1.5	Radiation interaction with matter.....	33
1.6	Thesis organization.....	34
1.7	Bibliography.....	36

CHAPTER 2 MOLECULES SCREENING

2.1	Evaluated structures and their selection criteria.....	42
2.1.1.	Introduction.....	42
2.1.2.	Tested molecules.....	44
2.2	Experimental screening.....	46
2.2.1.	Purification step.....	47
A.	Introduction.....	47
B.	Purification procedure.....	48
2.2.2.	Pre-crystallization step.....	49
A.	Screening of different solvent to find the best one.....	50

B. Crystallization step to define the general features of the obtained crystals.....	52
C. Definition of the solubility at room temperature.	53
2.2.3. Protocol for crystal growth.....	53
2.3 Characterization techniques.....	55
2.3.1. Synchrotron.....	55
2.3.2. XRD.....	56
2.4 Results and discussion.....	61
2.4.1. Pre-crystallization step.....	61
2.4.2. General characterizations.....	62
2.5 Summary.....	93
2.6 Bibliography.....	95

CHAPTER 3 OSSCs GROWTH

3.1 Crystallization theory.....	100
3.1.1. Introduction.....	100
3.1.2. Driving force.....	102
3.1.3. Nucleation.....	106
3.1.4. Post-nucleation growth.....	109
3.1.5. Steady-state theory.....	109
3.2 Growth parameters and their influence on the crystallization output.....	114
3.2.1. Introduction.....	114
3.2.2. Impurities.....	116
3.2.3. Supersaturation.....	117
3.2.4. Temperature.....	117
3.2.5. Volume of the growing vessel.....	118
3.3 Experimental techniques used to investigate growth results.....	118
3.3.1. Optical microscopy.....	119

3.3.2. Atomic force microscopy and roughness parameters.....	123
3.4 Materials and methods.....	127
3.4.1. Pre-growth purification.....	128
3.4.2. Crystallization setup.....	128
3.4.3. Instruments.....	129
3.5 Results and discussion.....	131
3.5.1. Effect of concentration.....	132
3.5.2. Effect of temperature.....	143
3.5.3. Effect of solution volume.....	151
3.6 Summary.....	156
3.7 Bibliography.....	158

CHAPTER 4 OSSCs FOR REAL DEVICES

4.1 Overview of the present work.....	167
4.2 Formation of self assembled monolayers (SAMs).....	169
4.2.1. Surfaces.....	169
4.2.2. Self Assembled Monolayers.....	170
4.3 The idea behind the work.....	173
4.4 Characterization of the surfaces for a proper SAM functionalization.....	176
4.5 Experimental techniques.....	177
4.5.1. XPS.....	177
4.5.2. Cyclic Voltammetry.....	181
4.5.3. SPELEEM.....	186
4.5.4. GI_XRD.....	188
4.6 Materials and methods.....	189
4.6.1. Electrodes cleaning procedure.....	189
4.6.2. Clean Electrodes characterization before functionalization.....	192
4.6.3. Electrodes functionalization with SAMs.....	193
4.6.4. Determination of SAMs on electrodes surface.....	194

4.6.5. OSSC binding on Au electrodes.....	195
4.7 Results and discussion.....	195
4.7.1. Electrodes cleaning procedure.....	195
4.7.2. Clean Electrodes surface characterization.....	201
4.7.3. Determination of SAMs on electrodes surface.....	205
4.7.4. OSSCs binding on electrodes surface.....	208
4.8 Bibliography.....	210

CHAPTER 5	GENERAL CONCLUSIONS	217
-----------	---------------------	-----

LIST OF ABBREVIATIONS

OLED	Organic Light Emitting Diode
OFET	Organic Field Effect Transistor
OSC	Organic Solar Cell
LCD	Liquid Crystal Display
OPV	Organic PhotoVoltaics
OS	Organic Semiconductor
OSSC	Organic Semiconductor Single Crystal
LUMO	Lowest Unoccupied Molecular Orbit
HOMO	Highest Occupied Molecular Orbit
XRD	X-Ray Diffraction
PVD	Physical Vapour Deposition
VTE	Vacuum Thermal Evaporation
CMOS	Complementary Metal-Oxide Semiconductor
PEN	Poly Ethylene Naphthalene
ID	Interplanar Distance
UNIBO	University of Bologna
SNR	Signal Noise Ratio
AFM	Atomic Force Microscopy
XPS	X-ray Photoelectron Spectroscopy

ESCA	Electron Spectroscopy for Chemical Analysis
SEM	Scanning Electron Microscope
ESEM	Environmental SEM
UHV	Ultra High Vacuum
RMS	Root Mean Square
CCD	Charge Coupled Device
SAM	Self Assembled Monolayers
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
LEEM	Low Energy Electron Microscopy
PEEM	Photo Emission Electron Microscopy
XPEEM	X-ray Photo Emission Electron Microscopy
MEM	Mirror Electron Microscopy
GID	Grazing incidence Diffraction
RAIRS	Reflection and Absorption IR Spectroscopy

CHAPTER 1: Introduction

In this chapter, an overview on organic electronics will be treated in **section 1.1**. The fundamental properties of semiconductors will be presented in **section 1.2** where a careful description is devoted to the organic semiconductors, which are the basis of the field of organic electronics. In **section 1.3**, the techniques for growing organic semiconducting single crystals will be illustrated. Since there are some open problems in the field of detection of ionizing radiation, not yet answered by Si-based devices technology, a proposal on this topic will be reported in **section 1.4**. After introducing the open needs, in **section 1.5** the organization of the work carried out will be described.

1.1 ORGANIC ELECTRONICS

We live in an increasingly electronic world, with computers occupying a central part of our lives. In 2012 there were an estimated average of 30-40 processors per person with some individuals surrounded, on a daily basis, by as many as 1000 processors.

While silicon- and, more generally, inorganic-based semiconductors have solved many of the challenges associated with our increased use of electronics, there are still some open problems that these materials cannot currently engage with, like for example the fabrication of flexible and low cost electronics. Organic semiconducting materials, whether used in combination with silicon or not, hold the potential to be applied in these fields.

The breaking discovery of electrical charge carrier transport in organic polymers in the late 1980s by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa^{1,2,3}, who were awarded with the Nobel Prize in Chemistry in 2000, opened the way to the exploration of these materials also as potential semiconductors. Indeed very early studies had highlighted non negligible charge carrier mobilities in organic single crystals^{4, 5}. This field started to attract major attention after the demonstration of the first **Organic Light Emitting Diode** device (OLED) in 1987 by Tang and Van Slyke⁶. Since then, the field of organic electronics has stimulated a tremendous research interest into organic semiconductors.

Today chemists and physicists, together with engineers and material scientists, are synthesizing and manipulating a wealth of new organic semiconducting materials, allowing a constant improvement of the peculiar properties of organic semiconductors and expanding the world of electronics in ways unimaginable until a few years ago. Therefore organic semiconductors have made their way from a rather exotic and academic topic, studied by a few specialists in molecular physics, to a mature research field^{7,8}.

In particular, there are already some commercially available applications of organic semiconductors and a number of products have reached the market. Consumers are using organic electronic devices, such as smartphones built with OLED displays, often without even being aware of the organic nature of the electronic technology in their hands, as shown in

FIGURE 1.1 .

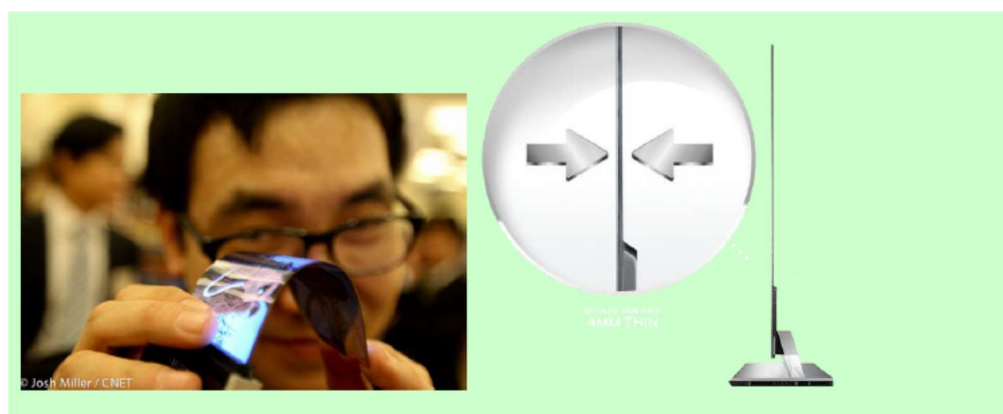


FIGURE 1.1: Left: Samsung flexible plastic OLED display; the phone can be folded to an eighth of its size. Source: Josh Miller/CNET. Right: Both Samsung and LG Electronics have announced near-future releases 4-mm thick OLED display TVs. Source: LG Electronics.

Today applications related to organic electronics can be divided into essentially three major fields, namely:

1. **Organic Light Emitting Diodes**, OLEDs,
2. **Organic Field Effect Transistors** (OFETs),
3. **Organic Solar Cells** (OSCs).

A fourth field, that of sensors is also explored, but, up to now, in a not commercially successful way, due to still unsolved reliability problems. For this reason, this field won't be further described in this overview chapter of thesis.

So far, OLEDs devices have had the largest impact in the field of organic electronics. The well known touch-screen display on the Galaxy S series of smartphones manufactured by Samsung Electronics is the archetype of the outstanding progress already achieved in this field. Most of the other smartphones, as well as computers, tablets, high definition televisions and other similar devices, use Liquid Crystal Display (LCD) technology - an organic-inorganic hybrid electronic technology that requires a backlight to produce the image displayed on the screen. Instead the Galaxy S uses a technology that doesn't require a backlight: OLED display technology. OLEDs emit their own colored light to produce images. Because they do not need backlights, OLED displays are thinner and lighter than LCD displays.

In contrast to such electro-luminescent devices, in many instances the realisation of OFETs for practical applications requires fairly large charge carrier mobilities of the organic materials used in the device. Unfortunately, these charge carrier mobilities are found to depend very sensitively on a number of parameters, including the degree of order, contaminations due to charge carrier traps, and other structural imperfections of the bulk material, such as domain boundaries. A real breakthrough with regard to understanding and optimising charge carrier mobilities in organic materials has thus not been achieved yet, and electronic devices using organic semiconductors as an active material are still in the laboratory rather than on the market. With the synthesis of new organic materials, chemists have increased charge-carrier mobilities for small-molecule OFETs of one order of magnitude (from $< 1 \text{ cm}^2 \cdot (\text{V}\cdot\text{s})^{-1}$ in 2000 to $8\text{-}11 \text{ cm}^2 \cdot (\text{V}\cdot\text{s})^{-1}$ today⁹). Initially, the improved mobilities were obtained only under very clean conditions in ultrahigh vacuum chambers. However, recent results suggest that high performance OFETs can be fabricated using simple and

relatively inexpensive techniques, such as solution processing. By 2020, with the synthesis of even more advanced materials, it has been foreseen that mobilities could increase to as much as $100 \text{ cm}^2 \cdot (\text{Vs})^{-1}$.⁹

Organic photovoltaics (OPV), or organic solar cells (OSC), is still in its infancy but it is receiving a substantial and strongly increasing amount of attention. While current OPV technology boasts conversion efficiencies that exceed 10%, reaching even 12%, some researchers predict organic solar cells will reach 15-20 % efficiency⁹. Despite its lower efficiency compared with silicon-based devices, organic solar cells offer the advantages of low cost, large area production, which might lead to a cost-effective use, and the potential for flexible devices. For example, in 2011, Eight19, a Cambridge, UK-based company devoted to the development and manufacture of organic solar cells, launched a program called Indigo to provide off-the-grid solar-powered energy to rural markets⁹. In this way, organic solar cells are being installed on rooftops in African villages that lack access to standard electricity, providing rural populations with a safer and cheaper alternative to kerosene, as shown in

FIGURE 1.2.



FIGURE 1.2 Accessible electronics: The Pay-as-you-go organic solar cell technology is being distributed throughout rural areas of southern Africa and elsewhere, providing a low-cost and safe alternative to kerosene. Source: Eight19

In the future, there are several potential properties of organic electronics that may become very important. The most often quoted one is related to their cost. Many companies invest a substantial amount of money and effort into developing organic electronic devices suitable for the mass market, motivated by the prospect of ‘cheap’ electronics. For example, the vision of being able to simply print electronic circuits on a substrate, using existing print technology, is very attractive.

Organic materials can be processed at low temperatures (well below 150 °C), thus allowing the combination of organic electronics into the flexible plastic substrate to build devices with a flexibility, stretchability and softness (‘soft electronics’) not allowed by silicon or other inorganic materials. The possibility to use flexible plastic substrates to obtain thin, flexible organic electronics has been shown by several groups^{10,11,12,13,14}. In addition, the use of plastic-based substrates, coupled with recent developments in solution deposition and inkjet printing for laying down organic light emitting polymers and active matrix thin film transistor arrays, strongly supports the possibility of cost-effective processing in high volumes. For these reasons the potential applications of organic electronics span a broad range of fields, including information and communications, national security, environmental health, as well as medicine and biomedical research⁹. Devices made with organic materials also have the potential to interface with biological systems in ways that are not possible with inorganic materials⁹.

Despite organic electronics has peculiar properties that will be hardly matched by inorganic semiconductors - first of all its flexibility - nevertheless it is improbable that this technology will completely replace silicon-based electronics. Rather, the vision for the future suggest that organic semiconductors will be used in synergy with silicon materials, creating an expanded electronic landscape – one filled with new materials that make electronics more functional, accessible, and sustainable.

Recently researches working in the field have proposed three visions for the future of organic electronics:

1. organic electronic devices will carry on tasks that silicon-based electronics cannot perform, expanding the functionality and accessibility of electronics;

2. organic electronic devices will be more energy-efficient and eco-friendly than today's electronics, contributing to a more sustainable electronic world;
3. organic electronic devices will be manufactured using more resource-friendly and energy efficient processes than today's methods, further contributing to a more sustainable electronic world.

Realizing the previous visions requires overcoming several major scientific and engineering challenges. Arguably, the greatest one is creating electronic structures at industry level scale with high yield and uniformity. This is true regardless of type of material or application. While the electronics industry has already achieved enormous success with some organic electronic structures, such as those being used to build OLED-based smartphones, most organic electronic structures are being synthesized on only very small scales, with performances, reproducibility and reliability being the major problems. Until wide-scale industry-level production is achieved, future visions for organic electronics will remain just that – visions.

1.2 SEMICONDUCTORS

1.2.1 INORGANIC SEMICONDUCTORS

'What is a semiconductor?' In most current dictionaries, a semiconductor is still defined as *'a nonmetallic solid that has electrical conductivity between that of a conductor and an insulator'*. According to several sources, the first occurrence of the word ('Halbleiter' in German) dates back to 1911¹⁵, at a time when electrical conduction in solids was not fully understood. Classical physics served well at accounting for electrical conduction in metals, but was contradicted by the 'anomalous' behaviour of various non-metals, among whose were silicon and a variety of binary compounds, for example oxides and sulphides. The 'anomalous' phenomena associated with these materials - for which the word 'semiconductor' was invented – included:

1. the positive variation of conductivity with temperature,
2. photoconductivity,

3. rectification,
4. photovoltaic effect.

The puzzle was only resolved with the advent of quantum mechanics and the subsequent development of the band theory of solids¹⁶. The following definition, more in accordance with our current state of knowledge, can be found in a modern encyclopaedia: *'A semiconductor is a material that is an insulator at very low temperature, but which has a sizable electrical conductivity at room temperature. The distinction between a semiconductor and an insulator is not very well-defined, but roughly, a semiconductor is an insulator with a band gap small enough that its conduction band is appreciably thermally populated at room temperature.'* Semi-insulators could be a more appropriate definition for these materials, but it is too late for such a correction.

The above definition applies to intrinsic semiconductors, namely to materials that present the mentioned properties without any addition of dopant. What makes semiconductors so useful in electronics, however, is that their electronic properties can be modified in a controllable manner by adding tiny amounts of an advisedly chosen impurity. This is the well-known process of doping, that generates extrinsic semiconductors. The difference between intrinsic and extrinsic semiconductors is illustrated in **FIGURE 1.3**, which represents the energy diagram of metals, insulators, and semi-conductors, as pictured in the framework of the now well-accepted band theory of solids.

The theory delineates a clear distinction between a metal, which has a partially-filled conduction band, and an insulator characterized by a filled valence band and an empty conduction band. However, an insulator is perfectly insulating only at $T = 0$ K. As soon as its temperature is elevated, electrons can be thermally excited from the valence band to the conduction band. Because electrical conduction can occur in partially filled bands, both bands contribute to conduction and, as thermal energy is low ($kT = 25$ meV at room temperature), thermally activated conduction can only be observed in low energy-gap insulators, also called intrinsic semiconductors.

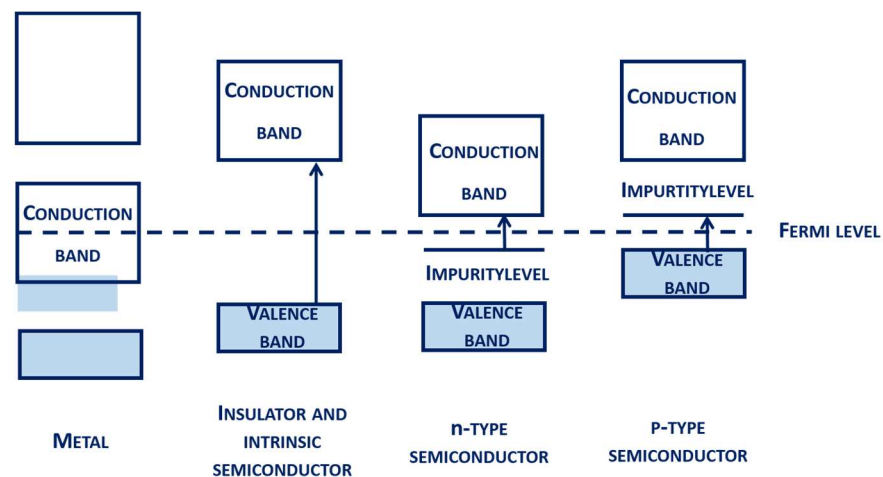


FIGURE 1.3: energy diagram of a metal, an insulator and an extrinsic semiconductor.

The temperature dependence of the conductivity of a typical doped (extrinsic) semiconductor is shown in **FIGURE 1.4**.

The curve contains three separated domains:

1. high temperature range,
2. intermediate temperature range,
3. low temperature range.

At high temperatures, the intrinsic domain is characterized by thermally activated behaviour. The intermediate domain is the so-called saturation (or exhaustion) regime in which the conductivity is practically temperature-independent. Finally, at low temperature the carriers are frozen. In terms of electronic devices, the only domain of interest is the exhaustion regime, where the density of charge-carriers practically equals that of the dopant.

A critical property for the practical application of all semiconductors is the environmental stability: the material must be resistant to degradation upon heating or irradiation, to oxidation by wet oxygen and to photo-oxidation. In this respect,

inorganic semiconductors are certainly much more reliable than organic ones, although these latter showed recently satisfactory environmental stability requirements¹⁷.

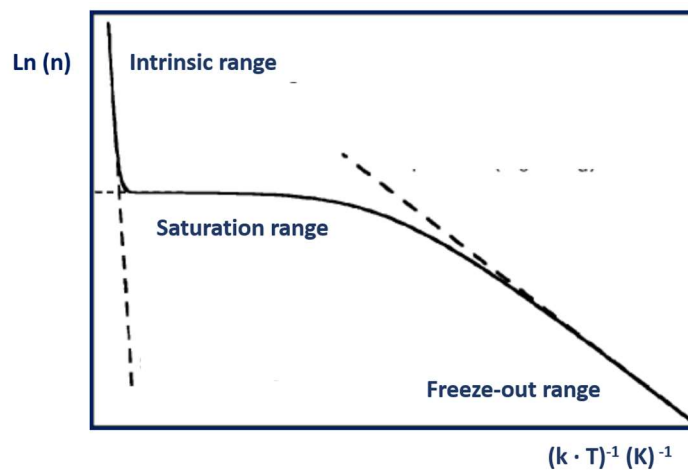


FIGURE 1.4: Temperature dependence of the charge carrier density. The Arrhenius plot.

On the other hand, silicon and the other inorganic semiconductors, whether in polycrystalline form or not, are rigid materials and their electronic properties strongly depend on the crystal grain size: the smaller are the grains, the higher number of grain boundaries a charge carrier will encounter. In fact, grain boundaries are charge carrier trap sites and they greatly limit device performance. To overcome these problems, processes to increase grain size are required but the necessary high temperatures are incompatible with flexible substrates¹⁸.

In the form of amorphous silicon (α -Si), thin flexible silicon films can be fabricated as well. Because of the absence of a crystal lattice, electronic performance of amorphous silicon is multiple orders of magnitude worse than that of (poly)crystalline silicon, but still high enough for some applications. However,

processing temperatures required to obtain α -Si films suitable for practical applications are not compatible with flexible substrates either. This is a clear example highlighting one of limits to what silicon, and in general inorganic semiconductors, can do, despite its electronics has solved many of the challenges associated with our increased use of electronics.

Concerning costs, silicon electronics is and will remain an expensive technology¹⁹. Production of electronic-grade silicon is an expensive process, as are the subsequent steps - vacuum evaporation and lithography - needed to make chips out of the material. Due to the high costs, application of silicon in large-scale electronics is not likely⁹. Again, this is a clear example highlighting one of limits to what silicon can do.

For these reasons, chemists are synthesizing a wealth of new organic materials for use in electronic devices that create novel properties impossible to replicate with silicon. These materials hold tremendous promise to expand the present electronic landscape in ways that could radically change the approach of society with technology.

1.2.2 ORGANIC SEMICONDUCTOR

While inorganic semiconductors have superior environmental stability and performances with respect to organic ones, the latter have a better processability and their physical properties can be more easily tailored by chemists. Therefore, about 50 years after the invention of Si-based transistors, organic semiconductors are being explored as a new class of materials for electronic and optoelectronic applications. The joint effort in materials development, fundamental research and device engineering^{20,21} have meanwhile led, as already mentioned in the previous paragraphs, to the first commercial products based on organic semiconducting materials.

The nature of bonding in organic semiconductors is fundamentally different from their inorganic counterparts. Indeed, organic compounds are van-der-Waals-bonded solids (FIGURE 1.5) implying a considerably weaker intermolecular bonding as compared to covalently bonded semiconductors like Si or GaAs.

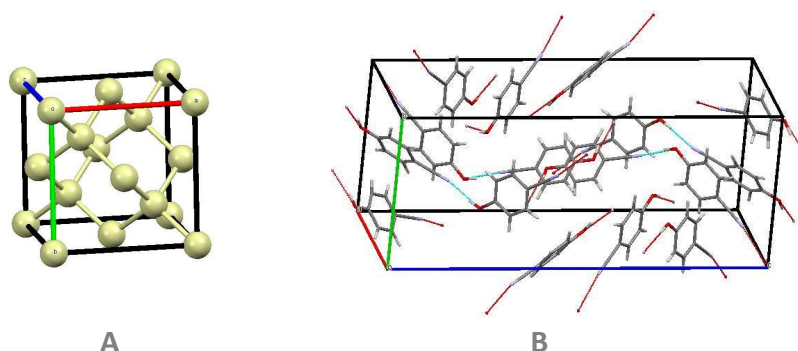


FIGURE 1.5: comparison between crystalline lattice of a typical inorganic compound (right) and a typical organic compound (left). A. Silicon crystalline lattice, characterized by covalent bondings. B. 4-hydroxycyanobenzene crystalline lattice shows how each molecule interacts via Van der Waal interactions with the surrounding ones.

The consequences are visible in mechanical and thermodynamic properties of organic semiconductors, OSs, such as lower hardness or lower melting point with respect to inorganic ones and, even more important, in a much weaker delocalization of electronic wavefunctions among neighbouring molecules, which has direct implications for optical properties and charge carrier transport. An advantage of organic materials, most notably polymers but also crystalline materials like rubrene (when these are thin enough, in general 5÷500 μm or less)²², is that films of the material can be bended without breaking them. This is true down to certain limits that depend on the considered OS. Interestingly these limits are much smaller in terms of bending radius than those of their inorganic counterparts. Moreover, upon bending, a layer of such a material will retain its electronic properties, because there is no covalent crystalline lattice to be damaged.

The presence of Van der Waals interaction inside the crystalline lattice has another important consequence: these compounds are in general soluble in numerous organic solvents, even at room temperature. This fact allows low-temperature processing, such as printing techniques. Low-temperature solubility

distinguishes OSs from covalently bonded inorganic semiconductors, which often can only be dissolved in high-temperature acidic or alkaline solutions.

There are two major classes of organic semiconductors²³:

1. polymers;
2. low-molecular weight materials.

Both have in common a conjugated π -electron system - the key to the charge conduction - formed by the p_z orbitals not involved in the sp^2 -hybridization of C atoms in the molecules. In order to explain and understand the electrical properties of organic compounds it is necessary to describe the electronic configuration of the carbon atom and the way it forms chemical bonds with other atoms.

On **FIGURE 1.6A** orbitals of just two adjacent carbon atoms are presented. The results of sp^2 -hybridization in each carbon atom are three sp^2 hybridized orbitals and therefore three σ bonds in the horizontal plane: one of these connects each carbon atom through σ -bond to the adjacent one. The electrons in p_z orbitals linearly combine to provide a weaker π -bond. Energy levels of electrons in σ and π -bonds are presented on **FIGURE 1.6B**.

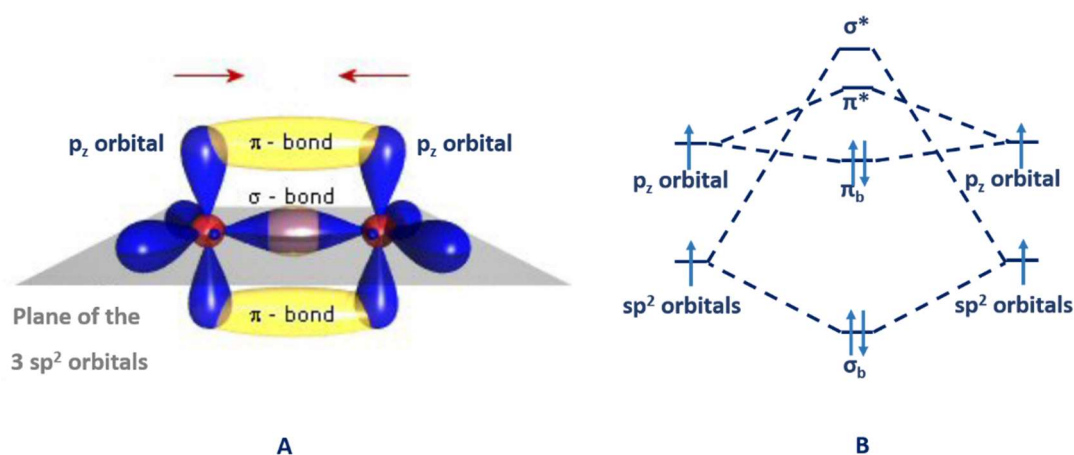


FIGURE 1.6: A. orbitals of 2 bonded C atoms; B. energy levels of occupied and unoccupied levels for σ and π -bonds.

In benzene ring on the **FIGURE 1.7** 6 C atoms are connected through 6 strong σ -bonds and 3 π -bonds delocalized over the whole ring. Chemists usually refer to these forms as to π -conjugated molecules.

Delocalized π -electrons

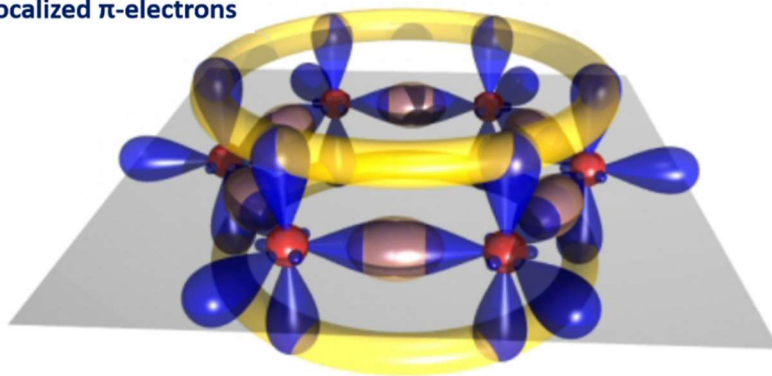


FIGURE 1.7A: Benzene ring with delocalized system of π -bonds

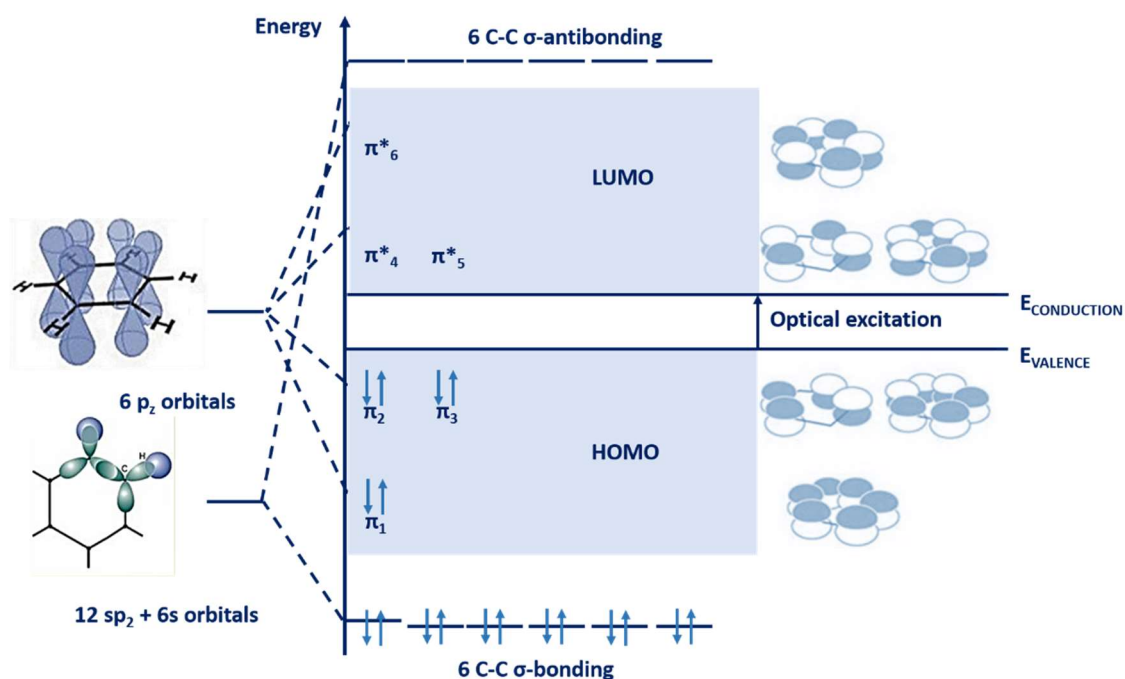


FIGURE 1.7B: energy levels of σ -bonds (12 + 6 electrons) and energy levels of delocalized π -bonds (6 electrons). Levels of π -bonds form 2 bands, named HOMO and LUMO.

The groups of levels resemble valence and conduction bands in inorganic semiconductors, but in organic semiconductors they are usually named HOMO (the Highest Occupied Molecular Orbit) and LUMO (the Lowest Unoccupied Molecular Orbit) since the structure is basically related to the molecular properties. Similarly as in inorganic semiconductors, charge carriers (i.e. electrons and holes) can “travel” through these bands resulting in current conduction.

The σ bond, which forms the backbone of the molecule, is more stable than the π bond. As a result of this, the least energetic electron excitation of conjugated molecules is observed in the case of the π - π^* type (HOMO-LUMO) transition. When the energy gap between HOMO and LUMO is between 1.5 and 3 eV, the compound is considered to be an organic semiconductor. In this case the HOMO-LUMO transition causes the absorption or emission of visible radiation. The energy gap may be controlled by the degree of conjugation of the individual systems. This feature opens various possibilities to tune the optoelectronic properties of organic semiconducting materials. Some prototype materials are given in **FIGURE 1.8**.

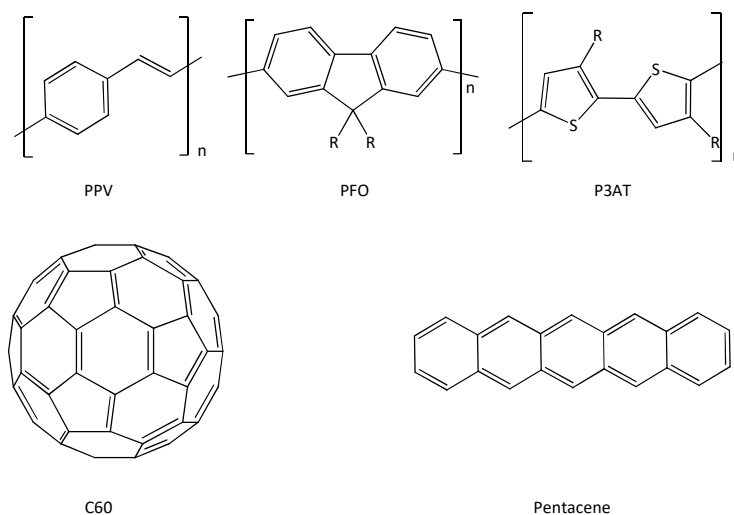


FIGURE 1.8: Molecular structure of some prototype organic semiconductors: PPV, poly(p-phenylenevinylene); PFO, polyfluorene; P3AT, poly(3-alkylthiophene); fullerene, C60;

1.2.2.1 Polymers

Polymers are large molecules composed by repeating structural units, called monomers, characterized by a relatively low molecular mass with respect to the final polymer. Each monomer is bonded to the others through covalent bonds. More specifically, conductive polymers are usually defined as organic polymers able to conduct electricity, exhibiting a conductive or a semiconductive behaviour. Conductive polymers can be roughly grouped into three different categories:

1. conjugated polymers;
2. polymers containing aromatic cycles;
3. conjugated polymers containing aromatic cycles.

All the molecules belonging to the previous categories have in common the alternation of single and multiple bonds (usually, double bond) in their structure. This is shown for example in **FIGURE 1.9** for the simplest conjugated molecule, polyacetylene.

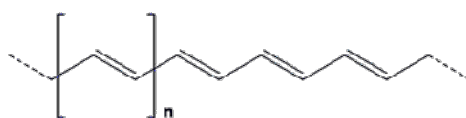


FIGURE 1.9: polyacetylene

Considering a polymer chain with N atoms using the quantum mechanical model for a free electron in a one dimensional box, the wave functions for the electrons of the polymer chain is given by:

$$E_n = \frac{n^2 \cdot h^2}{8 \cdot m \cdot L^2} \quad \text{EQUATION 1.1}$$

where n is a positive integer, h is the Plank constant, m the electron mass and L the conjugation length, which is equal to $N \cdot d$ in the case of N atoms separated by a distance d within the polymer chain. Therefore, if the π -electrons of the N atoms

occupy the delocalized molecular orbits, with 2 electrons per orbit, then the HOMO should have an energy given by:

$$E_{HOMO} = \frac{\left(\frac{N}{2}\right)^2 \cdot h^2}{8 \cdot m \cdot L^2}$$
EQUATION 1.2.1

whereas, the LUMO will have an energy of:

$$E_{LUMO} = \frac{\left(\frac{N}{2} + 1\right)^2 \cdot h^2}{8 \cdot m \cdot (N \cdot d)^2}$$
EQUATION 1.2.2

All energies are supposed to be measured with respect to vacuum energy level as reference. Thus, the energy required to excite an electron from the HOMO to the LUMO is given by their energies difference:

$$E_g = \frac{h^2}{8 \cdot m \cdot d^2 \cdot N}$$
EQUATION 1.3

It is evident that the band gap is inversely proportional to the conjugation length, and, as a consequence, to the number of atoms in the polymer chain. If the band gap is high the material is an insulator, if it is low the material is a conductor. Semiconducting polymers refer to polymeric materials with a band gap between 1.5 to 3 eV. This capability of decreasing the E_g by simply tuning the conjugation length justify why semiconducting polymers have been extensively studied as constituent materials for optoelectronic devices and why they have been experiencing a considerably increase of interest. As a result of this effort, it is now well established that the performances of semiconducting polymers critically depends on their chemical and structural order. In general, low charge carriers mobility is observed for most polymer semiconductors as a result of their inability to establish satisfactory structural order in the solid state.

It is outside the frame of the present intention to describe deeper inside conjugated polymers properties since they have not been treated in the current work. A detailed account can be found in literature^{24, 25}.

Therefore, active research is being carried out in order to find sufficiently ordered organic semiconductors. In this view, organic semiconducting single crystals represent a very promising option.

1.2.2.2 Organic semiconducting single crystals (OSSCS)

Crystals have attracted human civilization from prehistoric times, owing to their beauty and rarity, but their large-scale applications for devices have been realized only in the last six decades, based on silicon and analogous inorganic materials (Germanium, etc.). With respect to organic electronics, the importance of organic single-crystal research stems from several specific benefits that these materials offer with respect to fundamental studies:

1. high structural order (in particular, absence of grain boundaries),
2. high chemical purity,
3. availability of several efficient methods for fabrication of high-quality crystals.

The first two properties have been shown to be very important for observations of band-like transport in photoconductors based on molecular crystals in the pioneering time-of-flight measurements performed by Karl and co-workers²². The last point is especially important for the practical application of organic semiconducting single crystals (OSSCs), that rely on inexpensive and effective crystal growth techniques to ensure commercial success of these materials.

The immense efforts of the organic electronics research community in the early 2000s resulted in the first successful demonstration of high-performance devices based on single crystals of rubrene in 2002–2003^{26, 27}. This was followed, as reported in literature, by analogous demonstrations using single crystals of tetracene^{28, 29} and pentacene^{30, 31} thus overcoming the fabrication bottleneck in this area (FIGURE 1.10).

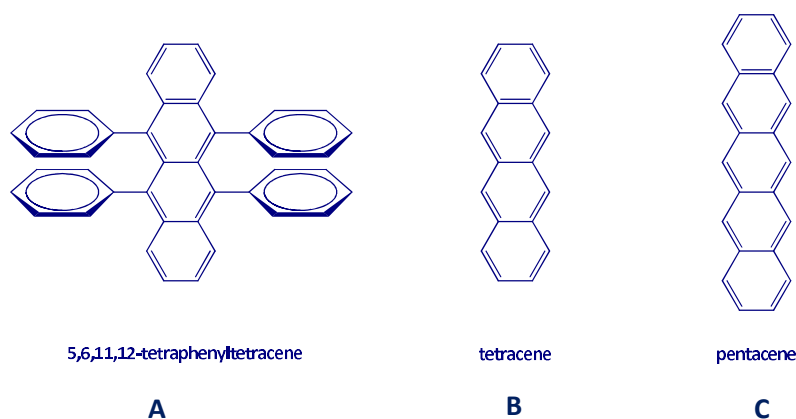


FIGURE 1. 10: Molecular structure of rubrene (A), tetracene (B) and pentacene (C).

These demonstrations have turned on an ever-growing activity in organic single-crystal devices, with the aim of exploring fundamental limitations and intrinsic electronic properties of organic semiconductors. To date, the highest reproducible charge-carrier mobility in organic semiconductors has been achieved in single-crystal rubrene oFETs. As shown in **FIGURE 1.10A**, rubrene is a condensed polyaromatic molecule, and large crystals can be obtained with a very high degree of order and purity. Rubrene can be grown in a variety of macroscopic morphologies, ranging from thick and bulky robust crystals to ultrathin (0.2–1 μm), flexible crystalline sheets. The bulky crystals can be easily handled and used in fabrication of freestanding devices. Depending on the crystal orientation and on the choice of the gate dielectric, the intrinsic hole mobility in rubrene can reach up to $20 \text{ cm}^2 \cdot (\text{V}\cdot\text{s})^{-1}$ at room temperature³². This value is higher than the mobility threshold required for a wide range of commercial applications, such as those currently utilizing α -(Si) FETs with $\mu \sim 1 \text{ cm}^2 \cdot (\text{Vs})^{-1}$. However, it is much lower than μ in high-purity single crystal Si ($\sim 500 \text{ cm}^2 \cdot (\text{Vs})^{-1}$).

In addition to the demonstration of relatively high charge-carrier mobilities, research in OSSCs have already evidenced a series of important discoveries. These include, for instance, the observation of:

1. intrinsic (not dominated by traps) polaronic transport at the surface of organic semiconductors (i.e., the motion of charge coupled to local lattice distortion)³³,

2. an intrinsic structure-property relationship in the form of mobility anisotropy observed experimentally^{34,35} and studied theoretically³⁶,
3. observation of a band-semiconductor Hall effect in molecular solids³⁷, and non-activated (band-like) charge transport observed in conductivity measurements³⁸, as well as in ultrafast optical experiments³⁹,
4. determination of the intrinsic anisotropic mechanical properties of flexible organic single crystals⁴⁰.

The ultrathin crystals can be electrostatically attached (laminated) to substrates such as SiO₂ or flexible plastics. This property of ultrathin crystals was utilized by Briseno and co-workers in developing flexible single-crystal rubrene oFETs on Kapton (a thin insulating plastic substrate), still with very good electrical performance ($\mu \sim 5 \text{ cm}^2 \cdot (\text{V}\cdot\text{s})^{-1}$), that can be bent to a radius of $R \sim 6 \text{ mm}$ without degradation of electrical properties⁴¹.

This pioneering work set the stage for OSSCs-incorporation within flexible devices, following a general tendency already observed in organic electronics with polymers and thin, polycrystalline films.

1.3 OSSCs GROWTH TECHNIQUES

Although systematic understanding of the subject of crystal growth began during the last quarter of the 19th century with Gibbs' phase equilibrium concept based on a thermodynamical treatment, man practiced crystal growth and crystallization processes as early as 1500BC in the form of salt and sugar crystallization. Thus, crystal growth can be treated as an ancient scientific activity. However, the scientific approach to the field of crystal growth started in 1611, when Kepler correlated crystal morphology and structure, followed by Nicolous Steno, who explained the origin of a variety of external crystal shapes (the so-called crystal habit). Since then, crystal growth has evolved steadily to attain its current technologically established field status.

Prior to commercial growth or production of crystals, man depended only on the availability of natural crystals for both jewellery and devices. The scientific and technological

interest in crystal growth started during World War II. Prior to that, applications of crystals and crystal growth technology did not catch the attention of technologists. The growth of small or thin crystals in the early days, which involved uncontrolled or poorly controlled crystal growth parameters without much sophistication in instrumentation or crystal growth equipment, slowly led to the growth of large bulk crystals during World War II.

Today the list of uses of artificially grown crystals is growing exponentially for a variety of applications, such as electronics, optics, nonlinear devices, oscillators, polarizers, radiation detectors, lasers, etc. Besides the inorganic one, the world of organic crystal growth is expanding greatly to make crystal growth activity more cost-effective. Today, the quality, purity, and defect-free nature of crystals is a prerequisite for their technological application^{42, 43}.

In general, crystal growth is essentially a process of arranging atoms, ions, molecules or molecular assemblies into long range, regular, three-dimensional periodic order.

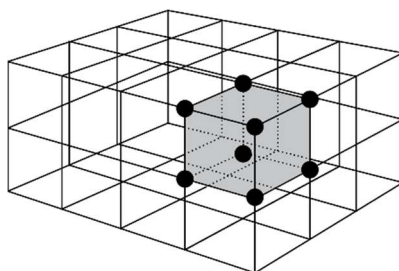


FIGURE 1.11: three-dimensional periodic order of a perfect crystal.

However, real crystals are never perfect, mainly due to the presence of:

1. different kinds of local disorder,
2. long-range imperfections (dislocations).

Moreover, they could be polycrystalline in nature. Hence, the ultimate aim of a crystal grower is to produce perfect single crystals of desired shape and size and to characterize them in order to verify their purity and quality for end users. Accordingly, crystal growth techniques and characterization tools have advanced greatly in recent years. This has

facilitated the growth and characterization of a large variety of technologically important single crystals.

So far many semiconducting organic molecules have been synthesized, but only a few of them have been processed into solid samples for electrical charge transport measurements, and even fewer have been crystallized into freestanding single crystals large enough for electrical measurements. For electrical measurements, unless using rather sophisticated lithographic processes, single crystals a few micrometers in size have to be grown at least. Single crystals that are a few tens micrometers in size are required for structure determination (i.e., XRD). Therefore, a large number of organic crystal growth methods have been developed, and most of them have been based on modified inorganic crystal growth methods.

All crystal growth processes can be broadly classified according to the scheme presented in

TABLE 1.

PROCESS NATURE	GROWTH TECHNIQUE	INITIAL STATE	DRIVING FORCE	FINAL STATE
LIQUID-SOLID	Melt growth	molten	T decrease	crystal
	Solution growth	Solid(s) + liquid	1. solvent evaporation 2. Temperature decrease	crystal
Gas-solid		Vapor(s)	T decrease	crystal

TABLE 1: Classification of crystal growth processes.

Since crystal growth is a highly interdisciplinary subject, covering various branches of science, and since it is extremely difficult to discuss the entire subject in this overview section, the following discussion will be focused on the three most common growth techniques:

1. melt growth,

2. vapour phase-growth,
3. solution growth.

The nature of the evaluated molecules, their interactions and the technological needs/limits for the chosen application determine the most suitable growth method for the considered compound.

Melt growth of crystals is undoubtedly the most popular method of growing large single crystals at relatively high growth rates. In fact, more than half of technological inorganic crystals are currently obtained by this technique⁴⁴. The method has been popularly used for growth of inorganic semiconductors and metals, oxides, halides, etc. Melt growth requires that the material:

1. melts without decomposition,
2. has no polymorphic transitions,
3. exhibits low chemical activity (or manageable vapour pressure at its melting point).

The **thermal decomposition** of a substance and chemical reactions in the melt can disturb the stoichiometry of the crystal and promote formation of physical or chemical defects. Similarly, the interaction between the melt and the crucible or the presence of a third component derived for example from the crystallization atmosphere, can affect melt growth. Crystallization can be carried out in a vacuum, in a neutral atmosphere (He, Ar, N₂), or in a standard atmosphere (air, O₂).

One of the earliest melt techniques used to grow large quantity of high-melting materials was the Verneuil method (flame fusion technique), first described by Verneuil in 1902⁴². This marks the beginning of the commercial production of large quantities of high-quality crystals, which were essentially used as gems or for various mechanical applications. Today, the technique is popular for growth of a variety of high-quality crystals for laser devices and precision instruments, as well as of substrates. The essential features are a seed crystal, the top of which is molten and is fed with molten drops of source material, usually as a powder forced through a flame or a plasma. The Czochralski method, developed in 1917 and later modified by several researchers, became the most popular technique to grow large-size single crystals, impossible to be obtained by any other techniques in such large

quantities⁴². An open crucible is used to melt the material. The seed is slowly immersed in the melt and then pulled up, under careful rotation. The crystal grows following the orientation of the small seed. The open crucible exposes the melt to air, favouring oxidation of the hot organic compounds. This is hence method applicable only to a few thermally stable organic materials.

The melt crystal growth methods are most frequently used for growing large crystals of inorganic semiconductors. Due to the high vapour pressure and thermal instability of most organic semiconductors around melting temperatures, the melt growth approach has been explored only for a few organic molecules, i.e. those sharing features of low cost and wide availability: naphthalene, anthracene, phenanthrene, pyrene, tetracene, and stilbene. These molecules are relatively stable at the melting temperature, but may polymerize or decompose during long heat treatments or under intense light. In any case, for these materials, large high quality single-crystalline ingots were obtained.

Vapour-phase growth, or Physical Vapour Deposition (PVD), or Vacuum Thermal Evaporation (VTE), is often employed in the fabrication of OSSCs for electronic devices because of its high throughput.

Various techniques exist in vapour-phase growth, differentiated by the nature of the source material and by the mechanism exploited to transport it to the growing crystal surface. Conceptually, the simplest vapour growth technique is the sublimation: the source material is placed at one end of a sealed tube and heated. As a consequence, it sublimates and it is carried to the cooler region of the tube, where it condenses and crystallizes. This vapour-phase growth involves three main stages:

1. vaporization,
2. transport,
3. deposition.

The process is carried out in a vacuum chamber, to lower the temperature required for the compound vaporization, hence minimizing the material degradation. Deposition of the vaporized molecules and subsequent condensation occurs on a substrate usually located several centimetres from the source, placed above it. This 'bottom up' geometry prevents

the source material from spilling out of the sublimation boat, and also avoids contamination of the substrate by flaking of material previously deposited onto the vacuum chamber wall, thereby creating dust that would ordinarily land on the substrate surface if a 'top down' deposition geometry were used.

VTE-grown crystals tend to have a low concentration of point defects and low dislocation densities compared with crystals grown from the melt, as the temperatures employed in VTE are usually much lower than the melting temperature of the source compounds. Moreover, if the material undergoes a phase transformation or melts incongruently, vapour growth may be the only choice for the growth of single crystals. The main advantage of this method, besides its easiness, is that molecular impurities are effectively separated due to the temperature gradient created along the growth tube, and thus efficient chemical purification is achieved. Most organic molecules possess sufficient vapor pressure to enable their VTE processing. Therefore, to date VTE-based methods are the most common growth techniques. Some materials, such as anthracene, tetracene, pentacene, and rubrene, have been crystallized in sealed ampoules in the form of needles, platelets or even large bulk single crystals. Oligothiophenes and acenes, for example, have been grown from the vapour phase, and resulting single crystals have been used for physical measurements as well as device preparation. Many organic molecules, designed and synthesized for exploration of their semiconducting properties, have been evaporated during heating and crystallized in the form of small (only a few to tens of micrometers long) crystals. Such small crystals may have sufficient quality that the crystal structure can be determined by diffraction methods (where dimensions of the order of $50 \times 50 \times 5 \text{ }\mu\text{m}^3$ are needed)⁴².

VTE has several shortcomings: it can be wasteful of material, and it is difficult to maintain a uniform deposition rate because the organic material sources are typically thermally insulating. Hence, they are only heated in regions where the organic source is in contact with the resistively heated boat, creating pockets in the source powder that occasionally collapse under gravity, resulting in powder bubbling or rapid changes in evaporation rate. Nevertheless, commercial applications of organic semiconductors is mainly based on VTE and very-large-area full-colour displays have been demonstrated using this process.

With respect to OSSCs growth, VTE growth provides very good results in terms of chemical purity, structural order and electrical performance. However, due to the mentioned limitations, the technique is not low-cost at an industrial scale. Therefore, while the vapour growth is well developed and delivers some of the highest order and purity small-molecule organic single crystals, **solution growth techniques** are perhaps the most favourable for industrial applications, especially considering previously mentioned printing techniques^{45, 46}. In fact, solution growth is used for a variety of organic crystalline products for daily life such as food-relevant compounds, medicines, fertilizers, pesticides, etc⁹. This wide application of the technique is due to its advantages with respect to VTE and growth from melt, which include suitability for substances that melt incongruently, are thermally sensitive, or have several high-temperature polymorphic modifications; moreover, even in the absence of such restrictions, solution growth is rather effective.

Organic semiconductors can be soluble in numerous organic solvents, even at room temperature. Moreover, solution growth allows a considerable degree of control over process parameters, which include the growth temperature, the solution viscosity and concentration. The equipment needed for solution growth is very simple and low-cost, and the resulting crystals, when the technique is correctly carried out, have a very good morphology and a very small number of defects.

Most organic molecules are soluble in organic solvents over a range of temperatures and pressures. This fact allows for low-temperature processing such as printing, spraying, casting, laminating, etc. to mention just a few. Of course, printing of materials implies the deposition of liquid drops onto a substrate. Growing OSSCs from printed solutions requires hence an optimization of general crystal growth from solution techniques. Based on the properties of the given organic molecule to be crystallized, several solution methods are available:

1. solvent evaporation method,
2. slow cooling method,
3. vapour diffusion method,
4. liquid–liquid diffusion method.

The solvent evaporation method is the simplest and most effective method to grow single crystals, and most organic crystals used for crystal structure analysis are grown by this method. Organic solvents, such as dichloromethane, chloroform, toluene, benzene, and chlorobenzene are used to solubilize the organic semiconductor. If a beaker containing a solution is not hermetically sealed, the solvent can slowly evaporate forming supersaturated solution. (FIGURE 1.12A).

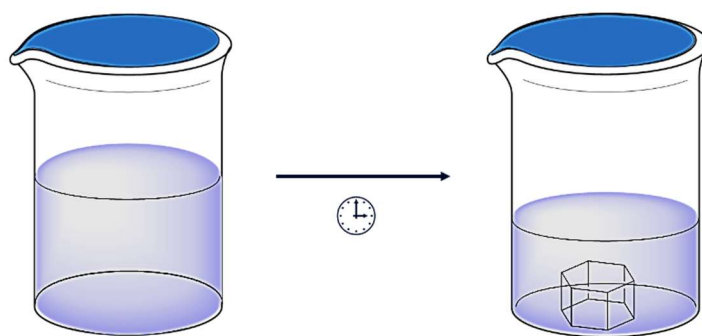


FIGURE 1.12A: Solution-based methods for the growth of organic semiconductor single crystals. Solvent evaporation method. Molecules crystallize due to oversaturation resulted from solvent evaporation.

Then nuclei spontaneously form, growing into larger crystals. As the solubility of some organic semiconductors in certain organic solvents is very high, sometimes the drop casting method is preferred. This method is a type of solvent evaporation method, widely explored for the fabrication of single-crystalline films for field-effect transistor measurements⁴².

The slow cooling method is suitable for organic semiconductors whose solubility in organic solvents is moderate at room temperature but changes considerably with temperature (FIGURE 1.12B).

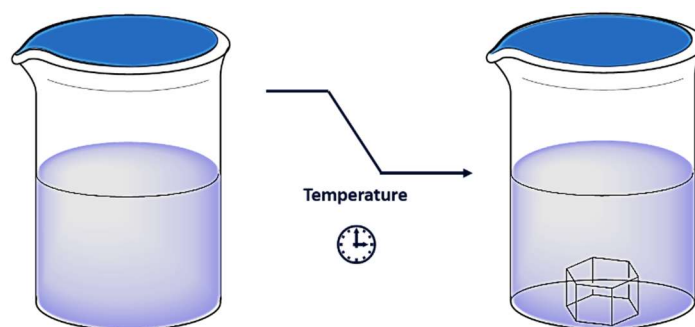


FIGURE 1.12B Solution-based methods for the growth of organic semiconductor single-crystals. Slow cooling method. Molecules crystallize due to a decrease of solute solubility.

As the temperature increases, more organic semiconductor material can be dissolved in solution until a saturated solution forms. When the temperature of the saturated solution slowly decreases, organic semiconductor material spontaneously forms nuclei and additional material deposits onto these seeds, forming at the end of the cooling step large crystals. The process can be repeated several times, oscillating the temperature around the saturation temperature in such a way that only a small portion of material dissolves and crystallizes in the following temperature oscillation period. This process results in preferred dissolution of the smallest seeds and crystallization on the remaining seeds. In this way, large organic crystals, even cm-sized, can be formed. The solvent evaporation method can be combined with the slow cooling method to obtain even larger organic crystals.

The vapour diffusion method (**FIGURE 1.12C**) is used to grow organic semiconductors that are highly soluble in a particular organic solvent, namely **2**, but have poor solubility in other solvents, namely **1**. To form a saturated solution, organic semiconductors are dissolved in solvent **2** bearing in mind that:

1. solubility of the compound to be crystallized in solvent **2** has to be as high as possible,
2. solvent **2** vapour pressure has to be as low as possible.

The beaker containing the saturated solution is then placed in a larger beaker that contains the volatile solvent **1** that only slightly dissolves the organic semiconductors. When the larger beaker is sealed, the volatile solvent **1** evaporates, and its vapour diffuses into the saturated

solution of the organic semiconductor dissolved in the solvent **2**. This diffusion changes the solution composition of the organic semiconductor. Indeed the new solvent is now composed by both the good pristine solvent **2** and by the solvent **1** and this change leads to an oversaturated solution, which causes the crystallization process to take place.

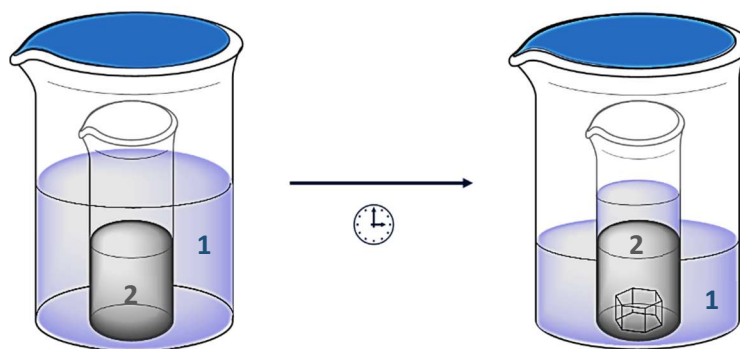


FIGURE 1.12C Solution-based methods for the growth of organic semiconductor single-crystals. Vapour diffusion method. Molecules crystallize because solvent **1** evaporates and diffuses into solvent **2**, leading to an oversaturated solution.

Two layers of different solvents are used in the liquid–liquid diffusion method, and the solubility of the crystallizing material in these two solvents is different. As shown in **FIGURE 1.12D**, the organic semiconductor is dissolved in the high-solubility solvent to form a saturated solution. The low-solubility solvent diffuses into the high-solubility solvent layer, causing the formation of a saturated solution at the interface between the solvent layers.

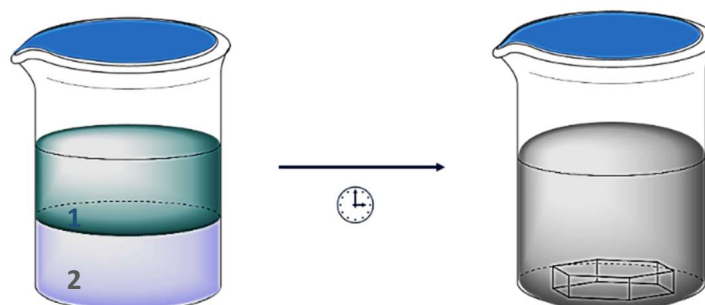


FIGURE 1.12D: Solution-based methods for the growth of organic semiconductor single-crystals. Liquid–liquid diffusion method. Molecules crystallize because solvent **1** inter diffuses with solvent **2** and results in a decrease of solution solubility in solvent **2**.

The liquid–liquid diffusion method generates high-quality small crystals, mostly micrometer sized, because the crystals are growing at the solvent interface without any stress from substrates.

Among the aforementioned techniques, the slow solvent evaporation is the one most approaching the actual behaviour of printed solution drops from which single crystals can develop. Inkjet printing represents a very interesting type of process from an industrial point of view, since it is completely additive (i.e., no material waste once the solution has been deposited onto the substrate), it allows lateral resolutions down to a few tens of microns, it is already optimized for industrial use and the printing equipment and overall process is usually inexpensive, if compared to the equipment needed for VTE or melt-based techniques. Moreover, inkjet printing is compatible with flexible substrates, i.e. substrates that can either be bent during usage or can be shaped once into a non rigid form.

1.4 AIMS OF THE WORK

So far, as seen in **section 1.1**, organic semiconducting materials have been receiving great attention for application in optoelectronics. Among possible applications in this field, a particularly attractive one is that of ionizing radiation detectors. This field has been constantly growing thanks to its vast and numerous industrially and socially relevant application. For example, X-rays are used in Biomedicine (Radiography), Radiotherapy (as a treatment for the therapy, including palliation, of cancer), industrial quality control (automated inspection of industrial parts) and security applications (control of luggage, cargos trucks and even people, before and during shipment by air, sea and road), and other niche but important applications in the scientific field (like in the cultural heritage study, protection and conservation where many artefacts are often X-rayed to reveal fundamental feature like under-drawings, alterations, restorations, etc)⁴⁸.

Many of these applications would take advantage of large area, low-cost, thin and flexible ionizing radiation sensing systems but the currently available technologies, based on bulky and rigid inorganic semiconductors, cannot deliver such a device.

Presently, on the available radiation detectors are of three different types: i) based on gas-filled containers (like Geiger counters) that directly count the ionizing photons or

particles; ii) based on a solid or liquid materials capable of producing visible photons upon exposure to the radiation (scintillators), which are coupled to photodiodes that then detect the visible photons emitted by the scintillator; iii) based on solid materials capable of directly converting X-ray photons into an electrical signal (direct detectors, also called solid state detectors). This latter type offers the great advantage to avoid the need of two or more coupled device (scintillators and photodiodes), which grants satisfactory performances but increases the complexity and lowers the overall performances.

State-of-the-art solid state X-rays detectors are based on inorganic materials and offer top detecting performances. High purity Si and Ge were the first materials to be used as solid-state detectors, and are still widely employed thanks to their extremely good energy resolution (below 0.2%) which, however, can only be achieved at cryogenic temperatures, thus hindering the practical realization of a large area sensor system based on a 'direct detection' process⁴⁸. This prompted the development of novel compound semiconductors such as CdTe, SiCd, CdZnTe, which can offer excellent performance at room temperature, superior in a few aspects to Ge. Nonetheless, the difficulty to grow large-size, high-quality crystals of these II–VI compound materials at a low cost is limiting their application in very high-tech and specific detectors, e.g. in satellites and as pioneering medical diagnostic tools. A non-negligible further drawback of these materials is their limited availability, and often their toxicity. Moreover they are rigid and heavy. These limitations have prompted the need to find alternative novel semiconducting materials and technologies enabling the fabrication of direct detectors on large areas.

The main requirements for a good solid state semiconductor detector are common to all semiconductors and are briefly detailed below:

1. high resistivity ($> 10^9 \Omega \cdot \text{cm}$) and low leakage current. Low leakage currents when an electric field is applied during operation are critical for low noise operation. The necessary high resistivity is achieved by using larger band gap materials ($> 1.5 \text{ eV}$) with low intrinsic carrier concentrations,
2. a small enough band gap so that the electron–hole ionization energy is small ($< 5 \text{ eV}$) This ensures that the number of electron–hole pairs created is reasonably large and results in a higher signal to noise ratio.

3. high atomic number (Z) and/or a large interaction volume for efficient radiation–atomic interactions. For high-sensitivity and efficiency, large detector volumes are required to ensure that as many incident photons as possible have the opportunity to interact in the detector volume,
4. high-purity, homogeneous, defect-free materials, to ensure good charge transport properties, low leakage currents, and no conductive short circuits between the detector contacts,
5. electrodes which produce no defects, impurities or barriers to the charge collection process and which can be used effectively to apply a uniform electric field across the device. This requirement is also related to the need to avoid material polarization effects which may affect the time response of the detector,
6. surfaces should be highly resistive and stable over time to prevent increases in the surface leakage currents over the lifetime of the detector.

It is quite obvious that not all of the above requirements can be easily met by a single material, but the dramatic advancements in the organic semiconductor research field have recently stimulated studies on the potential application of organic semiconductors as solid-state detectors.

So far organic semiconductor have been mainly used as detectors for ionizing radiation in the indirect conversion approach, namely as scintillators, which convert ionizing radiation into visible photons⁴⁹. In alternative, OSs have been proposed as photodiodes to be coupled to other technologies-based scintillators⁴⁷. Recent examples of organic device used as direct photon detectors have been presented for operation in the UV- NIR range, with very interesting values for figures of merit such as photoconversion efficiency, speed, and minimum detectable signal level⁴⁸ and even though the simultaneous attainment of all these relevant parameters is demonstrated only in a limited number of papers, real applications are within reach for this technology, where the best reported photoresponsivity outperform a-Si-based devices.

Organic semiconductors are also very promising candidates for the detection of higher energy photons (X-rays and γ -rays) and recently it has been reported⁴⁹ how organic semiconducting single crystals provide a direct, stable and linear electrical photoresponse to

increasing X-rays dose rates, proving to be good ionizing radiation sensors operating at room-temperature^{50,51}. In this article authors have shown how, among all the organic semiconductors, solution-grown OSSCs are ideal candidates to directly detect X-ray radiation, as their particular properties overcome most of the major limitations inherent to organic materials discussed to date and briefly reviewed in the **section 1.2**. Moreover, the evaluated crystals can be grown from solution, and it is possible to tune their sizes up to mm³⁵².

From this early work, in 2013 the EU project 'i-FLEXIS' has been set up in order to develop an innovative, large-area and low-cost integrated X-ray sensor system based on OSSCs as detecting elements. I-Flexis pushed for a real-time, direct X-ray detection, room temperature operation and a 'designed for industrial production' approach, delivering operationally reliable, robust and environmentally friendly devices. This Project wanted to integrate three major novel components implemented to achieve a totally new sensing system:

1. organic single crystal as the active, X-ray direct sensing material,
2. flexible transparent electronics integrated in low cost plastic substrates,
3. read-out electronics based on fully printed organic/inorganic CMOS platform, away from the conventional silicon technology.

Each of these three new technological concepts, considered as a single device, represents already a breakthrough and disruptive technology in their own field. The i-Flexis Project aimed to combine these three novel concepts, never applied before to ionizing radiation sensing, to implement them using nanotechnology as a mean for enhancing their performance and to integrate them in a final sensor system.

The here presented research stems from the i-Flexis project, and it has been mainly focused on OSSCs growth from solutions in quasi-equilibrium conditions and with lab-scale methods (slow solvent evaporation in beakers). The aim of this approach has been that of gaining the fundamental knowledge on crystal growth for maximizing grown crystals yield and quality, and to control the growth parameters for the production of crystals to be used for X-ray detection. These steps are essential to transfer the crystal growth proper conditions

from the laboratory to the factory, via inkjet printing technologies. In particular, the main aims of the work have been the following ones:

1. identification of structures able to deliver solution grown self-standing single crystals with meaningful X-rays response;
2. acquisition of sufficient know-how on the solution growth technique by slow solvent evaporation method in order to obtain crystals of the desired size and with the proper surface morphologies suitable to be used in the field of ionizing detection. The ultimate goal has been the transfer of the so-gained know-how from laboratory to inkjet printing in order to provide a base for an industrial production of single crystals;
3. identification of a method suitable for the bonding of the grown crystals on flexible substrates equipped with gold electrodes.

1.5 RADIATION INTERACTION WITH MATTER.

To organize the following overview, it is convenient to arrange the four major categories of radiation into the following matrix:

CHARGED PARTICULATE RADIATIONS		UNCHARGED RADIATIONS
HEAVY CHARGED PARTICLES (characteristic distance $\approx 10^{-5}$ m)	←	NEUTRONS (characteristic length $\approx 10^{-1}$ m)
FAST ELECTRONS (characteristic distance $\approx 10^{-3}$ m)	←	X-RAYS AND γ-RAYS (characteristic length $\approx 10^{-1}$ m)

TABLE 2: Major categories of radiation.

The entries in the left column represent the charged particles that, because of the electric charge carried by the particle, continuously interact by means of the Coulomb force with the electrons present in any medium through which they pass. The radiations in the right column are uncharged and therefore are not subject to the Coulomb force. Instead, these radiations must first undergo an interaction that radically alters the properties of the incident radiation in a single encounter. In all

cases of practical interest, the interaction results in the full or partial transfer of energy of the incident radiation to electrons or nuclei of the constituent atoms, or to charged particle products of nuclear reactions. If the interaction does not occur within the detector, these uncharged radiations (e.g., neutrons or gamma rays) can pass completely through the detector volume without revealing the slightest hint that they were ever there. The horizontal arrows shown in the diagram illustrate the results of such interactions. An X- or gamma ray, through the processes described below, can transfer all or part of its energy to electrons within the medium.

Although a large number of possible interaction mechanism are known for gamma rays in matter, only three major types play an important role in radiation measurements: *photoelectric absorption*, *Compton scattering*, and *pair production*. All of these processes lead to the partial or complete transfer of the gamma-ray photon energy to electron energy.

Photoelectric absorption: in this process, a photon undergoes an interaction with an absorber atom in which the photon completely disappears. In its place, an energetic photoelectron is ejected by the atom from one of its bound shells. The interaction is with the atom as a whole and cannot take place with free electrons. The photoelectron appears with an energy given by where $h\nu$ is the energy of the original photon and E_b represents the binding energy of the photoelectron in its original shell. For gamma-ray energies of more than a few hundred keV, the photoelectron carries off the majority of the original photon energy. In addition to the photoelectron, the interaction also creates an ionized absorber atom with vacancy in one of its bound shell. This vacancy is quickly filled through capture of a free electron from the medium and/or rearrangement of electrons from other shells of the atom. Therefore, one or more characteristic X-ray photons may also be generated.

Compton scattering: this interaction takes place between the incident gamma-ray and an electron in the absorbing material. The photon transfers a portion of its energy to the electron (assumed to be initially at rest), which is then known as a recoil electron.

1.6 THESIS ORGANISATION.

The thesis content has been organized in the following three steps:

1. in **Chapter 2** the screening of several different molecules, crystallized from solution as free-standing single crystals (by slow solvent evaporation method), is described. The results of the work is aimed to the selection of those structures able to provide the best

results in terms of both crystals output and preliminary X-rays response characterization. The latter part of the work has been carried out from i-FLEXIS collaborating groups on the self-standing crystals provided by this first part of work . Based on both evaluations the most promising molecules have been identified and therefore the subsequent work has been focused on them;

2. in **Chapter 3** a thorough exploration of the influence of the main growth parameters, those easily controllable in the industrial production of single-crystals, is described. The main scope of the work has been the production of crystals with desired size and quality, with respect to those required in the field of radiation detection. A discussion over the rationale for the found influence of the analysed parameters over the crystal size and quality is provided;
3. in **Chapter 4**, investigations over a possible method to connect the crystals to nanostructured electrodes defined onto flexible PEN substrate have been carried out, finding interesting methods based on the use of self-assembled monolayers.

BIBLIOGRAPHY

- ⁰¹ C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa: Synthesis of highly conducting films of derivatives of polyacetylene - J. Am. Chem. Soc. – 100 - 1013÷1015 – 1978;
- ⁰² C. K. Chiang, C. R. Fischer, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid: Electrical Conductivity in Doped Polyacetylene - Phys. Rev. Lett. – 39 – 1098 – 1977;
- ⁰³ H. Shirakawa, E. J. Louis, A. G. McDiarmid, C. K. Chiang and A. J. Heeger: Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)_x - J. Chem. Soc. Chem.Comm. - 579÷580 – 1977;
- ⁴ R. G. Kepler: Charge Carrier Production and Mobility in Anthracene Crystals - Phys. Rev. – 119 - 1226÷1235 – 1960;
- ⁵ P. Mark and W. Helfrich: Space-Charge-Limited Currents in Organic Crystals - Journal of Applied Physics – 33 - 205 – 1962;
- ⁰⁶ C. W. Tang, and S. A. Van Slyke: Organic electroluminescent diodes - Appl. Phys. Lett. – 51 – 913÷915 – 1987;
- ⁰⁷ W. Brütting: Physics of Organic Semiconductors - Wiley-VCH – Berlin – 2005;
- ⁰⁸ I. H. Campbell and D. L. Smith: Physics of Organic Electronic Devices - Solid State Physics - 55 - Academic Press - San Diego – 2001;
- ⁹ X. Zhang, P. Bäuerle, T. Aida, P. Skabara and C. Kagan: Organic Electronics for a better tomorrow: innovation, acessibility and sustainability – San Francisco – California – 2012;
- ⁰¹⁰ J.A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, H.E. Katz, V. Kuck, K. Amundson, P.Drzaic: Paper-like electronic displays: large-area rubber-stamped plastic sheets of electronics

-
- and microencapsulated electrophoretic inks - Proc. Of National Academy of Sciences – 98 - 4835÷4840 – 2001;
- ⁰¹¹ M. Halik, H. Klauk, U. Zschieschang, G. Schmid, W. Radlik: Polymer gate dielectrics and conducting polymer contacts for high-performance organic thin film transistors - IEDM Technical Digest - 557÷ 560, 2002;
- ⁰¹² C.D. Sheraw, L. Zhou, J.R. Huang, D.J. Gundlach, T.N. Jackson, M.G. Kane, I.G. Hill, M.S. Hammond, J. Campi, B.K. Greening, J. Francl and J. West: Organic Thin-Film Transistor-Driven PolymerDispersed Liquid Crystal Displays on Flexible Polymeric Substrates - Appl. Phys. Lett. - 80 - 1088÷1090 - 2002;
- ¹³ M.G. Kane, J. Campi, M.S. Hammond, F.P. Cuomo, B. Greening, C.D. Sheraw, J.A. Nichols, D.J. Gundlach, J.R. Huang, C.C. Kuo, L. Jia, H. Klauk and T.N. Jackson: Analog and digital circuits using organic thin-film transistors on polyester substrates - IEEE Electron Device Letters - 21 - 534÷536 – 2000;
- ¹⁴ J. Krumm, E. Eckert, W.H. Glauert, A. Ullmann, W. Fix, W. Clemens: A polymer transistor circuit using PDHTT - IEEE Electron Device Letters - 25 - 399÷401 - 2004;
- ¹⁵ G Busch: Early history of the physics and chemistry of semiconductors-from doubts to fact in a hundred years - European Journal of Physics – 10 – 4;
- ¹⁶ F. A. Stahl: The emergence of semiconductors: Nineteenth century modern physics - Am. J. Phys. - 71 - 1170÷1173 – 2003;
- ¹⁷ D. M. de Leeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand: Hybrid light emitting transistors (Presentation Recording) - Synth. Met. – 87 - 53 -1997;
- ¹⁸ Y. Sun and J. A. Rogers: Inorganic Semiconductors for Flexible Electronics - Adv. Mater. – 19 - 1897÷1916 – 2007;
- ¹⁹ IDTechEx: Printed electronics vs Silicon Electronics – www.electronicweekly.com – 25 - 2006;

- ²⁰ G. Hadziioannou and P. F. van Hutten: Semiconducting Polymers - Wiley – VCH - Weinheim - 2000;
- ²¹ W. Brütting: The Physics of Organic Semiconductors - Wiley-VCH - Weinheim - 2005;
- ²² A. L. Briseno, R. J. Tseng, M.-M. Ling, E. H. L. Falcao, Y. Yang, F. Wudl and Z. Bao: High-Performance Organic Single-Crystal Transistors on Flexible Substrates - Adv. Mater. – 18 - 2320÷2324 – 2006;
- ²³ R. Farchioni and G. Grosso: Organic Electronic Materials: conjugated polymers and low molecular weight organic solids – Springer - Berlin - 2013;
- ²⁴ J. Fraxedas: Molecular Organic Materials. From molecules to crystalline solids – Cambridge University Press – 2006;
- ²⁵ M. Schwoerer, H. C. Wolf: Markus Schwoerer, Hans Christoph Wolf – Wiley-VCH – 2007;
- ²⁶ V. Podzorov, V.M. Pudalov and M.E. Gershenson: Field-effect transistors on rubrene single crystals with parylene gate insulator - Appl. Phys. Lett. - 82 – 1739÷1741 – 2003;
- ²⁷ V. Podzorov, S.E. Sysoev, E. Loginova, V.M. Pudalov and M.E. Gershenson: Single-crystal organic field effect transistors with the hole mobility $\sim 8 \text{ cm}^2(\text{Vs})^{-1}$ - Appl.Phys. Lett. - 83 – 3504÷3506 - 2003;
- ²⁸ R.W.I. de Boer, T.M. Klapwijk and A.F. Morpurgo: Field-effect transistors on tetracene single crystals - Appl. Phys. Lett. - 83 - 4345÷4347 – 2003;
- ²⁹ C.R. Newman, R.J. Chesterfield, J.A. Merlo and C.D. Frisbie: Transport properties of single-crystal tetracene field-effect transistors with silicon dioxide gate dielectric - Appl. Phys. Lett. - 85 - 422÷424 – 2004;
- ³⁰ J. Takeya, C. Goldmann, S. Haas, K.P. Pernstich, B. Ketterer and B. Batlogg: Field-induced charge transport at the surface of pentacene single crystals: A method to study charge dynamics of two-dimensional electron systems in organic crystals - J. Appl. Phys. - 94 - 5800÷5804 - 2003;

-
- ³¹ J. Takeya, T. Nishikawa, T. Takenobu, S. Kobayashi, Y. Iwasa, T. Mitani, C. Goldmann, C. Krellner and B. Batlogg: Effects of polarized organosilane self-assembled monolayers on organic single-crystal field-effect transistors - Appl. Phys. Lett. - 85 - 5078÷5080 – 2004;
- ³² V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J.A. Rogers and M.E. Gershenson: Intrinsic Charge Transport on the Surface of Organic Semiconductors - Phys. Rev. Lett. - 93 – 086602-1÷086602-4 – 2004;
- ³³ Vitaly Podzorov: Organic single crystals: Addressing the fundamentals of organic electronics – Mrs bulletin – 38 – 1 – 15÷24 – 2013;
- ³⁴ V.C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R.L. Willett, M.E. Gershenson and J.A. Rogers: Elastomeric transistor stamps: reversible probing of charge transport in organic crystals - Science - 303 - 1644÷1646 – 2004;
- ³⁵ Y. Xia and C.D. Frisbie: Tetracene air-gap single-crystal field-effect transistors - Appl. Phys. Lett. - 90 – 162106-1÷162106-3 -2007;
- ³⁶ F. Ortmann, F. Bechstedt and K. Hannewald: Charge transport in organic crystals: Theory and modelling - Phys. Status Solidi - B - 248 – 511÷525 – 2011;
- ³⁷ V. Podzorov, E. Menard, J.A. Rogers and M.E. Gershenson: Hall Effect in the Accumulation Layers on the Surface of Organic Semiconductors - Phys. Rev. Lett. - 95 – 226601-1÷226601-4 2005;
- ³⁸ N.A. Minder, S. Ono, Z. Chen, A. Facchetti and A.F. Morpurgo: Band-like electron transport in organic transistors and implication of the molecular structure for performance optimization - Adv. Mater. - 24 - 503÷508 – 2012;
- ³⁹ O. Ostroverkhova, D.G. Cooke, F.A. Hegmann, J.E. Anthony, V. Podzorov, M.E. Gershenson, O.D. Jurchescu and T.T.M. Palstra: Ultrafast carrier dynamics in pentacene, functionalized

-
- pentacene, tetracene, and rubrene single crystals - Appl. Phys. Lett. - 88 – 162101-1÷162101-3 – 2006;
- ⁴⁰ M.A. Reyes-Martinez, A. Ramasubramaniam, A.L. Briseno and A.J. Crosby: The intrinsic mechanical properties of rubrene single crystals - Adv. Mater. - 24 – 41 - 5548÷5552 – 2012;
- ⁴¹ A.L. Briseno, R.J. Tseng, M.M. Ling, E.H.L. Falcao, Y. Yang, F. Wudl and Z. Bao: High-performance organic single-crystal transistors on flexible substrates - Adv. Mater. - 18 - 2320÷2324 – 2006;
- ⁴² H.J. Scheel: Historical introduction. In: Handbook of Crystal Growth - 1a - D.T.J. Hurle – Elsevier - Amsterdam - 1÷41 – 11993;
- ⁴³ D. Elwell and H.J. Scheel: Crystal Growth from High Temperature Solution – Academic - London - 1975;
- ⁴⁴ H. Jiang and C. Kloc: Single-Crystal growth of organic semiconductors – Mrs Bulletin – 38 – 28÷33 – 2013;
- ⁴⁵ S.R. Forrest: The path to ubiquitous and low-cost organic electronic applications on plastic - Nature – 428 - 911÷918 - 2004;
- ⁴⁶ E. Reichmanis, H. Katz, C. Kloc and A. Maliakal: Plastic electronic devices: from materials design to devices applications - Bell Labs Tech. J. – **10** - 87÷105 – 2005;
- ⁴⁷ G.F. Knoll et al: Radiation detection and measurement – Wiley –Hoboken – NJ – 2011;
- ⁴⁸ K.J. Baeg, M. Binda, D. Natali, M. Caironi and Y.Y. Noh: Organic light detectors: photodiodes and phototransistors - Adv. Mater. – 25 – 4267÷4295 – 2013;
- ⁴⁹ F.A. Boroumand, M. Zhu, A. B. Dalton, J. L. Keddie and P. J. Sellinan: Direct x-ray detection with conjugated polymer devices - Appl. Phys. Lett. – 91 – 033509-1÷033509-3 – 2007;

-
- ⁵⁰ B. Fraboni, A. Ciavatti, F. Merlo, L. Pasquini, A. Cavallini, A. Quaranta, A. Bonfiglio, A. Fraleoni-Morgera: Organic Semiconducting Single Crystals as Next Generation of Low-Cost, Room-Temperature Electrical X-ray Detectors – *Adv. Mat.* – 24 – 2289÷293 – 2012;
- ⁵¹ B. Fraboni, A. Ciavatti, L. Basiricò and A. Fraleoni-Morgera: Organic semiconducting single crystals as solid-state sensors for ionizing radiation – *Farad. Disc.* – 174 – 219÷234 – 2014;
- ⁵² A. Fraleoni Morgera, L. Benevoli, B. Fraboni: Solution growth of single crystals of 4-hydroxycyanobenzene (4HCB) suitable for electronic applications – *J. Crys. Grow.* – 312 – 23 - 3466÷3472 – 2010;

CHAPTER 2: Identification of structures able to deliver solution grown self-standing single-crystals with required X-ray detection.

In this chapter the general procedure adopted to select the best molecules for the purposes of the project will be described. In more detail, the evaluated structures and the reasons why they have been chosen will be described in **section 2.1**. The molecules screening method, including description of the purification procedures and of the solvents selection criteria, will be treated in **section 2.2**. The experimental techniques carried out to evaluate the crystal yield and quality will be described in **section 2.3**. The obtained results, in terms of crystals yield and quality, are reported in details in **section 2.4**, where an addendum devoted to the obtained charge mobilities is also provide.

2.1 EVALUATED STRUCTURES AND THEIR SELECTION CRITERIA

2.1.1. INTRODUCTION

In **Chapter 1** it has been shown that most organic molecular crystals are materials that behave like insulators, with electrical resistivities in the range of $10^{13}\div 10^{18}$ $\Omega \cdot \text{cm}$ at room temperature. However, it has also been highlighted how some organic

molecules with delocalized π -electrons - such as conjugated hydrocarbons, phthalocyanines, oligothiophenes - may form colored crystals. This feature clearly indicates a small energy gap between the HOMO - the highest occupied molecular orbital - and the LUMO - the lowest unoccupied molecular orbital. Crystals of such substances often show semiconducting behavior.

In the first chapter it has been shown how the pristine studies of physical properties of organic semiconductors have been performed on polycrystalline or amorphous thin-film devices, due to their ease of fabrication. However, grain boundaries, inhomogeneous distribution of impurities, and high defect densities make thin-film devices unattractive for studies of intrinsic properties^{1, 2}. On the other hand, single crystals - systems characterized by a high symmetry of molecules and by the absence of grain boundaries - are ideal candidate for a systematic investigation of the intrinsic properties of organic semiconductors. Indeed, so far, results obtained on these systems have ever been more reproducible than those obtained on amorphous or polycrystalline thin-film samples³. In general, organic semiconductors crystallize in low-symmetry unit cells. Therefore, all physical properties are tensorial properties with often large anisotropies, that can be properly evaluated in single crystals. The availability of high-purity and high-quality single crystals of organic semiconductors is thus crucial in exploring the physics of such materials and can be very helpful in new materials design and in building devices with novel functionality and high performances^{3, 4}.

In this frame, a series of aromatic structures have been investigated in terms of their ability to form OSSCs of desired size and morphology and as potential X-rays detecting elements in direct devices. The former part of the work has been integral part of this thesis – and will be therefore described in deep detail - while the latter one has been performed, on the single-crystals crystallized in this first part of the work, by other colleagues involved in i-Flexis project. The overall results have been compared and matched in order to select only a few structures suitable for the already described purposes.

2.1.2. TESTED MOLECULES

As shown in **FIGURE 2.1**, a starting plethora of molecules, all commercially available, have been chosen based on precise structural and physical differences:

1. 4-hydroxycyanobenzene (4HCB),
2. 1,8-naphthalimide (NTI),
3. 1,5-Dinitronaphtalene (DNN),
4. 2,4-dinitro-1-naphthol (commercial name: Martius Yellow, MY),
5. 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (DMTPDS),
6. Mn(II)phthalocyanine (MnPc),
7. Zn(II)phthalocyanine (ZnPc),

The first three molecules, shown in **FIGURE 2.1** have been screened^{5, 6, 7, 8} based on previous demonstrations of their applicability as room temperature, low-voltage direct X-ray detectors. Moreover, 4HCB is rather interesting as, although being a very small molecule, it presents carrier mobilities approaching $10^{-1} \text{ cm}^2 \cdot (\text{V} \cdot \text{s})^{-1}$ ⁹. 4HCB is characterized by the presence of a push-pull (-OH/-CN) conjugated system. In this frame, it has been deemed worth of attention to compare its electronic properties with those of other small systems having a naphthalenic core, like DNN and NTI.

MY has been chosen as it has a naphthalenic core analogous to that of DNN, but bearing a push-pull-pull system (-OH/-NO₂/-NO₂) instead of a double pull system (-NO₂/-NO₂), as shown in **FIGURE 2.2**.

Finally, DMTPDS has been chosen due to the presence in its chemical structure of two silicon atoms, whose presence could have been beneficial for the overall X-ray cross section of the resulting crystals. In fact, it is known that the introduction of high Z elements in polymeric thin film X-rays detectors increases the X-ray attenuation of the material¹⁰.

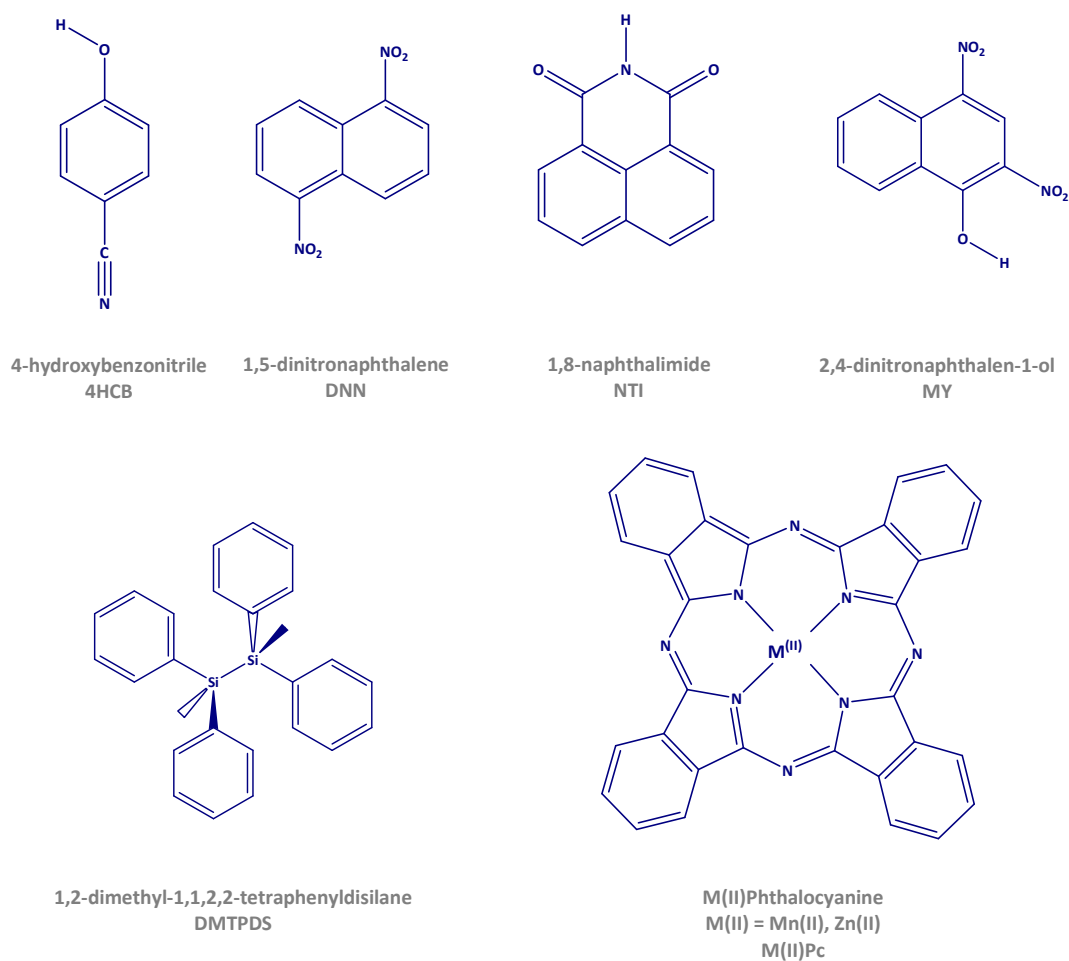


FIGURE 2.1: chemical structures of the molecules evaluated in the first step of the work carried out.

Structures on top: 4HCB, DNN, NTI and MY. Structures on bottom: DMTPDS and M(II)Pc.

On the same basis, i.e. the presence of metallic atoms in the molecule, phthalocyanine-based molecules, Pc, have been chosen. These compounds are very interesting, due to their good stability, their interesting electronic properties already shown in several previous studies¹² and their capabilities to be ink-jet printed¹³. Moreover, in addition to the presence of the metallic moiety, Pcs had the additional feature of presenting a very large aromatic structure, in principle allowing interesting comparisons with the series formed by 4HCB, DNN, NTI and DMTPS with respect to the effect of this characteristic over the electronic and X-rays response properties of the resulting crystals.

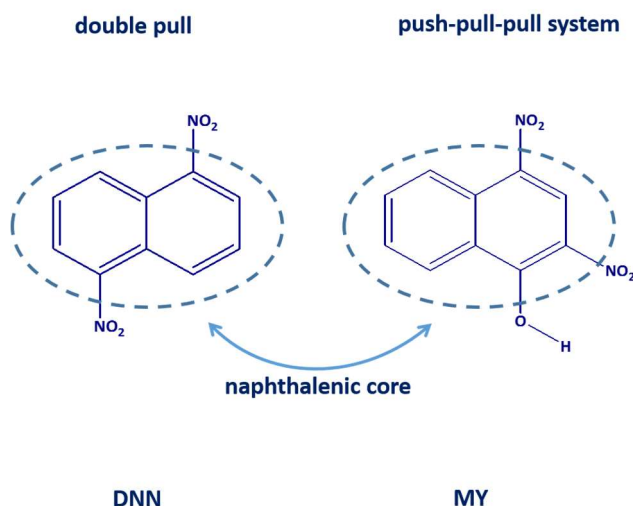


FIGURE 2.2: chemical structures of DNN on left and MY on right. The figure highlights the analogous naphthalenic core of the two structures and the presence in MY of an additional electron-donor (PUSH) system, absent in the DNN structure. Indeed the -NO_2 group belong to the electron-attractor (PULL).

2.2 EXPERIMENTAL SCREENING

The overall work has been divided into the following three steps:

1. purification of the semiconductor,
2. pre-crystallization test,
3. solubility determination.

The first step has been carried out because, for the present research purposes, batches of organic semiconductor materials have been purchased from chemical suppliers. Because the yield of an organic reaction is rarely 100%, the analyzed molecules are often mixed with numerous, not always well-characterized, contaminants. It is well known in literature that the presence of small amounts of specific impurities in a supersaturated mother phase can significantly change the nucleation of crystals, the growth¹⁴ and aggregation of nuclei¹⁵, the morphology of growing crystals¹⁶, the crystalline phase¹⁷ and also the opto-electronic

features of the obtained crystals¹⁸. Therefore, before crystals growth, the source materials need to be pre-purified.

The second step has been carried out to investigate the molecules and molecules/solvents ability to provide suitable single-crystals in terms of desired size and morphology to the purposes of X-ray detection device production.

2.2.1. PURIFICATION STEP

A. Introduction

Contaminants may be molecules introduced as reagents of a chemical reaction, products formed by side-reactions or decomposition processes as well as by reduction, oxidation, decomposition or photoinduced processes during storage. In comparison with classical inorganic semiconductors, such as Si or GaAs, where 6N (99.9999%) purity or better is available, organic semiconductors are significantly contaminated with purity in the range of 95–98%. Therefore, as briefly introduced in the introduction of this section, the source materials need to be purified¹⁹.

This topic has received great attention since it is of relevant theoretical and practical interest in the growth of crystals of industrial importance. The ability of impurities to change the growth behavior has been studied by many authors ^{11, 12, 20, 21, 22, 23, 24}. It is well known that the influence of impurities on the crystal habit and on the growth rate is based on the adsorption of ions, atoms or molecules of foreign species at kinks, ledges and terraces of a growing crystal. In fact, the crystal habit is based on a difference in adsorption energies on different facets. Impurity molecules will be preferentially adsorbed on surfaces where the free adsorption energy is maximum. It has been possible to predict this preferred surface adsorption using computational approaches²⁵. **FIGURE 2.3** shows a typical case of habit change due to the presence of some contaminant.

Impurities can act in different ways. When they interact with the solute or solvent, they can have strong influences on the solubility and consequently on the supersaturation and kinetic processes. When impurities are adsorbed on

crystals, they can have thermodynamic and kinetic effects. The dominant effect is on the rates of exchange in which the adsorbed molecule and growth units are involved.

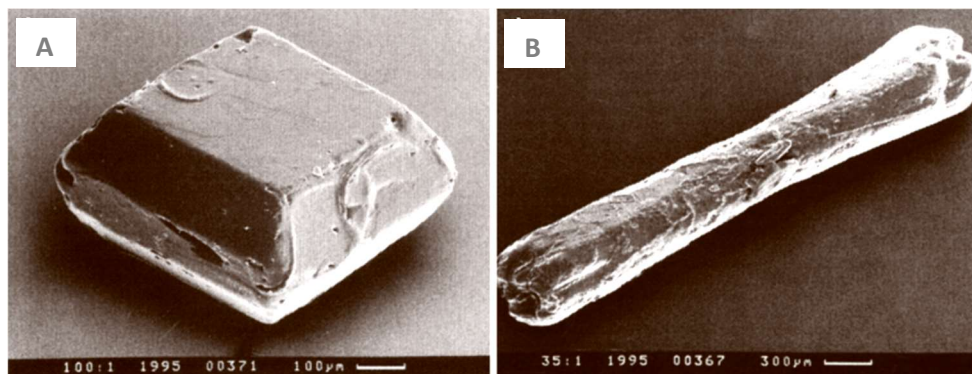


FIGURE 2.3: (A) Ammonium sulfate crystals grown from pure solution and (B) in presence of 100 ppm Al^{3+} . [ref]

B. Purification procedure

Many purification methods are available to get rid of impurities in crystallizable compounds: zone refining, sublimation or distillation and, due to the solubility of organic semiconductors in organic solvents, recrystallization is also feasible. In the frame of the project carried out, the latter method has been evaluated as the most suitable one, due to both planning motivations (i.e. the main goal of the i-FLEXIS project was the growth of OSSCs from inkjet printed solutions) and to practical motivation (i.e. to avoid possible degradation issues of the evaluated materials when other methods involving high temperatures are used). The product of such purification requires also subsequent removal of traces of solvents.

Re-crystallization is one of the oldest purification techniques for the production of pure specimen and crystals for fundamental analyses. One of the most effective approaches for growth of both inorganic and organic crystals from solution is the temperature decrease, provided that the material has a positive temperature coefficient of solubility (i.e., lowering the temperature the compound solubility must decrease significantly). In this method, a saturated

solution of the material to be grown is prepared and heated at a chosen temperature, usually near the boiling point of the solvent. Then, by slowly lowering the temperature, the growth process starts. The temperature of the solution is lowered at a controlled and programmed rate, typically $0.05\div 1.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, depending on the solubility of the selected material. The complete crystallization process may take from one to several hours. To terminate the growth process the grown crystals are taken out of the solution without thermal shock.

Following this procedure, the powders of the selected molecules have been first dissolved in the proper solvent (*vide infra*) and then re-crystallized from it. All the mentioned compounds, with purity in the range of 95–99%, have been purchased from chemical suppliers. The as-received compounds have been characterized by means of ^1H -NMR spectroscopy, UV-VIS spectroscopy and melting point determination. After each cycle of purification the previous mentioned characterizations have been carried out. By comparison of the spectra obtained after each purification cycle with those obtained from the starting compound, the proper number of purification cycles have been determined. All compounds have been used to carry on the pre-crystallization step immediately after their pre-growth purification.

2.2.2. PRE-CRYSTALLIZATION STEP

After the pre-purification step, as previously mentioned, the pre-crystallization step has been modulated in consecutive three steps:

1. screening of the different solvents to find the best one/ones,
2. crystallization step to define the general features of the obtained crystals,
3. determination of the solubility at room temperature.

In the following paragraphs a short description of the work carried out is summarized.

A. SCREENING OF DIFFERENT SOLVENTS TO FIND THE BEST ONE/ONES.

Before starting the solvent screening procedure, any possible reaction between the target molecule and the chosen solvents has been evaluated to avoid this circumstance. If the functional groups had suggested any kind of possible reaction, the solvent has been rejected.

The first essential step for any crystallization is the choice of solvent. Therefore, the first step of the pre-crystallization test has been the screening of the possible solvents to be used to grow the crystals from each of the previous mentioned compounds. Besides high-purity starting materials, solution growth requires a good solvent. The solvent has been chosen by taking into account the following parameters:

1. high solubility for the given solute,
2. good solubility gradient with temperature (only for purification purposes),
3. low viscosity,
4. low volatility.

If the solubility is too high, it is then difficult to grow bulk single crystals and, if it is too small, solubility restricts the size and growth rate of the crystals. Hence, in first approximation, the solubility of the solute in the chosen solvent has been determined before starting the growth process. For the explained reasons, solubility values higher than 1 M at room temperature have been decreased, while those solvents, whose compound solubility has been lower than 10^{-3} M, have been rejected. This operation has been done since outside this solubility window the results obtained, in terms of crystal growth, are in general very poor. In the former case the crystals have not been suitable for XRD characterization²⁶ while in the latter case the obtained crystal have always been so small to be useless to the purposes of the research, as experimentally verified and in perfect agreement with the literature^{23, 27}.

As reported in literature²⁸, the solubility parameter δ can often be used in estimating the solubility of nonelectrolytes in organic solvents:

$$\delta = \left(\frac{\Delta U}{V_m} \right)^{\frac{1}{2}} = \left(\frac{\Delta H - RT}{V_m} \right)^{\frac{1}{2}} \quad \text{EQUATION 2.1}$$

where V_m is the molar volume of the solvent, ΔU is the molar energy, and ΔH is the molar enthalpy; δ is a solvent property that measures the work necessary to separate the solvent molecules. Often a mixture of two solvents, one having a δ value higher and the other one having it lower than that of the solute, is a better solvent than either of the two solvents separately²⁹. A selection of δ -values is given in **TABLE 1**.

Another property has been considered for selecting solvent for crystal growth: the dipole moment difference between the solute and the solvent. Lower is the difference, better the solubility of the solute into the solvent. Most typical organic solvents have a dipole moment less than about 3 debye. Therefore, in the case of a solute having a similar value of dipole moment, a much wider choice of solvents is possible.

The preliminary determination of the solubility of the tested molecules has been carried out in properly sealed test-tubes. A small amount of the compound has been weighted (generally 1 mg), and drops of solvent have been added to the system every 1÷5 minute till the complete solubilization of the total amount of compound. If the solubility obtained has been lower than 10^{-3} M the solvent has been immediately rejected. Solvents with solubility higher than this threshold have been subjected to the second step of the pre-crystallization.

All the test-tubes used to roughly define the solubility have been cleaned immediately prior use. The protocol settled up for their cleaning consists of three different steps: i) bath in a mixture of $\text{HNO}_3 + \text{H}_2\text{SO}_4$ (1 : 3) for 12 hours; ii) three cycles of washing with milli-Q water of 15 minutes each in an ultrasound bath at 50°C ; iii) three cycles of washing with acetone of 5 minutes each in an ultrasound bath at room temperature.

SOLVENT	Δ (MPa ^{1/2})	SOLVENT	Δ (MPa ^{1/2})
Methanole	29.6	Ciclo-hexanone	20.3
Ethanol	26.0	Acetone	20.2
N-methyl-formammide	32.9	1,2-dicholoroethane	20.0
1,2-ethanediol	29.9	chlorobenzene	19.4
N,N-dimethylformammide	24.8	chloroform	19.0
dimethylsulfoxide	24.5	benzene	18.8
acetonitrile	24.3	tetrahydrofuran	18.6
1-butanol	23.3	tetrachloromethane	17.6
Ciclo-hexanole	23.3	cyclohexane	16.8
Tert-butanol	21.7	n-hexane	14.9

TABLE 1: Solubility parameters δ , at 25 °C, of some organic solvents evaluated during the present work.

B. CRYSTALLIZATION STEP TO DEFINE THE GENERAL FEATURES OF THE OBTAINED CRYSTALS

All the 5 mL vessel used as crystallizers have been cleaned immediately before their use, following the above mentioned cleaning protocol.

Based on the solubility value obtained in the step of the pre-crystallization, a proper amount of pre-purified compound has been taken and used to prepare a saturated solution. Analytical grade solvents have been used to solvate the organic semiconductor with the aim of minimizing as possible the amount of impurities introduced into the system.

The so-prepared solutions have been put in the crystallization vessels (normal atmosphere). The vessels have been hence closed with a proper cap and the lateral regions have been sealed with parafilm. A small hole (approximately

200 μm of diameter) has been done in the center of the cap, allowing a slow and controlled solvent evaporation.

The growth batches have been placed under a hood at room temperature conditions and conveniently isolated from the hood forced air using a further vessel external to the growth one. The hood temperature has been measured by a thermometer. After the complete evaporation of the solvent, the parafilm and the cap have been removed, and the obtained crystals gently removed from the vessel using a spatula.

Where mm-sized free-standing single and poly-crystal have been found, they have been characterized by means of optical microcopy. This characterization allow for the determination of the sizes and the surfaces morphology of the obtained crystals. In some cases, IR absorption spectroscopy has been carried out on crystals to evaluate their purity.

Only the crystals that gave good results in these tests have been subjected to the third step, in order to define semiconductor solubility in the selected solvent/s at room temperature.

C. DETERMINATION OF THE SOLUBILITY VALUE AT ROOM TEMPERATURE

Since most often no solubility data were available for the considered solute/solvent pairs, initial solution have been prepared by placing large amounts of solid powder in the selected solvent. The solutions have been allowed to be stirred in sealed sample-holder at room temperature for 2-3 days to reach saturation. The equilibrium concentration of the saturated solution, C_0 , has been determined by a standard method of weighting solution samples before and after solvent drying until a constant sample weight, following a procedure reported in literature³⁰.

2.2.3. PROTOCOL FOR CRYSTALS GROWTH

For each molecule, the systems that gave the best results, if any, have been used to grow OSSCs for deeper analysis of sizes and morphologies – with respect to the

mentioned purposes - and for additional characterization, such as X-rays diffraction, UV-Vis spectroscopy and X-ray response characterization to define the mobility properties of the evaluated crystals. The former work has been integral part of this thesis work while the latter characterization has been performed by a collaborating group at the University of Bologna.

Glass beakers have been used as crystallizers, and have been pre-treated immediately prior their use, following the previously described cleaning method. Only 100 mL beakers have been employed to carry on the growth except otherwise stated.

A proper amount of pre-purified compound has been taken and used to prepare the saturated solution. Analytical grade solvents have been used to solvate the organic semiconductor with the aim of minimizing as possible the amount of impurities introduced into the system. When the solution has been prepared, the beaker has been hence closed with an Al foil and the lateral regions have been sealed with parafilm to avoid any uncontrolled loss of solvent. A small hole (approximately 200 μm of diameter) has been done in the center of the Al foil, allowing, in this way, a slow and controlled solvent evaporation.

The growth batches have been placed under the hood at room temperature, as highlighted by a thermometer placed under the hood, and conveniently isolated from the hood forced air using a further vessel external to the beaker. The crystallization has been considered completed after the evaporation of the total amount of solvent. The parafilm and the Al foil have been hence removed, and the resulting crystals (Free-standing single and poly-crystals) have been gently recovered using a spatula. A Typical example of crystal size obtained with this method are shown in **FIGURE 2.4**.

The so-obtained crystals have been characterized by means of optical microscopy, UV-Vis spectroscopy and XRD. In some cases also IR-spectroscopy has been carried out.

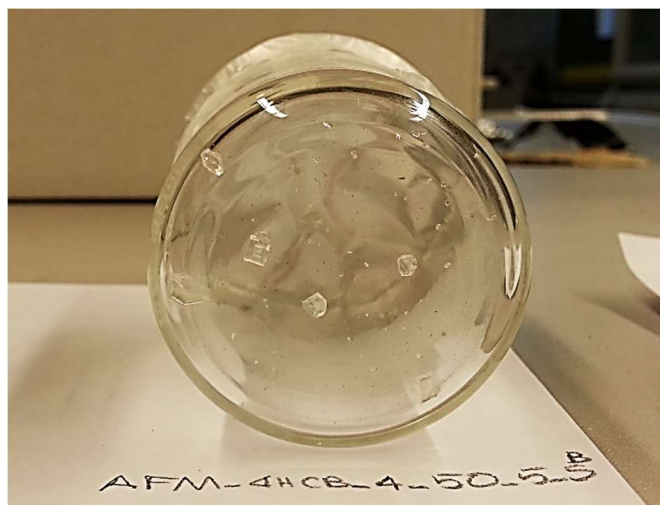


FIGURE 2.4: 4HCB crystals on the bottom of a 100 mL beaker, after the evaporation of the total amount of solvent.

2.3 CHARACTERIZATION TECHNIQUES

2.3.1. SYNCHROTRON

Synchrotron radiation is inherently advantageous for advanced and thorough materials characterization for several reasons:

1. high brightness and high intensity, many orders of magnitude more than with conventional X-ray tubes (3rd generation sources typically have a brilliance larger than 10^{18} photons $\cdot$ s $^{-1}$),
2. high collimation, i.e. small angular divergence of the photon beam,
3. high level of light polarization,
4. large tunability in wavelength by monochromatization.

The crystal structure of semiconductors is required in order to explain/predict their conduction properties. For this goal, very precise crystal structures including charge

density studies are needed. Synchrotron diffraction is an invaluable technique for characterizing the structures of such organic compounds.

Diffraction can be classified under two main classes, depending upon the nature of the examined sample. Polycrystalline samples are generally studied by powder diffraction, while single crystals are studied by single crystal diffraction. In the following a short description of the technique is given.

2.3.2. XRD

Single-crystal X-ray diffraction is a non-destructive analytical technique able to provide detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering.

As shown in **FIGURE 2.5** Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. In fact, crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter primarily X-ray waves, via the electrons present in the atoms, and this scattering process produces secondary spherical waves. This phenomenon is known as elastic scattering and the electron is known as the 'scatterer'. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$n\lambda = 2d \sin\theta$$
EQUATION 2.2

here d is the spacing between diffracting planes, θ is the incident angle, n is any integer and λ is the wavelength of the beam. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

These specific directions appear as spots on the diffraction pattern, called reflections. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal). X-rays are used to produce the diffraction pattern because their wavelength λ is typically the same order of magnitude ($1\div 100$ Å) as the spacing d between planes in the crystal, but in principle any wave impinging on a regular array of scatterers produces diffraction, as predicted first by Francesco Maria Grimaldi in 1665. To produce significant diffraction, the size of the scatterers and the wavelength of the impinging wave should be similar in size.

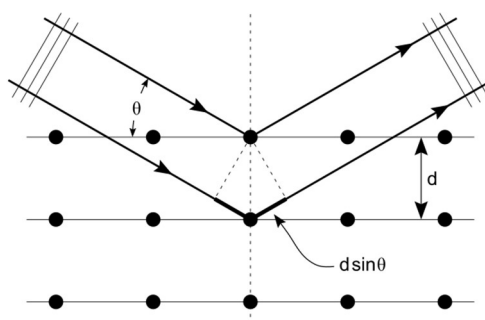


FIGURE 2.5: The incoming beam causes each scatterer to radiate a small portion of its intensity as a spherical wave. If scatterers are arranged symmetrically with separation d , these spherical waves will add constructively only in directions where their path-length difference $2d \sin \theta$ equals an integer multiple of the wavelength λ . In this case, part of the incoming beam is deflected by an angle 2θ , producing a reflection spot in the diffraction pattern.

These diffracted X-rays are then detected, processed and counted. By changing the geometry of the incident rays, the orientation of the centered crystal and the detector, all possible diffraction directions of the lattice should be attained.

Data collection has been performed at the XRD-1 X-ray diffraction beamline of Elettra Synchrotron, Trieste (Italy) (monochromatic wavelength 0.82660 Å) using a

Dectris Pilatus 2M area detector with the rotating crystal method. The diffraction datasets have been collected using crystals – obtained from the growth batches - glued on a glass fiber, at room temperature. In some cases data collection have also been performed at lower temperature to investigate the possible existence of polymorphs. In these cases the control over the temperature has been obtained with a nitrogen stream (supplied through an Oxford Cryostream 700). The diffraction data were indexed and integrated using XDS, and scaled with SCALA. The structures have been solved by direct methods using SIR2011.

To verify the single-crystal nature of the obtained crystals and to confirm, if already known, the crystalline structure, X-ray diffraction analysis have been carried out. If already known, the structure and morphological phase have been confirmed.

The crystal structure of semiconductors is required in order to explain/predict their conduction properties. For this goal, very precise crystal structures including charge density studies are needed. Synchrotron diffraction is an invaluable technique for characterizing the structures of such organic compounds.

In order to achieve high performance in organic optoelectronic devices, control of the molecular packing is important^{31, 32}. Many organic semiconductor adopt p-stacking structures³³, where the slips along the molecular long axis (longitudinal offset) and the molecular short axis (transverse offset) determine the intermolecular transfer^{34,35}. In an organic semiconductor the energy gap (the HOMO-LUMO difference) is an important parameter to verify the semiconducting properties of the material when employed as an active layer of an organic transistor. Moreover according to the studies of Kakinuma and Mori³⁴ on naphthalene bisimides (with brickwork packings) when conduction takes place along a specific direction of the crystallographic axes, then the transistor performances (i.e. mobility) depend on some geometrical parameters that correlate with the transfer integral (orbital overlap). It is important to underline that the part of the work dealing with the performances of the optoelectronic devices has not been part of the present thesis. On these basis, to validate the studied materials from a physical point of view, the following parameters have been determined:

1. energy gap as shown in **FIGURE 2.6**,
2. ID: interplanar distance as shown in **FIGURE 2.7A**,
3. D_x : displacement along the molecular long axis - longitudinal offset- as shown in **FIGURE 2.7B**,
4. D_y : displacement along the molecular short axis - transverse offset - as shown in **FIGURE 2.7B**.

The last three parameters, related to the intermolecular transfer integral and therefore to the mobility and to the optoelectronic performances, have been shared with the partner engaged in the physical characterization of the single crystalline systems. Deeper details are reported in literature³⁶.

The UV-Vis spectra have been used to roughly evaluate the bandgap of the semiconductor, as summarized in **TABLE 18**.

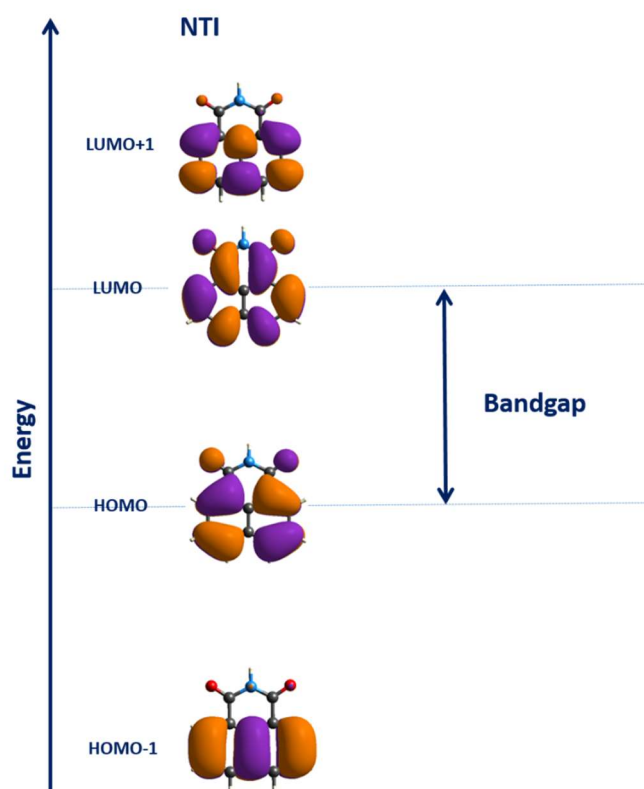


FIGURE 2.6: the HOMO-LUMO levels and the consequent bandgap, which is one of the two informations required to determine the semiconductor mobility.

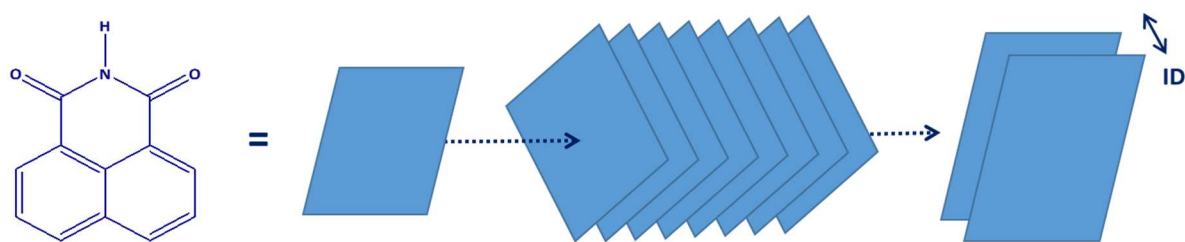


FIGURE 2.7A: the interplanar distance, ID, one of the three geometrical parameters necessary to determine the charge mobility.

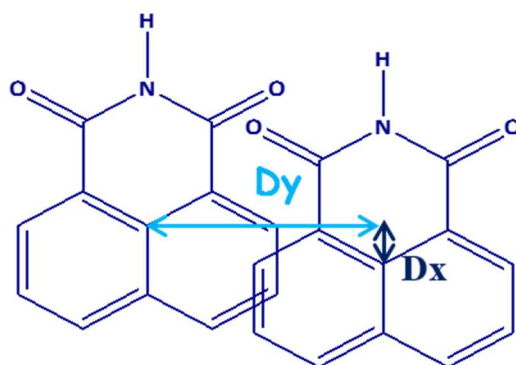


FIGURE 2.7B: the two displacements along the two axis, the long one, D_y , and the short one, D_x . These are two out of the three geometrical parameters necessary to determine the charge mobility.

2.4 RESULTS AND DISCUSSION

2.4.1. PRE-CRYSTALLIZATION STEP

The above described protocols for crystal growth have been applied to the series of organic molecules mentioned in **section 2.1**, and showed in **FIGURE 2.1**. In the following, a summary of the results of these screening is presented.

A. 4-HCB

A. screening of the different solvents,

Based on the parameters introduced in **section 2.2**, solvents shown in **TABLE 2** have been evaluated.

SYSTEM	SOLVENT	C (mg · mL ⁻¹)	M (mol · L ⁻¹)	EVALUATION
A ¹ _ 4HCB	ETHYLIC ETHER	32	2.6 · 10 ⁻¹	A
B ¹ _ 4HCB	TOLUENE	28	2.3 · 10 ⁻¹	A
D ¹ _ 4HCB	ETHYLIC ETHER + P.E. (9 : 1)	25	2.0 · 10 ⁻¹	A
E ¹ _ 4HCB	ETHYLIC ETHER + TOLUENE (4 : 1)	30	2.5 · 10 ⁻¹	A
F ¹ _ 4HCB	ETHANOLE	>> 1 M	<< 10 ⁻³	R
G ¹ _ 4HCB	ISOPROPAPOLE	>> 1 M		R

TABLE 2: solvents evaluated to solvate 4HCB. 'A' means 'accepted' and therefore subjected to the second step of the pre-crystallization. 'R' means 'rejected'.

Based on the first approximation of obtained solubility values, these tests evidenced that the best suited solvents are:

1. ethylic ether,
2. toluene,
3. ethylic ether + toluene (4:1),
4. ethylic ether + petroleum ether.

These four solvents have been therefore used to carry on the second step of the pre-crystallization test to select a few best solvents with respect to the sizes and surface morphologies.

B. crystallization step

The reference growth has always been obtained starting from a saturated concentration of the solution. The volume of the prepared solution has always been 5 mL. The evaporation time took from 1 week to 3 weeks, depending on the solvents nature. In the frame of the present purposes low-boiling point solvents have been preferred to the high-boiling point ones. Five batches per each solvent have been prepared in order to obtain a meaningful comparison.

All the evaluated solvents gave platelet-shaped crystals, as shown in **FIGURE 2.8**.

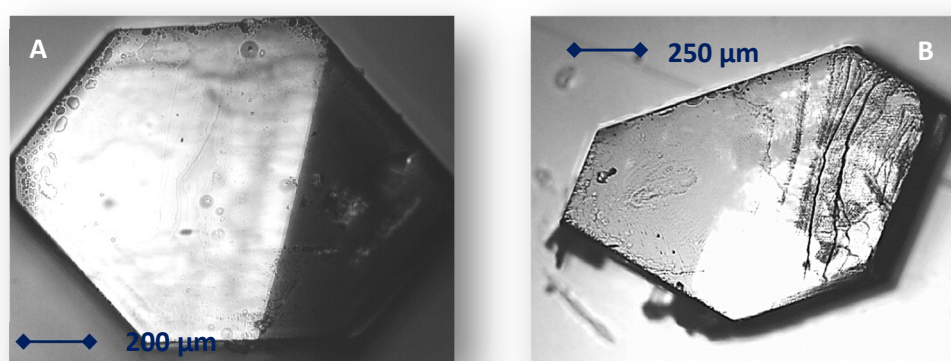


FIGURE 2.8: two micrographs of the typical surfaces obtained for 4HCB crystals grown in the same growth conditions except for the two different solvents. (A) flat surfaces obtained in toluene. (B) Stepped surfaces obtained in ethylic ether.

The average surfaces of the obtained crystals, both single and poly-crystal, have been mm²-sized as summarized in **TABLE 3**. The mean size of the surfaces obtained for crystals grown in (ethylic ether + petroleum ether) has been considered as not suitable for the purposes of the project and this solvent mixture has been therefore rejected. The thickness of the crystals grown in toluene have always been larger than that found for other solvents (typically twice or triple than that of crystals grown in ethylic ether), highlighting interesting changes in the crystalline habit of 4HCB.

SOLVENT	MEAN SURFACE	MEAN THICKNESS
	(μm^2)	(μm)
ETHYLIC ETHER	$6,2 \cdot 10^7$	690
TOLUENE	$1,8 \cdot 10^7$	$1,0 \cdot 10^3$
ETHYLIC ETHER + TOLUENE (4:1)	$1,8 \cdot 10^7$	$1,0 \cdot 10^3$
ETHYLIC ETHER + PETROLEUM ETHER	$4,2 \cdot 10^6$	580

TABLE 3: average surfaces size and thickness obtained for 4HCB single-crystal grown in those solvents selected throughout the solvent selection protocol.

Also differences in terms of morphology of surfaces have been observed. Indeed a careful analysis under the optical microscope allow to understand that the surfaces obtained in ethylic ether have always been less flat – in the same growth conditions - than those obtained using toluene as a solvent, as shown in **FIGURE 2.8**. Surfaces obtained in ethylic ether+toluene phase have always been comparable (by optical microscopy analysis) to those obtained in toluene alone.

Upon these results, 4HCB-based single crystals grown using the above presented protocols have been sent to University of Bologna (UNIBO in the following) for X-rays response studies, and the related results are summarized in **section 2.4**.

C. Determination of the solubility at room temperature.

Based on the procedure described in the previous subsection the solubility values summarized in **TABLE 4** have been obtained for the solubility of the 4HCB into the selected solvents at room temperature.

SEMICONDUCTOR	SOLVENT	[S]	
		(mg · ml ⁻¹)	(mol · L ⁻¹)
4HCB	ETHYLIC ETHER	32	2.6 · 10 ⁻¹
4HCB	TOLUENE	28	2.3 · 10 ⁻¹
4HCB	ETHYLIC ETHER + TOLUENE (4 : 1)	30	2.5 · 10 ⁻¹

TABLE 4: Average solubilities of 4HCB in those solvents selected throughout the selection protocol, properly created to select those single-crystals suitable for the purposes.

B. NTI

A. screening of the different solvents,

Based on the parameters introduced in **section 2.2**, solvents shown in **TABLE 5** have been evaluated.

Based on the first approximation of obtained solubility values, these tests evidenced that the best suited solvents are:

1. chloroform + N,N-dimethylsuphoxide (4:1),
2. ethylic ether + N,N-dimethylsuphoxide (2.25 : 1.55),
3. acetone + N,N-dimethylsuphoxide (4: 1.85),
4. N,N-dimethylsuphoxide,

5. tetrahydrofurane,

6. tetrahydrofurane + chlorbenzene (3% v/v).

SYSTEM	SOLVENT	C (mg · mL ⁻¹)	M (mol · L ⁻¹)	STATUS
A ¹ _NTI	THF + 1,2-PROPANDIOLE (5 : 1)	----	<< 10 ⁻³	R
B ¹ _NTI	CHCl ₃ + BENZONITRILE (1 : 1)	----	<< 10 ⁻³	R
C ¹ _NTI	1,2-DICHLOROBENZENE	----	<< 10 ⁻³	R
D ¹ _NTI	BENZONITRILE	----	<< 10 ⁻³	R
E ¹ _NTI	CH ₃ CN	----	<< 10 ⁻³	R
F ¹ _NTI	BENZONITRILE + MeOH (1 : 1)	----	<< 10 ⁻³	R
G ¹ _NTI	CHLOROFORM + DMSO (4 : 1)	2.1	1.1 · 10 ⁻²	A
H ¹ _NTI	ETHYLIC ETHER + DMSO (2.25 : 1.55)	2.8	1.4 · 10 ⁻²	A
I ¹ _NTI	ACETONE + DMSO (4 : 1.85)	1.86	9.4 · 10 ⁻³	A
L ¹ _NTI	DMSO	7.3	3.7 · 10 ⁻³	A
M ¹ _NTI	THF	2	1.0 · 10 ⁻²	A
N ¹ _NTI	THF + CHLOROBENZENE 3%	2	1.0 · 10 ⁻²	A

TABLE 5: solvents evaluated to solvate NTI. 'A' means 'accepted' and therefore subjected to the second step of the pre-crystallization. 'R' means 'rejected'.

These six solvents have been therefore used to carry on the second step of the pre-crystallization test in order to select only those solvents able to provide mm-sized single-crystals with surface morphologies able to be implemented in a x-ray sensing device.

B. crystallization step

The reference growth has always been obtained starting from a saturated concentration of the solution. The volume of the prepared solution has always been 5 mL. The evaporation time took from 1 week to 3 weeks, depending on the solvents nature. In the frame of the present purposes low-boiling point solvents have been preferred to the high-boiling point ones. Five batches per each solvent have been prepared in order to obtain a meaningful comparison.

All the evaluated solvents gave needle-shaped crystals, as shown in **FIGURE 2.9**.



FIGURE 2.9: typical needle-shaped NTI single crystal showing the typical flat surfaces obtained growing the semiconductor in THF

As summerized in **TABLE 6** only crystals – we focused on single-crystals but the output has been the same also for poly-crystals- grown in THF have been mm²-sized in surface.

SOLVENT	MEAN SURFACE	MEAN THICKNESS
	(μm^2)	(μm)
Chloroform + DMSO	---	---
Ethylic ether + DMSO	---	---
Acetone + DMSO	---	---
DMSO	---	---
THF	$6.42 \cdot 10^5$	200
THF + chlorobenzene	---	---

TABLE 6: Average solubility of NTI in THF, the only solvent selected throughout the selection protocol, properly created to select those single-crystals suitable for the

All the other solvents gave crystal extremely thin and small. It was not possible even their manipulation. Therefore all the other solvents except THF have been rejected. Also differences in terms of morphology of surfaces have not been observed under the optical microscope due to the same reason.

Upon these results, only NTI single crystals grown in THF have been sent to UNIBO for X-rays response studies. The related results are summarized in **section 2.4**.

C. determination of the solubility at room temperature.

Based on the procedure described in the previous subsection the solubility values summarized in **TABLE 7** have been obtained for the solubility of the NTI into the selected solvent at room temperature.

SEMICONDUCTOR	SOLVENT	[S]	
		(mg · ml ⁻¹)	(mol · L ⁻¹)
NTI	THF	2	2.0 · 10 ⁻²

TABLE 7: Average solubility of NTI in THF, the only solvent selected throughout the selection protocol, properly created to select those single-crystals suitable for the

D. DNN

A. screening of the different solvents,

Based on the parameters introduced in **section 2.2**, solvents shown in **TABLE 8** have been evaluated.

Upon these tests, systems subjected to the second step have been:

1. tetrahydrofurane,
2. acetone.

These two solvents have been therefore used to carry on the second step of the pre-crystallization test

Based on these first approximations solubility value obtained, these tests clearly suggest that the best solvents are:

1. acetone,
2. THF .

These two solvents have been therefore used to carry on the second step of the pre-crystallization test in order to select, if the case, only the one able to provide mm-sized single-crystals with surface morphologies able to be implemented in a x-ray sensing device.

SYSTEM	SOLVENT	C (mg · mL ⁻¹)	M (mol · L ⁻¹)	STATUS
A ¹ _ DNN	1,2-DICHLOROBENZENE	2.15	3.8 · 10 ⁻²	R
B ¹ _ DNN	NITROBENZENE	5.25	2.4 · 10 ⁻²	R
C ¹ _ DNN	1,2-PROPANDIOLE	-----	<< 10 ⁻³	R
D ¹ _ DNN	1,2-PROPANDIOLE + CHCl ₃ (3:4)	2.8	7 · 10 ⁻³	R
E ¹ _ DNN	2-METHYL-2-PIRROLIDONE	2.5	1.14 · 10 ⁻¹	R
F ¹ _ DNN	BENZONITRILE	-----	<< 10 ⁻³	R
G¹_ DNN	ACETONE	2	9.1·10⁻³	A
N²_ DNN	THF	2	9.1·10⁻³	A

B. crystallization step

The reference growth has always been obtained starting from a saturated concentration of the solution. The volume of the prepared solution has always been 5 mL. The evaporation time took from 1 week to 3 weeks, depending on the solvents nature. In the frame of the present purposes low-boiling point solvents have been preferred to the high-boiling point ones. Five batches per each solvent have been prepared in order to obtain a meaningful comparison.

Both the evaluated solvents gave needle-shaped crystals, as shown in **FIGURE 2.10.**



FIGURE 2.10: Optical microscopy image of a DNN single crystal.

The average surfaces of the obtained single-crystals, on which we focused, have been mm²-sized, as summarized in **TABLE 9**.

SOLVENT	AVERAGE SURFACE	AVERAGE THICKNESS
	(μm ²)	(μm)
THF	$5.88 \cdot 10^5$	250
ACETONE	$5.37 \cdot 10^5$	200

TABLE 9: average surfaces size and thickness obtained for DNN single-crystals grown in the second step of the pre-crystallization step.

A careful analysis under the optical microscope allows to understand that the surfaces of the obtained crystals have always been quite irregular and stepped, as shown in **FIGURE 2.11**.

Upon these results, the higher quality single crystals grown using both solvent have been sent to UniBo for X-rays response studies, and the related results are summarized in **section 2.4**.

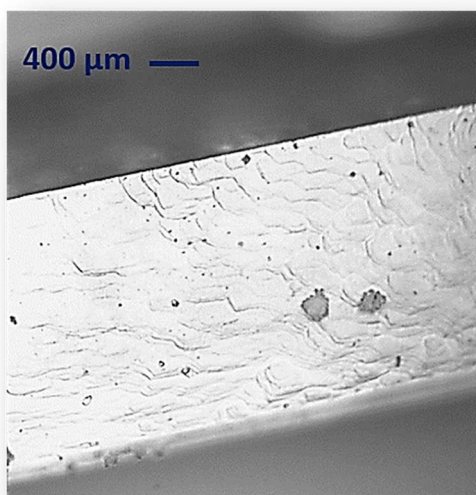


FIGURE 2.11: typical stepped surfaces obtained for DNN crystals grown in THF.

C. Determination of the solubility at room temperature.

Based on the procedure described in the previous subsection the solubility values summarized in **TABLE 10** have been obtained for the solubility of the DNN into the selected solvents at room temperature.

SEMICONDUCTOR	SOLVENT	[S]	
		(mg · ml ⁻¹)	(mol · L ⁻¹)
DNN	acetone	2	9.1 · 10 ⁻³
DNN	THF	2	9.1 · 10 ⁻³

TABLE 10: Average solubility of DNN in those solvents selected throughout the selection protocol, properly created to select those single-crystals suitable for the purposes.

E. MY

A. screening of the different solvents.

Based on the parameters introduced in **section 2.2**, solvents shown in

TABLE 11 have been evaluated.

SYSTEM	SOLVENT	C (mg·mL ⁻¹)	STATUS 1°STEP
A ¹ _MY	CHLOROFORM	7.3	A
A ² _MY	CHCl ₃ + 1,2-PROPANEDIOLE (3 : 1)	3.8	A
B ¹ _MY	THF	3.12	R
C ¹ _MY	ISOPROPANOLE	----	R
D ¹ _MY	BENZONITRILE	9.3	A
E ¹ _MY	METHANOLE	2.6	A

TABLE 11: solvents evaluated to solvate MY. ‘A’ means ‘accepted’ and therefore subjected to the second step of the pre-crystallization. ‘R’ means ‘rejected’.

Upon these tests, solvents subjected to the subsequent steps are listed in the following:

1. chloroform,
2. benzonitrile,
3. chloroform + 1,2-propanediol,
4. methanole.

These four solvents have been therefore used to carry on the second step of the pre-crystallization test in order to select a few solvents able to provide the single-crystals suitable to the purposes.

B. crystallization step

The reference growth has always been obtained starting from a saturated concentration of the solution. The volume of the prepared solution has always been 5 mL. The evaporation time took from 1 week to 3 weeks, depending on the solvents nature. In the frame of the present purposes low-boiling point solvents have been preferred to the high-boiling point ones. Five batches per each solvent have been prepared in order to obtain a meaningful comparison.

All the evaluated solvents gave needle-shaped crystals, as shown in [FIGURE 2.12](#). The sizes of the obtained single-crystals, on which we focused, have been mm-sized. The yield of poly-crystals has always been higher than that of single-crystals. Despite the high purity of the pre-purified compound, both solvents gave crystals with visible orange inclusions inside, as shown in [FIGURE 2.13](#).

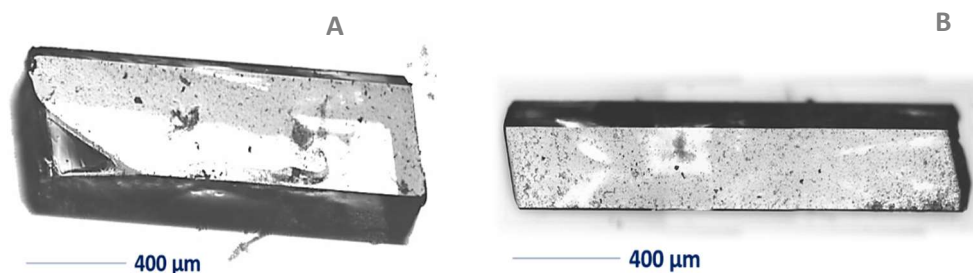


FIGURE 2.12: two micrographs of the surfaces obtained for MY crystals grown in two different solvents. (A) typical surfaces obtained for crystals grown in chloroform. (B) Typical stepped surfaces obtained for crystals grown in benzonitrile.



FIGURE 2.13: visible orange inclusions inside MY crystals.

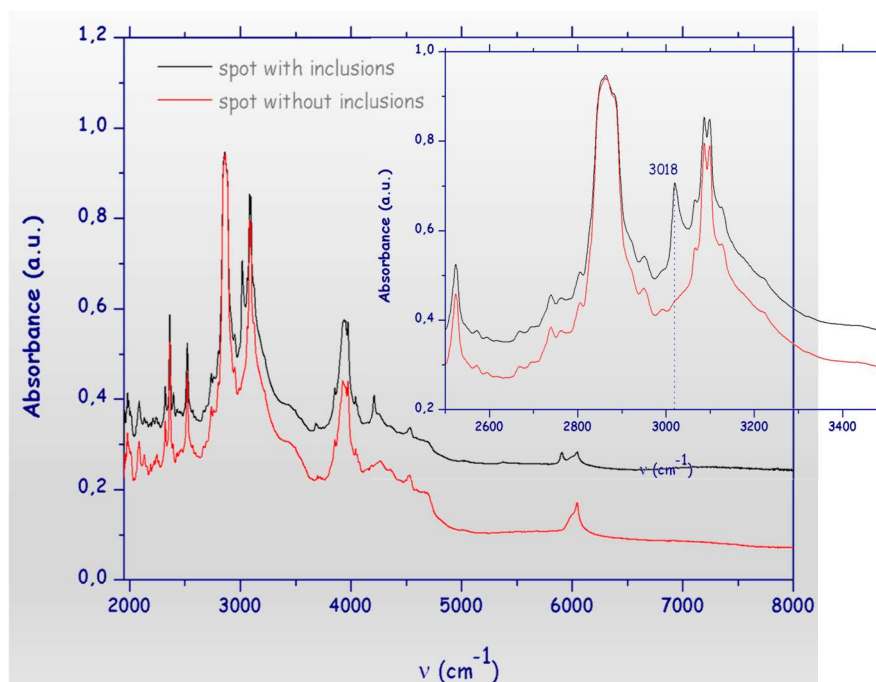


FIGURE 2.14: comparison between the typical spectrum acquired on a region without the orange inclusions (red line) and the typical spectrum acquired on a region with the orange inclusions (black line). The red line is basically superposable with the spectra obtained from crystals immediately after the compound purification

To define the presence of any reaction occurring during crystallization/storage, some IR spectra focused on specific crystal zones with the help of a dedicated IR microscope (courtesy of the SISSI beamline of Sincrotrone Trieste) have been acquired both in regions of MY crystals that showed orange inclusions, as well as in zone not showing such inclusions, as shown in **FIGURE 2.14**. These spectra have been compared also with those obtained immediately after the pre-purification step. Only the orange inclusions spectra provided the peak at 3018 cm^{-1} . This has been rationalized as a chemical reaction taking place during the crystallization process or immediately after. These inclusions have been observed with all the solvents evaluated, hence it can be concluded that they are not due to co-crystallization with solvents molecules but to some intrinsic degradation of MY. No polymorphism has been observed for MY based on XRD measures therefore the inclusions can not be ascribed to the presence of polymorph forms.

The thickness of the obtained crystals have always been comparable with all the evaluated solvents, therefore no visible changes in crystalline habit have been observed. The average surfaces of the grown crystals are shown in the following **TABLE 12**.

SOLVENT	AVERAGE SURFACE	AVERAGE THICKNESS
	(μm^2)	(μm)
chloroform	4647	2458
benzonitrile	18488	4862
chloroform + 1,2-propanediol	2160	1158
(3 : 1)		
methanole	1500	988

TABLE 12: Average surfaces size and thickness obtained for MY single-crystals grown in the second step of the pre-crystallization step.

Moreover, no significant differences in terms of morphology of surfaces have been observed among crystals grown from different solvents. Based on the overall observations only chloroform and benzonitrile have been subjected to the following characterization tests. The former has been chosen since it provides faster single-crystals of the same quality than those grown in all the other evaluated solvents. Benzonitrile has been chosen since it provides larger crystals.

Upon these results, MY single crystals grown using both these solvents have been sent to UniBo for X-rays response studies. The related results are summarized in **section 2.4**.

C. Determination of the solubility at room temperature.

Based on the procedure described in the previous subsection the solubility values summarized in **TABLE 13** have been obtained for the solubility of the NTI into the selected solvents at room temperature.

SEMICONDUCTOR	SOLVENT	[S]	
		(mg · ml ⁻¹)	(mol · L ⁻¹)
MY*	CHCl ₃	7.3	3.1 · 10 ⁻²
MY*	benzonitrile	9.3	4.0 · 10 ⁻²

TABLE 13: Average solubilities of MY in those solvents selected throughout the selection protocol, properly created to select those single-crystals suitable for the

F. DMTPDS

A. screening of the different solvents.

Based on the parameters introduced in **section 2.2**, solvents shown in

TABLE 14 have been evaluated.

SYSTEM	SOLVENT	C (mg·mL ⁻¹)	M (mg·mL ⁻¹)	STATUS
A ¹ _DMTDS	acetone	4.12	1.7·10 ⁻²	R
B ¹ _DMTDS	acetone + chloroform	3.4	1.4·10 ⁻²	A
B ² _DMTDS	2-butanone	6.68	2.8·10 ⁻²	R
C ¹ _DMTDS	2-butanone + Chloroform	5.6	2.3·10 ⁻²	R
C ² _DMTDS	chloroform	28	1.2·10 ⁻¹	A
D ¹ _DMTDS	toluene	5.3	2.2·10 ⁻²	A

TABLE 14: solvents evaluated to solvate DMTPDS. 'A' means 'accepted' and therefore subjected to the second step of the pre-crystallization. 'R' means 'rejected'.

After these tests, the solvents used for the subsequent steps were identified as follows:

1. chloroform,
2. toluene,
3. acetone + chloroform.

These three solvents have been therefore used to carry on the second step of the pre-crystallization test in order to select the most performin one in terms of sizes and surface morphologies of the obtained crystals.

B. crystallization step

The reference growth has always been obtained starting from a saturated concentration of the solution. The volume of the prepared solution has always been 5 mL. The evaporation time took from 1 week to 3 weeks, depending on the solvents nature. In the frame of the present purposes low-boiling point solvents have been preferred to the high-boiling point ones. Five batches per each solvent have been prepared in order to obtaine a meaningful comparison.

All these solvents have provided only polycrystals, as shown in **FIGURE 2.15**.

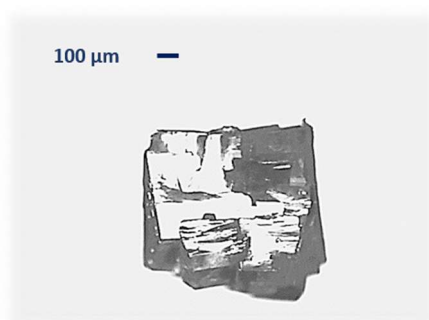


FIGURE 2.15: typical result obtained

for DNN poly-crystals grown in

chloroform.

Acetone + chloroform gave the smallest polycrystals therefore this solvent has been rejected. To investigate the possibility of obtaining single-crystals, many tests have been carried out using solutions with decreased concentration. The following concentration values have been tested:

1. three forth of the saturated solution concentration:

- $9 \cdot 10^{-2}$ M in chloroform,

- $1.7 \cdot 10^{-2} \text{M}$ in toluene,
2. the half of the saturated solution concentration:
- $6 \cdot 10^{-2} \text{M}$ in chloroform,
 - $1.1 \cdot 10^{-2} \text{M}$ in toluene,
3. one forth of the saturated solution concentration:
- $3 \cdot 10^{-2} \text{M}$ in chloroform,
 - $5.5 \cdot 10^{-3} \text{M}$ in toluene,

All the evaluated cases gave only $2 \div 10$ polycrystals, whose mean surfaces have been on mm^2 range but never higher than 25 mm^2 . The mean sizes are shown in the following **TABLE 15**.

SOLVENT	MEAN SURFACE	MEAN THICKNESS
	(μm^2)	(μm)
chloroform	$1.46 \cdot 10^6$	1000
toluene	$3.88 \cdot 10^6$	4562
Acetone + choloform	$5.55 \cdot 10^5$	568

TABLE 15: mean surfaces size and thickness obtained for DMTPDS single-crystals grown in the second step of the pre-crystallization step.

Both the absence of a single-crystals yield and the poor surface morphology suggest for the DMTPDS semiconductor to be accepted with reserve to the last, third step. Nonetheless, to try to obtain a first result in terms of X-rays response, the higher quality poly-crystals have been sent to UniBO for the electrical characterization.

C. Determination of the solubility at room temperature.

Based on the procedure described in the previous subsection the solubility values summarized in **TABLE 16** have been obtained for the solubility of the NTI into the selected solvents at room temperature.

SEMICONDUCTOR	SOLVENT	[S]	
		(mg · ml ⁻¹)	(mol · L ⁻¹)
DMTDS*	chloroform	28	1.2 · 10 ⁻¹
DMTDS*	toluene	5.3	2.2 · 10 ⁻²

TABLE 16: Average solubilities of 4HCB in those solvents selected throughout the selection protocol, properly created to select those single-crystals suitable for the

G. MPc

A. Screening of the different solvents

Based on the parameters introduced in **section 2.2**, solvents shown in **TABLE 14** have been evaluated. Based on the result, they all have been rejected. Indeed the highest solubility has been found in the order of 10⁻⁴ M for acetonitrile. In all the other evaluated cases the solubility have been even lower.

SYSTEM	SOLVENT	M (mol · L ⁻¹)	SYSTEM OBTAINED	STATUS
A ¹ _MPCy	EtOH	<< 10 ⁻³	2 phases system: Green solution + precipitate	R
B ¹ _MPCy	acetone	<< 10 ⁻³	2 phases system: Green solution + flocculate precipitate	R
C ¹ _MPCy	Methyl-ethyl ketone	<< 10 ⁻³	2 phases system: Green solution + flocculate precipitate	R
D ¹ _MPCy	THF	<< 10 ⁻³	Dark green monophasic system	R
E ¹ _MPCy	CHCl ₃	<< 10 ⁻³	Dark marron monophasic system	R
F ¹ _MPCy	toluene	<< 10 ⁻³	2 phases system: Green solution + flocculate precipitate	R
G ¹ _MPCy	benzonitrile	<< 10 ⁻³	Dark marron monophasic system	R
H ¹ _MPCy	chlorobenzene	<< 10 ⁻³	Dark marron monophasic system	R
I ¹ _MPCy	acetonitrile	~ 10 ⁻⁴	2 phases system: Green solution + flocculate precipitate	R
M ¹ _MPCy	Toluene + THF	<< 10 ⁻³	Dark green monophasic system	R

TABLE 17: solvents evaluated to solvate MPCy. 'A' means 'accepted' and therefore subjected to the second step of the pre-crystallization. 'R' means 'rejected'.

For this reason both the phtalocyanine have been rejected as molecule to grow crystal suitable for the purposes of the i-Flexis Project and therefore the subsequent two steps have not been performed.

2.4.2. GENERAL CHARACTERIZATIONS

For defining the characteristics of the crystals better fitting the i-FLEXIS project needs, a series of characterization have been carried out. In the following, the most significant ones will be described and commented.

A. UV-Vis Spectroscopy on solutions

As reported in literature⁴², in order to determine an approximative optical bandgap of the crystal it is possible to carry out UV-Vis spectroscopic investigations on the solutions from which the crystals are grown.

Each tested compound has been measured five times, to ensure the repeatability of the results. The following **TABLE 18** summarizes the obtained results.

SEMICONDUCTOR	SOLVENTS	M (mol·L ⁻¹)	ΔE (eV)
4HCB ⁴³	----	-----	~ 4.19
NTI	THF	10 ⁻⁴	~ 3.49
DNN	acetone	10 ⁻⁴	~ 3.26
MY	chloroform	10 ⁻⁴	~ 2.85
DMTPDS	chloroform	10 ⁻⁴	~ 4.41

TABLE 18: first approximation of the bandgap values obtained from UV-Vis spectra following a method reported in literature.

As is visible, the largest bandgap is associated to DMTPDS, followed by 4HCB, while the smallest one belongs to MY. NTI and DNN has a very similar optical bandgap.

B. XRD Characterization

The collected XRD data have been post-processed and shared with i-Flexis collaborating groups, who have used them – together with band-gap determination - to correlate with carrier mobility. In this way it has been possible to identify those molecule most suitable for the purposes of the Project, which has been the main goal of this first part of the work.

A. HCB

Crystals of 4-hydroxycyanobenzene are orthorhombic, space group with two independent molecules in the unit cell. They have similar dimensions, indicating a probable contribution from the quinonoid resonance structure and are joined alternately head-to-tail by O-H... N hydrogen bonds to form infinite helical chains around 2_1 axes parallel to c . As shown in [FIGURE 2.16](#) the grown crystals structure confirmed the known one⁴⁴.

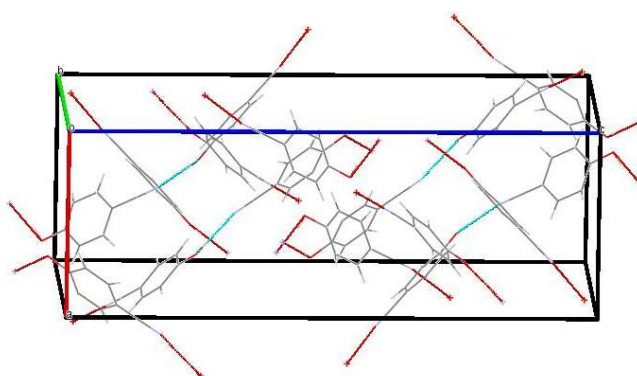


FIGURE 2.16: crystalline structure of 4HCB.

- Cell length:

a: 9.190(4) Å,

b: 10.750(3) Å,

c: 25.460(4) Å,

- Cell angles:

α : 90°,

β : 90°,

γ : 90°,

- Cell volume: 2515.26 Å³,
- Space group: P b c n
- Z: 16,
- Z': 0.

Some interesting observations, arose since it is well known that 4HCB possesses a marked charge transport anisotropy⁴⁵. This anisotropy is associated to the peculiar crystal unit cell arrangement, that sees a good overlapping of benzenic π -clouds along the a axis, a less good but still sufficient overlapping along the axis b and no overlapping at all along the axis c, in good agreement with the known charge carrier mobilities (about 10⁻¹, 10⁻² and 10⁻⁵ cm²·(V·s)⁻¹ for the axes a, b and c, respectively).

B. NTI

Crystals of 1,8-naphthalimide are monoclinic, space group P 2₁/n, with two molecules in the unit cell. As shown in **FIGURE 2.17** the structure has been confirmed⁴⁶ and details of the molecular geometry and dimensions have been obtained. As shown in **FIGURE 2.17** two different dimers are present: the parallel and the antiparallel one.

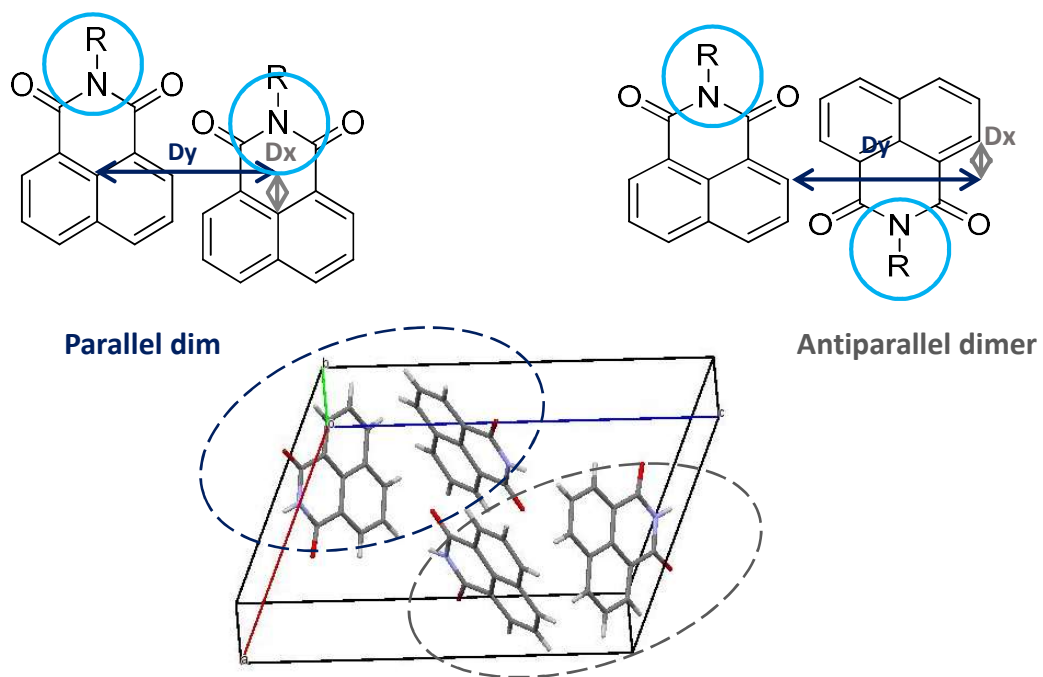


FIGURE 2.17: crystallographic structure of NTI

- Cell length:
 a : 11.009 Å,
 b : 5.4134 Å,
 c : 15.675 Å,
- Cell angles:
 α : 90°,
 β : 108.92°,
 γ : 90°.
- Cell volume: 883.698 Å³,
- Space group: P 2₁/n,

- Z: 0,
- Z': 0.

The herringbone structure of the molecular packing is shown in **FIGURE 2.18** and the evaluated geometrical parameters are the following:

1. I.D.:

Parallel dimer = 3.43 Å,

Antiparallel dimer = 3.43 Å;

2. D_Y:

Parallel dimer = 4.16 Å,

Antiparallel dimer = 4.04 Å;

3. D_X :

Parallel dimer = 3.43 Å,

Antiparallel dimer = 3.43 Å;

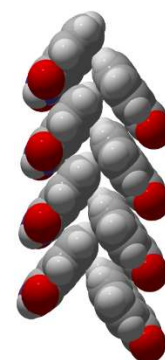


FIGURE 2.18: the herringbone packing of NTI molecule

The calculated centroid is shown in **FIGURE 2.19**

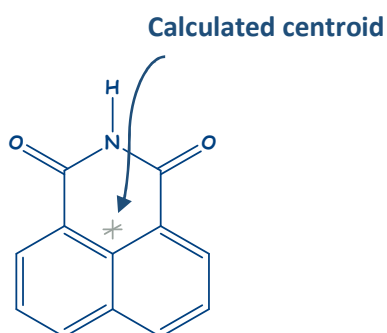


FIGURE 2.19: the calculated centroid of NTI molecule

These evaluated geometrical parameters and the herringbone packing, typical of systems with a good π - π interaction, suggest that the electronic properties of the NTI crystal should be good.

C. DNN

Crystals of 1,5-dinitronaphthalene are monoclinic, space group P21/a, with two molecules in the unit cell. As shown in **FIGURE 2.20** the structure has been confirmed⁴⁷ and details of the molecular geometry and dimensions have been obtained. The nitrogen atom and all the carbon atoms lie on one plane, but the planes of the nitro groups are rotated about the C-N bonds 49 ° out of the aromatic plane.

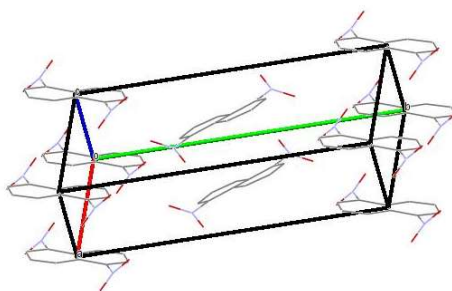


FIGURE 2.20: 1,5- dinitronaphthalene unit cell

- Cell length:

a: 7.760 Å,

b: 7.760 Å,

c: 3.700 Å,

- Cell angles:

α : 90°,

β : 101.80°,

$\gamma: 90^\circ$,

- Cell volume: $458.678 \text{ \AA}^3$,
- Space group: $P 2_1/a$,
- $Z: 2$,
- $Z': 0$.

The herringbone structure of the molecular packing is shown in **FIGURE 2.21** and the evaluated geometrical parameters are the following:

1. I.D.= $3.700 \text{ \AA}$,
2. $D_Y = 0 \text{ \AA}$,
3. $D_X = 0 \text{ \AA}$.

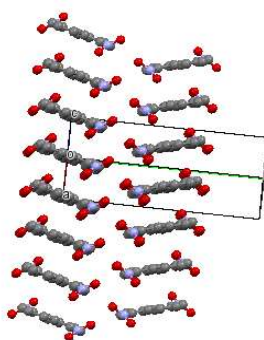


FIGURE 2.21: the herringbone packing

The calculated centroid is shown in **FIGURE 2.22**

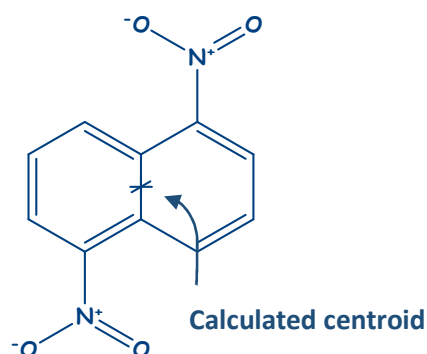


FIGURE 2.22: the calculated centroid

In this case the herringbone structure helps to achieve a decent electronic performance in terms of charge carrier mobility, which reaches about $10^{-3} \text{ cm}^2 \cdot (\text{V} \cdot \text{s})^{-1}$.

C. X-RAYS RESPONSE

The best single-crystals (except DMTPDS obtained only in polycrystalline form) prepared during the preliminary tests deeply described in this Chapter have been sent to i-FLEXIS partner group UNIBO for electrical and X-rays-response characterization. A detailed account of the results of their work is not present in the following since it has not been part of the present thesis. Some interesting results are hereafter shortly summarized in order to define the complete frame that allowed the selection of the better performing structures. The selection criteria were based on both X-rays response and crystallization output of the evaluated semiconductor.

Since this x-ray response characterization has not been carried out as this thesis work but is strictly connected to it, the results has been included but their description has not to be considered as exhaustive.

To carry out these characterizations, crystals have been electrically contacted as shown in **FIGURE 2.23**, where the two typical contact geometries used for platelet-like and needle-like crystals are shown, and a bias has been applied to the contacts.

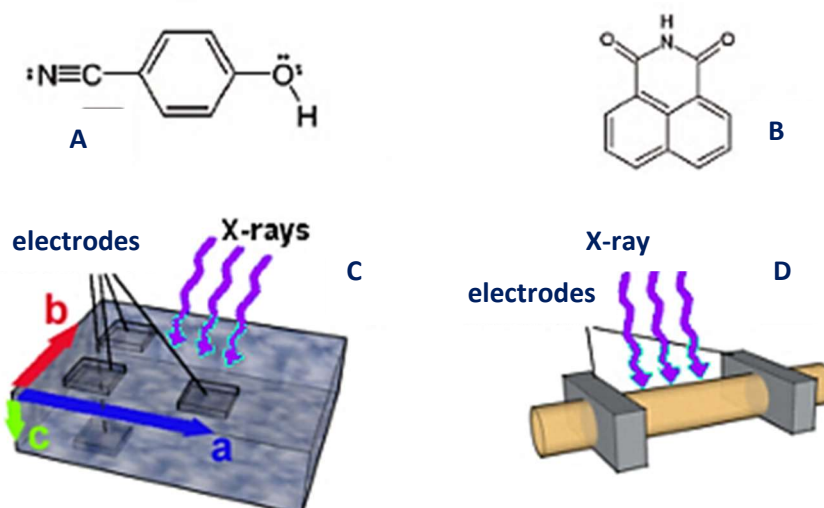


FIGURE 2.23: molecular structure of 4HCB (A) and NTI (B), respective crystal habit and related electrical contacts layout (C,D)

The current flowing through the crystal between the contacts has been recorded as:

$$\Delta I = I_{\text{on}} - I_{\text{off}}$$

EQUATION 2.3

where I_{on} is the current recorded under X-rays and I_{off} is the current recorded in absence of X-rays. Typical results of these analyses for 4HCB and NTI are shown in **FIGURE 2.24**.

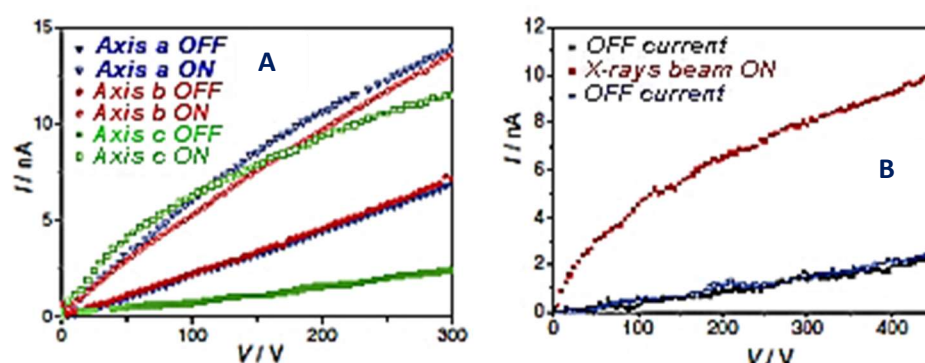


FIGURE 2.24: X-rays response under a 35 KeV X-rays beam switched on and off for 4HCB (A) and NTI (B).

A summary of the results is reported in **TABLE 19**:

	4HCB	NTI	DNN	MY	DMTPDS
Mobility (cm^2/Vs)	1×10^{-1} (a axis)				
	2×10^{-2} (b axis)	ca. 5×10^{-5}	1×10^{-3}	5×10^{-5}	6.5×10^{-5}
	2×10^{-5} (c axis)				
S @10 V (nC/Gy)	7 (a,b axes);				
	40 (c axis)	4.4	6.1	6.2	1.57
Max sensitivity/@V	175 (c axis) @ 500 V	13 @ 50 V	6.1 @ 10 V	19 @ 150 V	5.6 @ 50 V
SNR @10 V	15 (a,b axes);				
	56 (c axis)	34	4	9	11.4

TABLE 19: summary of the most meaningful results obtained for the analysed structures.

A detector sensitivity is defined as:

$$s = \frac{\Delta I}{D}$$
EQUATION 2.4

where D is the dose rate and ΔI is defined by EQUATION 2.3 .

Sensitivity is an important figure of merit in evaluating the performance of a detector. The Signal-to-Noise ratio (SNR) is the parameter giving an idea of the incidence of the noise on the overall collected signal.

Since the crystals evidenced, during the electrical characterization, different bias responses, the calculated sensitivities and SNRs showed even remarkable different values when not considering the bias at which it has been calculated. Therefore, to allow a reliable comparison between the crystals, a general bias reference value of 10 V has been taken for both values (in line with the i-FLEXIS project objectives of realizing portable, hence low-power consuming devices).

As is visible from the data reported in TABLE 19, the most performing crystal is 4HCB, that along its thickness (c axis) has a sensitivity @10 V about ten times that of the other crystals. This is likely due to the fact that along that axis the overall charge carrier transport is very poor and that, in this situation, the X-rays-generated photocarriers - though limited in absolute number (the recorded "on" currents are in the order of a few nA) - give rise to a notable ΔI due to the extremely low dark current (which is normally around a few tens of pA). Moreover, the same 4HCB have a top sensitivity of 175 nC/Gy @500 V, which makes it an interesting candidate for practical applications, considering that

commercial silicon-based detectors reach sensitivities up to 150 nC/Gy^{48, 49}.

4HCB single-crystals have been tested with different types of electrodes, namely Au deposited via precursor chloride solution, Ag epoxy paste and graphite. The best results have been achieved with Au electrodes.

The remaining crystals have measurable sensitivities, but none of them is able to achieve results as good as those of 4HCB. Nevertheless the following have been selected:

1. 4HCB,
2. DNN,
3. NTI.

Finally, one of the most surprising finding is that DMTPDS, despite incorporating a relatively high-Z atom (silicon), does not show particularly effective sensitivities towards the used X-rays. This finding has been attributed to the scarce quality of the obtained crystals, that hinder a good charges transport and their collection at the electrodes.

2.5 SUMMARY

OSSCs have been grown from solutions in quasi-equilibrium conditions and with lab-scale methods in order to select the best compound/s for the purposes of the project. Small and rigid organic molecules have been chosen. All the tested molecules included aromatic rings, interacting together through π - π interactions and van der Waals forces in the crystalline solid.

For each molecule, a pre-crystallization test, modulated in 3 steps, has been performed to find out the best solvents for each considered molecule and the best crystallization conditions for obtaining high quality crystals.

In the second step, crystals have been grown using those solvents accepted in the first step. Five batches per each solvent have been prepared. The obtained crystals have been studied in order to determine a first, rough order of magnitude of their sizes and surface morphologies. This allowed for the definition of the best solvent/solvents to be used to grow each semiconductor. After this step MY have been accepted with reserve due to its brittleness and due to the presence of orange inclusions, ascribed to a possible reaction during the crystallization process or storage . Also DMTPDS have been accepted with reserve since it basically mainly provides polycrystals with highly stepped surfaces.

The morphological characterization of the obtained single-crystals have been carried out by means of optical microscopy, while UV-Vis absorption spectroscopy of the starting solutions has been performed in order to estimate the bandgaps of the respective crystals. IR absorption spectroscopy has also been performed on some crystals in order to ascertain their purity. To verify the single-crystal nature of the obtained crystals and to confirm, if already known, the crystalline structure, X-ray diffraction analysis have been carried out.

The data collected with UV-Vis spectroscopy and XRD measurements have been shared with colleagues working in other research groups involved in the project, to define the mobility properties of the evaluated crystals.

This procedure allow for the definition of the best molecules to the purposes of the project based on both x-ray response and crystallizability:

1. 4HCB,
2. NTI.

Also DNN has been positively evaluated, but, since its performances are lower than NTI in terms of surfaces of the obtained crystals and in terms of number of obtained polycrystals per batch, it has chosen to focus the following part of the research only on 4HCB – as a representative of platelet-shaped crystal – and on NTI – as a representative of needle-shaped habit.

BIBLIOGRAPHY

- ⁰¹ G. Horowitz and M. Hajlaoui: Mobility in polycrystalline oligothiophene field-effect transistors dependent on grain size - *Adv. Mater.* – 12 - 1046÷1050 – 2000;
- ⁰² T.W. Kelley and C.D. Frisbie: Gate voltage dependent resistance of a single organic semiconductor grain boundary - *J. Phys. Chem. B* – 105 - 4538÷4540 – 2001; organic semiconducting single-crystals as next generation of low-cost, room-temperature electrical X-ray detectors: *Adv. Mater.* – 24 - 2289÷2293 - 2012
- ⁰³ M.E. Gershenson, V. Podzorov and A.F. Morpurgo: Colloquium: Electronic transport in single-crystal organic transistor - *Rev. Mod. Phys.* – 78 - 973÷989 – 2006;
- ⁰⁴ N. Karl: Charge-carrier mobility in organic crystals. In: *Organic Electronic Materials Part II: Low Molecular Weight Organic Solids* - Springer Series in Material Science – 41 - ed. by R. Farchioni and G. Grosso – Springer - Berlin Heidelberg - pp. 283÷326 – 2001;
- ⁰⁵ B. Fraboni, A. Ciavatti, F. Merlo, L. Pasquini, A. Cavallini, A. Quaranta, A. Bonfiglio and A. Fraleoni-Morgera: organic semiconducting single-crystals as next generation of low-cost, room-temperature electrical X-ray detectors: *Adv. Mater.* – 24 - 2289÷2293 - 2012
- ⁰⁶ B. Fraboni, A. Ciavatti, L. Basiricò and A. Fraleoni –Morgera: Organic semiconducting single crystal as solid-state sensors for ionizing radiation - *Farady Discussions* – 174 – 219÷234 – 2014;
- ⁰⁷ A. Ciavatti, E. Capria, A. Fraleoni-Morgera, G. Tromba, D. Dreossi, P.J. Sellin, P. Cosseddu, A. Bonfiglio and B. Fraboni: Toward low-voltage and bendable x-ray direct detectors based on organic semiconducting single crystals – *Adv. Mater.* – 27 – 7213÷7220 – 2015;
- ⁸ L. Basiricò, A. Ciavatti, M. Sibilia, A. Fraleoni-Morgera, S. Trabattoni, A. Sassella and B. Fraboni: Solid state organic X-ray detectors based on Rubrene single crystals - 62 – 4 - 1791÷1797 – 2015;
- ⁹ B. Fraboni, C. Femoni, I. Mencarelli, L. Setti, R. Di Pietro, A. Cavallini and A. Fraleoni-Morgera: Solution-grown, macroscopic, organic single crystals exhibiting anisotropic charge-transport properties – *Adv. Mat* – 21 – 1835÷1839 – 2009;

- ¹⁰ A. Intaniwet, C.A. Mills, M. Shkunov, P.J. Sellin and J.L. Keddie: Heavy metallic oxide nanoparticles for enhanced sensitivity in semiconducting polymer x-ray detectors.- Nanotechnology - 23 – 2012;
- ¹² F.H. Moser: The Phthalocyanines. Properties - A.L. Thomas Eds. – CRC - Boca Raton – 1983;
- ¹³ J. P. Mensing, A. Wisitsoraat, A. Tuantranont , T. Kerdcharoen: Inkjet-printed sol–gel films containing metal phthalocyanines/porphyrins for opto-electronic nose applications – Sensors and Actuators B: Chemical – 176 - 428÷436 – 2013;
- ¹⁴ S. Veintemillas-Verdaguer: Chemical aspects of the effects of impurities in crystal growth - Prog. Crystal Growth and Charact. - 32 - 75÷109 – 1996;
- ¹⁵ K. Sangwal: Effects of impurities on crystal growth processes - Progress in Crystal Growth and Characterization of Materials – 32 – 1÷3 – 3÷43 – 1996;
- ¹⁶ S. Seif, K. Bhat, A. K. Batra, M. D. Aggarwal and R. B. Lal: Effect of Cr(III) impurity on the growth kinetics of potassium dihydrogen phosphate and triglycine sulfate crystals grown from aqueous solutions – Mat. Lett. - 58 - 991÷994 - 2004;
- ¹⁷ H. Füredi-Milhofer and S. Sarig: Interactions between polyelectrolytes and sparingly soluble salts - Prog. Cryst. Growth Charact. - 32 - 45÷74 – 1996;
- ¹⁸ N. Zaitseva, L. Carman, I. Smolsky, R. Torres and M. Yan: The effect of impurities and supersaturation on the rapid growth of KDP crystals - Journal of Crystal Growth - 204 - 512÷524 – 1999;
- ¹⁹ Allan S. Myerson: Handbook of Industrial Crystallization – Butterworth – Heinemann – 2001,
- ²⁰ I. Owczareka and K. Sangwal: Effect of impurities on the growth of KDP crystals. Mechanism of adsorption on (101) faces - J. Cryst. Growth – 102 - 574÷580 – 1990;
- ²¹ E. Kirkova, M. Djarova and B. Donkova: Inclusions of isomorphism impurities during crystallization from solutions - Prog. Cryst. Growth Charact. – 32 - 111÷134 – 1996;

- ²² E. Mielniczek-Brzoska, K. Gielzak-Kocwin and K. Sangwal: Effects of Cu(II) ions on the growth of ammonium oxalate monohydrate crystals from aqueous solutions. Growth kinetics, segregation coefficient and characterization of incorporation sites - J. Cryst. Growth – 212 - 532÷542 – 2000;
- ²³ N. Kubota, M. Yokota and J.W. Mullin: Supersaturation dependence of crystal growth in solutions in the presence of impurity - J. Cryst. Growth – 182 - 86÷94 – 1997;
- ²⁴ P.S. Delineshev: Growth of crystals in the presence of impurities, a hypotheses based on a kinetic approach - Cryst. Res. Technol. - 33(6) - 891÷897 – 1998;
- ²⁵ A.S. Myerson and S.M. Jang: A comparison of binding energy an metastable zone width for adipic acid with various additives - J. Cryst. Growth – 156 - 459÷466 – 1995;
- ²⁶ G. Dhanaraj, K. Byrappa, V. Prasad, M. Dudley: Handbook of crystal growth - Springer-Verlag - Berlin – 2010;
- ²⁷ B. Fraboni, A. Fraleoni-Morgera and N. Zaitseva: Ionizing Radiation Detectors Based on Solution-Grown Organic Single Crystals – Adv. Funct. Mat. - 26, 2276÷2291 – 2016;
- ²⁸ G. Dhanaraj, K. Byrappa, V. Prasad, M. Dudley: Handbook of crystal growth – Springer – 2010;
- ²⁹ A.F. Barton: Handbook of Solubility Parameters and Other Cohesion Parameters – CRC - Boca Raton – 1983;
- ³⁰ N. Zaitseva, L. Carman, A. Glenn, J. Newby, M. Faust, S. Hamel, N. Cherepy and S. Payne: Application of solution techniques for rapid growth of organic crystals – J. Cryst. Grow. - 314 163÷170 – 2011;
- ³¹ D. Shukla, S. F. Nelson, D. C. Freeman, M. Rajeswaran, W. G. Ahearn, D. M. Meyer and J. T. Carey: Correlation of mobility and molecular packing in organic transistors based on cycloalkyl naphthalene diimides - Chem. Mater. - 20 - 7486÷7492 – 2008;
- ³² S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward and M. F. Toney: Structural Characterization of a Pentacene Monolayer on an Amorphous SiO₂ Substrate with Grazing Incidence X-ray Diffraction - J. Am. Chem. Soc. - 126 - 4084÷4085 – 2004;

- ³³ E. Hadicke and F. Graser: Structures of Eleven Perylene-3,4:9,10-bis(dicarboximide) Pigments - *Acta Crystallogr. - Sect. C: Cryst. Struct. Commun.* - 42 - 189÷195 – 1986;
- ³⁴ C. R. Newman, C. F. Frisbie, D. A. da Silva Filho, J.-L. Bredas, P. C. Ewbank and K. R. Mann: Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors - *Chem. Mater.* - 16 - 4436÷4451 – 2004;
- ³⁵ T. Kakinuma, H. Kojima, M. Ashizawa, H. Matsumoto and T. Mor: Correlation of mobility and molecular packing in organic transistors based on cycloalkyl naphthalene diimides - *J. Mater. Chem.* - C – 1 - 5395÷5401 - 2013,
- ³⁶ V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. Bredas: Charge Transport in Organic Semiconductors - *Chem. Rev.* – 107 - 926÷952 – 2007;
- ⁴² M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith: Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites – *Science* – 338 - 643÷647 – 2012;
- ⁴³ B. Fraboni, C. Femoni, I. Mencarelli, L. Setti, R. Di Pietro, A. Cavallini and A. Fraleoni-Morgera: Solution-grown, macroscopic, organic single crystals exhibiting anisotropic charge-transport properties – *Adv. Mat* – 21 – 1835÷1839 – 2009;
- ⁴⁴ T. Higashi and K. Osaki: p-Cyanophenol - *Acta Cryst.* - B33 - 607÷609 -1977;
- ⁴⁵ B. Fraboni, C. Femoni, I. Mencarelli, L. Setti, R. Di pietro, A. Cavallini and Alessandro Fraleoni Morgera: Solution-grown organic single crystals exhibiting three-dimensional anisotropic charge-transport properties – *Adv. Mat.* – 21 – 1835÷1839 – 2009;
- ⁴⁶ A. Yu. Kovalevsky, I. I. Ponomarev, M. Yu. Antipin, I. G. Ermolenko, O. V. Shishkin: Influence of steric and electronic effects of substituents on the molecular structures and conformational flexibility of 1,8-naphthalenedicarboximides - *Russian Chemical Bulletin* - 49 - 70÷76 – 2000;
- ⁴⁷ J. Trotter: The Crystal Structure of 1,5-Dinitronaphthalene - *Acta Cryst.* – 13 – 95÷99 - 1960;
- ⁴⁸ M. Bruzzi , F. Nava , S. Russo , S. Sciortino , P. Vanni - *Diam. Relat.Mater.* - 10 - 657 – 2001;

-
- ⁴⁹ M. A. E. Abdel-Rahman , A. Lohstroh , I. Jayawardena , S. J. Henley - Diam. Relat. Mater. - 22
- 70 – 2012;

CHAPTER 3: Organic Semiconducting Single

Crystals growth

In this chapter, the systematic study of the main parameters affecting crystallization by slow solvent evaporation will be described, with experiments carried out over the two most representative semiconductors properly selected in the first part of the work. In more detail, the theoretical bases of crystallization from solution and particularly on the nucleation thermodynamics and kinetics, will be introduced in **section 3.1**. Subsequently, in **section 3.2** the crystal growth dependence from some thermodynamic parameters will be described in deeper detail. In **section 3.3** the description of the techniques carried out to analyse the results will be presented. The general procedure adopted throughout the experimental work will be described in **section 3.4**. In closing, the results of the data obtained will be discussed in **section 3.5**.

3.1 CRYSTALLIZATION THEORY

3.1.1. INTRODUCTION.

Due to the strong needs of the semiconductor and opto-electronic industries, in which thin films and single crystals are used as basic materials, the science of crystal growth has also made great progress during the twentieth century.

Crystal growth is the process of the birth and development of a solid phase with a regular structure out of a disordered and irregular state, and thus it can be regarded as a first-order phase transition. In the case of solution growth, a liquid-solid transition takes place. Both the phase transition and the formation of a crystal, the final product, do not occur instantaneously but during a defined and relatively long (usually minutes/hours) time.

The science dealing with phase transitions is thermodynamics. In particular, thermodynamics discusses which phase will eventually be formed when a material is maintained under the same conditions for an infinite time, and the phase reaches the minimum energy state - equilibrium state - under given thermodynamic conditions, temperature and pressure. It is only when a driving force causes a system to depart from its equilibrium condition that a nucleus of a crystal is formed and the growth begins.

Solid, melt, solution, and vapour phases may be distinguished as ambient phases in which crystals can grow. These can be systematically classified depending on whether they are condensed or dilute phases, and whether solute-solvent interactions are involved or not. Solution growth is a case of dilute phase growth in which solute-solvent interactions are engaged. The driving force for the process to take place is due to both heat and mass transfers, but the degree of their respective contributions depends on the type of ambient phase involved. To grow crystals in a diluted ambient phase, a condensation process is required, and so mass transfer plays an essential role. The contribution of heat generated by crystallization in this case is small compared with that of the mass transfer. On the other hand, for crystallization in a condensed phase, such as a melt phase, heat transfer plays the essential role, and the contribution from the mass transfer is very small, because the difference in concentration between the solid and liquid phases is very small, smaller than 1 or 2%¹. Solution growth belongs to the first group, therefore it is a process where mass transfer plays the essential role.

3.1.2. DRIVING FORCE

The interfaces between the crystal and the solution phase are the unique places where growth and dissolution takes place. An equilibrium state corresponds to a dynamic state where the variations of concentrations - mass exchange - become zero at the interfaces of the two phases. This corresponds, on the phase diagram of a solution, to a specific point on a solubility curve where neither temperature nor concentration changes take place, which means that neither growth nor dissolution of a crystal occurs.

To achieve growth or dissolution of a crystal, it is necessary to attain a situation away from the equilibrium state, either by lowering the temperature or by concentrating the solute by solvent evaporation. The degree of departure from the equilibrium state corresponds to the driving force for growth or dissolution to take place. In a temperature-concentration graph **FIGURE 3.1** this situation is visualized in the Miers region, confined between the dotted line and the solubility curve indicated by the solid line.

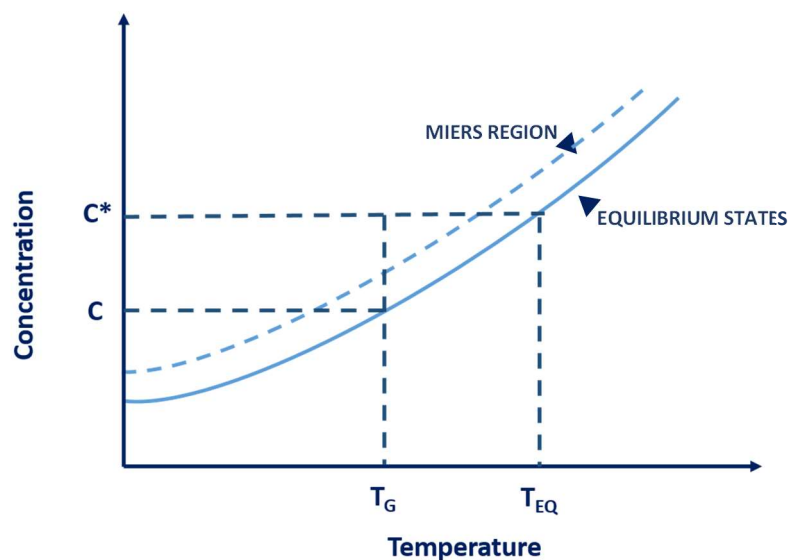


FIGURE 3.1: Solubility curve (solid line, equilibrium concentration curve) and the region in which nucleation and growth hardly occur (the Miers region, in between the dotted and solid lines). T_{EQ} and C^* are the equilibrium temperature and concentration, respectively; and T_G and C are the growth temperature and concentration, respectively.

The driving force for crystallization actually derives from supersaturation with respect to the solute, whose growth is required. Its supersaturation can be expressed in a number of ways. In the case of solution growth, where mass transfer plays the essential role, the concentration driving force, ΔC , corresponds to the difference between the concentration C^* at the equilibrium temperature T_{EQ} and the saturated solution and the concentration C at the growth temperature T_G and is expressed as follows:

$$\Delta C = C - C^* \quad \text{EQUATION 3.1}$$

The supersaturation ratio, S , is defined as follow:

$$S = \frac{C}{C^*} \quad \text{EQUATION 3.2}$$

The relative supersaturation is:

$$\sigma = \frac{C - C^*}{C^*} \quad \text{EQUATION 3.3.1}$$

or alternatively:

$$\sigma = S - 1 \quad \text{EQUATION 3.3.2}$$

If, at a given temperature, the concentration of a solution can be measured and the corresponding saturation concentration of the equilibrium state is known, then the supersaturation can be estimated.

The supersaturation required to start a crystallization can be achieved in different ways, among which two are the most widely used:

1. solution cooling,
2. evaporation of the solvent.

Meirs and Isaac reported a detailed investigation on the relationship between supersaturation and spontaneous crystallization². The results of their analysis are shown in **FIGURE 3.2**, which shows three zones, termed as regions I, II, and III. The lower continuous line indicates the normal solubility of the evaluated solute. The temperature and concentration at which spontaneous crystallization occurs are represented by the upper broken curve, generally referred to as the supersolubility curve. The three zones are defined as:

- I. the stable (undersaturated) zone: here crystallization is not possible,
- II. the metastable zone: here spontaneous crystallization is improbable; however, if a seed crystal is placed in such a metastable solution, growth will occur,
- III. the unstable or labile (supersaturation) zone: here spontaneous crystallization is more probable.

The attainment of supersaturation is not sufficient to initiate crystallization. The formation of embryos or nuclei with a number of minute solid particles present in the solution, often-termed centres of crystallization, is a prerequisite.

The degree of driving force can be generalized by the difference of the chemical potentials between the two phases:

$$\Delta\mu = \mu^S - \mu_\infty^S = \mu^S - \mu_\infty^{crystal} \quad \text{EQUATION 3.4}$$

where μ^S is the chemical potential of the supersaturated solution phase, μ_∞^S the chemical potentials of the saturated phase and $\mu^{CRYSTAL}$ the chemical potential of the solid phase. From this, a generalized driving force may be expressed as:

$$\Delta\mu = k_B T \ln \left(\frac{C}{C^*} \right) = k_B T \ln S \quad \text{EQUATION 3.5}$$

where k_B is the Boltzmann constant and T is the absolute temperature. The driving force will be expressed in terms of a generalized driving force, $\Delta\mu/k_BT$, throughout this chapter.

The process of crystal growth is divided into the following three steps:

1. a driving force is applied: it causes the system to depart from its equilibrium state and to move towards a supersaturated (or supercooled) state;
2. nucleation starts and some embryos (clusters of atoms or molecules) are formed in the system. Some of these clusters, out of the many that repeatedly forms and dissolves, grow larger than a critical size;
3. once an embryo reaches the critical size, turning in this way into a critical nucleus, it can grow larger. This process corresponds to the growth stage in its strictest sense.

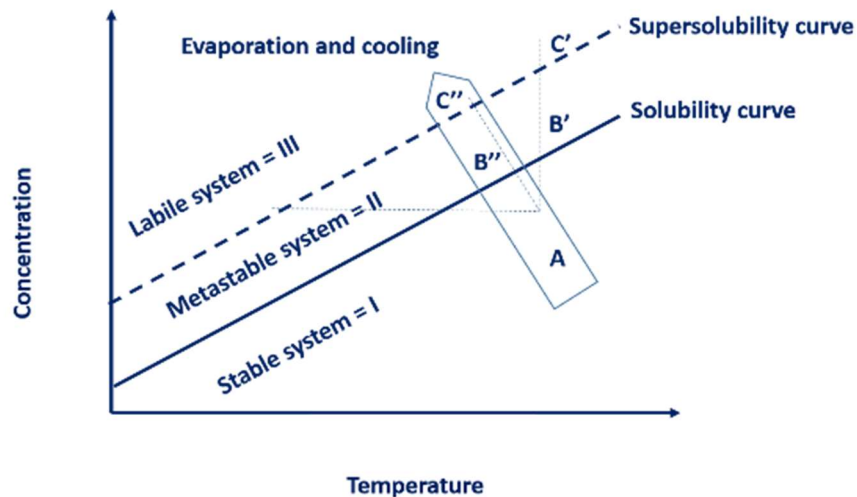


FIGURE 3.2: Miers and Isaac solubility curve which shows the three zones, termed regions I, II, and III describing respectively three behaviour of the system.

3.1.3. NUCLEATION

When a driving force is applied to a solution, it causes the process to proceed by the formation of a supersaturated state and the nucleation step of the crystal growth takes place. Nucleation is the process of generating, within a metastable phase, initial clusters of a new and more stable phase (embryos). In a supersaturated system a few molecules joining together form an embryo, a system that may further grow or may dissolve.

The free energy per molecule of the new phase is less than that of the solvated phase but this only applies to the bulk of the new phase. The surface is a different matter because the surface molecules are less bounded to their neighbours than those in the bulk, therefore their contribution to the free energy of the new phase is greater. The difference between the free energy per molecule of the bulk and that of the surface is referred to as the interfacial free energy, γ . As shown in **FIGURE 3.3** the interfacial free energy is always a positive term and acts to destabilize the embryo. As a consequence, at very small sizes (when many of the molecules reside at the surface), the embryo is unstable. Adding even one more molecule just increases the free energy of the system. On average, such an embryo will more likely dissolve rather than grow. But once the nucleus gets large enough, the drop in free energy associated with formation of the bulk phase becomes sufficiently high that the surface free energy is unimportant, and every addition of a molecule to the lattice lowers the free energy of the system.

In quantitative terms, this situation can be described as follows. The formation of a solid particle within a homogeneous solution results from the expenditure of a certain quantity of energy. The total quantity of work, W^{TOT} , required for the formation of a stable nucleus is equal to the sum of the work required to form the surface, W_s , a positive quantity, and the work required to form the bulk of the particle, W_v , a negative quantity, that is:

$$W^{TOT} = W_S + W_V \quad \text{EQUATION 3.6.1}$$

Therefore, the total change in Gibbs free energy, $\Delta^{TOT}G$, between the crystalline phase and the surrounding mother liquor results in a driving force, which stimulates crystallization. This $\Delta^{TOT}G$ is the sum of the surface free energy and the volume free energy:

$$\Delta^{TOT}G = \Delta G_S + \Delta G_V \quad \text{EQUATION 3.6.2}$$

For a spherical nucleus:

$$\Delta^{TOT}G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V \quad \text{EQUATION 3.6.3}$$

where r is the radius of the nucleus, γ is its interfacial tension, and ΔG_V is the free energy change per unit volume; the first term in the above equation expresses the formation of new surface, and the second term expresses the difference in chemical potential between the crystalline phase, $\mu^{CRYSTAL}$, and the surrounding mother liquor, μ^s . At the critical condition, the free energy formation obeys the condition $d\Delta G/dr = 0$. Hence, the radius of the critical nucleus is expressed as:

$$r^* = \frac{2\gamma}{\Delta G_V} \quad \text{EQUATION 3.7}$$

The critical free energy barrier is:

$$\Delta G^* = \frac{6\pi\gamma^3 v^2}{3(\Delta\mu)^2} \quad \text{EQUATION 3.8}$$

The number of molecules in the critical nucleus is:

$$X^* = \frac{4}{3}\pi\gamma(r^*)^3$$

EQUATION 3.9

The crucial parameter between a growing crystal and the surrounding mother liquor is the interfacial tension γ .

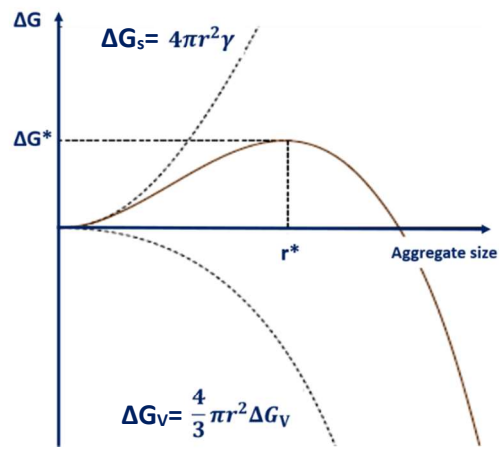


FIGURE 3.3: Free energy of aggregates as a function of aggregate size. The nucleation free-energy barrier is ΔG^* at an aggregate size r^* .

The time required for the formation of a nucleus depends strongly on the activation energy of the nucleation process, ΔG^* , and, thus, on the supersaturation. Once formed, a nucleus grows slowly at first, because the free energy is nearly constant as a function of size. Attachment and detachment are nearly equally likely, and the nucleus grows (if it does) by a slow random walk process^{3,4}. Thus there is a lag time before truly stable aggregates are formed.

3.1.4. POSTNUCLEATION GROWTH

Once a crystal has become larger than the critical size, its growth becomes thermodynamically favoured, and it proceeds to reach macroscopic sizes. To do so, molecules must be transported through the bulk solution to the surface of the crystal, where they may attach. Since the structure is already formed, the solute component will be incorporated into the crystal at the expense of a much smaller energy than that necessary for nucleation. Here, the interface structure between the solid - appeared as a result of nucleation - and liquid phases becomes important. This is because the growth mechanism will be different depending on whether the interface is atomically rough or smooth. In any case, the growing crystal must be supplied with molecules, which, in the absence of convection, are transported through the solution by diffusion. A concentration gradient necessarily develops, and, in the layer nearer the crystal, the solution is relatively depleted of molecules. This is called volume or bulk diffusion. The concentration gradient is not linear from the bulk ambient phase, away from the nuclei, and the surface of the nuclei or crystal. This was already clear from investigations conducted before the 1930s, as shown in **FIGURE 3.4**. The region with a sharp gradient is called the diffusion boundary layer and the concentration gradient in this layer plays an essential role in crystal growth, since its presence determine a difference of chemical potential and therefore the presence of a driving force for the growing process to take place. This has, moreover, the important consequence that nucleation is inhibited in the vicinity of a growing crystal.

3.1.5. THE STEADY-STATE APPROACH

In accordance with current rate theory, the rate at which the critical nuclei form is therefore:

$$J = A \cdot e^{\left(\frac{-\Delta G^*}{kT}\right)} \quad \text{EQUATION 3.10.1}$$

Bearing in mind the **EQUATION 3.7** the previous becomes:

$$J = A \cdot \exp \left(-\frac{6\pi\gamma^3 v^2}{3 (\Delta\mu)^2} \right) \quad \text{EQUATION 3.10.2}$$

The pre-exponential term A has been discussed in the theories of Becker, Doring and others^{5, 6} who used the kinetic theory to calculate the rate of condensation on to the embryo. The very rapid increase in nucleation rate as the supersaturation increases, predicted by EQUATION 3.10.2, has been confirmed by experimental observations. The agreement between the experimental kinetic factor, A , and those calculated from the Becker-Doring theory was very good for some systems.

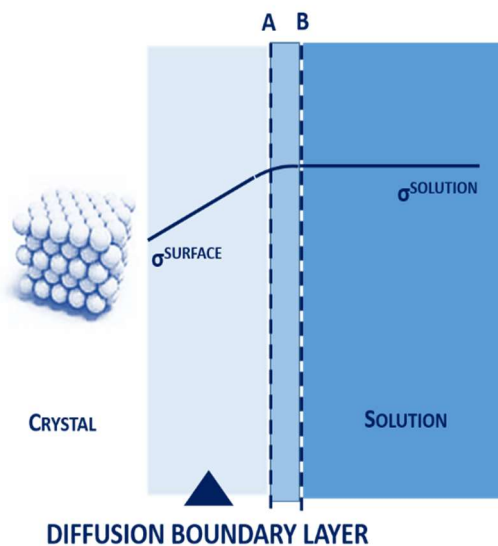


FIGURE 3.4 Schematic illustration explaining the concentration gradient around a growing crystal and the presence of the diffusion boundary layer. Bulk diffusion indicated by diffusion boundary layer (for A or B). The concentration gradient is $(\sigma_{\text{SURFACE}} - \sigma_{\text{SOLUTION}})$.

The surfaces of the growing crystals may be:

1. flat, F,
2. stepped, S,
3. kinked, K.

However, crystals of visible size are usually bounded by slowly growing F-faces, which grow by the attachment of growth units at energetically favourable sites.

FIGURE 3.5 shows different positions for the attachment of growth units at a flat crystal–solution interface of a simple cubic lattice. A growth unit attached at a surface terrace, T, has one out of the six potential nearest neighbours; a growth unit attached on a surface at a smooth ledge, L, has two out of the six potential nearest neighbours; a growth unit attached at a kink site, K, has three out of the six potential nearest neighbours. Therefore, a growth unit arriving at a surface terrace, ledge or kink simply loses one, two or three degrees of freedom. If ϕ is the binding energy per pair, the corresponding binding energy of a growth unit attached at these sites is ϕ , 2ϕ , and 3ϕ , respectively.

The probability of capture of a growth unit at a given site depends on the term:

$$e^{\frac{n\phi}{k_B T}} \quad \text{EQUATION 3.11}$$

where n is the number of bonds formed, k_B is the Boltzmann constant and T is the temperature in Kelvin, therefore the growth unit has a much higher probability of becoming a part of the crystal at a kink site than at a ledge or surface terrace. Consequently, in contrast to ledges, the contribution of kinks is overwhelmingly high in the rate v of displacement of a step along the surface and in the rate R of displacement of the surface normal to it. Similarly, the contribution to the face growth rate, R , by the direct attachment of growth units at the terrace is negligible.

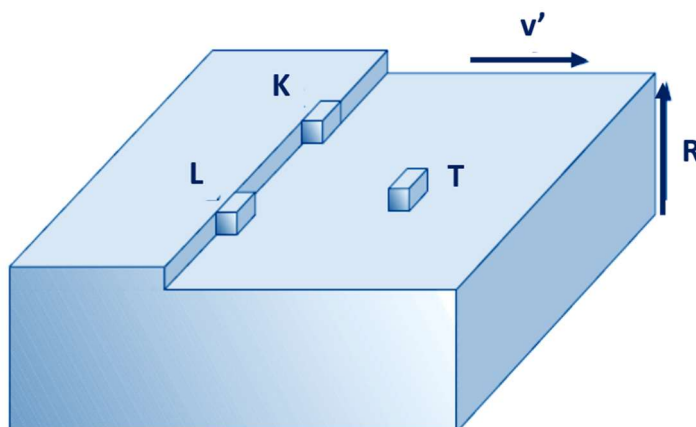


FIGURE 3.5: Different positions for the attachment of growth units at a flat crystal–medium interface of a simple cubic lattice

From the above discussion, the kinetics of crystal growth occurs in the following stages:

1. transport of growth units to the growing surface by bulk diffusion and their capture onto the surface terrace,
2. migration of growth units adsorbed onto the terrace to the step by surface diffusion and their capture at the step,
3. migration of growth units adsorbed onto the step to the kink site and their integration into the kink,
4. transport of the released heat of the process and solvent molecules from the solvated atoms/molecules.

It should be noted that growth kinetics, characterized by the rates v' and R , depends on the crystal structure, the structure of the crystal–medium interface (i. e. rough or smooth), the presence of dislocations emerging on the growing face, the supersaturation of the growth medium, the growth temperature, stirring and impurities present in the growth medium. These are the factors that definitely determine the surface morphology of the crystal.

Many theories on interface structures have been expounded and therefore many different terms have been introduced, as in the following:

THEORY	TERMS
KOSSEL, STRANSKI	COMPLETE FACE, INCOMPLETE FACE
BURTON, CABRERA, FRANK	SINGULAR FACE, NON-SINGULAR FACE
HARTMAN, PERDOK	FLAT FACE (F FACE), STEPPED FACE (S FACE), KINKED FACE (K FACE)
PRESENT-DAY TERMINOLOGY	SMOOTH FACE, ROUGH FACE

Instead of referring to complete and incomplete faces, Burton, Cabrera, and Frank used the terms singular and non-singular faces, in the sense of one face showing a sharp minimum (cusp) and one showing no minimum, respectively, on a polar diagram of surface energy. This classification is based on the calculation of statistical mechanics and is closely related to the discussion of the equilibrium form. Hartman and Perdok classified crystal faces into F (for flat face), S (stepped), and K (kinked face), depending on the numbers of periodic bond chains (PBCs) that were found in a crystal structure by connecting strong bonds. It is clear that these faces correspond to the $\{100\}$, $\{110\}$, and $\{111\}$ faces of a Kossel crystal, respectively. Today, the terms smooth and rough interface are commonly used alongside perfect and imperfect faces, and singular and non-singular faces.

As can be seen from the Kossel crystal, the roughness of an interface depends on which faces we are considering, i.e. on the crystallographic directions. It also varies depending on the crystal species, the temperature, and the driving force. Increasing the temperature or driving force will cause a smooth interface to change into a rough interface. The transition point that exists in going from a smooth to a rough interface as the temperature increases is called a roughening transition. The existence of roughening transitions has been demonstrated by computer simulation. A roughening transition resulting from increasing driving force is called a kinetic roughening transition. Depending on the degree of roughness of an interface, the growth mechanism or growth rate versus the driving force relation changes, and so the interface roughness is an essentially important concept in analyzing the morphology of crystals and element

partitioning. Extensive computer experiments have been made since the 1980s to investigate how interface structure changes as $\Delta\mu/kT$ changes, to determine whether the roughening transition takes place and to establish how the growth rate versus the driving force relation (and thus the growth mechanism) change depending on changes in $\Delta\mu/kT$.

3.2 GROWTH PARAMETERS AND THEIR INFLUENCE ON CRYSTALLIZATION OUTPUT

3.2.1. INTRODUCTION

Obtaining the control of size, quality and crystal habit of organic semiconductor - for structural investigations in conduction mechanisms physics and opto-electronic engineering - is still a challenge in many laboratories worldwide. Indeed, in opto-electronic engineering, crystallization conditions affect both the OSSC properties (and hence the solid-state properties of device) and its habit. It should be emphasized that even minor changes in crystallization conditions - for example: supersaturation, temperature, cooling or evaporation rate and impurity concentration - can induce significant changes in the crystal properties^{7, 8} and morphologies. These effects have been recognized as the major batch-to-batch variation problems, leading to inconsistency in the final device formulation properties.

Crystals of the same phase can exhibit a great variety of crystal habits. This was one of the major difficulties at the beginning of crystal study and partly still remains, notwithstanding the enormous theoretical and experimental progress. This subject has both scientific and applied relevance. In many industrial sectors, crystal habit change is necessary to prevent crystal caking, crystal filters occlusions, obtain more convenient crystal products (again in terms of shape, size, purity, quality, etc.), simplify storage and package, etc. Empiricism played an important role in industrial crystallization in the past, but has been

progressively supported and replaced by knowledge of crystal growth mechanisms and phenomenological rules.

Variations in crystallization conditions may, in general, also confer instability upon the product leading to disordered and amorphous states, polymorphism and, in some cases, even the occurrence of solid-state reactions⁹.

In order to apply the concepts of crystal engineering to organic semiconductors, the reproducibility of the solid-state properties, stability and morphology must, first of all, be attained. The complexity and variety of crystallization problems warrant investigations of the more fundamental aspects of crystal growth. It is therefore clear that, in order to achieve full control over the characteristics of organic compounds, a greater insight into their crystallization procedures has to be gained.

On one hand, the thermodynamic quantities describing the energetics of crystal growth and especially of nucleation are surface free energy and the volume free energy, as seen in EQUATION 3.7. For the crystallization process to take place, it must be that:

$$\Delta^{TOT}G = 4\pi r^2\gamma + \frac{4}{3}\pi r^3\Delta G_V < 0 \quad \text{EQUATION 3.12}$$

the first term in the above equation expresses the formation of new surface, and the second term expresses the difference in chemical potential between the crystalline phase, μ , and the surrounding mother liquor, μ_0 .

The crucial parameters between a growing crystal and the surrounding mother liquor are the interfacial tension, γ , the solubility, the temperature of the solution, the composition of the solution and the presence of impurities.

On the other hand, the growth kinetics of a face depends on its growth mechanisms and contributes to define the crystal habit, therefore a detailed knowledge of these aspects is essential for production of crystals of specific physical or morphological properties. The growth rate of a face describes the

advancement of its surface in the normal direction per unit time. It depends upon both internal and external factors. Internal factors include the surface structure of faces, which are, in turn, related to the bulk crystal structure, and their degree of perfection. Defects usually occur in the crystals and can emerge at the surface, affecting the growth kinetics. The external factors include the supersaturation, the solute concentration, which is related to solubility, the temperature of the solution, the composition of the solution, mechanical conditions such as the use of stirring, and the presence of impurities or a magnetic or gravitational field. Due to the ultimate goal of the project this PhD research is part of, the use of the stirring or other external influences have been intentionally not considered.

One of the basic questions of industrial formulation is to define what experimental conditions provide the crystals more suitable to the purposes. Since the growth output are determined by various inter-relating factors, it is inevitable that to form a clear picture we would need to analyse the origin of each factor case by case. On this basis the crystal growth dependence from some different growth parameters has been studied in order to investigate the changes in crystallization outputs as a consequence of the parameter changes, the ultimate goal being the achievement of OSSCs of desired dimensions and quality, suitable to the purposes of the Project.

3.2.2. IMPURITIES

As described in **Chapter 2**, various researchers^{10, 11, 12, 13} have already studied the effects of the presence of inorganic and organic impurities on the kinetics of growth, assessing that impurities can have a substantial effect on the kinetics of crystal nucleation and, hence, the resulting morphology^{14, 15, 16, 17, 18, 19}. These molecules induce their effects by interacting with the crystal faces during growth. Some impurities can completely suppress growth, some enhance growth, while others can act selectively on each crystal face, consequently modifying the crystal morphology²⁰. Mullin²³ stated that the suppression of nucleation may result from changes in the equilibrium solubility or in the solution structure or by physical or chemical adsorption of the impurity on homogeneous or heterogeneous nuclei.

3.2.3. SUPERSATURATION

Supersaturation can have a profound affect on crystal growth, resulting in morphological changes in the crystallizing compound^{21, 22, 23, 24}. It is also known to affect many of the physical properties of crystals, including the solvent content, melting point, enthalpy and entropy of fusion, as well as the dissolution rate.

By varying either the solution composition or the supersaturation, the probability of nucleation can be controlled and addressed. Indeed, the probability of nucleation is strongly affected by the value of the critical size, hence nucleation can be controlled, to some extent, by modulating the critical size²⁵, which is in turn a function of the interfacial energy. The smaller the interfacial energy, the smaller the critical size and the more likely nucleation becomes for any given supersaturation.

3.2.4. TEMPERATURE

An especially important parameter is temperature, though it is often poorly controlled. Crystals grow when the total free energy of the system can be decreased. Thus, the driving force for crystallization is the free energy difference between the solid and the supersaturated solution:

$$\Delta^{TOT}G = \Delta^{TOT}H - T\Delta^{TOT}S$$
EQUATION 3.13

where $\Delta^{TOT}H$ and $\Delta^{TOT}S$ are the differences in enthalpy and entropy of the crystalline and fluid phase, respectively. It is then clear that temperature governs the balance between enthalpy and entropy effects in the free energy, which are typically comparable in magnitude. Moreover, depending on whether crystallization is enthalpy- or entropy-driven, the growth unit – semiconductor molecule in the evaluated case - may become either more or less soluble at higher temperature. Moreover, temperature influences also other factors that act on the growth rates: solubility, surface roughness, solvent/solute-interface interactions, and chemical equilibria. Since these factors work in a selective way

on different crystal facets, a change in temperature may cause relevant changes in crystal habit, as shown in experiments since the beginning of the 20th century^{26, 27, 28}. Interestingly, temperature is relatively easy to set and precisely program, making it an attractive control parameter to separately optimize conditions for nucleation and growth.

3.2.5. VOLUME OF THE GROWING VESSEL AND VOLUME OF THE SOLUTION

During crystallization, the parameters characterizing the solution may change with time. The rate at which changes occur is important: if high supersaturation is reached too rapidly, many crystals nucleates before the concentration of the solution is significantly depleted²⁹. The remaining molecules are then insufficient to sustain growth of all these nuclei to a large size, generating in such a way small crystals. Fast growth rates also favour the formation of crystals with poor morphology³⁰.

3.3 EXPERIMENTAL TECHNIQUES USED TO INVESTIGATE GROWTH RESULTS

Characterization of crystals has become an integral part of crystal growth and process development. Crystals crystallinity, sizes, surface morphologies together with composition and elemental purity determine most of semiconductors properties such as electrical conductivity, photoconductivity, luminescence and optical absorption, and these properties influence their performance in applications. Therefore, investigating such parameters is critical to gain a proper control over the process.

Techniques for observing crystals and their complex surface morphologies have been described in detail by Verma³¹ and Amelincks³². So far, knowledge of crystal growth has principally been based on data acquired using optical microscopy^{33, 34}, electron microscopy^{35, 36, 37} and supported by the theories of Burton, Cabrera and Frank³⁸, Bennema^{39, 40, 41}, Gilmer⁴², and Chernov⁴³.

Moreover, in recent years a relevant improvement has been achieved when atomic force microscopy, AFM, has been applied to study the nanometer scale features of crystal faces^{44, 45}.

These characterization methods have different ranges of capabilities and limitations, and hence they should be used complementarily⁴⁶. All the mentioned techniques are described in the following sub-sections.

3.3.1. OPTICAL MICROSCOPY

A detailed account of the mechanical description of optical microscopes has been reported by Needham⁴⁷. Optical microscopy, in its simplest form, employs a series of lenses to focus a beam of visible light, after it has interacted with a sample. This provides an image of the sample which is usually observed through an eyepiece. The resolution of the optical microscope is restricted by the wavelength of visible light, which thus precludes atomic-scale imaging. A block diagram of an optical microscope is shown in **FIGURE 3.6**.

The optical microscopy characterization, in reflection and transmission, has been carried out to evaluate the geometrical (sizes) and surface morphological features⁴⁸ of crystals, such as the growth spirals, which however are not always observable via direct microscopic imaging. In fact, the step separation of a spiral, λ_0 , is related to the critical radius of two-dimensional nuclei, r_c , in the following manner:

$$\lambda_0 = 19 \cdot r_c \quad \text{EQUATION 3.14}$$

and r_c has the following relation to step free energy and the driving force:

$$\Delta G(r_c) = \frac{16\pi \cdot \gamma^3 \cdot (v)^2}{3\Delta\mu^2} \quad \text{EQUATION 3.15}$$

where v is the molecular volume of the bulk nucleated phase. Therefore, λ_0 becomes smaller as the driving force increases. Also, λ_0 will vary with changes in γ ,

reflecting the difference in temperatures, impurities, and solute–solvent interaction, resulting in the variation in the normal growth rates of crystal facets.

Therefore, the factors affecting the crystal habit are the same as those affecting the roughness of the steps and λ_0 . When the step separation is wide enough, typical spiral step patterns observable by optical microscopy may appear, but if the separation becomes narrower than the resolution power of the optical microscope, the spirals appear in the forms of polygonal pyramids or conical growth hillocks. Even if spiral patterns are not directly observable, we may assume that these growth hillocks are formed by the spiral growth mechanism. Examples representing the two cases are compared in **FIGURE 3.7**.

The values of λ_0/h are different for different growth phases and conditions. They are typically in the order of $10^2 \div 10^3$ on crystals grown from the solution phase (because the step separation is narrower)⁴⁹. It is extremely unlikely that the whole surface of a crystal face is covered by step patterns with constant λ_0 . In general, λ_0 becomes narrower towards the edge. This is due to the fact that the driving force is higher at the edge than at the center, i.e. the Berg effect.

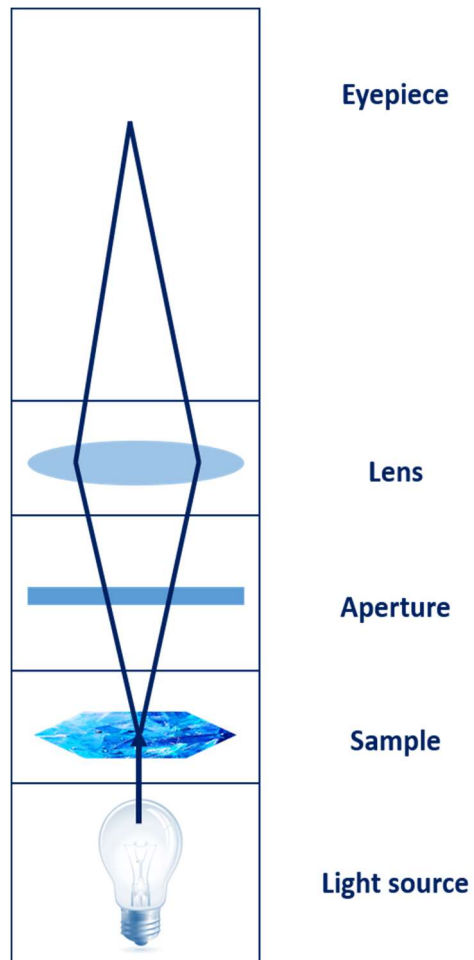


Figure 3.6: block diagram of a conventional optical microscope.

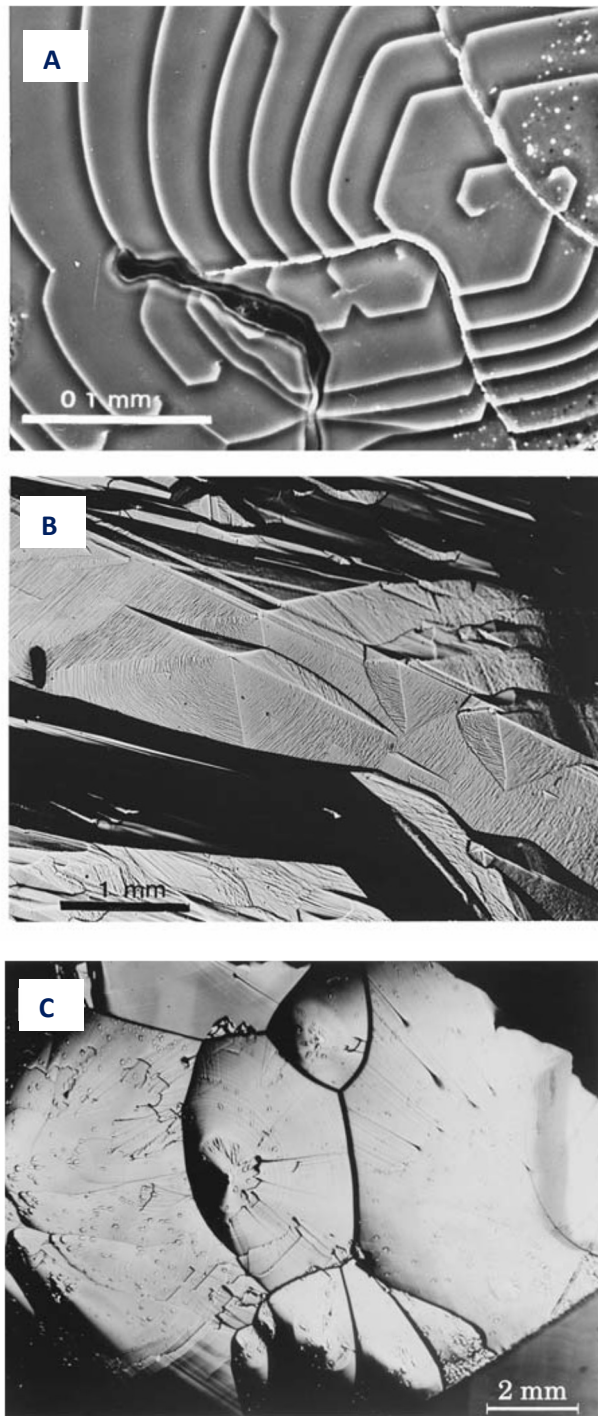


FIGURE 3.7: (A) Typical spiral pattern and spiral growth hillocks which appear as (B) polygonal and (C) conical pyramids due to narrow step separation.

3.3.2. ATOMIC FORCE MICROSCOPY (AFM) AND ROUGHNESS PARAMETERS

The above described technique have drawbacks. Optical microscopy have relatively limited resolution, and electron microscopy technique, with the exception of Environmental SEM (ESEM), must be performed in vacuum and 4HCB cannot be analysed in vacuum condition since its tendency to sublime is high well below 100°C.

Over the past decade, a powerful technique, known as AFM, has been successfully applied in the study of crystals growth, establishing itself as a leading technique in the nanoscale investigation of surface topography and mechanisms of crystal growth. Nowadays its application to the study of surface topography is almost ubiquitous since, in contrast to the above mentioned techniques, AFM allows the direct observation of crystal surfaces also in solution, at near molecular resolution. Indeed, in 1986 AFM was first reported to image material surfaces with high resolution in aqueous solutions, thus enabling the study of a wide range of solid-liquid interfaces⁵⁰.

The theory behind AFM and its methodology are well documented^{51, 52, 53, 54, 55} and, hence, shall be only briefly described here. Most modern instruments can operate in contact, non contact and tapping mode and, based on the topography of the analysed surface and on the experimental needs. All these modes have been used in the experiments described in this thesis.

AFM was first introduced to the field of crystal growth by Durbin and Carlson in 1992⁵⁶, who observed the growth of steps on the surface of lysozyme crystals in mother liquor. Its subsequent application has substantially changed the way we view simple molecular crystals⁶³. A vast number of researchers have taken advantage of AFM to investigate the mechanisms of crystal growth. Crystalline materials whose growth has been probed using AFM range from inorganic systems, such as calcite^{57, 58}, potassium sulphate^{59, 60}, and potassium hydrogen phthalate⁶¹, to complex macromolecules.

Surface morphology is an important issue when the main interest is to understand the nature of material surfaces, and it plays an important role in the functional performance of many engineering components, so much that the American

National Standards Institute's B46.1 specification takes care to give definition of the surface texture ('the repetitive or random deviation from the normal surface that forms the three dimensional topography of a surface'). Before 1990 the characterization of a sample surface texture was typically carried out via a contact stylus profiler⁶² (Whitehouse et al., 1975), that had several limitations.

On the other hand AFM has been developed to obtain a three-dimensional image of a material surface at a molecular scale. *Lay* is the term used to indicate the direction of the dominant pattern of texture on the surface. On a surface, the lay is in the front-to-back direction, as shown in **FIGURE 3.8**:

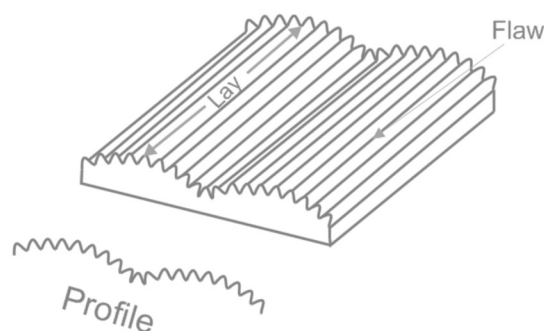


FIGURE 3.8: Surface lay (adapted from B. C. MacDonald & Co., 2011)

The surface profile is just the height from the top of the peak to the bottom of the trough. It is usually at least three times the roughness average height. Roughness is often described as closely spaced irregularities or with terms such as 'uneven', 'irregular' and other similar ones as shown in **FIGURE 3.9**. Similar to some surface properties such as hardness, the value of surface roughness depends on the scale of measurement. In addition, the concept of roughness has statistical implications, as it takes into consideration factors such as sample size and sampling interval. It is

quantified by the vertical spacing of a real surface from its ideal form. If these spacing are large, the surface is rough; if they are small the surface is smooth.

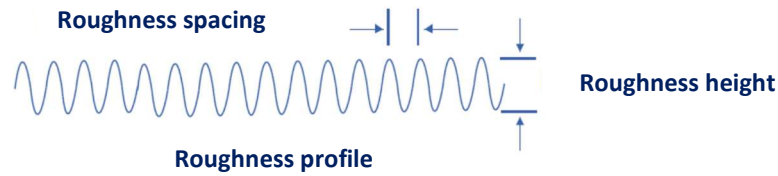


FIGURE 3.9: Roughness (adapted from B. C. MacDonald & Co., 2011).

The roughness can be characterized by several parameters and functions (such as height parameters, wavelength parameters, spacing and hybrid parameters. The following parameters and functions related to the height and spacing will be discussed as well as their calculation:

1. roughness average, R_A ;
2. root mean square roughness, R_Q ;

These, are the most significant parameters in the case of roughness. Among the height parameters, the roughness average, R_A , is the most widely used because it is the simplest parameter to obtain when compared to others. The roughness average is described as follows⁸⁵:

$$R_a = \frac{1}{L} \int_0^L |Z_x| \cdot dx \quad \text{EQUATION 3.16}$$

where Z_x is the function that describes the surface profile analysed in terms of height, z , and position, x , of the sample over the evaluation length, L , as shown in FIGURE 3.10. Thus, R_A is the arithmetic mean of the absolute values of the height of the surface profile Z_x .

The average roughness has advantages and disadvantages. The advantages include, for example, the ease of obtaining the same average roughness of less sophisticated instruments like a profilometers; the possibility of repetition of the parameter, since

it appears statistically very stable. Also for these reasons it is recommended as a parameter for the characterization of random surfaces.

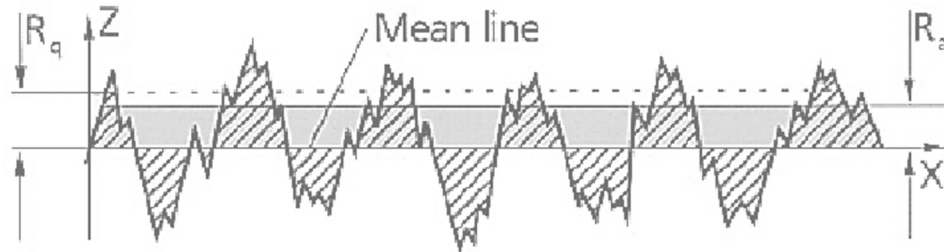


FIGURE 3.10: Profile of a surface (Z). It represents the average roughness R_a and R_q is the RMS roughness based on the mean line (B.C. MacDonald & Co, 2011).

The average roughness, as already said, is just the average absolute profile, making no distinction between peaks and valleys. However, the average roughness can be the same for surfaces with totally different roughness profiles, because it depends only on the average profile of heights. Therefore, surfaces that have different undulations are not distinguished by this parameter, as shown in **FIGURE 3.11**. For this reason, more sophisticated parameters can be used to fully characterize a surface when more significant information are necessary (for example, need for distinguishing between peaks and valleys).

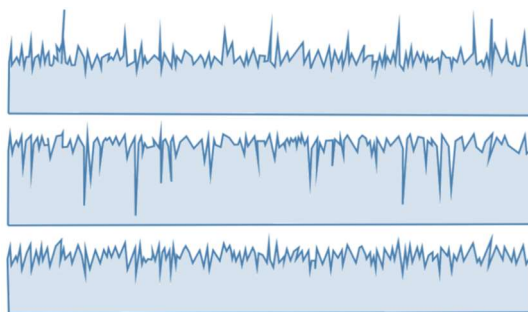


FIGURE 3.11: Different profiles of surfaces, with the same R_a (adapted from Predev, 2011).

The root mean square, RMS, is a statistical measure used in different fields. The root mean square of roughness, R_o , is a function that takes the square of the measures. The RMS roughness of a surface is similar to the roughness average, with the only

difference being the mean squared absolute values of surface roughness profile.

The function R_Q is defined as follow:

$$R_q = \sqrt{\frac{1}{L} \int_0^L |Z_x| \cdot dx} \quad \text{EQUATION 3.17}$$

The R_Q is more sensitive to peaks and valleys than the average roughness, due to the squaring of the amplitude in its calculation.

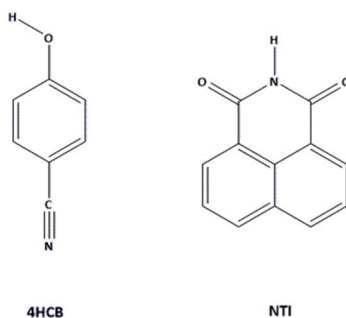
3.4 MATERIALS AND METHODS

As already discussed in **Chapter 2**, the first part of the research has been carried out in order to select, among a plethora of starting compounds, those showing the best growth features and the higher performances in terms of mobility. Upon the obtained results, two compounds have been selected and have mainly been investigated in the second part of the work:

1. 4-hydroxycyanobenzene (4HCB),
2. 1,8-naphthalimide (NTI).

The first one is the best representative of a semiconductor that gives platelet single-crystals, while the second is the best representative that gives needle-shaped single-crystals. Moreover both semiconductor have been provided an higher number of single-crystals than poly-crystals per each batch of growth.

Both compounds have been subjected to the same study and have been treated following the same protocol. To avoid useless repetitions, the obtained data are presented only for one of them (4HCB), even though the same trend has been obtained also for the other one (NTI).



3.4.1. PRE-GROWTH PURIFICATION

Due to the solubility of organic semiconductors in organic solvents, recrystallization from organic solvents have been chosen as the proper method to purify the starting compounds. This type of purification procedure is already known to provide OSSCs with well reproducible electronic behaviour^{63, 64, 65, 66, 67}.

Recrystallization is a purification process used to remove impurities from organic compounds that are solids at room temperature (see **Chapter 2, section 2.2** of this thesis for more details). Both 4HCB and NTI, with purity in the range of 95–99%, have been purchased from Sigma-Aldrich. The as-received compounds have been characterized by means of ¹H-NMR spectroscopy, UV-VIS spectroscopy and melting point determination and purified as described in **Chapter 2**. Once purified, both compounds have been used to grow crystal within two days after their pre-growth purification, and have been stored in the meanwhile in a dark room.

4HCB

Pre-purification step has been carried out using CHCl₃ as a re-crystallizing solvent. By comparison of the obtained spectra, the proper number of purification cycles has been set in two.

NTI

Pre-purification step has been carried out using THF as a re-crystallizing solvent. By comparison of the obtained spectra, the proper number of purification cycles has been set in three.

3.4.2. CRYSTALLIZATION SETUP

All the beakers used as crystallizers have been pre-treated immediately before their use. The protocol settled up for their cleaning has been described in **Chapter 2, section 2.2**.

A proper amount of pre-purified compound (see again **Chapter 2, section 2.2** for details) has been taken and used to prepare the solution with the final desired concentration. Analytical grade solvents have been used to solvate the organic

semiconductor with the aim of minimizing as possible the amount of impurities introduced into the system.

The prepared solution have been put into the properly cleaned beakers, that have been sealed with Al foil and parafilm to avoid any loose of solvent from the lateral region. A small hole (approximately 200 μm of diameter) has been made in the centre of the Al foil, allow for a slow and controlled solvent evaporation. The volume of the beakers used to grow the crystals has always been the same, namely 100 mL.

The growth batches have been placed in a thermostatic chamber at a proper temperature (20°C). The temperature inside the chamber was monitored by a thermometer that showed maximum temperature changes during the experiments being within $\pm 1^\circ\text{C}$. The crystallization has been considered completed when the total amount of solvent has been evaporated. Upon crystallization completion, the parafilm and the Al foil have been removed from the top and the walls of the beakers. Systems have been left in air for at least one day to allow the solvent traces to completely leave the system. After this period, crystals have been gently detached from the beaker's bottom surface with the help of a tiny spatula, and have been catalogued for the following analysis. To provide statistically reliable results, at least five batches per each growth experiment have been prepared. Each of them has been treated and analysed following the previous procedure, and the obtained results have been used to evaluate the mean value of the sizes and the mean value of the number of obtained single-crystals. The so-obtained data have been processed using Origin software. Optical microscopy images of the typical crystals obtained after complete solvent evaporation are shown in **Chapter 2**.

3.4.3. INSTRUMENTS

The 4HCB and NTI single-crystals have been extensively examined under a transmission and reflection optical microscope (Olimpus BH2-UMA (FIGURE 3.12) at a magnification up to 1600 x - Among the geometrical information, the characteristic shape has been determined together with the sizes of the sides. Moreover, the technique has been carried out to evaluate morphological features⁶⁸ of crystals such as the growth spirals. As shown in FIGURE 3.13 several types of common defects have

been detected with this technique, as highlight in the **section 3.3**, and have been observed: cracks, growth steps, sub-grain boundaries and hexagonal inclusions. These hexagonal inclusions have been found either at the centres of growth spirals or on a smooth surface without other obvious defects.

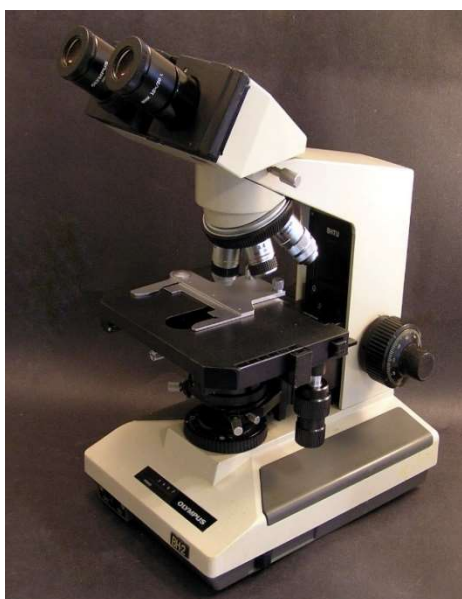


FIGURE 3.12 : Optical microscopy Olympus
BH2-UMA.

AFM analysis of the crystals surface has been performed using an A.P.E. Research Nanotechnology (Italy) Atomic Force Microscopy. V-shaped silicon nitride cantilevers with integrated pyramidal tips (Nanoprobes, Veeco, Santa Barbara, CA) have been used as probes.

Contact mode, non-contact mode and tapping mode imaging have been performed depending on the sample features

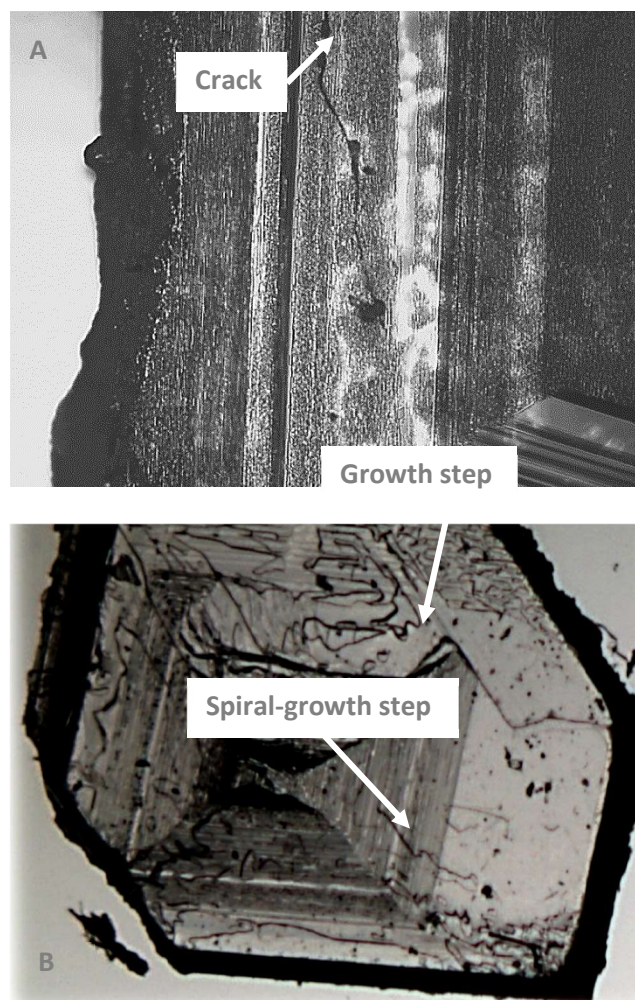


Figure 3.13: Optical micrographs of surface features on 4HCB single-crystal showing different type of common defects. Micrograph A acquired in reflection. Micrograph B acquired in transmission. Two different magnification. Side A image = 1160 μm . Side B image = 2320 μm .

3.5 RESULTS AND DISCUSSION

In order to properly obtain OSSCs of desired dimensions and quality, the crystal growth has been studied in terms of its dependence from the following parameters:

1. concentration of the solution,
2. growth temperature,

3. volume of solution.

The crystal parameters analyzed under the aforementioned variables are the following ones:

1. number of single crystals produced,
2. number of polycrystals produced,
3. number of total crystals (single and poly),
4. single crystals sizes,
5. sizes of the crystals' sides (with reference to Fig. 3.18, sides A, B and C),
6. surface quality.

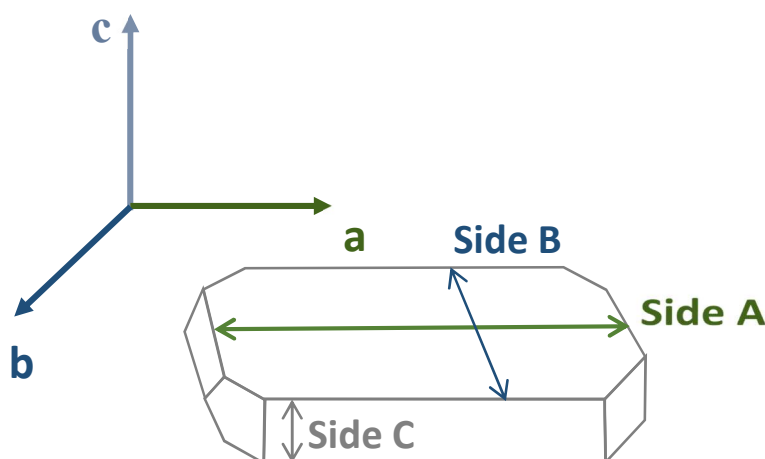


FIGURE 3.14: 4HCB single crystal grown from solution. In this representation sides are shown with their name.

1. EFFECT OF CONCENTRATION

A. Mean number and mean size of the obtained single-crystals

The evaluated concentrations for 4HCB in ethylic ether solvent spanned from 5 $\text{mg}\cdot\text{mL}^{-1}$ to 30 $\text{mg}\cdot\text{mL}^{-1}$, allowing to explore the effect of different supersaturation values. The evaluated concentration for NTI in THF spanned from 0.2 $\text{mg}\cdot\text{mL}^{-1}$ to 2

$\text{mg} \cdot \text{mL}^{-1}$. FIGURE 3.15 represents the solubility curve discussed in FIGURE 3.1 in different condition of solution equilibrium concentration, C^*_n , and evidences that the hereafter discussed experiments have been carried out at room temperature, varying hence the reference solubility curve in each experiment and therefore the supersaturation condition.

In FIGURE 3.16A the results of the mean number of obtained single- (left ordinates) and poly-crystals (right ordinates) are shown-

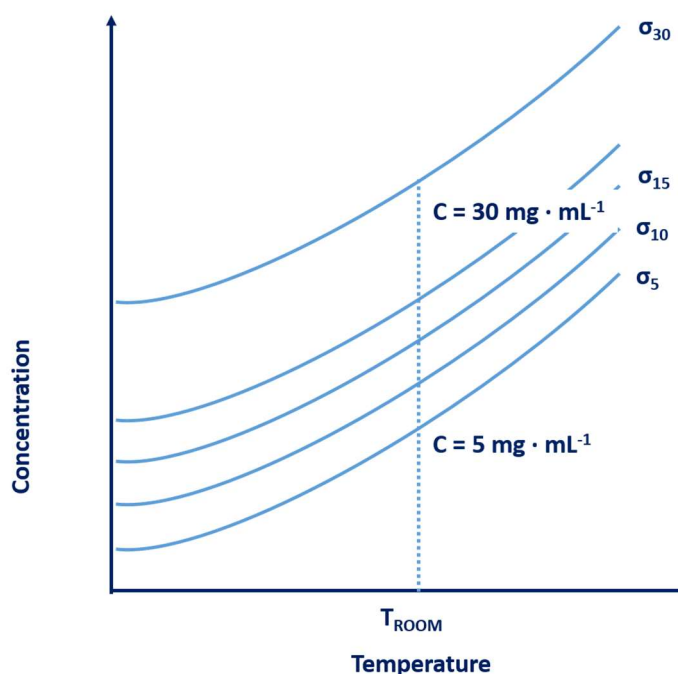


FIGURE 3.15: solubility curves (σ) as a function of the concentration of the solution.

The obtained trend clearly highlights that increasing the starting concentration of the solution leads to a decrease of the per-batch obtained single-crystals and polycrystals number. This can be better appreciated looking at the more analytical data shown in TABLE 1.

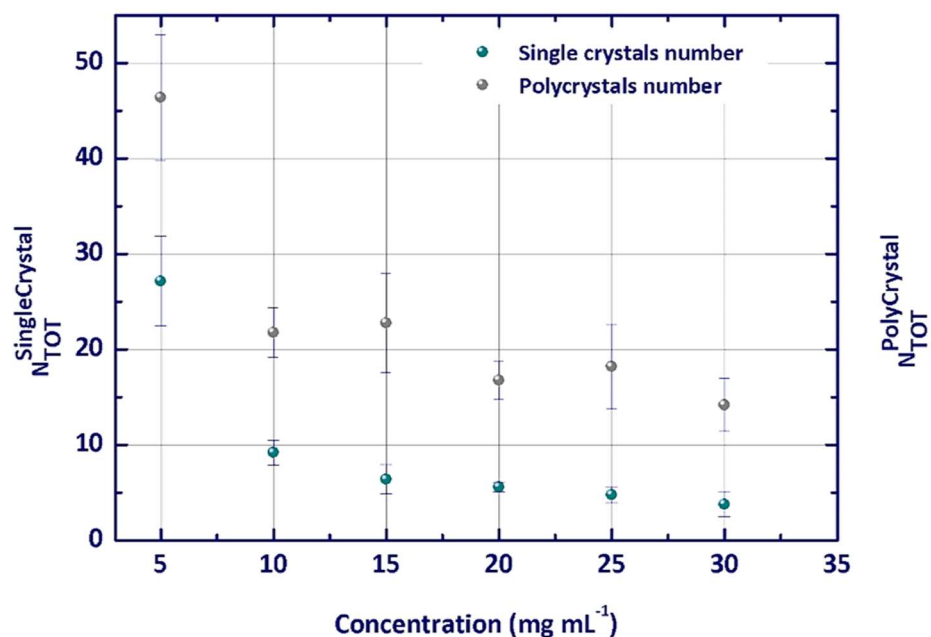


FIGURE 3.16A: obtained single crystals and polycrystals as a function of the initial concentration of the solution.

CONCENTRATION (mg · mL ⁻¹)	NUMBER ^{SC}	σ ^{SC}	NUMBER ^{PC}	σ ^{SC}
5	27,2	4,7	46,4	6,6
10	9,2	1,3	21,8	2,6
15	6,4	1,5	22,8	5,2
20	5,6	0,5	16,8	2,0
25	4,8	0,8	18,2	4,4
30	3,8	1,3	14,2	2,8

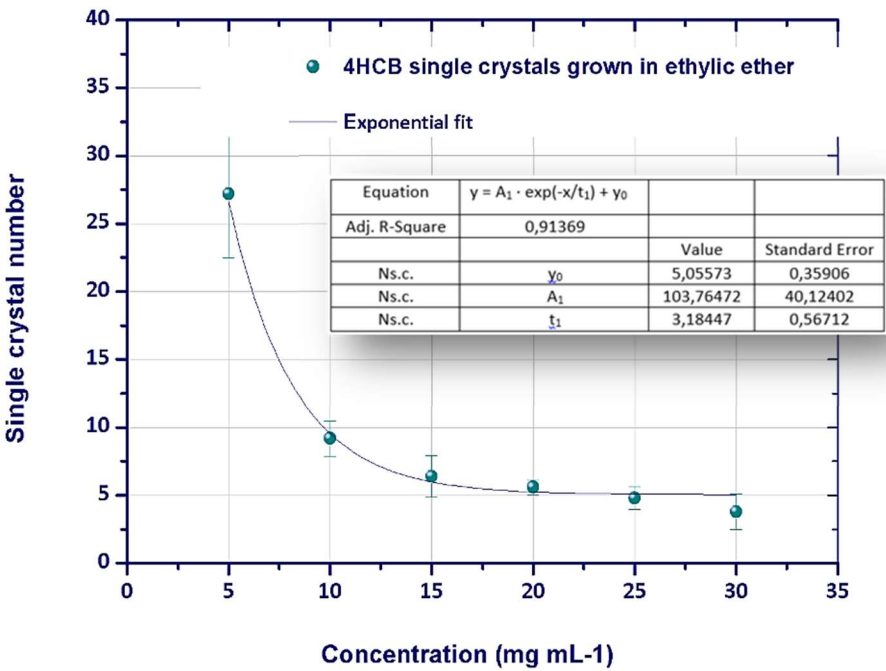
TABLE 1: obtained single crystals and polycrystals as a function of the starting concentration of the solution.

In the attempt to understand this behaviour, a fitting of the data points has been performed and, for both single crystals and polycrystals, the best fit is obtained by using a single exponential decay of the form:

$$y = y_0 + A_1 \cdot e^{-\left(\frac{x}{t_1}\right)}$$

EQUATION 3.18

An example of the exponential fit for 4HCB single crystals is reported in **FIGURE 3.16B**, for which the Adj. R² is 0.91369. Analogous dependence law has been found for NTI.



In a crystallization batch it is important to achieve the required crystal size, maximizing its quality and minimizing defects. Obtaining from a growth batch a few large crystals instead of several small crystals is – to this work purposes – one of most attractive goal together with the ability to properly tune the crystal quality (detailed characterization of the obtained crystals will be given below). In **FIGURE 3.17** the size of the 4HCB crystals side A, B and C (**FIGURE 3.14**) in function of the starting solution concentration is reported. The sides A and B, instead, experience even drastic changes, moving from around 1 mm at the lower concentration to more than 4 mm

at $30 \text{ mg}\cdot\text{mL}^{-1}$. Interestingly, a meaningful side size increase (about the triple of that achieved at $5 \text{ mg}\cdot\text{mL}^{-1}$) is reached already at around $15 \text{ mg}\cdot\text{mL}^{-1}$.

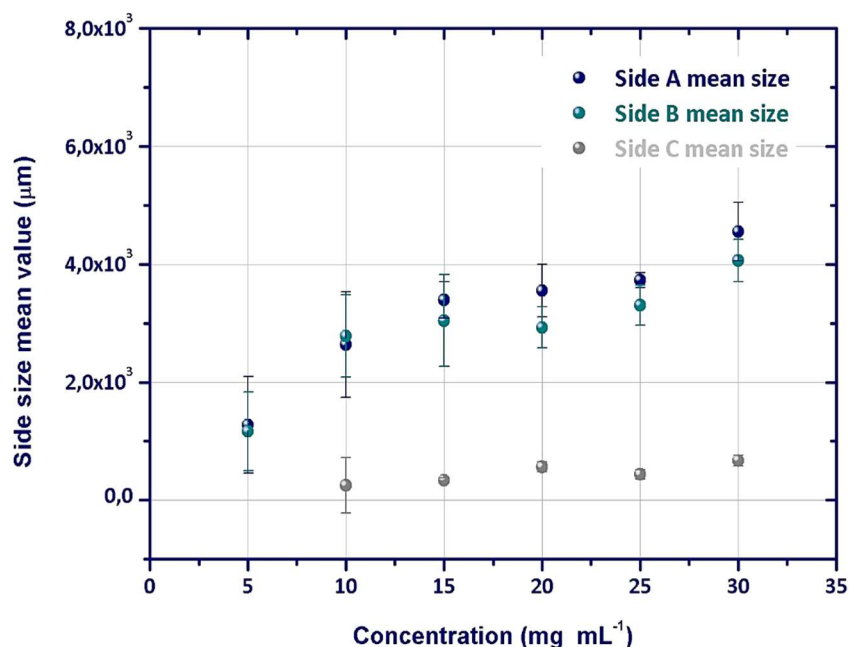


FIGURE 3.17: single-crystals and polycrystals mean sizes as a function of the initial concentration of the solution.

Considering both the graphs of **FIGURE 3.16A** and **FIGURE 3.17**, the observed trends clearly highlight that increasing the starting concentration of the solution leads to an increase of the single crystal sizes, till reaching a plateau that starts around 15 mg , as it can be better appreciated looking at the more analytical data shown in **TABLE 2**. This increase in single-crystal size is also associated with a decrease of the obtained single-crystal number. The same features have been obtained for NTI. The obtained results have been rationalized based on thermodynamics, as follows. Increasing the concentration of the solution leads to an increase of the supersaturation, and therefore to an increase of the driving force for the nucleation to take place. The consequences are both an increase of the nucleation rate and a decrease of the activation energy for the formation of the critical nucleus. The nuclei able to avoid redissolution (i.e., exceeding the critical size) are hence formed faster. When they

start to only grow, the nucleation rate goes rapidly to zero and all the remaining solute molecules are engaged for the growth of already formed nuclei, rather than forming new nuclei. To verify this rationalization some intensive and deeper studies on the kinetic of crystal growth are programmed and have to be carried out.

CONCENTRATION (mg · mL ⁻¹)	SIDE A (μm)	σ _A	SIDE B (μm)	σ _B	SIDE C (μm)	σ _C
5	1,3E3	8,2E2	1,2E3	6,7E2	--	--
10	2,6E3	9E2	2,8E3	7E2	2,5E2	4,7E2
15	3,4E3	3,1E2	3,0E3	7,8E2	3,4E2	4,4E1
20	3,5E3	4,4E2	3E3	3,5E2	5,6E2	8,2E1
25	3,7E3	1,3E2	3,3E3	3,4E2	4,4E2	8,0E1
30	4,5E3	5E2	4,1E3	3,6E2	6,7E2	8,9E1

TABLE 2: mean sides of the obtained single crystals as a function of the initial concentration of the solution.

CONCLUSIONS:

Summarizing the results obtained, both the trends suggest that for 4HCB grown in ethylic ether, at room temperature, in 100 mL glass beaker the best improvement in terms of yield and size – with respect to the purposes of the work - is achieved increasing the concentration in the range from 5 mg · mL⁻¹ to 15 mg · mL⁻¹ while from 20 mg · mL⁻¹ on, the improvement is not as high as in the previous range. The best results for 4HCB is achieved if the concentration is equal to 20 mg mL⁻¹. For NTI, grown in THF, at 20°C in 100 mL beaker the same goal is obtained working within the range between 1.8 mg · mL⁻¹ and 2 mg · mL⁻¹.

B. Optical microscopy analysis

4HCB crystals have been extensively investigated by optical microscopy. In particular, for each growth batch, the recovered crystals (both single and poly) have been extensively evaluated in terms of morphological defects and indications of the possible growing mechanism. The number of crystals from which the data have been evaluated are summarized in the blue column of the **TABLE 3**:

CONCENTRATION (mg · mL ⁻¹)	SINGLE-CRYSTAL TOT	POLY-CRYSTAL TOT	CRYSTAL TOT	σ
5	136	232	368	σ ₅
10	46	109	155	σ ₁₀
15	32	114	146	σ ₁₅
20	28	84	112	σ ₂₀
25	24	91	115	σ ₂₅
30	30	81	101	σ ₃₀

TABLE 3: number of single crystal analysed by means of optical microscopy to evaluate their sizes and surface morphologies.

FIGURE 3. 14 shows a sketch of the normal growth habit of 4HCB single crystals grown from ethylic ether solution, as provided from the CCD database. All 4HCB single crystals, at whatever starting concentration explored, were highly transparent, with no optically visible inclusions in them. Generally speaking, three main types of surface morphologies have been observed in the 4HCB single crystals:

1. smooth surfaces,
2. surfaces with growth steps,
3. surfaces with growth spirals.

Smooth surfaces and surfaces with growth steps have been usually obtained for crystals grown starting from solutions between 15 and 30 mg · mL⁻¹ concentration, while typical small steps, possibly suggesting a spiral growth mechanism, have been seen always present in crystals grown between 5 mg · mL⁻¹ and 10 mg · mL⁻¹. Typical images of facets found in crystals deriving from different starting solutions (i.e., solutions with a different supersaturation value σ) are shown in **FIGURE 3.18**. NTI analysis only provided smooth or stepped surface. Spiral growth have rarely been observed. The smooth surface have always been obtained between 1.5 and 2 mg · mL⁻¹, while for lower concentration the obtained surfaces have always been stepped.

The facets have been examined extensively, revealing also several types of common defects (see **section 3.3**): cracks, growth steps, sub-grain boundaries and hexagonal inclusions. The most common type of defect observed in 4HCB single-crystals are cracks, as shown in **FIGURE 3.13**. Cracks have been observed in 4HCB single crystals, regardless of their thickness, in less than 10% of the cases but in 90% of these case crystals have been grown at the lowest starting concentrations (5 mg · mL⁻¹ or 10 mg · mL⁻¹). Cracks have not been found in NTI single crystals, regardless their thickness.

CONCLUSIONS:

Summarizing the results obtained, the characterization under the optical microscope suggest that for 4HCB grown in ethylic ether, at room temperature, in 100 mL glass beaker the best improvement in terms of surfaces – with respect to the purposes of the work - is achieved increasing the concentration in the range from 10 mg · mL⁻¹ to 30 mg · mL⁻¹. The best results for 4HCB is achieved if the concentration is equal to 20 mg mL⁻¹. For NTI, grown in THF, at 20°C in 100 mL beaker the same goal is obtained working within the range between 1.0 mg · mL⁻¹ and 2 mg · mL⁻¹.

C. atomic force microscopy

Typical AFM images of facets of 4HCB crystals obtained from solutions at different σ are shown in **FIGURE 3.19**. This sequence of images shows different areas where different crystal growth mechanisms are obtained as a consequence of the different supersaturation value, σ . The supersaturation degree increases from top to bottom. As is visible, at low supersaturation (5 mg · mL⁻¹) evident growth spirals are found, with

step heights of a few nm (FIGURE 3.19A). Increasing the supersaturation (to 15 $\text{mg}\cdot\text{mL}^{-1}$) results in an stepped growth with step height, which roughly triples with respect to the 5 $\text{mg}\cdot\text{mL}^{-1}$ concentration (FIGURE 3.19B). Finally, the further increase of concentration to 25 $\text{mg}\cdot\text{mL}^{-1}$ results in typical surfaces resulted from adhesive type growth, with heights in the range of several tens of nm and a prominent increase of the surface roughness, feature detrimental to a possible connection of the surface of the crystal to an electrode (FIGURE 3.19C).

This trend is confirmed by roughness calculations carried out over crystals grown at different starting concentrations. TABLE 4 shows the results of these calculations: the roughness increases by increasing the solution concentration. The data have been calculated as average among 10 crystals per considered group of concentrations.

CONCENTRATION ($\text{mg} \cdot \text{mL}^{-1}$)	SUPPOSED GROWTH TYPE	RA (nm)	Rq (nm)
5 ÷ 10	SPIRAL GROWTH	0.56	0.80
15 ÷ 20	ISLAND GROWTH	0.96	1.63
25 ÷ 30	ADHESIVE	47.0	59.5

TABLE 4: roughness parameters of 4HCB single-crystals growth in ethylic ether in different supersaturation condition.

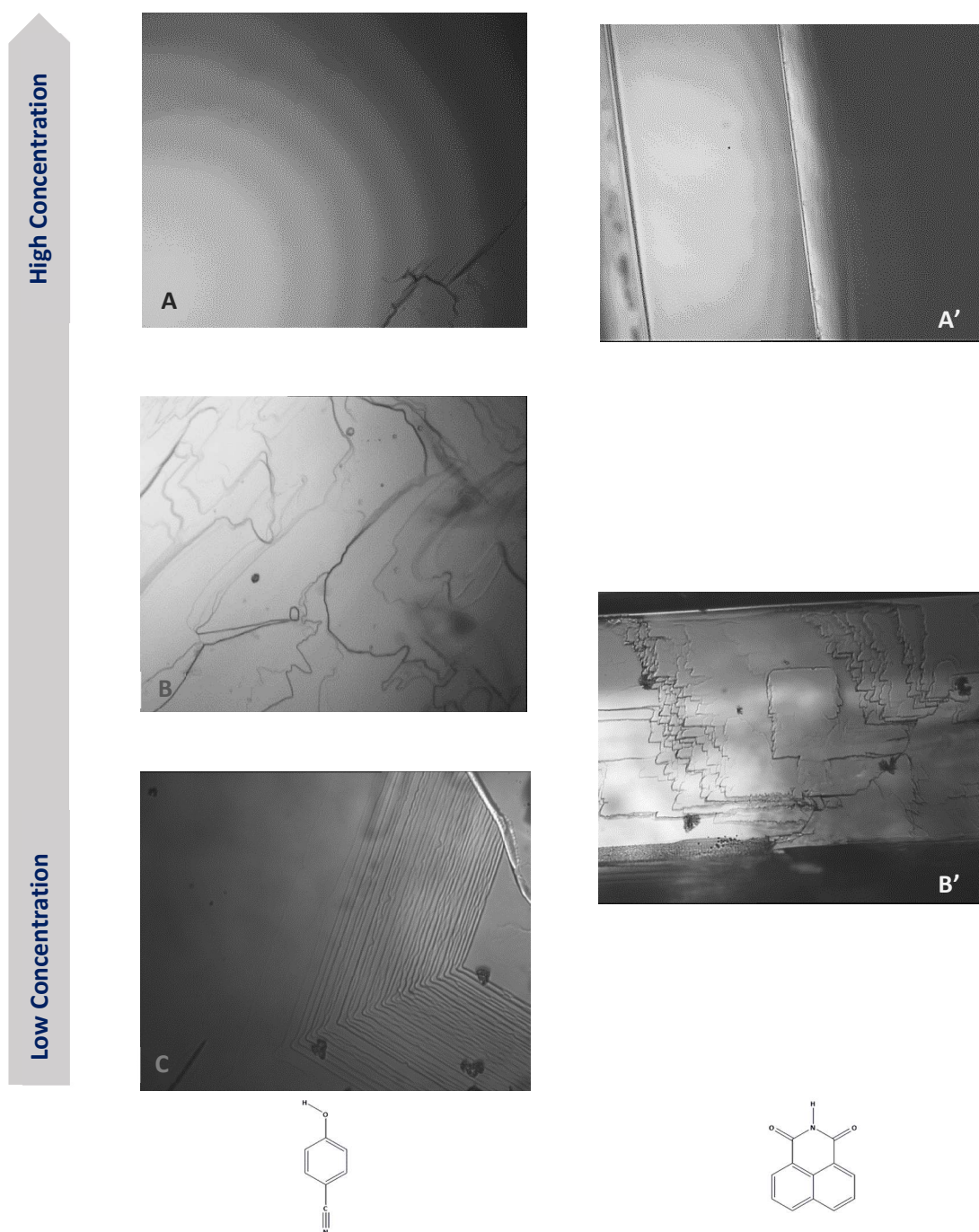


FIGURE 3.18: on the left: optical micrographs showing 4HCB surfaces grown in three different at three different starting concentration and therefore at three different supersaturations. Image A shows a typical average flat surface obtained in the range $20\div 30\text{ mg}\cdot\text{mL}^{-1}$. Image B shows a typical average surface obtained in the range $10\div 20\text{ mg}\cdot\text{mL}^{-1}$ while image C shows a typical surface obtained in the range of $5\div 10\text{ mg}\cdot\text{mL}^{-1}$. On the right: optical micrographs showing NTI surfaces grown at two different starting concentrations. Image A' shows a typical flat surface obtained in the range $1.5\div 2\text{ mg}\cdot\text{mL}^{-1}$ while image B' shows a typical stepped surface obtained under $1.5\text{ mg}\cdot\text{mL}^{-1}$. All the images side are $1660\text{ }\mu\text{m}$ except image B', whose larger side in $2320\text{ }\mu\text{m}$.

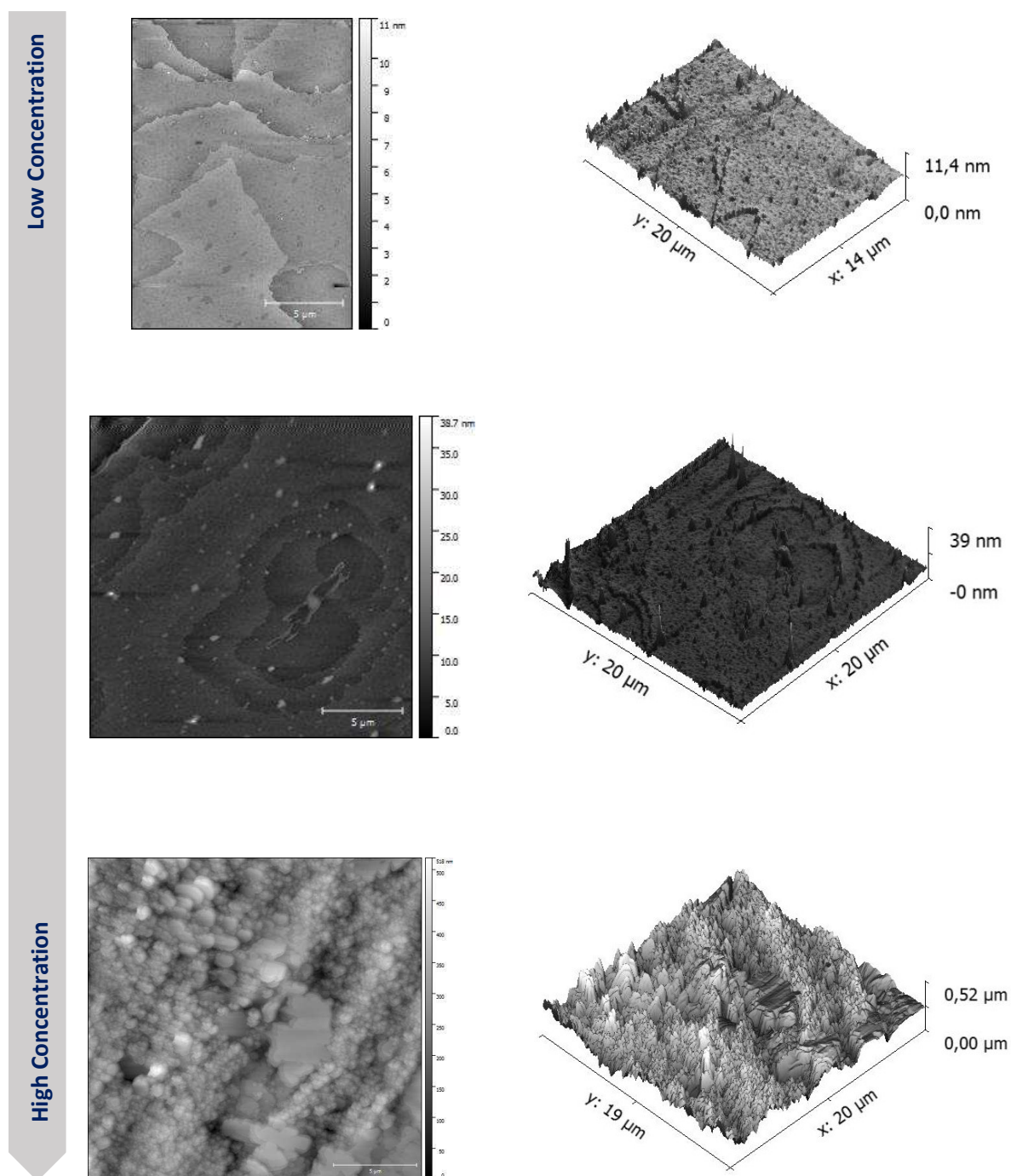


FIGURE 3.19: AFM micrographs taken on free-standing crystals grown in the same condition of temperature, volume of the beaker, solvent using 10 mL of solution but at different starting concentration. In particular, the supersaturation increases from the top images to the bottom ones.

CONCLUSIONS:

The concentration of the solution has shown a significant effect on the growth mechanisms. In particular, a drastic transition from flat to very rough average surfaces seems to occur at a critical concentration whose value depends on the evaluated couple solute/solvent. Therefore by studying the effect of the concentration for each couple, it is possible to tune the concentration value in order to avoid the production of crystals whose surface morphology is not suitable to the desired purposes and, in the same way, it is possible to drive the formation of crystals whose average surfaces match the required needs.

D. GENERAL CONSIDERATIONS OVER THE EFFECT OF CONCENTRATION ON THE CRYSTAL GROWTH MECHANISMS

Summarizing the observations from a statistical point of view (single-crystals mean size and mean number), optical microscopy and AFM it clearly appears that high-quality single crystals – with respect to the purposes of the present work - can be obtained tuning the starting solution concentration. In particular, it is possible to identify a precise concentration range from which the crystals of best quality can be grown, and this concentration is the range $15 \div 20 \text{ mg} \cdot \text{mL}^{-1}$ for 4HCB and $1.5 \div 2.0 \text{ mg} \cdot \text{mL}^{-1}$ for NTI. In fact, crystals grown in this range present the best characteristics in terms of large size, high surface quality and satisfactory yield (low number but high surface) per growth batch.

2. EFFECT OF TEMPERATURE

A. Mean number and mean size of the obtained single-crystals

The thermodynamic parameter under evaluation is the temperature of the solution during the crystallization process. The evaluated temperatures spanned from:

1. -16°C to 55°C for 4HCB,
2. -16°C to 60°C for NTI,

4HCB has been crystallized using ethylic ether as solvent with the starting concentration fixed in the previous part of the study as the best one, namely 20

$\text{mg} \cdot \text{mL}^{-1}$. However the use of this solvent did not allowed to study this trend in a sufficiently large temperature range. Therefore the same investigation has been carried out also in chloroform, which allows to reach about 55°C and therefore a larger temperature range. NTI has been crystallized using THF as solvent with the starting concentration fixed in the previous part of the work as the best one, namely $2 \text{ mg} \cdot \text{mL}^{-1}$.

The volume of the beakers used to grow the crystal has always been the same, namely 100 mL. Each of the five batches has been analysed as previously mentioned and the results, in terms of number of the obtained crystals and their size, has been plotted as a function of the temperature. **FIGURE 3.20** shows the results of the number of obtained crystals while **FIGURE 3.21** shows the results of the sizes. The standard deviation on the data has been calculated by the software.

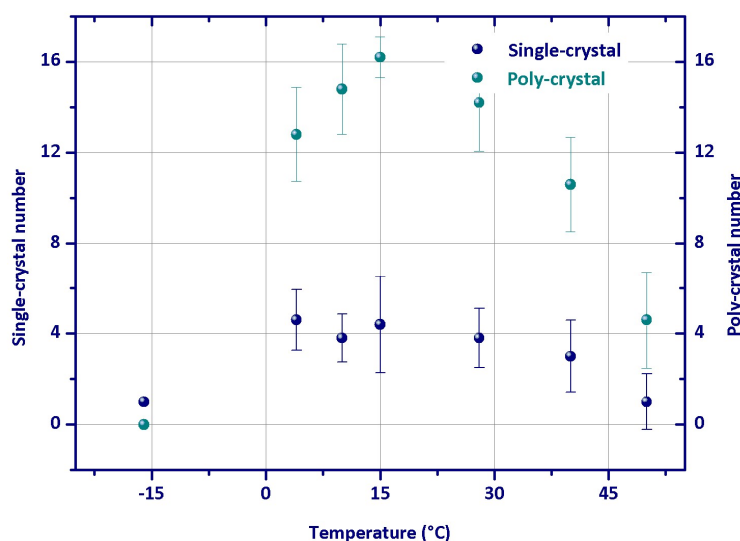


FIGURE 3.20: obtained single crystals and polycrystals as a function of the growth temperature.

Increasing the temperature from -16 to 15°C led to a first increase of both the single-crystals and polycrystals number **FIGURE 3.20**. A further temperature increase caused instead a decrease of the mean number of both obtained single-crystals and polycrystals, suggesting – as reported in literature^{69, 70} – a shift from a kinetic control

of the growth rates in the range between -16°C and 15°C to a thermodynamic control at higher temperature. This can be better appreciated looking at the more analytical data shown in **TABLE 5**. This shift can be identified in the range between 15°C and 20°C . The contextual increase of the precipitate amount reinforce this rationalization, that has nevertheless be further verified by some intensive and deeper study on the kinetic of crystal growth rates. These in-depth analysis are programmed and have not been done yet since they were outside the fundamental purposes of this second part of the work. From this trend it has been possible to identify, as the best range for the growth, the interval from -16°C to 15°C . With the only exception of the growth at 15°C . Also NTI has showed the same trend, highlighting a shift in the range 30°C - 40°C .

TEMPERATURE ($^{\circ}\text{C}$)	NUMBER ^{SC}	σ^{SC}	NUMBER ^{PC}	σ^{PC}
-16	1,0	0	0	0
4	4,1	1,3	1,3E1	2,8
10	3,8	1,0	1,5E1	1,9
15	4,4	2,1	1,6E1	1,9
28	3,8	1,3	1,4E1	2,8
40	3,0	1,6	1,1E1	3,3
50	1,0	1,2	4,6E0	2,6

TABLE 5: obtained single crystals and polycrystals as a function of the growth temperature

In general, increasing the temperature of the solution leads to a decrease of the single-crystals sizes, as is visible from **FIGURE 3.21**.

Increasing the temperature more, results in a prevalence of the precipitation with respect to the crystallization. This process depletes the solution, and therefore molecules that can undergo to the crystallization process decrease, negatively affecting the growth.

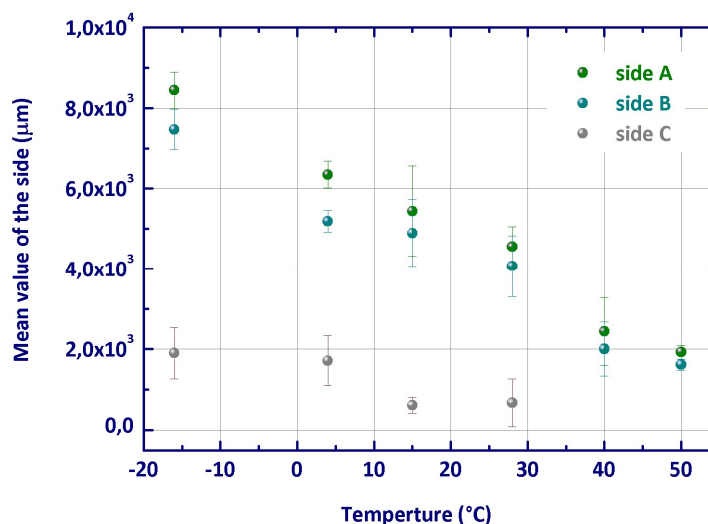


FIGURE 3.21A: single crystals mean number value as a function of the volume of solution used to grow the crystals.

CONCLUSIONS:

Summarizing, the best temperature condition for 4HCB crystal to be grown in chloroform with a concentration of $20 \text{ mg} \cdot \text{mL}^{-1}$ is between -16°C and 15°C as for 4HCB grown in ethylic ether while for NTI in THF the range spans between -16°C and 30°C - 40°C . Higher temperatures allow the precipitation to take place in all the evaluated cases, decreasing in this way both the yield and the sizes of the obtained crystals.

B. Optical microscopy analysis

FIGURE 3. 14 shows a diagrammatic representation of the normal growth habit of 4HCB single crystals grown from ethylic ether solution or from toluene solution or from a mix of the two (4:1 ratio) or from chloroform. All 4HCB single crystals, whatever the growth temperature explored in the lower temperature range (-16°C – 15°C), were highly transparent and there have been no optically visible inclusions in them. The faces have been examined extensively.

It has been observed that the morphology of single crystals changes with increasing temperatures, generating progressively more complicated morphologies of polycrystalline aggregates.

Typical images of these faces grown at different temperature are shown in **FIGURE 3.22**. This sequence of images shows areas obtained from single-crystals grown in different temperature conditions (4HCB single crystals grown in ethylic ether in $20 \text{ mg} \cdot \text{mL}^{-1}$ solution concentration) clearly show a roughening transition. In detail, at -16°C the interface is very smooth (**FIGURE 3.22A**). At 15°C more evident, but still small, steps suggesting a step-growth mechanism are visible (**Figure 3.22B**). Finally, at 28°C (**Figure 3.22C**) extremely rough surfaces are found. A transition from flat to rough can hence be located between 15 and 28°C . This trend is in perfect agreement with literature^{71, 72, 73, 74}. Indeed, it is well known that crystal roughness varies depending also on the temperature and the driving force. Increasing the temperature or driving force will cause a smooth interface to change into a rough interface.

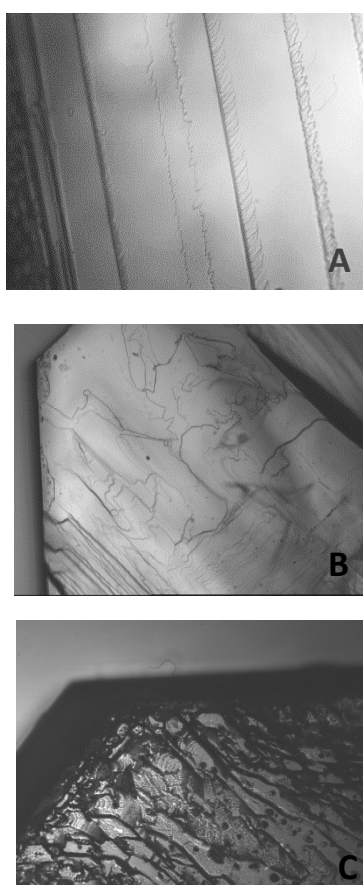


Figure 3.22: increase of the surface roughness due to the increase of the growth temperature from -16°C (A) to 15°C (B) to 28°C (C). Images larger side $2320 \mu\text{m}$.

Similar observations have been obtained for the NTI single crystals (FIGURE 3.23); however, in this case the roughening transition has been observed at much higher growth temperatures (40°C to 66°C).

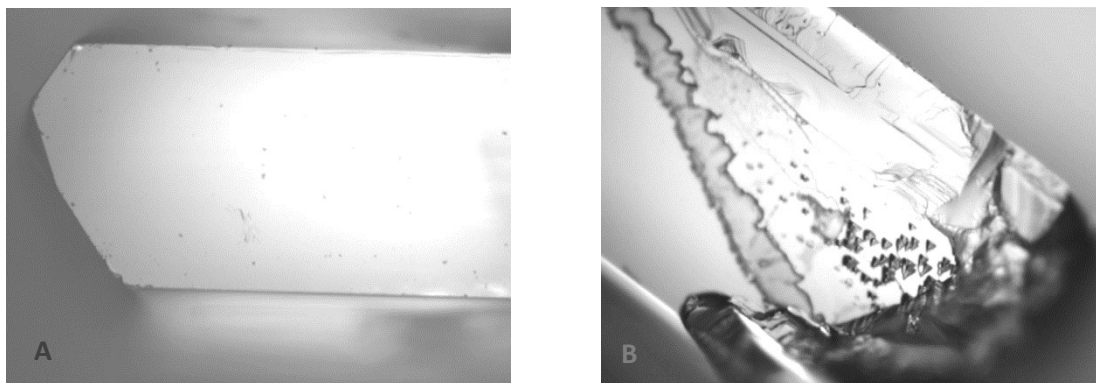


FIGURE 3.23: Comparison of two typical NTI surfaces for single crystals grown in the same growth condition except for temperature. The solvent is THF in both cases, the volume of the beaker is 100 mL in both cases. The concentration is the same, namely $1.5 \text{ mg} \cdot \text{mL}^{-1}$. Figure A the surface obtained at 4 °C. Figure B shows the typical surface obtained at 50°C. Images larger side 2320 μm .

Among the different types of common defects, cracks have been observed, as clearly shown in FIGURE 3.13. As for the case of concentration study, the density of cracks decreases as the thickness of the crystal increases. Cracks have been observed in 4HCB single crystals, regardless of their thickness, in less than 15% of the cases. In order to avoid the presence of cracks, it has been understood that thickness must be larger than 200 μm . No cracks have been observed for NTI single crystals regardless their thickness.

CONCLUSIONS:

Summarizing, the best temperature condition for 4HCB crystal to be grown in ethylic ether with a concentration of the solution of $20 \text{ mg} \cdot \text{mL}^{-1}$ is between -16°C and 15 °C – 20° C at maximum. In this range the obtained surfaces show quite smooth and regular surfaces.

C. Atomic Force Microscopy

The following sequence of images shows different areas where different crystal morphologies have been obtained as a consequence of the different growth temperature. AFM analysis of the as-grown 4HCB single-crystals have showed R_Q and R_A roughness parameters of the same order of magnitude in the range -16°C to 15°C , and have values typical of a very smooth surface in this range (below 1 nm for R_A , below 2 nm for R_Q). However, as is visible from **TABLE 6**, moving from 15°C to 28°C this parameter becomes ~ 35 times higher. Therefore, a clear roughening transition is obtained increasing the temperature at values higher than 20°C .

TEMPERATURE	R_A	R_Q
($^{\circ}\text{C}$)	(nm)	(nm)
-16	0,89	1.58
15	1.23	1.83
28	56.40	70.91

TABLE 6: roughness parameters of 4HCB single-crystals growth in ethylic ether at different growth temperature.

Similar observations have been obtained with the NTI single crystals; in this case the roughening transition has been observed at much higher growth temperatures (between 28°C to 40°C). In all the evaluated cases (i.e., both 4HCB and NTI) conical features, clearly seen on the surfaces, were the cause of the high surface roughness.

Typical AFM images of faces grown at different temperature conditions (keeping constant the concentration of the solution at $20 \text{ mg} \cdot \text{mL}^{-1}$ in ethylic ether, and using 100 mL beakers used as crystallization vessels) are shown in **FIGURE 3.24**. They provide the analytical roughness data reported in **TABLE 6**. In particular, in Fig. 3.31 it is possible to notice that the maximum height of spiking formations for the crystal grown at -

16°C is around 40 nm, while the analogous reference for the crystal grown at 28 °C is more than 2 µm high.

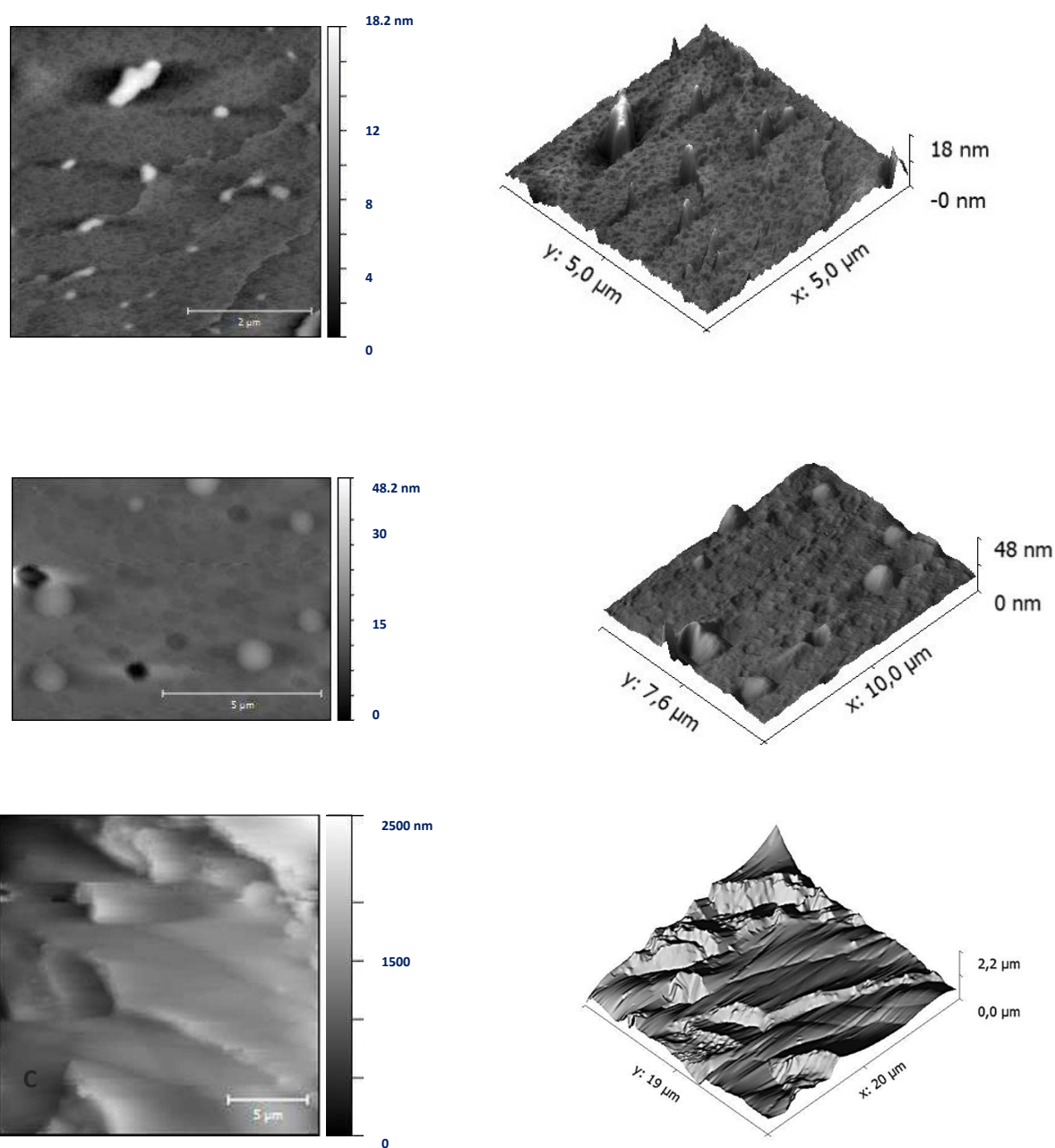


FIGURE 3.24: AFM micrographs taken on free-standing crystals grown in the same condition of concentration, volume of the beaker, solvent type, but at different growth temperature. The top image describes the surface morphology obtained at -16°C, while the bottom image describes the surface morphology obtained at 28°C.

The surface roughness of the studied single-crystals (bot 4HCB and NTI) is particularly relevant for some aspects of the i-FLEXIS project, as rough surfaces have problems in closely adhering to electrodes (this aspect will be better investigated in the next chapter).

CONCLUSIONS:

In any case, upon the above discussed findings, it has been understood that for achieving smooth and regular surfaces for 4HCB single crystals, growing temperatures under 20°C must be kept, which is a good value in view of practical applications of this type of crystal. The same value for NTI is instead 40°C, which, though being a bit higher, is still acceptable under an industrial point of view.

D. GENERAL CONSIDERATIONS OVER THE EFFECT OF CONCENTRATION ON THE CRYSTAL GROWTH MECHANISMS

Summarizing the observations from a statistical point of view (single-crystals mean size and mean number), optical microscopy and AFM it clearly appears that high-quality single crystals – with respect to the purposes of the present work - can be obtained tuning also the growth temperature. In particular, a drastic transition from flat to very rough average surfaces seems to occur at a critical temperature whose range again depends on the evaluated couple solute/solvent. Therefore by studying the effect of the temperature for each couple, it is possible to tune the growth temperature in order to minimize the production of crystals whose surface morphology is not suitable to the desired purposes and, in the same way, it is possible to drive and maximize the formation of crystals whose average surfaces match the required needs

3. EFFECT OF CRYSTALLIZATION VESSEL VOLUME

A. Mean number and mean size of the obtained single-crystals

For evaluating the effect of different crystallization volumes on the growth of 4HCB single crystals, several experiments using ethylic ether as solvent in quantities spanning from 5 mL to 30 mL have been carried out. These solution volumes have been placed in 100 mL volume beakers used to grow the crystal. Based on the results obtained from the previously discussed concentration and temperature studies, the concentration of the solution has been fixed to $20 \text{ mg} \cdot \text{mL}^{-1}$ and the growth

temperature at room temperature (about 20 °C). Each of the five batches has been analysed as mentioned in the introduction and the results in terms of number of the recovered crystals and corresponding sizes have been plotted as a function of the volume of solution. In **FIGURE 3.25** the average numbers of collected crystals are shown, while **FIGURE 3.26** reports the results of the average sizes value.

Increasing the volume of solution results in a slight decrease of the single-crystals average number value and in a strong decrease, down to 0 after the vessel volume reached 20 mL, of the polycrystals number. This trend has allowed to understand that the growth of 4HCB in ethylic ether solution ($20 \text{ mg} \cdot \text{mL}^{-1}$ concentration) is not significantly affected by increasing the volume of the solution in terms of single-crystals yield, but it is a key parameter to limit, and in proper conditions to eliminate, the presence of poly-crystals; therefore, indirectly, this is an improvement of the yield of the crystal growth.

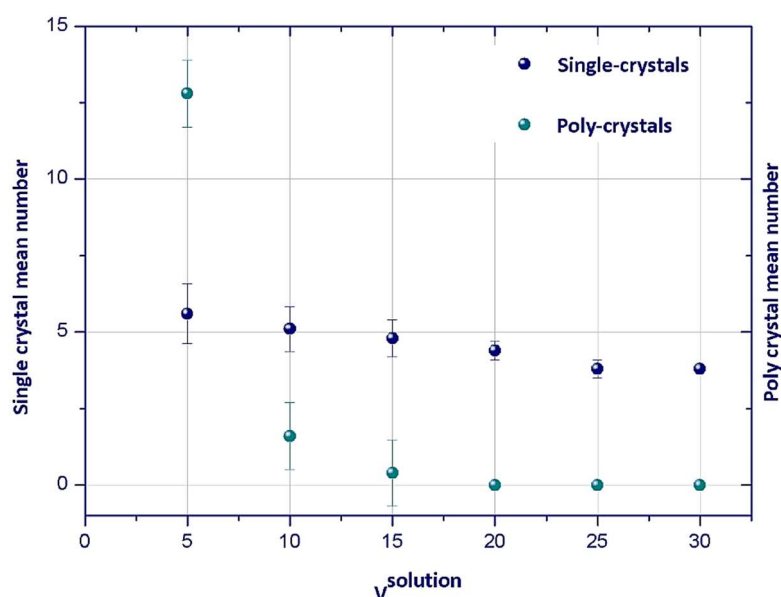


Figure 3.25: single crystal mean number value as a function of the volume of solution used to grow the crystals

Moreover, and more interestingly, increasing the volume of the solution leads to an increase of the single-crystals sizes. Also a change in the crystal habit is achieved in

this way, as evidenced from the increase of the A and B sizes, being C almost constant, as is visible from **FIGURE 3.26**.

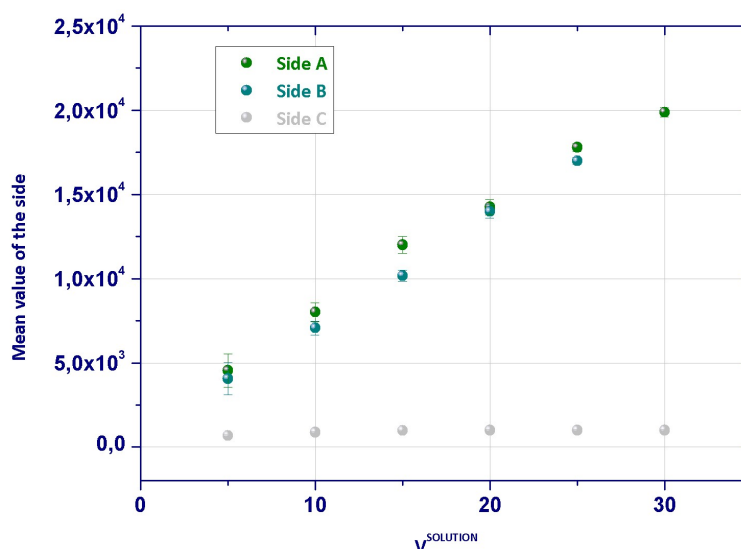


FIGURE 3.26: single crystal mean sizes as a function of the volume of solution used to grow the crystals

CONCLUSIONS:

Summarizing, the volume doesn't seem to be the key parameter to increase the yield of 4HCB single crystal production in ethylic ether at a concentration of $20 \text{ mg} \cdot \text{mL}^{-1}$, but it has been found that it is an important parameter to increase the sizes of the obtained single crystals. Indeed, this parameter has been demonstrated to be the most effective to be tuned to tailor the final sizes of the obtained crystals. Indeed, while the concentration tuning is able to allow increasing the crystal sizes till a plateau value, the vessel volume looks like being able to modify the crystal habit in a linear fashion, at least in the $5\text{-}30 \text{ mg} \cdot \text{mL}^{-1}$ range. While higher volumes have not been tested, this finding appears rather interesting in view of practical applications of 4HCB crystals.

B. Optical microscopy analysis

All the 4HCB single crystals obtained from the volume-dependence experiments were highly transparent, with no optically visible inclusions in them. The faces have been

examined extensively, and it has been observed that the morphology of single crystals changes with increasing the volume of the solution.

Typical images of these faces grown using different volumes of solution are shown in **FIGURE 3.27**. This sequence of images shows areas obtained from single-crystals grown from different starting volumes as a result of different crystal growth mechanisms, which in all the evaluated cases provide crystal with surfaces ranging from flat, at least to the optical microscope, to slightly stepped. The observations acquired suggest a shift from a step-growth mechanism to a spiral-growth mechanism taking place.

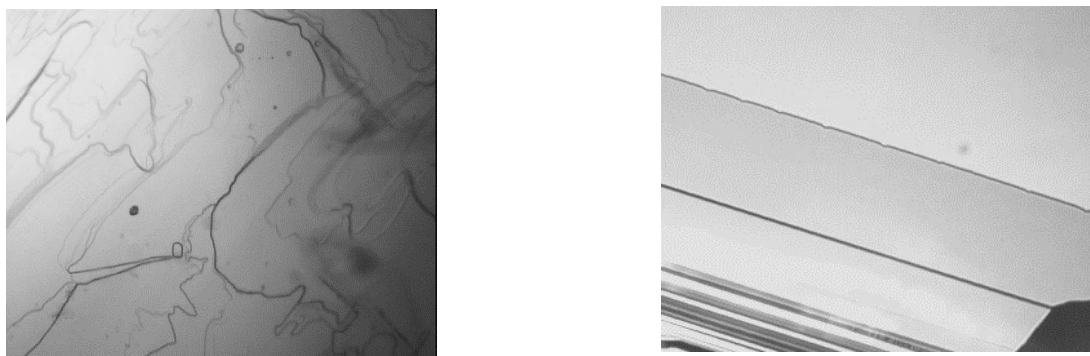


FIGURE 3.27: single crystals surfaces obtained using different volumes of solution. On the left, typical average stepped-surface obtained growing crystals using 10 mL of solution. On the right, typical average spiral-surface obtained growing crystals using 30 mL of solution. Images larger side 1660 μm .

CONCLUSIONS:

Summarizing, the solution volume effect on the surfaces morphology doesn't seem to be a key parameters, although a shift between step-growth and spiral growth can be stated. In any case in the range evaluated the surfaces always appears quite smooth and regular and suitable to the purposes of the present work.

C. Atomic Force Microscopy analysis

Typical AFM images of faces grown from different volumes of solution have been acquired. The starting concentration of the solution has been $20 \text{ mg} \cdot \text{mL}^{-1}$ in both

cases using ethylic ether as a solvent. 100 mL beakers have been used as crystallization vessels. Crystals have been grown at room temperature. Typical images of faces grown in different volumes of solution are shown in **FIGURE 3.28**, and the related roughness data are given in **TABLE 7**. Top image shows the average surface obtained using 10 mL of solution while the bottom one shows the average surface obtained growing the crystal from 20 mL of solution. From these data it is rather evident that the overall surface roughness doesn't change so much by increasing the solution volume. Also the heights of the observed steps in the two cases are very similar in the range of a few nm,

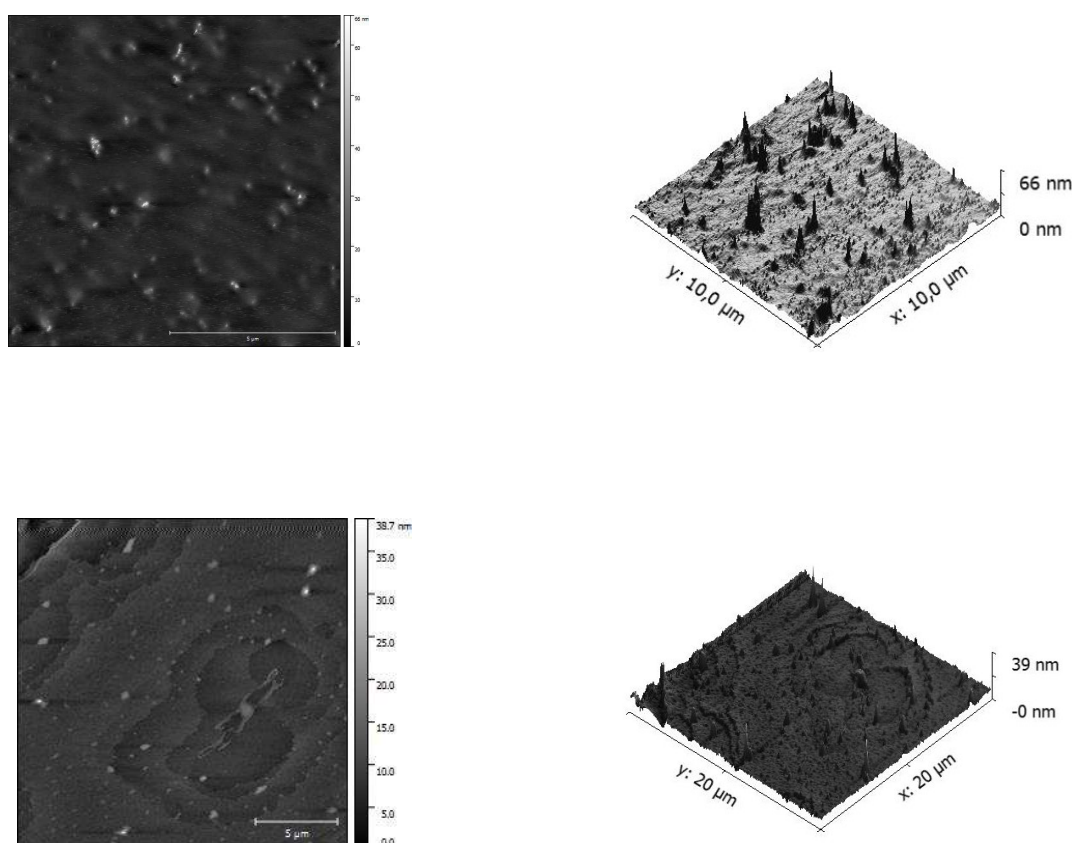


FIGURE 3.28: AFM micrographs taken on free-standing crystals grown in the same condition of concentration, growth temperature, solvent but using different volume of solution. The top image describes the surface morphology obtained from 10 mL of solution, while the bottom image describes the surface morphology obtained from 20 mL of solution.

VOLUME	RA	Rq
(mL)	(nm)	(nm)
5 ÷ 10	0,96	1,63
15 ÷ 30	1,90	3,07

Table 7: roughness parameters of 4HCB single-crystals

growth in ethylic ether from different volume of

It is therefore evident that the volume of the solution does not have a significant effect on crystal surface morphology.

CONCLUSIONS:

In summary, the effect of a volume increase in the solution growth process of 4HCB (NTI was not fully tested under this point of view) is that of limiting, even to the full suppression, the formation of polycrystals, while not altering in a detectable way the surface morphology, neither at the nanometric scale.

3.6 SUMMARY

In this chapter a systematic study of some of the main parameters affecting crystallization by slow solvent evaporation have been described. Experiments have been focused on the two most representative semiconductors properly selected in the first part of the work, namely 4HCB - as a representative of platelet-like crystal - and NTI - as a representative of needle-shaped crystal. The aim of this part of the work has been the achievement of control over the number, size, quality and crystal habit of organic semiconductor.

In summary, the effect of a concentration, growth temperature and volume of the solution have been investigated showing that by studying their effect for each couple solute/solvent, it is possible to tune their values in order to avoid the production of crystals

whose surface morphology is not suitable to the desired purposes and, in the same way, it is possible to drive the formation of crystals whose average surfaces match the required needs.

BIBLIOGRAPHY

- ⁰¹ I. Sunagawa: Crystals. Growth, morphology and perfections. – Cambridge University Press – 2006;
- ⁰² H.A. Meirs, F. Isaac: The spontaneous crystallization - Proc. R. Soc. Lond. – A – 79 - 322÷325 – 1987;
- ⁰³ Zettlemoyer AC, ed. 1969. Nucleation. New York: Dekker
- ⁰⁴ Andres PR. 1969. See Ref. 217, pp. 69– 108
- ⁰⁵ Bradley, Quart. Rev., 1951, 5, 315
- ⁰⁶ G.H. Nancollas and N. Purdie: The kinetics of crystal growth – 1964
- ⁰⁷ A. H.-L. Chow and D. J. W. Grant: Modification of acetaminophen crystals. III. Influence of initial supersaturation during solution-phase growth on crystal properties in the presence and absence of p-acetoxyacetanilide - Int. J. Pharm. – **42** - 123÷133- 1988;
- ⁰⁸ B. Y. Shekunov and P. York: Crystallization processes in pharmaceutical technology and drug delivery design. - J. Cryst. Growth - **211** - 122÷136 – 2000;
- ⁰⁹ S. R. Byrn: Mechanisms of solid-state reactions of drugs - J. Pharm. Sci. – **65** - 1÷22 – 1976;
- ¹⁰ Romé de l'Isle: Essai de Cristallographie - 1772;
- ¹¹ H. E. Buckley: Crystal Growth - New York - John Wiley & Sons - 195;
- ¹² Li Lian, K. Tsukamoto, and I. Sunagawa: Impurity adsorption and habit changes in aqueous solution grown in KCl crystals - J. Crystal Growth - 99 - 1156÷1161 – 1990;

- ¹³ M. Bienfait, R. Boistelle, and R. Kern, Formes de croissance des halogénures alcalins dans un solvant polaire, Les morphodromes de NaCl en solution et l'adsorption d'ions étrangers, in Adsorption et Croissance Cristalline, CNRS, 1965, pp. 515–35, 577–94
- ¹⁴ B. A. Hendriksen, D. J. W. Grant, P. Meenan and D. A. Green: Crystallisation of paracetamol (acetaminophen) in the presence of structurally related substances - J. Cryst. Growth – **183** - 629÷640 – 1998;
- ¹⁵ S. N. Black, R. J. Davey and M. Halcrow: The kinetics of crystal growth in the presence of tailor-made additives - J. Cryst. Growth – **79** - 765÷774 -1986;
- ¹⁶ R. J. Davey, S. N. Black, A. D. Goodwin, D. Mackerron, S. J. Maginn and E. J. Miller: Crystallization in polymer films. Control of morphology and kinetics of an organic dye in a polysilicone matrix - J. Mater. Chem. - **7** - 237÷241 – 1997;
- ¹⁷ T. Kato, T. Suzuki, T. Amamiya, T. Irie, M. Komiyama, and H. Yui: Effects of macromolecules on the crystallization of CaCO₃. The formation of organic/inorganic composites - Supramol. Sci. - **5** - 411÷415 – 1998;
- ¹⁸ L. Williams-Seton, R. J. Davey, H. F. Lieberman, and R. G. Pritchard: Disorder and twinning in molecular crystals: impurity-induced effects in adipic acid. - J. Pharm. Sci. – **89** - 346÷354 – 2000;
- ¹⁹ K. V. R. Prasad, R. I. Ristic, D. B. Sheen and J. N. Sherwood: Crystallization of paracetamol from solution in the presence and absence of impurity - Int. J. Pharm. – **215** - 29÷44 – 2001;
- ²⁰ J. W. Mullin: Industrial crystallization - Butterworth-Heinemann - London – 1993;

- ²¹ S. D. Finnie, R. I. Ristic, J. N. Sherwood and A. M. Zikic: Morphological and growth rate distributions of small self-nucleated paracetamol crystals grown from pure aqueous solutions - J. Cryst. Growth – **207** - 308÷318 – 1999;
- ²² E. A. Karpova and Y. S. Tarahovsky: Altering the morphology of crystals of a macromolecule without changing the unit cell (A case study of ribosome crystals) - J. Cryst. Growth – **232** - 610÷617 – 2001;
- ²³ R. I. Ristic, S. Finnie, D. B. Sheen and J. N. Sherwood: Macro- and micromorphology of monoclinic paracetamol grown from pure aqueous solution - J. Phys. Chem. – B - **105** - 9057÷9066 – 2001;
- ²⁴ I. Yoshizaki, T. Sato, N. Igarashi, M. Natsuisaka, N. Tanaka, H. Komatsu and S. Yoda: Systematic analysis of supersaturation and lysozyme crystal quality - Acta Cryst. - **D57** - 1621÷1629 – 2001;
- ²⁵ J. De Yoreo and Peter G. Vekilov: Principles of Crystal Nucleation and Growth – Nanoscale – 2 – 2346÷2357 – 2010;
- ²⁶ R. Boistelle: Survey of crystal habit modification in solution. In: Industrial Crystallization - ed. B y J.W. Mullin – Plenum - New York - 203÷214 – 1975;
- ²⁷ E.V. Khamskii: Some problems of crystal habit modification. In: Industrial Crystallization - ed. By J.W. Mullin – Plenum - New York - 215÷221 – 1975;
- ²⁸ S.D. Elwell and H.J. Scheel: Crystal Growth from High- Temperature Solutions – Academic - London – 1975;

-
- ²⁹ J. R. Luft, S. V. Arakali, M. J. Kirsits, J. Kalenik, I. Wawrzak: - J. Appl. Crystallogr. - 27 - 443÷452 -1994;
- ³⁰ R.C. DeMattei, R.S. Feigelson, P.C. Weber: Factors affecting the morphology of isocitrate lyase crystals - J. Cryst. Growth – 122 - 152÷160 – 1992;
- ³¹ A.R. Verma: Crystal Growth and Dislocations – Butterworths - London – 1953;
- ³² S. Amelinckx: The direct observation of dislocations. In: Solid State Physics - F. Seitz and D. Turnbull - Academic - New York - Suppl. 6 – 1964;
- ³³ G. L. Zipp and N. Rodríguez-Hornedo: Growth mechanism and morphology of phenytoin and their relationship with crystallographic structure - J. Phys. – D - **26** - B48÷B55 – 1993;
- ³⁴ G. L. Zipp and N. Rodríguez-Hornedo: The mechanism of phenytoin crystal growth - Int. J. Pharm. – **98** - 189÷201 – 1993;
- ³⁵ S. D. Durbin and G. Feher: Studies of crystal growth of proteins by electron microscopy - J. Mol. Biol. - **212** - 763÷774 – 1990;
- ³⁶ M. Michinomae, M. Mochizuki and M. Ataka: Electron microscopic studies on the initial process of lysozyme crystal growth - J. Cryst. Growth – **197** - 257÷262 – 1999;
- ³⁷ N. Braun, J. Tack, M. Fischer, A. Bacher, L. Bachmann and S. Weinkauff: Electron microscopic observations on protein crystallization: adsorption layers, aggregates and crystal defects - J. Cryst. Growth – **212** - 270÷282 – 2000;

-
- ³⁸ W. K. Burton, N. Cabrera and F. C. Frank: The growth of crystals and the equilibrium structure of their surfaces - Phil. Trans. R. Soc. - Lond - **A243** - 299÷358 – 1951;
- ³⁹ P. Bennema: Analysis of crystal growth models for slightly supersaturated solutions - J. Cryst. Growth – **1** - 225÷232 – 1967;
- ⁴⁰ P. Bennema: Interpretation of the relation of the rate of crystal growth and low supersaturation - J. Cryst. Growth – **1** - 278÷287 – 1967;
- ⁴¹ P. Bennema: Spiral growth and surface roughening: development since Burton, Cabrera and Frank - J. Cryst. Growth – **69** - 182÷197 – 1984;
- ⁴² G. H. Gilmer, R. Ghez and N. Cabrera: An analysis of combined surface and volume diffusion processes in crystal growth - J. Cryst. Growth – **8** - 79÷93 – 1971;
- ⁴³ A. A. Chernov: Formation of crystals in solutions - Contemp. Phys. – **30** - 251÷276 – 1989;
- ⁴⁴ I. Sunagawa: Surface microtopography of crystal faces. In: Morphology of Crystals - ed. by I. Sunagawa - Terra Scientific - Tokyo - 321÷365 – 1987;
- ⁴⁵ I. Sunagawa: Crystals, Growth, Morphology and Perfection - Cambridge Univ. Press - Cambridge – 2005;
- ⁴⁶ G. Dhanaraj, K. Byrappa, V. Prasad and M. Dudley: Handbook of crystal growth – Springer - 2010
- ⁴⁷ G. Needham: The practical use of the microscope - C. C. Thomas - Springfield – 1958;

-
- ⁴⁸ D.C. Miller and G.A. Rozgonyi: Defect characterization by etching, optical microscopy and x-ray topography. In: Handbook on Semiconductors - 3 - ed. by S.B. Keller - North-Holland - Amsterdam - 218÷246 – 1980;
- ⁴⁹ I. Sunagawa: Vapor growth and epitaxy of minerals and synthetic crystals - J. Crystal Growth – 45 - 3÷12 -1978,
- ⁵⁰ G. Binnig, C. F. Quate and C. Gerber: Atomic force microscope - Phys. Rev. Lett. – **56** - 930÷933 – 1986;
- ⁵¹ C. J. Roberts, P. M. Williams, M. C. Davies, D. E. Jackson, and S. J. B. Tendler: Atomic force microscopy and scanning tunnelling microscopy: refining techniques for studying biomolecules. Trends Biotechnol. – **12** - 127÷132 – 1994;
- ⁵² A. Ikai: STM and AFM of bio/organic molecules and structures - Surf. Sci. - **26** - 261÷332 – 1996;
- ⁵³ I. Amato: Candid cameras for the nanoworld - Science – **276** - 1982÷1985 – 1997;
- ⁵⁴ S. N. Magonov and D. H. Reneker: Characterization of polymer surfaces with atomic force microscopy - Annu. Rev. Mater. Sci. – **27** - 175÷222 – 1997;
- ⁵⁵ S. O. Vansteenkiste, M. C. Davies, C. J. Roberts, S. J. B. Tendler and P. M. Williams: Scanning probe microscopy of biomedical interfaces - Prog. Surf. Sci. - **57** - 95÷136 – 1998;
- ⁵⁶ S. D. Durbin and W. E. Carlson: Lysozyme crystal growth studied by atomic force microscopy - J. Cryst. Growth – **122** - 71÷79 – 1992;

-
- ⁵⁷ G. T. Palocz, B. L. Smith, P. K. Hansma, D. A. Walters, and M. A. Wendman: Rapid imaging of calcite crystal growth using atomic force microscopy with small cantilevers - *Appl. Phys. Lett.* – **73** - 1658÷1660 – 1998;
- ⁵⁸ P. A. Campbell, M. A. Mayer, G. Kerherve and D. L. Roux: Dynamic processes at surfaces: Crystal growth and dissolution studied by atomic force microscopy - *Microsc. Anal.* – **75** - 17÷19 – 2000;
- ⁵⁹ A. Mauri and M. Moret: Growth of potassium sulphate crystals in the presence of organic dyes: in situ characterization by atomic force microscopy - *J. Cryst. Growth* – **208** - 599÷614 – 2000;
- ⁶⁰ M. Moret: Influence of organic dyes on potassium sulphate crystal growth: a joint morphological and atomic force microscopy analysis - *Mater. Chem. Phys.* – **66** - 177÷188 – 2000;
- ⁶¹ G. R. Ester, R. Price and P. J. Halfpenny: The relationship between crystal growth and defect structure: a study of potassium hydrogen phthalate using X-ray topography and atomic force microscopy - *J. Phys. D.: Appl. Phys.* – **32** - A128÷A132 – 1999;
- ⁶² D J Whitehouse: Surface metrology - *Meas. Sci. Technol.* – **8** - 955÷972 – 1997;
- ⁶³ B. Fraboni, A. Ciavatti, F. Merlo, L. Pasquini, A. Cavallini, A. Quaranta, A. Bonfiglio and A. Fraleoni-Morgera: Organic Semiconducting Single Crystals as Next Generation of Low-Cost, Room-Temperature Electrical X-ray Detectors - *Adv. Mater.* - **24** – 17 - 2289÷2293 - 2012;
- ⁶⁴ B. Fraboni, C. Femoni, I. Mencarelli, L. Setti, R. Di Pietro, A. Cavallini and A. Fraleoni-Morgera: Solution-Grown, macroscopic Organic Single Crystals Exhibiting Three-Dimensional Anisotropic Charge-Transport Properties - *Adv. Mater.* – **21** - 18 - 1835–÷1839 – 2009;

-
- ⁶⁵ A. Fraleoni-Morgera, L. Benevoli and B. Fraboni: Solution growth of single crystals of 4-hydroxycyanobenzene (4HCB) suitable for electronic applications - J. Cryst. Growth – 312 – 23 - 3466÷3472 - 2010.
- ⁶⁶ B. Fraboni, A. Fraleoni-Morgera and A. Cavallini: Three-dimensional anisotropic density of states distribution and intrinsic-like mobility in organic single crystals - Org. Electron. – 11 – 1- 10÷15 – 2010;
- ⁶⁷ Laura Basiricò, Andrea Ciavatti, Mirta Sibilia, Alessandro Fraleoni-Morgera, Silvia Trabattoni, Adele Sassella and Beatrice Fraboni: Solid state organic X-ray detectors based on rubrene single crystals - IEEE Transactions on Nuclear Science – 62 - 1791 ÷ 1797 - 2015;
- ⁶⁸ D.C. Miller and G.A. Rozgonyi: Defect characterization by etching, optical microscopy and x-ray topography. In: Handbook on Semiconductors - 3 - ed. by S.B. Keller - North-Holland - Amsterdam - 218÷246 – 1980;
- ⁶⁹ D. J. Plazek and J. H. Magill: Physical Properties of Aromatic Hydrocarbons. I. Viscous and Viscoelastic Behavior of 1:3:5-Tri- α -Naphthyl Benzene - J. Chem. Phys. – **45** - 3038 – 1966;
- ⁷⁰ M. Ediger, L. Yu and P. Harrowell - J. Chem. Phys. – **128** – 2008;
- ⁷¹ I. V. Markov: Crystal Growth for beginners. Fundamentals of Nucleation, Crystal Growth and Epitaxy – Word scientific – 1998;
- ⁷² Ichiro Sunagawa: Crystals. Growth, Morphology, and Perfection – Cambridge University Press – 2005;
- ⁷³ S. Wang, B. Raghothamachar, M. Dudley and A. G. Timmerman: Crystal Growth and Defect Characterization of AlN Single Crystals - Mater. Res. Soc. Symp. Proc. - 892 - 892-FF30-06.1 ÷ 892-FF30-06.6 – 2011;

-
- ⁷⁴ M. T. Hussein, E. M. Nasir, A. H. Al-Aarajiy: Structural and Surface Morphology Analysis of Nickel Phthalocyanine Thin Films - Advances in Materials Physics and Chemistry – 3 - 113÷119 – 2013;

CHAPTER 4: OSSCs FOR REAL DEVICES

In this chapter, the description of the third part of the work, devoted to find a possible realization of a stable interaction between the electrodes and the OSSCs, will be presented. In detail, **section 4.1** is devoted to describe the overall overview of the work. Among the organic materials, self assembled monolayer are the best candidate to functionalize the electrodes surfaces in order to reach the mentioned goal. An overview on their use is described in **section 4.2**. The idea of exploring SAMs to the presented purposes is described in **section 4.3**. Due to the fundamental importance of the cleaning procedure of a substrate to the aim of its functionalization with self assembled monolayers, the procedure will be presented in deeper detail in **section 4.4**. Subsequently, in **section 4.5**, the experimental techniques applied to carry out this third part of the work will be illustrated. The materials and methods will be presented in **section 4.6** and the results will be discussed in **section 4.7**.

4.1 OVERVIEW OF THE PRESENTED WORK

The main objective of the i-Flexis European Research Project, under the frame of which the present PhD research has been carried out, is to develop OSSCs-based X-ray sensing devices.

In the first part of the PhD work, it has been seen how the best molecules with the proper electronic properties, suitable for X-ray detectors, have been selected.

In the second part of the work, the investigation of parameters affecting the outcomes of crystallization, in terms of control over crystal yield and size, have been carried out. This step

of the work has moreover allowed to define the best experimental conditions to maximize the surface quality in terms of decreasing of roughness. Indeed this feature is detrimental for a good strategy on connection of a self-standing single crystal to whatever interface. The final step of the work has been focused on exploring a possible, viable, good strategy for ensuring a good crystal adhesion to electrodes, which is needed for practical applicability of free-standing crystals. Two approaches are mainly feasible:

1. real growth of the single-crystals directly on the microelectrodes,
2. near-equilibrium growth of the self-standing crystals and subsequent bonding on the microelectrodes.

The former approach is the one to which the i-FLEXIS Project was aiming for, and can be achieved by depositing on the substrate a conveniently formulated solution, from which crystals are grown. This can be obtained by industrially compatible techniques, like for example printing. On the other hand, before being able to print on a substrate a solution to grow single crystals well adherent to an underlying, highly heterogeneous substrate, such as interdigitated metallic electrodes on a plastic substrate, the system must be well understood and controlled in its ideal, reference state. To face and try to solve these open needs, the last part of this PhD work has been carried out.

In particular, Au electrodes have been fabricated, on 1 mm thick PEN (poly-ethylene-naphthalene, a polymer capable of giving flexible films), by a collaborating group of the i-Flexis Project (FIGURE 4.1):



FIGURE 4.1: on the left a schematic representation of the electrode.

On the right an image depicting some electrodes.

Due to the possibility of obtaining platelet crystals, the preferred crystal habit for the i-Flexis project aims, 4HCB has been chosen as the target crystal.

In order to promote good adhesion of the 4HCB crystals via electrostatic interactions to the underlying electrodes, a strategy based on the electrodes functionalization with the self-assembled monolayers (SAMs), has been attempted. The tested SAM-precursor molecules are shown in **FIGURE 4.2**.

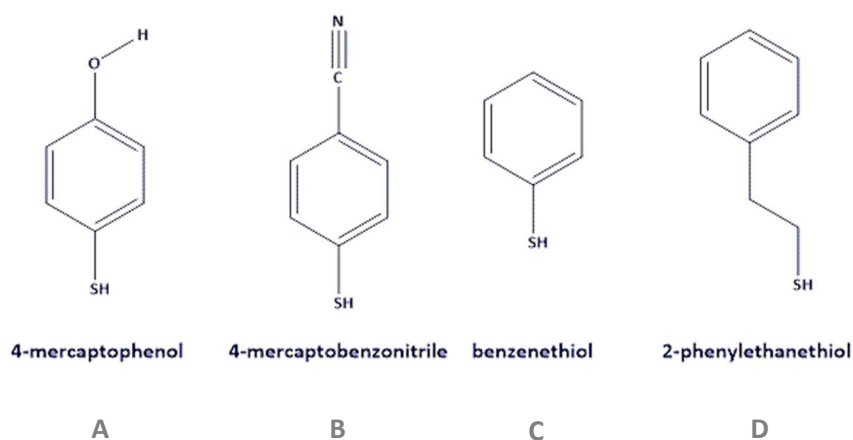


FIGURE 4.2: chemical structures of the four thiols used to functionalize Au electrodes with the aim of realize a stable connection between electrode itself and the single-crystal semiconductor.

4.2 FORMATION OF SELF-ASSEMBLED MONOLAYER ON ELECTRODES

4.2.1. SURFACES

Surface atoms or molecules experience a different environment than those in the bulk. The absence of net forces on one side of the interface implies that the surface atoms and molecules have different free energies, electronic states, relativities, mobilities and structures and, thus, the whole surface region is at a relatively higher energy than the bulk. Therefore, the binding of adsorbates is generally strongly favoured on surfaces, either by the formation of chemical bonds (chemisorption) or by weak van der Waals interactions causing

physical adsorption (physisorption)¹. Indeed, the adsorption of organic molecules on metals modifies their interfacial properties by lowering the free energy of the interface between the metal and the ambient external environment. Many chemical processes (such as corrosion and heterogeneous catalysis) take place at the surface of solids. The adsorption of organic materials (for example, thiols or disulphides) can modify surface properties or the chemical behaviour by modifying the chemical reactivity of the surfaces². Therefore, in this way, it is possible to induce corrosion resistance, conductivity or wettability.

4.2.2. SELF-ASSEMBLED MONOLAYERS (SAMs)

The research on organic thin films has old roots. In the eighteenth century, Benjamin Franklin observed the spontaneous spreading of oil on the surface of a pond³. In the nineteenth century, Agnes Pockles and Lord Rayleigh performed studies at the air-water interface⁴. As shown in **FIGURE 4.3** Irving Langmuir investigated monolayers of amphiphilic molecules on the water surface⁵ and Katherine Blodgett did the first study on the deposition of long chain fatty acids on solid substrates⁶. Zisman conducted the first systematic studies related to Self-Assembled Monolayers (SAMs) of primary aliphatic amines and monocarboxylic acids on platinum and Pyrex substrates⁷.

In these earlier studies, the macroscopic properties (such as surface tension and wetting properties) of these layers have been explored at the macroscopic level, rather than at the molecular one, due to the lack of appropriate tools. With the spectroscopic and microscopic tools available in the last years, it has been possible to correlate macroscopic and microscopic properties of these structures, and several methods for preparing molecular monolayers are today available⁸.

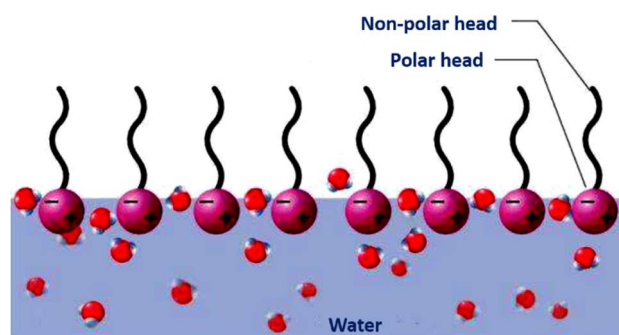


FIGURE 4.3: Langmuir monolayer of amphiphilic molecules on the water surface.

SAMs provide a convenient, flexible and simple system for tailoring the interfacial properties of metals or semiconductors, but also metal oxides or plastics, realizing a true bridge between the macroscopic world (surface up to hundreds of cm^2 can be functionalized with SAMs) and the nanoscopic one. SAMs have been applied in many fields spanning from the development of sensors⁹ and interfaces¹⁰ to micro fabrication^{11, 12, 13, 14, 15}.

SAMs are highly ordered, molecular, organic assemblies formed spontaneously by chemisorption and self organization from solution or gas phase onto surfaces of solids (i.e. Au Ag or Cu). The adsorbates organize spontaneously (and sometimes epitaxially) into crystalline or poly-crystalline structures. As Au is the reference substrate chosen in the present work(as discussed in **Chapter 1**), the work has been concentrated only on SAMs on Au surfaces.

A self-assembling molecule is defined by three chemical entities, as shown in **FIGURE 4.4**, each of which plays an important role in the assembly process:

1. the head group,
2. the spacer group,
3. the terminal (or end) group.

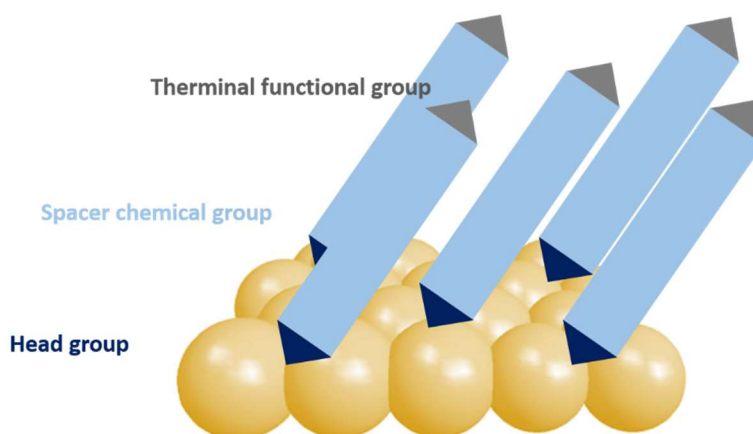


FIGURE 4.4: schematization of molecular self-assembly on Au substrate.

The head group is a surface-active functionality with high affinity for a specific substrate, Au in the present case. The head group is responsible for the chemisorption of the SAMs molecules on the substrate surface. The apparent pinning of the head group to a specific site through a chemical bond (covalent or ionic) results from strong substrate-molecular interaction.

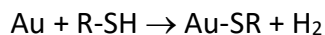
The second part is the spacer group. The spacer group can be an alkyl chain or an aromatic backbone. The forces that come into play in simple alkyl molecules and molecules containing polar aromatic groups are Van der Waals interactions and electrostatic interactions, respectively. A wide range of fundamentals groups can be introduced into the SAMs spacer group without any destabilisation^{16, 17, 18, 19, 20, 21, 22, 23}.

The third part is the end group. This end group can be of any desired functionality. The properties of this terminal group define the surface properties of the assembled monolayer. Therefore, the macroscopic properties of the SAM-functionalized surface, like wettability and adhesion, can be altered by changing the end functional groups of SAMs.²⁴

Self-assembly is a term of supramolecular chemistry²⁵ and is generally used to define the interactions among molecules in solution or solid state to give special arrangement or architectures. This is also used for formation of micelles and other systems formed by the surfactants. In this Chapter the term SAMs is used to refer to the chemisorption of aromatic thiols, those shown in **FIGURE 4.2**, on a Au surface. Moreover, in the following discussion, the term SAM will be used to refer to both a monolayer formation or to a multilayer.

Au is, in general, the reference substrate for SAM preparation, due to an extensive base of work reported in literature about it^{10, 19, 23, 24, 25}. Moreover, the electrodes used in the i-FLEXIS project have been based on Au, after a careful selection over some different alternatives, as discussed in **Chapter 2**. For these reasons, also for this part of work carried out, Au has been the electrode of reference to realize the connection.

The adsorption of thiols and disulphides on clean Au gives monolayers through the formation of gold-thiolate species. The reaction between thiols and Au surface is an oxidative addition producing surface bound thiolates, followed by a reductive elimination of the hydrogen, as shown in **EQUATION 4.1**:



EQUATION 4.1

However, the possibility of formation of water cannot be ruled out in the experiments involving the immersion of the substrates in solution²¹.

In this work, SAMs have been used in order to promote a satisfactory physical adhesion of the self-standing crystals to gold electrodes.

4.3 THE IDEA BEHIND THE WORK

To physically join a self-standing crystal to a substrate, one possible option would be to use a conventional glue²⁶, (like for example cyanoacrylate adhesives). However, this option, in the case of organic semiconductors, can seriously degrade the transport properties at the interfaces. Nonetheless, other possibilities for connect a self-standing OSSC to an electrode could be used, including for example the use of non-covalent but surface-extended interactions between the crystal and the substrate. For example, hydrogen bonds are known to be about one order of magnitude weaker than the covalent carbon-carbon bonds (83÷85 kcal·mol⁻¹); on the other hand, ten hydrogen bonds can establish an interaction as strong as C-C covalent bond. On these bases, a non-covalent bonding approach to the problem of physically promoting the adhesion of a crystal to an underlying substrate has been investigated. In particular, it has been devised a method based on the use of SAM chemically bound to the Au electrode and able to establish non-covalent bonds with an above lying crystal.

To reach this goal, 4 different SAMs have been chosen, as shown in **FIGURE 4.2**. They are all characterized by including an aromatic ring, so to maximize, in perspective, the electrical conductance between the crystal and the electrode through the monolayer, once this has been formed^{27, 28}. Two different groups of aromatic SAMs have been chosen. The first one is characterized by the ability to form both π - π interactions and H bonds (see structures A and B in **FIGURE 4.2**), while the second group is characterized by the ability to form only π - π interactions, (structures C and D in **FIGURE 4.2**). Moreover, structures A and B recall the one of 4HCB itself, as shown in **FIGURE 4.5**.

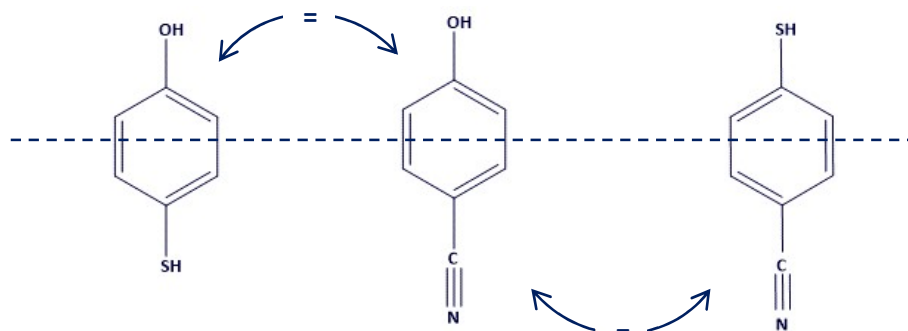


FIGURE 4.5: structural equivalence between 4HCB and the chosen SAMs.

Therefore, the mentioned SAMs are designed to create on top of the Au electrode a monolayer chemically and structurally similar to the crystal molecules, as shown in FIGURE 4.6.

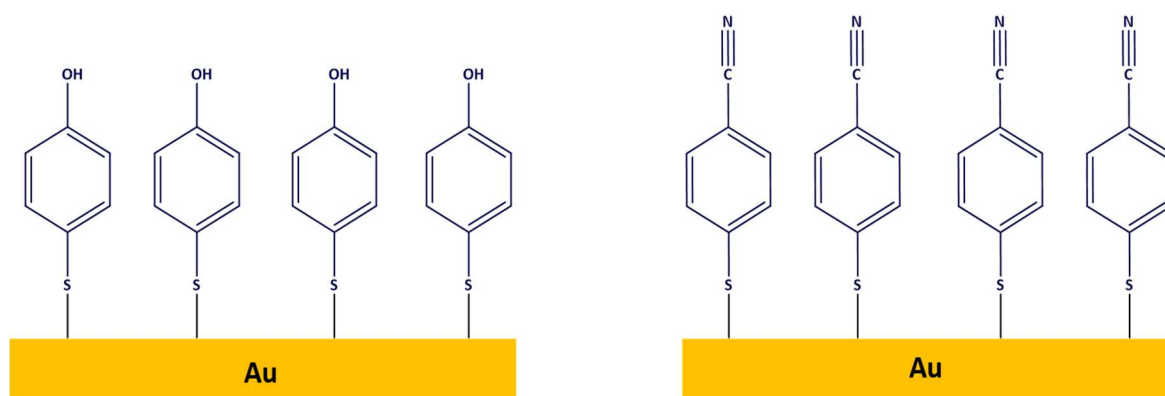


FIGURE 4.6: chemical functionalization of Au with the aromatic SAMs, containing also functional groups capable of forming H-bonding.

With this approach it was deemed possible to attain a good adherence of the crystal to the modified substrate. In fact, in general hydrogen bonds are known to possess the highest energies among non-covalent interactions²⁹; moreover, the hydrogen bond between a hydroxyl group and the nitrile group has been found to be around $3\div 7 \text{ Kcal}\cdot\text{mol}^{-1}$ either via experimental or theoretical calculations^{30, 31, 32}.

The ab face of the crystalline unit cell of the 4HCB crystal, of size of about $100 \text{ \AA}^2$, exposes two terminal -OH groups, two terminal $-\text{NO}_2$ groups and four less accessible (due to some sterical hindrance) benzene rings (see **FIGURE 4.7**). Considering that an average 4HCB single crystal has about 1 cm^2 (i.e., about $10^{16} \text{ \AA}^2$) surface area of the ab facet, around $2 \cdot 10^{16}$ -OH functional groups, $2 \cdot 10^{16}$ of $-\text{NO}_2$ and $4 \cdot 10^{16}$ of benzene groups are ideally available for establishing electrostatic interactions with the substrate. Even though the strength of a standard H-bond is about one order of magnitude lower than a covalent C-C bond the very large amount of available interaction sites should ensure a good adhesion between the crystal and the substrate functionalized with the described SAMs, provided that both the crystal surface exposed to the SAM-functionalized substrate and the latter substrate are flat enough to maximize the number of mutual interactions.

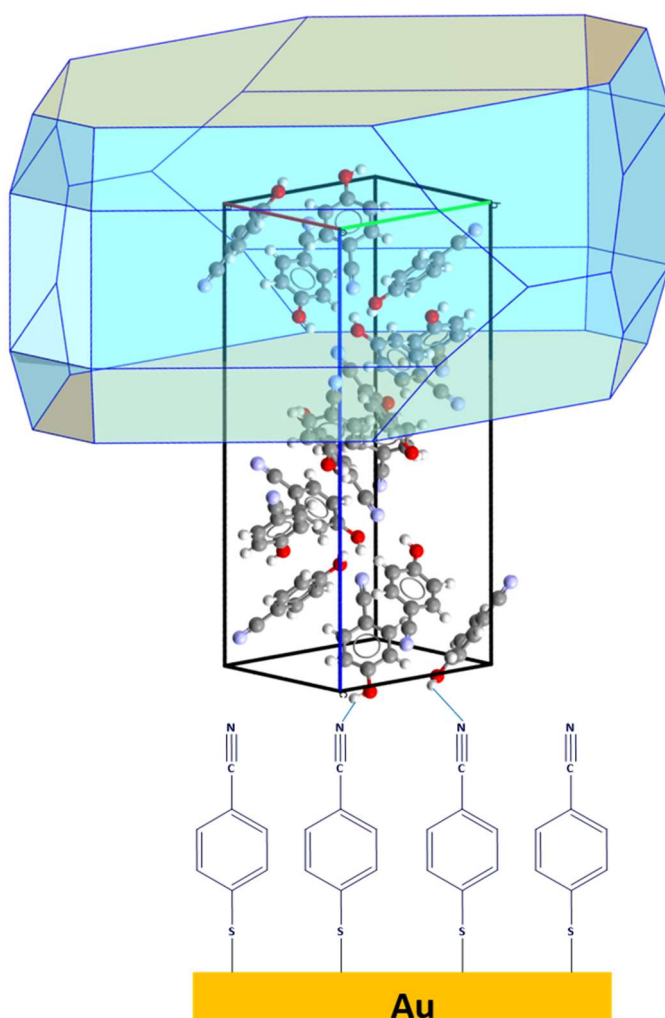


FIGURE 4.7: Sketch of the proposed interactions between the 4HCB single crystals and the underlying SAMs. In the crystal unit cell, the grey atoms are Carbons, the whitish ones are evidenced Hydrogens, the red ones are Oxygens, the bluish ones are Nitrogens. The H-bonds established between the crystal molecules and the monolayer are evidenced as dashed cyan lines.

4.4 CHARACTERIZATION OF THE SURFACES FOR PROPER SAM FUNCTIONALIZATION

A consistent part of the SAM functionalization approach has been devoted to the investigation of methods to reliably obtain clean Au film surfaces. Indeed, cleaning of surfaces to remove hydrocarbon and other inorganic contaminants is nowadays recognized as a necessary part of virtually all industrial processes where surfaces must be functionalized in any way. Examples range from soldering to self-assembly, to adhesion bonding. A film of hydrocarbon - only a few atomic layers thick - is able to prevent bonding between phases; inorganic contaminants - i.e. Cl^- , F^- - can react with the surface of either phases to cause unreliable bonding and the possibility of corrosive failure of the device once in service. In the past, most surface cleaning procedures have involved the use of volatile organic solvents such as fluorinated and chlorinated hydrocarbons, the ultimate sources of Cl^- , F^- .

These contamination effects have been observed also in electrochemical experiments. In particular, Au is also used as an electrochemically active surface on which the behaviours of chemical samples are studied³². The peak currents in cyclic voltammetry will be dependent on the surface composition of the Au. Upon exposure to a non cleanroom laboratory environment the Au surface is subject to numerous ambient contaminants, affecting binding kinetics of thiols in addition to electrochemical effects³³. These are the reasons why Au, especially the evaporated one, must be cleaned immediately before its chemical modification for these uses³⁴.

Another important characteristic of the used substrates to the end of a reproducible SAM formation is their roughness. In fact, it has been emphasized in several studies that the state of the surface, including the surface roughness, affects markedly the reproducibility of self-assembled monolayers on Au³⁵.

Based on these observations a careful choice of the proper cleaning method has been carried out in order to find the best methods, able to provide:

1. a clean surface,
2. a reproducible electrode roughness.

Upon these requirements, three treatments have been tested to clean the surface of the Au. Following cleaning, the Au samples have been characterized using cyclic voltammetry (CV) to investigate Au electrochemical activity. Surface composition has been investigated using X-ray photoelectron spectroscopy (XPS) to determine its elemental composition. Surface morphology has been evaluated by AFM. The results obtained in this step have been applied in the following steps of work to reliably ensure clean and reproducible Au surfaces and to maximize stable coverage of thiols monolayers.

Some solvent cleaning protocols are effective in some applications, but often surface contaminants are only partially removed, and in addition impurities present in the cleaning solvents can be unintentionally introduced. Therefore, during the past ten years, a number of 'dry' cleaning processes have been developed, which use electronically excited atoms and molecules to react with surface hydrocarbons, to decompose them to volatile molecules easily eliminated from the surface during the treatment.

Overall, the cleaning methods evaluated in this step of the work are listed below:

1. O₂ and Ar plasma treatment^{36, 37},
2. potassium hydroxide + hydrogen peroxide⁴⁰ + potassium hydroxide potential sweep⁴⁰,
3. acetone cleaning.

It must be reminded that cleaning effects are temporary. Removal of contaminants and the chemical reactions developed on the substrate surface during cleaning render the surface more active, hence more prone to recontamination. Thus particular attention has been devoted to characterize the cleaned system immediately after their cleaning procedure.

4.5 EXPERIMENTAL TECHNIQUES

4.5.1. XPS

X-ray Photoelectron Spectroscopy (XPS) is one of the most widely used surface analysis spectroscopic technique. It can be applied to a broad range of materials and it provides valuable quantitative and qualitative chemical information from the surface of the analysed material (with an average depth of analysis of approximately 5 nm). The chemical information XPS can provide are:

1. elemental composition of the surface,
2. empirical formula of pure materials,
3. elements that contaminate a surface,
4. chemical or electronic state of each element in the surface,

As shown in **FIGURE 4.8**, X-ray photoelectron spectroscopy is based upon a single photon in/electron out process. It is typically accomplished by exciting core level electrons of surface atoms with a monochromatic x-ray beam (typically, ~ 1-2 keV) to an unoccupied state in the continuum. An electron energy analyser is used to measure the kinetic energy of the emitted photoelectrons and their number. Therefore, the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be determined, and a photoelectron spectrum can thus be recorded. From the kinetic energy and the energy of the impinging photons it is possible to determine the binding energy of the atoms whose photoelectrons have been analysed, using the following relation

$$E_{\text{BE}} = h\nu - E_{\text{KE}} \quad \text{EQUATION 4.2}$$

For each and every element, there is a characteristic binding energy associated with each core atomic orbital, therefore each element give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study. Furthermore, the intensity of the peaks is related to the concentration of the elements within the sampled region. Thus, the technique provides a quantitative analysis of the surface composition. This is the reason why it is sometimes known by the alternative acronym, ESCA (Electron Spectroscopy for Chemical Analysis). This technique requires ultra-high vacuum (UHV) conditions.

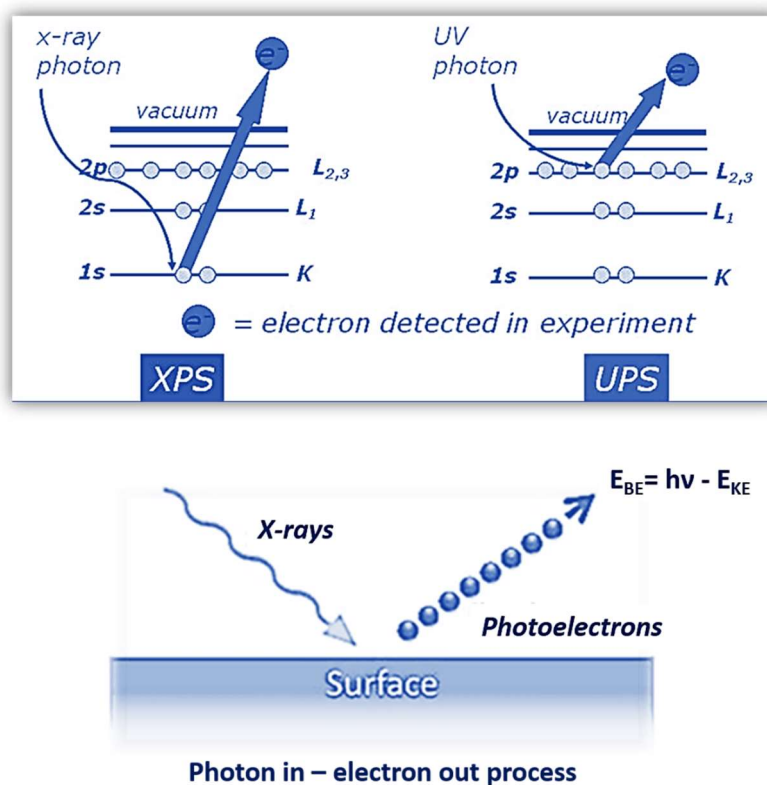


FIGURE 4.8: schematic representation of the XPS process on the left. On the right the same process is depicted describing an UPS experiment to evaluate the valence band work function.

The basic requirements for a photoemission experiment are:

1. a source of fixed-energy radiation,
2. an electron energy analyser (able to disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy),
3. a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions).

Such a system is illustrated schematically below in **FIGURE 4.9:**

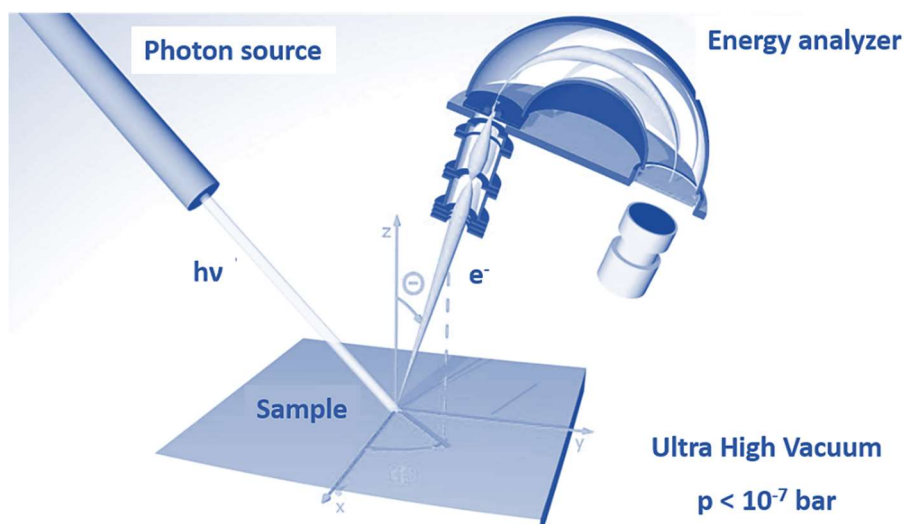


FIGURE 4.9: schematic representation of the basic requirements of an XPS

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring but also upon:

1. the formal oxidation state of the atom,
2. the local chemical and physical environment,

Changes in either 1 or 2 give rise to small shifts in the peak positions in the spectrum - so-called chemical shifts. Such shifts are readily observable and interpretable in XPS spectra because the technique is:

1. of high intrinsic resolution (as core levels are discrete and generally of a well-defined energy),
2. a one electron process (thus simplifying the interpretation).

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulomb interaction between the photo-emitted electron and the ion core. This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.

XPS measurements have been performed in a UHV apparatus based on a modified XPS system with a double-anode X-ray source. For the measurements reported here,

an Al K_{α} X-ray source with an energy resolution of about 0.8 eV has been used at normal incidence. The base pressure of the apparatus has been below $3 \cdot 10^{-10}$ mbar.

4.5.2. CYCLIC VOLTAMMETRY

Cyclic voltammetry has become a popular tool in the last fifteen years for studying electrochemical reactions and therefore it is nowadays the most widely used technique in this field. An increasing number of inorganic chemists have been using cyclic voltammetry to evaluate the effects of ligands on the oxidation/reduction potential of the central metal ion in complexes and multinuclear clusters³⁸. This type of information plays an integral part in many of the approaches directed toward solar energy conversion^{39, 40}.

There are several good texts that deal with the theory and practice of modern voltammetry in depth^{41, 42, 43}.

A. Voltammetry

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry:

1. linear sweep,
2. cyclic voltammetry.

For each of these cases a voltage or series of voltages are applied to an electrode and the corresponding current that flows is monitored.

B. Linear Sweep Voltammetry

In linear sweep voltammetry, LSV, a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown in **FIGURE 4.10**. The characteristics of the linear sweep voltammogram depend on a number of factors including:

1. the rate of the electron transfer reaction(s),
2. the chemical reactivity of the electroactive species,
3. the voltage scan rate.

In LSV measurements the current response is plotted as a function of voltage. The scan begins from the left hand side of the current/voltage plot where no current flows. As the voltage is swept further to the right (to more reductive values) a current begins to flow and eventually reaches a peak before dropping. To rationalise this behaviour it is necessary to consider the influence of voltage on the equilibrium established at the electrode surface. Here the rate of electron transfer is fast in comparison to the voltage sweep rate. Therefore at the electrode surface an equilibrium is established identical to that predicted by thermodynamics.

The exact form of the voltammogram can be rationalised by considering the voltage and mass transport effects. As the voltage is initially swept from V_1 the equilibrium at the surface begins to alter and the current begins to flow. The current rises as the voltage is swept further from its initial value as the equilibrium position is shifted further to the right hand side, thus converting more reactant. The peak occurs, since at some point the diffusion layer has grown sufficiently above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation. In this situation the current begins to drop just as it did in the potential step measurements.

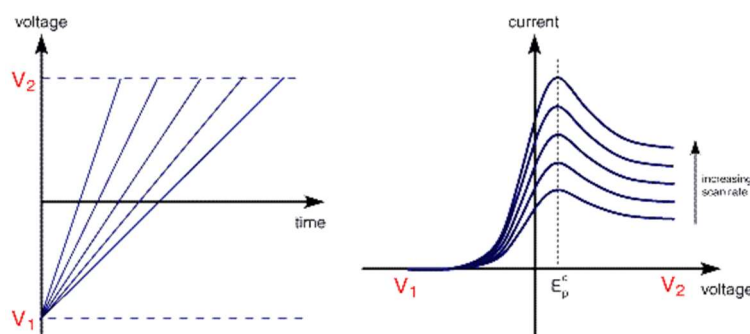


FIGURE 4.10: Linear increase of the potential vs time

The **FIGURE 4.10** shows a series of linear sweep voltammograms recorded at different scan rates. Each curve has the same form but it is apparent that the total current increases with increasing scan rate. This again can be rationalised by considering the size of the diffusion layer and the time taken to record the scan. Clearly, the linear sweep voltammogram will take longer to record as the scan rate is decreased. Therefore, the size of the diffusion layer above the electrode surface will be different

depending upon the voltage scan rate used. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently, the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode the magnitude of the current will be lower at slow scan rates and higher at high rates. This highlights an important point when examining LSV (and cyclic voltammograms), although there is no time axis on the graph the voltage scan rate does strongly effect the behaviour seen. A final point to note from the figure is the position of the current maximum, it is clear that the peak occurs at the same voltage and this is a characteristic of electrode reactions which have rapid electron transfer kinetics. These rapid processes are often referred to as reversible electron transfer reactions. This leaves the question as to what would happen if the electron transfer processes were 'slow' (relative to the voltage scan rate). For these cases the reactions are referred to as quasi-reversible or irreversible electron transfer reactions. The figure below shows a series of voltammograms recorded at a single voltage sweep rate for different values of the reduction rate constant k_{red} .

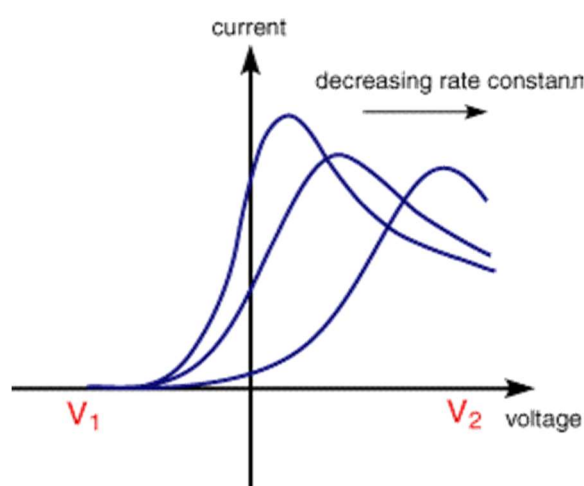


FIGURE 4.11: Change of the rate constant

C. Cyclic Voltammetry

Cyclic voltammetry, CV, is very similar to LSV. In this case, the voltage is swept between 2 values (see below) at a fixed rate, however now, when the voltage reaches V_2 , the scan is reversed and the voltage is swept back to V_1 .

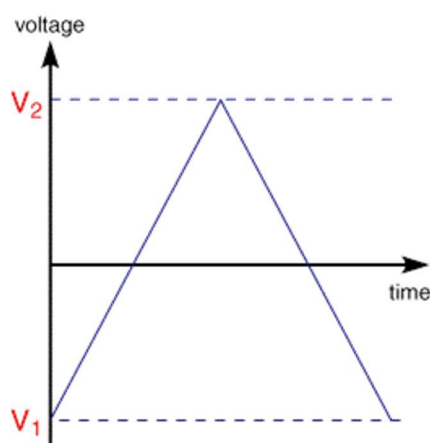


FIGURE 4.12: Voltage as a function of time

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in below. Again, the solution contains only a single electrochemical reactant:

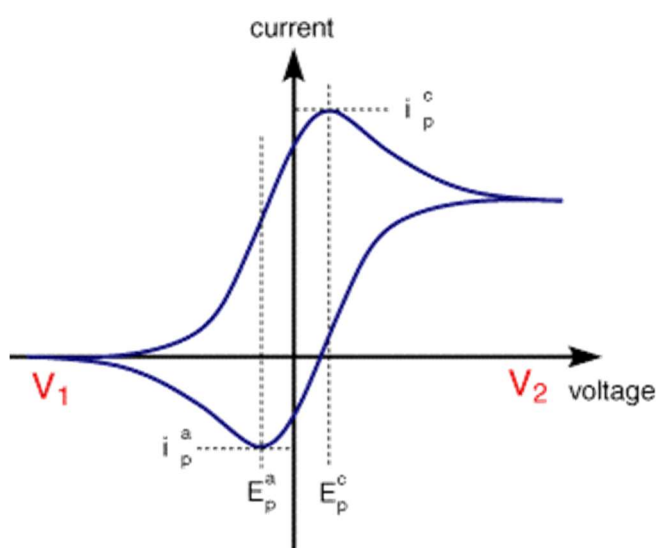


FIGURE 4.13: current as a function of voltage for CV

The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product (Fe^{2+} back to reactant Fe^{3+}). The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward sweep but otherwise the behaviour can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

1. The voltage separation between the current peaks is:

$$\Delta E = E_p^a - E_p^c \quad \text{EQUATION 4.12}$$

2. The positions of peak voltage do not alter as a function of voltage scan rate
3. The ratio of the peak currents is equal to one:

$$\frac{i_p^a}{i_p^c} = 1 \quad \text{EQUATION 4.13}$$

4. The peak currents are proportional to the square root of the scan rate.

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen in **FIGURE 4.14**. As with LSV, the influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. The CV for cases where the electron transfer is not reversible show considerably different behaviour from their reversible counterparts. By analysing the variation of peak position as a function of scan rate it is possible to gain an estimation for the electron transfer rate constants.

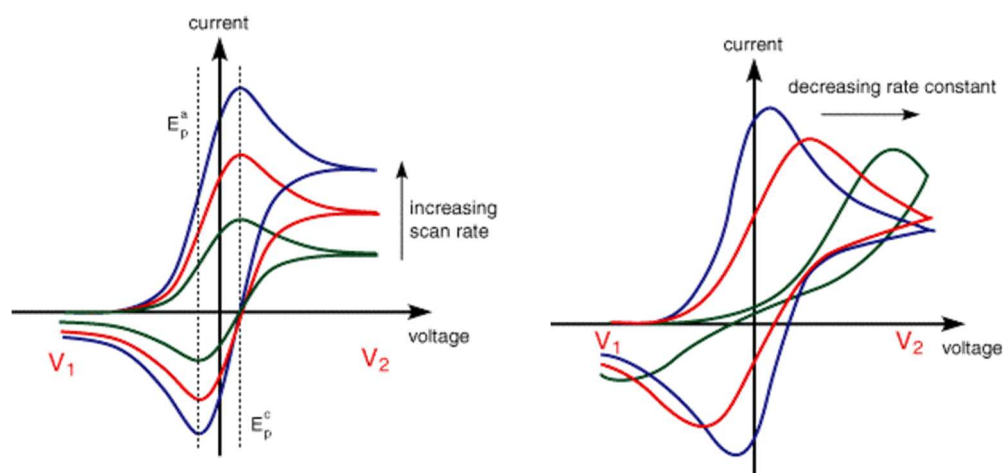


FIGURE 4.14: Scan rate and rate constant dependence of the I-V curves

4.5.3. SPELEEM (XPEEM + LEEM)

By using photons or electrons as probe, the SPELEEM allows a multi-technique approach of complementary imaging to the study of surfaces and thin films . This instrument combines the structural sensitivity of Low Energy Electron Microscopy (LEEM, lateral resolution < 10 nm) with the flexible spectroscopy of energy-filtered PEEM. The combination of LEEM with energy filtered XPEEM enables to carry out a variety of complementary analytical surface characterization methods with both chemical and structural sensitivity⁴⁴. In the following the main features of the two techniques are given.

XPEEM - a chemical and electronic structure sensitive analytic method - is a full-field and direct imaging technique. The microscope images a restricted portion of the specimen area illuminated by x-ray beam and photoemitted electrons are collected at the same time by the optics setup, which produce a magnified image of the surface. The key element of the microscope is the objective lens, also known as cathode or immersion lens, of which the sample is part. The PEEM detects electrons emitted from atomic core levels with kinetic energy expressed from [EQUATION 4.1](#). Typically $h\nu$ is kept fixed, with energies in the range provided by the source. The energy filter is used to select the kinetic energy, E_{kin} , of photoelectrons, which allows measuring the binding energies of emitting atoms or accessing the surface electronic structure.

LEEM is a structure sensitive technique which uses elastically backscattered electrons to image a crystalline surface with a lateral resolution of few tens nm. Microprobe measurements are limited to surface areas of 2 microns in diameter. Which properties does LEEM allow to probe? Different contrast mechanisms are available in LEEM for structure characterization:

1. surface structure,
2. film thickness,
3. step morphology.

The use of a contrast aperture positioned in the diffraction plane allows employing primary or secondary diffracted beams for imaging. When the primary diffracted beam (or "00" beam) is selected, the performing of *bright-field* LEEM is allowed. Here, the contrast is purely structural (*diffraction contrast*) and depends on the local differences in diffraction for the different surface phases present on the sample. By selecting a secondary diffracted beam, a *dark field image* of the surface is produced. Here all areas that contribute to the formation of the selected beam appear bright.

Spectroscopic operation can be implemented either in real space (spectroscopic imaging, or XPEEM) or microprobe angle-resolved photoemission spectroscopy mode (microprobe-XPS). Schematic diagrams representing the electron optical configuration of the microscope are shown in **FIGURE 4.15**.

The measurements were performed with the spectroscopic photoemission and low-energy electron microscope (SPELEEM) installed at the Nanospectroscopy beamline of the Elettra synchrotron laboratory (Italy). In the SPELEEM, the specimen can be probed either with low energy electrons (0-750 eV) provided by an LaB₆ source, or using monochromatized soft X-rays in the range 40-1000 eV. The SPELEEM is equipped with a hemispherical bandpass energy filter, which is normally operated at a pass energy of 908 eV.

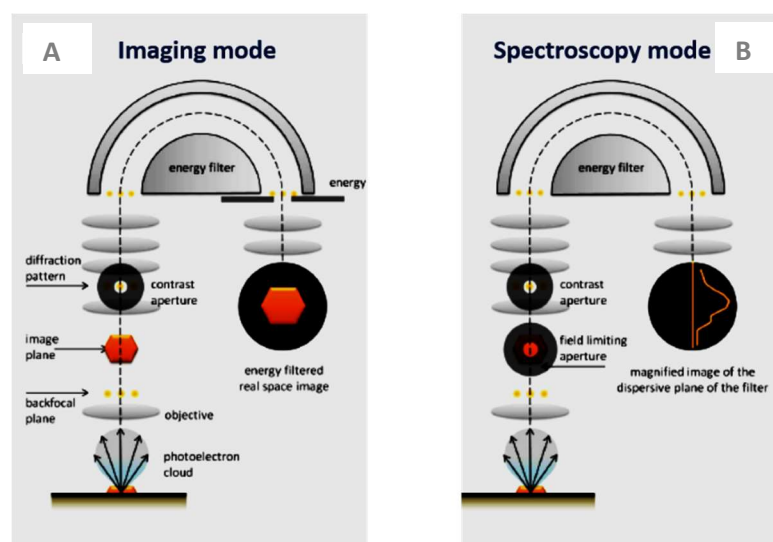


FIGURE 4.15: Electron optics configuration of the SPELEEM microscope in two different operation modes: A: spectroscopic imaging; B: micro spectroscopy operation.

4.5.4. GI-XRD

In conventional X-ray diffraction, an incident x-ray beam penetrates deep into a material. Therefore, X-rays diffraction methods provides signals and therefore information referred to the bulk of the evaluated system. To provide information on the topmost layers of a thin film it is required to perform a $\theta/2\theta$ scan with a fixed grazing angle of incidence, popularly known as GI-XRD.

GI-XRD was originally developed by Marra, Eisenberger and Cho in 1979⁴⁵. The fixed angle is generally chosen to be slightly above the critical angle for total reflection of the film material. In these conditions, the incident beam is evanescent and penetrates only the top 100 Å or less into the surface^{46, 47}. In a GID experiment, the incident x-ray beam impinges onto the surface of a film at an incident angle of 1° or less, and the detector is placed in a horizontal plane parallel to the film surface to collect diffraction from lattice planes which are perpendicular to the surface. GID data can be collected using a $\theta/2\theta$ (or radial) scan and/or an ω scan, as shown in **FIGURE 4.16**. In a $\theta/2\theta$ scan, both the film and the detector are scanned at a speed of 1:2 to record diffraction along a fixed direction on the substrate. In an ω scan the detector

is stationary at a fixed 2θ angle, while the film rotates about its surface normal to record in-plane diffraction from lattice planes which have the fixed value of d-spacing. Actually, the measures performed for this work have been recorded in a ω scan.

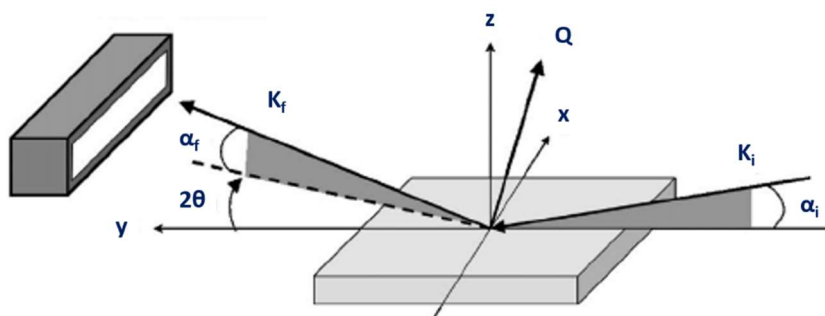


FIGURE 4.16 Schematic of the GID geometry.

In symmetric Bragg diffraction, one-dimensional crystallographic information along the surface normal is obtained. In GI-XRD, two-dimensional information parallel to the surface is measured.

GI-XRD have been performed at the XRD1 Beamline in Elettra Sincrotrone Trieste (main features already described in **Chapter 2**).

4.6 MATERIALS AND METHODS

4.5.1. ELECTRODES CLEANING PROCEDURE

Following fabrication and dicing all samples have been stored under the hood in the lab. It is known that, in ambient lab storage conditions, the gold surface is quickly covered by adventitious particles⁴⁸, thus the electrodes stored in lab conditions have been used as standard 'contamination' references.

Four different variety of common gold cleaning methods have been investigated among the plethora found in literature^{53, 54, 55, 56, 57}..:

1. O₂ and Ar plasma treatment,
2. KOH and H₂O₂,
3. KOH potential sweep,

4. solvent cleaning,

The applied treatments are described below, including solution concentrations and voltammetry parameters.

O₂ AND Ar PLASMA TREATMENT

Gold samples spent 1 min in a Merck Eurolab PR-100 under O₂ flux and 5 minutes under Ar flux. The working parameters are summarized in **TABLE 1**. This treatment is commonly used when working with biological samples as a way to restore or regenerate the gold surface after experiments^{49, 50, 51}. Abbreviated 'O₂/Ar' method in the results.

WORKING PARAMETERS	O ₂	Ar
FLUX (sccm)	30	20
V _{BIAS} (V)	100	250
POWER (W)	20	35
Time (min)	1	5

TABLE 1: working parameters used to clean the gold electrode following the procedure 'O₂/Ar'.

KOH AND H₂O₂

This method has been used by Heiskanen et al.⁵³ as an intermediate step in a gold cleaning protocol. Samples spent 10 min in a solution of $5 \cdot 10^{-2}$ M KOH and 25% H₂O₂ before rinsing with Milli-Q water. Abbreviated 'KOH + H₂O₂' system in the results.

KOH POTENTIAL SWEEP

This is the second part of the cleaning protocol used by Heiskanen et al.⁵⁷. After the treatment above described, electrodes have been placed in $5 \cdot 10^{-2}$ M KOH and connected to a potentiostat. The electrode potential has been swept from -200 to -1200 mV (vs. Ag/AgCl) once, at $50 \text{ mV} \cdot \text{s}^{-1}$ scan rate, and then rinsed in Milli-Q water. Cleaning times have been explicitly chosen, based on literature, for non-voltammetric techniques, while all voltammetric techniques have been carried out within 2 min. Abbreviated 'KOH sweep' system in the results.

SOLVENT CLEANING

Samples spent 10 min in acetone before rinsing with Milli-Q water. Abbreviated 'Acetone' in the results. The same treatment has been tested at 60°C but the increased temperature had caused the Au to detach from the PEN surface therefore this approach has been rejected.

Before and after cleaning, each electrode has been subjected to the following characterizations:

1. XPS,
2. CV,
3. AFM.

A PS Trace 2.3 Palm Instruments Electrochemical Analyzer has been used to perform all CV. The probe solution has been 10^{-2} M ferri/ferro-cyanide $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple and $2 \cdot 10^{-1}$ M KCl (reference/counter-electrolyte) in Milli-Q water. A chlorinated silver wire has been the Ag/AgCl pseudo-reference electrode. All electrochemical measurements have been conducted using 10 mL of fresh probe solution, without stirring, per each measure. All the mentioned compounds have

been diluted with Milli-Q water. Each cleaning method has been applied to five gold samples for statistical relevance.

4.5.2. CLEAN ELECTRODES CHARACTERIZATION BEFORE FUNCTIONALIZATION

In order to properly bond the self-standing single-crystals onto the microelectrodes a detailed characterization of the electrodes surfaces has been carried out. The complete analytical characterization has been carried out by means of:

1. optical microscopy,
2. scanning electron microscopy,
3. atomic force microscopy,
4. grazing-incidence X-ray diffraction,
5. low energy electron microscopy.

The optical and electron microscopy have been carried out to evaluate the surface smoothness and the morphology of the microelectrode. Its polycrystalline nature has been investigated by means of grazing-incidence X-ray diffraction and low energy electron microscopy.

An Olympus BH2-UMA optical microscope ([Figure 3.12](#)) has been used to image all samples under a range of magnification settings up to 1600x.

A Zeiss Supra 40 high resolution Field Emission Gun SEM with Genimi column has been used to image all samples under a range of magnification settings at a voltage of approximately 2kV.

The atomic force microscopy have been carried out with already described equipment (see **Chapter 3**).GI-XRD have been performed at the XRD1 beamline in Elettra Sincrotrone Trieste (main features already described in **Chapter 2**) both on PEN substrate and PEN+Au. The measurements have been carried out using a incident X-ray beam impinging onto the substrate surface at an incident angle $< 1^\circ$, with the detector placed in a horizontal plane parallel to the film surface, using an ω scan pattern, in standard atmosphere (i.e., not in UHV conditions).

All the evaluated sample have been pre-treated using 'KOH + H₂O₂' + 'KOH potential sweep' methods to clean the Au surface. All characterizations have been performed immediately after the cleaning procedure. Each characterization has been performed on an average value of five samples, in order to obtain statistically significant and reliable result.

4.5.3. ELECTRODES FUNCTIONALIZATION WITH SAMs

The most common protocol for preparing SAMs on Au is immersion of a freshly prepared or clean substrate into a dilute (10^{-3} – 10^{-2} M) ethanol solution of thiols for ~ 12-18 h at room temperature. This procedure is widely used and has been set up based on early studies on SAMs. The experimental parameters are the ultimate results of a combination of studies devoted to the optimization of the reproducibility of SAMs⁵⁴. It is well known that high coverage can be obtained quickly (milliseconds to minutes) from millimolar solutions, but only a slow (order of hours) reorganization process provide a maximization of the molecules density and therefore a minimization of the defects. Based on these observations, substrates have been pre-treated using 'KOH + H₂O₂' + 'KOH potential sweep' methods to clean the Au surface and have been immediately immersed into freshly prepared ethanol solution ($1 \cdot 10^{-3}$ M) of the SAM under evaluation.

Forming SAMs at temperatures above 25 °C can improve the kinetics of formation and reduce the number of defects in them^{55, 56}. Elevated temperatures increase the rate of desorption for adventitious materials and solvent molecules physisorbed on the surface of the substrate and make it possible for the system to cross activation barriers for processes such as chain reorganization and lateral rearrangements of the adsorbates more easily than at room temperature. Uosaki and co-workers suggest that the effect of temperature is particularly relevant during the first few minutes of the formation of a SAM when most of the adsorption and reorganization of the SAM is taking place.

Based on these data of literature, Au substrate immersed into the ethanol solution have been heated up at 40°C for the first 10 minutes and have been therefore cooled

down to room temperature and then to 4°C. The systems have been therefore left at this temperature for 8 days.

Solution concentration and immersion time have been chosen after a careful study of the literature. On one hand, most spectroscopic and experimental evidence suggests that the average properties of SAMs formed from thiols (wettability, mass coverage, and the structure deduced by Reflection and absorption IR Spectroscopy, RAIRS, do not change significantly when exposed to 10^{-3} M solutions of thiols for more than 12-18 h. On the other hand, other observations acquired by electrochemistry⁵⁷, Scanning Tunneling Microscopy⁵⁸ and again RAIRS⁵⁹ indicate that SAMs structure should, in principle, evolve over immersion times of ~7-10 days. These results imply that the coverage of the surface increases with increasing the immersion times and therefore suggest three consequences:

1. the number of defects in the SAMs should decrease,
2. the conformational defects along the spacer group should decrease,
3. the conformational defects between the spacer groups should decrease.

The typical time allowed for formation (12-18 h) is convenient experimentally, but for some applications, formation over many days can improve the reproducibility of subsequent experiments, as in the case, for example, of the studies of electron transfer through SAMs⁶⁰.

4.5.4. DETERMINATION OF SAMs ON SURFACES

In order to properly bond the self-standing single-crystals onto the functionalized microelectrodes, a detailed characterization after the functionalization is required. Due to the ultimate roughness of the electrode surface, many conventional technique of characterization have been rejected, i.e. AFM. The characterization described in the following section is the first part of the total work to be done to obtain a fully description of the functionalized layer. In this very first step, it has been possible to verify just the presence of a functionalization. To achieve some insights on the functionalization degree some additional experiments are planned for the

future, as described in **Chapter 5**. During the present work, the following characterization have been performed:

1. SPELEEM (XPEEM+LEEM);
2. GI-XRD.

The presence of a functionalization has been confirmed with SPLEEM and nothing more concerning the morphology of the layer on the surface. It has not possible to conveniently define the presence of monolayer or multilayer. GI-XRD have been performed not in UHV condition and in this working set-up it has not been possible to verify the presence of the monolayer and, for this reason, a deeper insight on these aspects is foreseen for the future in UHV condition.

4.5.5. OSSCs BINDING TESTS ON AU ELECTRODES

The binding tests between the functionalized electrode and self-standing single-crystals have been carried out following a general method adapted from already reported ones^{61, 62, 63, 64, 65, 66}. In more detail, both the single-crystal and the SAM-functionalized electrode have been dipped into a stirred saturated solution (ethylic ether) of the semiconductor (4HCB), and then the crystal has been deposited onto the functionalized electrode on its *ab* face. Then the system has been carefully cooled down at a fixed rate of cooling to the final value of 6°C. After about 12 h the so-treated crystal+substrate system was recovered and brought back to room temperature for the adhesivity tests.

4.7 RESULTS AND DISCUSSIONS.

4.7.1 ELECTRODE CLEANING PROCEDURE

The electrodes have been treated as described in **section 4.5**. After the cleaning process, the electrodes have been immediately subjected to the described characterization. If this has not been possible, the electrodes have been immediately immersed in ultrapure water in properly cleaned sample-holder and have been transferred to the characterization technique instrument within 5 minutes. The results of these characterizations are hereafter reported.

A. XPS results

The core level Au(4f) spectra contains two sets of distinct peaks, with the Au(4f_{7/2}) peaks at 84.6 and the Au(4f_{5/2}) at 86.2 eV. The binding energy, BE, of the main peak at 84.6 eV is slightly higher, as reported in literature⁶⁷. The shoulder at higher BE can be assigned to Au³⁺ (Au₂O₃) species, following previous assignments reported in literature⁶⁸.

XPS spectra recorded from 'O₂/Ar' method, 'KOH+H₂O₂' method + 'KOH sweep' method and 'acetone' method, on polycrystalline gold substrates are shown in **FIGURE 4.17**. An higher intensity of Au peak on the surface is a clear signal indicating cleaner surface. The samples treated with 'O₂/Ar' method gave the most intense peak and therefore the cleanest Au surface. The samples treated with 'KOH+H₂O₂'+'KOH sweep' methods have the second highest Au peak intensity.

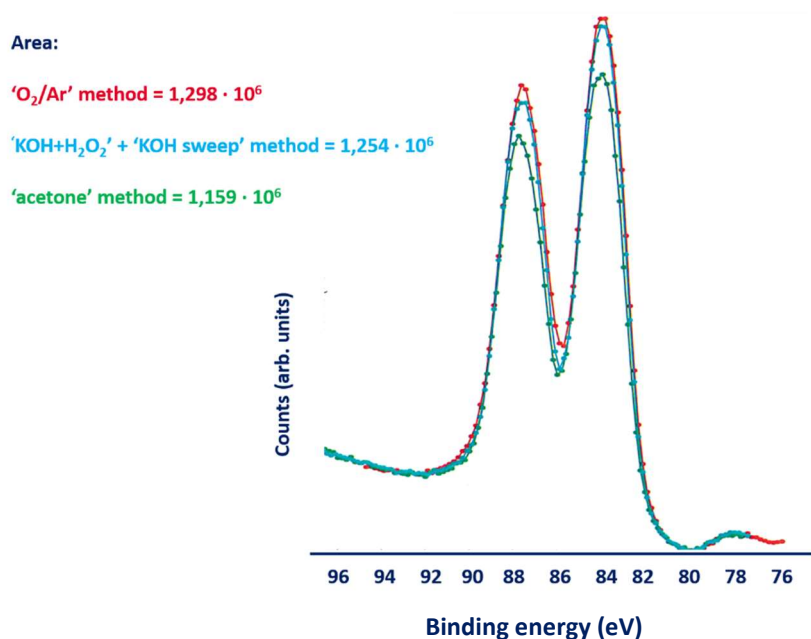


FIGURE 4.17: Au 4 f XPS peaks obtained from the three cleaning methods.

B. Electrochemical results

The potential-difference between the peak cathodic and anodic currents, ΔE_p , is used as a measure of electrochemical cleanliness of the electrode surface, as shown in **FIGURE 4.13**, the smaller ΔE_p the cleaner the surface. In % ΔE_p the higher the value, the cleaner the surface.

Theoretically, for single-electron transfer reactions such as in the $[\text{Fe}(\text{CN})_6]^{3-}/^{4-}$ couple on a perfect Au surface, the potential-difference should be $\Delta E_p = 58\text{mV}$ ⁶⁹ and therefore any increase in this value should be interpreted as caused by surface contaminations.

CLEANING METHODS	ΔE_p	
	$\Delta\%$	σ_E
O_2/Ar	-9.8	3.1
$\text{KOH} + \text{H}_2\text{O}_2 + \text{KOH sweep}$	-28.4	3.1
acetone	-7.1	12.0

TABLE 2: Potential difference each gold cleaning method. A negative sign indicates a percentage decrease from uncleaned values.

The large standard deviation in the ' O_2/Ar ' cleaned samples suggests a possible contamination of the reactor. The combination of ' $\text{KOH}+\text{H}_2\text{O}_2$ +'KOH sweep' methods appear to deliver the cleanest gold, while the very common 'acetone' cleaning method delivers the less clean surface.

C. AFM results

Per each cleaning procedure, contact-mode AFM has been carried out on five samples before and immediately after the cleaning. FIGURE 4.18 and TABLE 4.2 describe the results. As is visible from FIGURE 4.18A, uncleaned sample scans appear very rough, with large bumps of more than 200 nm, and a substrate surface with marked roughness ($R_A = 3.90$ e $R_Q = 5.45$)

After cleaning with acetone, the situation is partially improved, with major bumps less than 100 nm high, and a generally much smoother surface (FIGURE 4.18B , $R_A = 3.15$ nm and $R_Q = 4.26$ nm).

AFM of gold substrates treated with the 'KOH + H₂O₂' + 'KOH Sweep' method evidenced drastically reduced roughness (FIGURE 4.18B , with a few large bumps not higher than 30 nm, and a generally very smooth surface. ($R_A = 2.30$ e $R_Q = 2.88$)

Finally, electrodes treated with the 'O₂/Ar' method provide a roughness not repeatable at all, highlighting in this way that this cleaning method is not a proper one with respect to the purposes of functionalization.

It is noteworthy to underline that this type of progressive improvement in the overall roughness of the gold/PEN substrate upon application of the proper cleaning procedure is statistically reliable, except for 'O₂/Ar', as later discussed. Nonetheless, it must be similarly remarked that even the best performing treatment, i.e. the 'KOH + H₂O₂' + 'KOH Sweep' method, was not able to level the substrate below an average roughness of $R_A = 2.30 \pm 0.13$, $R_Q = 2.79 \pm 0.09$

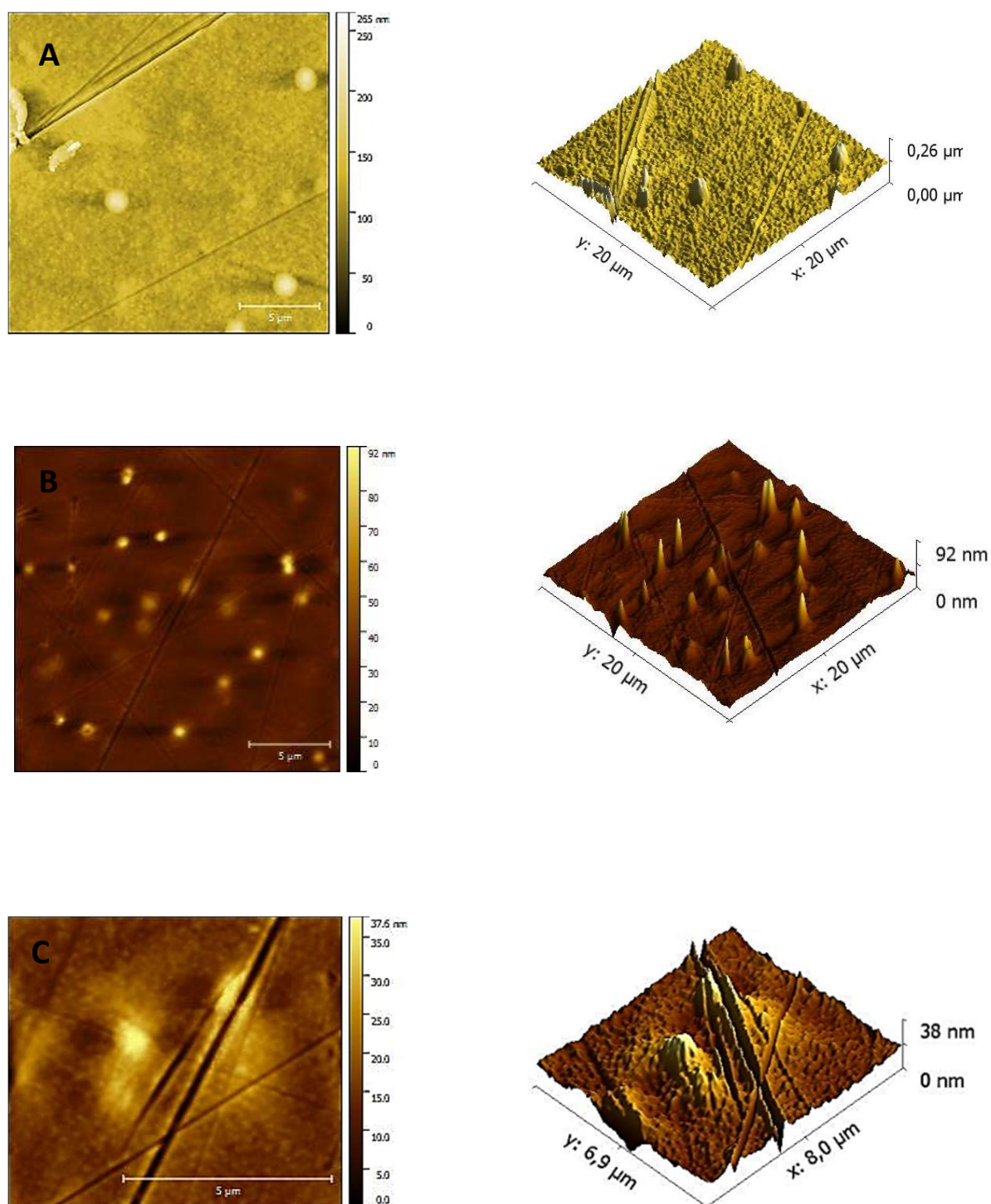


FIGURE 4.18: Figure A shows the AFM micrograph of a 'reference' dirty electrode. Figure B shows the AFM micrograph of an electrode cleaned up with 'acetone' cleaning method. Figure C shows the AFM micrograph of an electrode cleaned up with the combined 'KOH+H₂O₂'+'KOH sweep' cleaning methods.

This value is typical of commercial PEN substrates, which show in the better cases R_A around 100 nm⁷⁰ and likely reflects the almost perfect gold surface smoothing achieved with the treatment, that however is not able to level the underlying polymeric layer. A slightly better result in terms of surface levelling was sometimes achieved by the 'O₂/Ar' method (data not shown), but with very scarce reproducibility, possibly due to the unoptimized process with respect to the considered substrate. For this reason, the 'O₂/Ar' method, despite being able to provide very good results in terms of elimination of surface contaminants, was not further considered for practical applications.

Another point worth to be underlined is that, even though the improvement brought by the optimized cleaning treatment was notable, also in the best case the residual substrate roughness was still too high to allow the use of AFM for exploring in detail the presence of the tested SAMs on the surface. Therefore, the success of the SAM functionalization was investigated, as already mentioned, with different techniques .

CLEANING METHODS	R_A (nm)	R_Q (nm)
uncleaned	3,90	5,45
O ₂ /Ar*	2.80	3.87
KOH + H ₂ O ₂ + KOH sweep	2,30	2,88
acetone	3.15	4.26

TABLE 3: Summary of AFM data underling that all samples, after cleaning, exhibit nearly identical roughness despite their prior differences.

D. Conclusions

After investigating 3 cleaning methods, it has been demonstrated that the combination of 'KOH + H₂O₂' + 'KOH sweep' cleaning methods is the best technique to provide clean and as smooth as possible Au on PEN substrates. The 'acetone' method alone appears to be unacceptable in term of cleanliness and final surface roughness, while the 'O₂/Ar' methods doesn't provide an enough reproducible surface morphology. Based on these observations, in the following, all the electrodes are meant treated by the combination of 'KOH + H₂O₂' + 'KOH sweep' cleaning methods.

Another point worth to be underlined is that, even though the improvement brought by the optimized cleaning treatment was notable, also in the best case the residual substrate roughness was still too high to allow the use of AFM for exploring in detail the presence of the tested SAMs on the surface. Therefore, the success of the SAM functionalization was investigated with techniques different from AFM.

4.7.2 CLEAN ELECTRODE SURFACE CHARACTERIZATION

A. Optical and electron microscopy

The optical and electron microscopy have been carried out to evaluate the surface smoothness and the morphology of the gold electrode, as shown in **FIGURE 4.19**

It has been possible to determine an excellent uniformity of the Au deposition. No particular morphological defects have been detected, except for regular scratches on the surface, attributed to the PEN fabrication process (**FIGURE 4.19B** and **FIGURE 4.19C**). In about the 3% of all the screened electrodes, protrusions with traces of Au delamination have been found (**FIGURE 4.19C**), which have been related again to the presence of in homogeneities in the PEN layer. Indeed, in all the evaluated cases the diameter of the protrusions span from 0.5 μm to 1 μm . All

the samples presenting these defects have been discarded, and have not been used for the functionalization with SAMs.

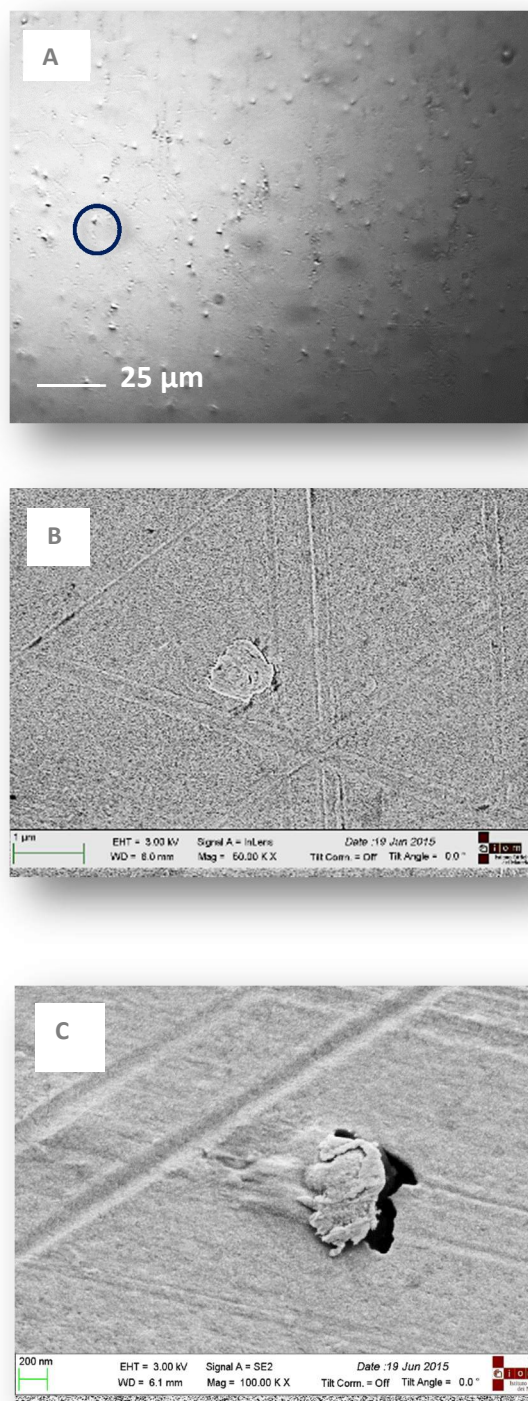


FIGURE 4.19: Figure A shows an optical micrograph of a cleaned electrode. Figure B and C show SEM micrographs of an electrode, evidencing . Figure C shows an electron micrograph magnification of the typical protrusion, due to inhomogeneities of the PEN substrate, found in 3% of the electrodes.

B. Grazing incidence x-ray diffraction

GI-XRD has been carried out on PEN+Au while on PEN substrate the measures have been acquired in transmission mode.

The ω scan pattern for the Au reflections from the film is plotted on the right of **FIGURE 4.20**. As a reference, the pattern- acquired in transmission - for the PEN reflections is also shown on the right of **FIGURE 4.20**. The ω scan patterns are plotted in an angular scale of $\omega - \theta$ so that the orientation of the Au film and the PEN substrate can be compared directly by a rotation of 90° . These measurements confirmed the well known polycrystalline nature of PEN⁷¹, with some preferential growth direction dictated by the axial stretch production process, as shown in **FIGURE 4.20**.

Measures on PEN+Au revealed the polycrystalline nature also of the deposited Au, with the same preferential growth direction seen in the PEN alone, as shown in **FIGURE 4.20**.

C. Low energy electron microscopy

This surface characterization technique has been carried out to confirm the surface polycrystalline nature of Au and the morphology of the electrode, to determine the average size of the domains and the homogeneity of the deposition.

The measurements were performed with the spectroscopic photoemission and low-energy electron microscope (SPELEEM) installed at the Nanospectroscopy beamline of the Elettra synchrotron laboratory – Italy⁷². In the SPELEEM, the specimen can be probed either with low energy electrons (0-750 eV) provided by a LaB₆ source, or using monochromatized soft X-rays in the range 40-1000 eV. In the here discussed case, low energy electrons of 0.9 eV have been used, working therefore in the LEEM-MEM threshold, which provides a very high sensitivity to morphology. This analysis allowed to confirm the polycrystalline nature of the Au surface, whose grain size are in the order of tens of nm, as shown in **FIGURE 4.21**.

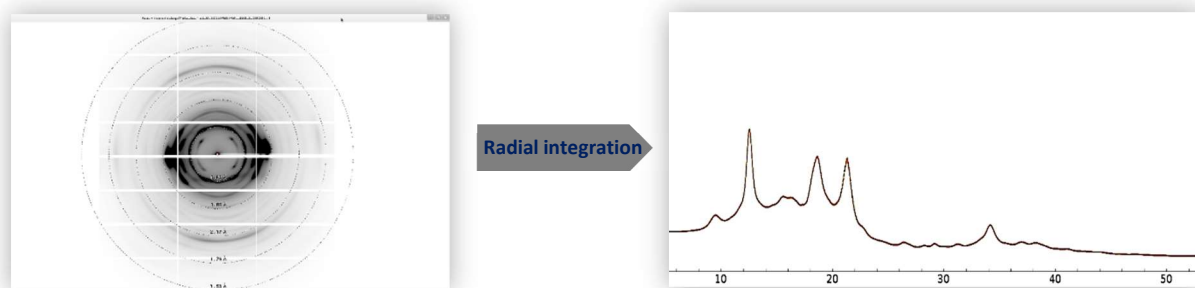


FIGURE 4.20: On the left, the diffraction pattern of PEN and, on the right, its radial integration. The diagram clearly shows the poly-crystalline nature of the PEN and also highlights some preferential directions of growth.

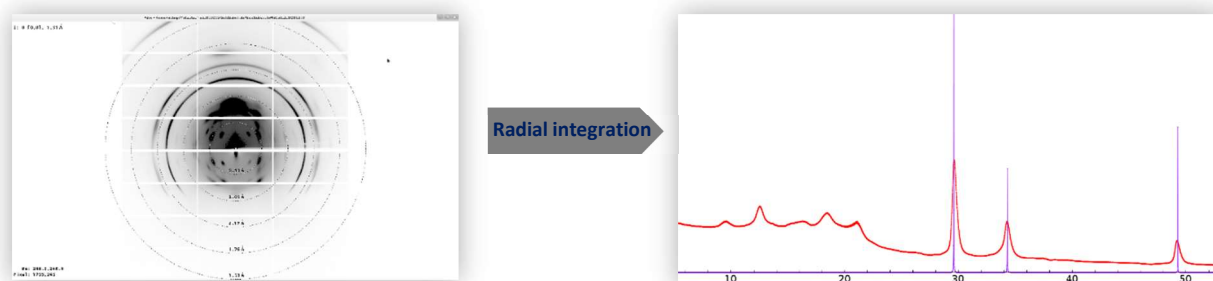


FIGURE 4.20: On the left, the diffraction pattern of Au and, on the right, its radial integration. The diagram clearly shows the poly-crystalline nature of the Au and also highlights the same preferential directions of growth already seen in PEN substrate.

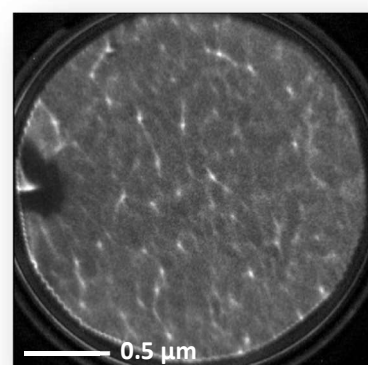


FIGURE 4.21: On the left, the cleaned Au electrode mounted inside the sample holder to be inserted into the UHV chamber. On the right, a typical micrograph obtained for the substrate.

4.7.1 DETERMINATION OF SAMs ON ELECTRODE SURFACE

A. SPLEEM

The result of a SPELEEM characterization carried out on a 4-mercaptobenzonitrile-treated electrode is shown in **FIGURE 4.22** (also the other SAMs have been probed, but for the sake of concision only the 4-mercaptobenzonitrile results are shown here, as this is the SAM that gave the best results in terms of final adhesion effectiveness) Besides a large Au 4f signal originating from the underlying gold film, the spectrum contains three features that can be assigned to the C 1s, N 1s and S 2p signals of the bounded SAM molecules. To derive precise information on the chemical nature of these elements within the SAMs molecule, the individual element spectra have been acquired. **FIGURE 4.22** shows the individual peaks for 4-mercaptobenzonitrile-SAMs on Au electrode. The N 1s core-level spectrum arises as a double component, peaking at around 248.5 and 249.3 eV. We hypothesize that this double signal is due to the fact that N occurs in two chemical environments, namely the intramolecular C-N bond and the intermolecular C-N bond. However, both a low cross section and a low photon flux density in the spectral region of the N 1s electron excitation prevented more exhaustive data to be acquired.

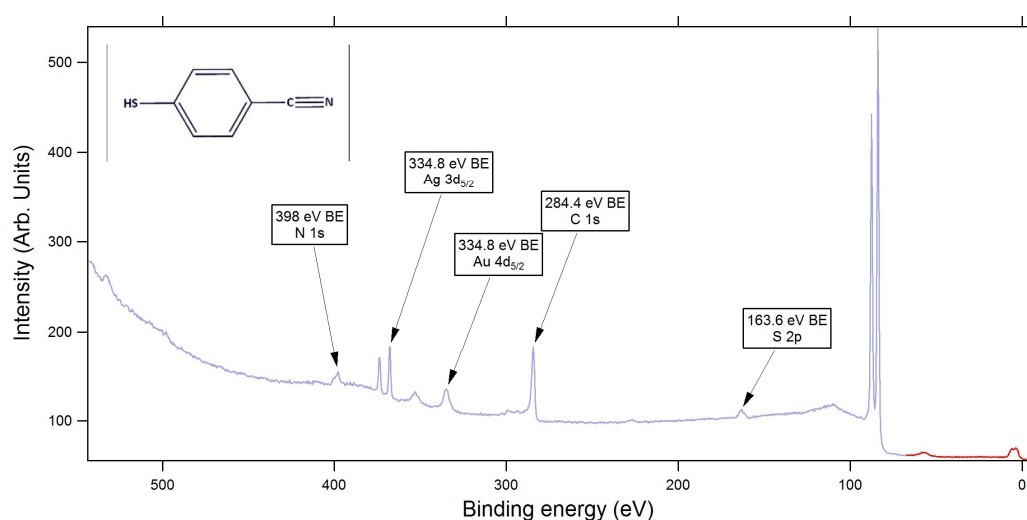


FIGURE 4.22: overview spectrum of 4-mercaptobenzonitrile -SAMs on polycrystalline Au.

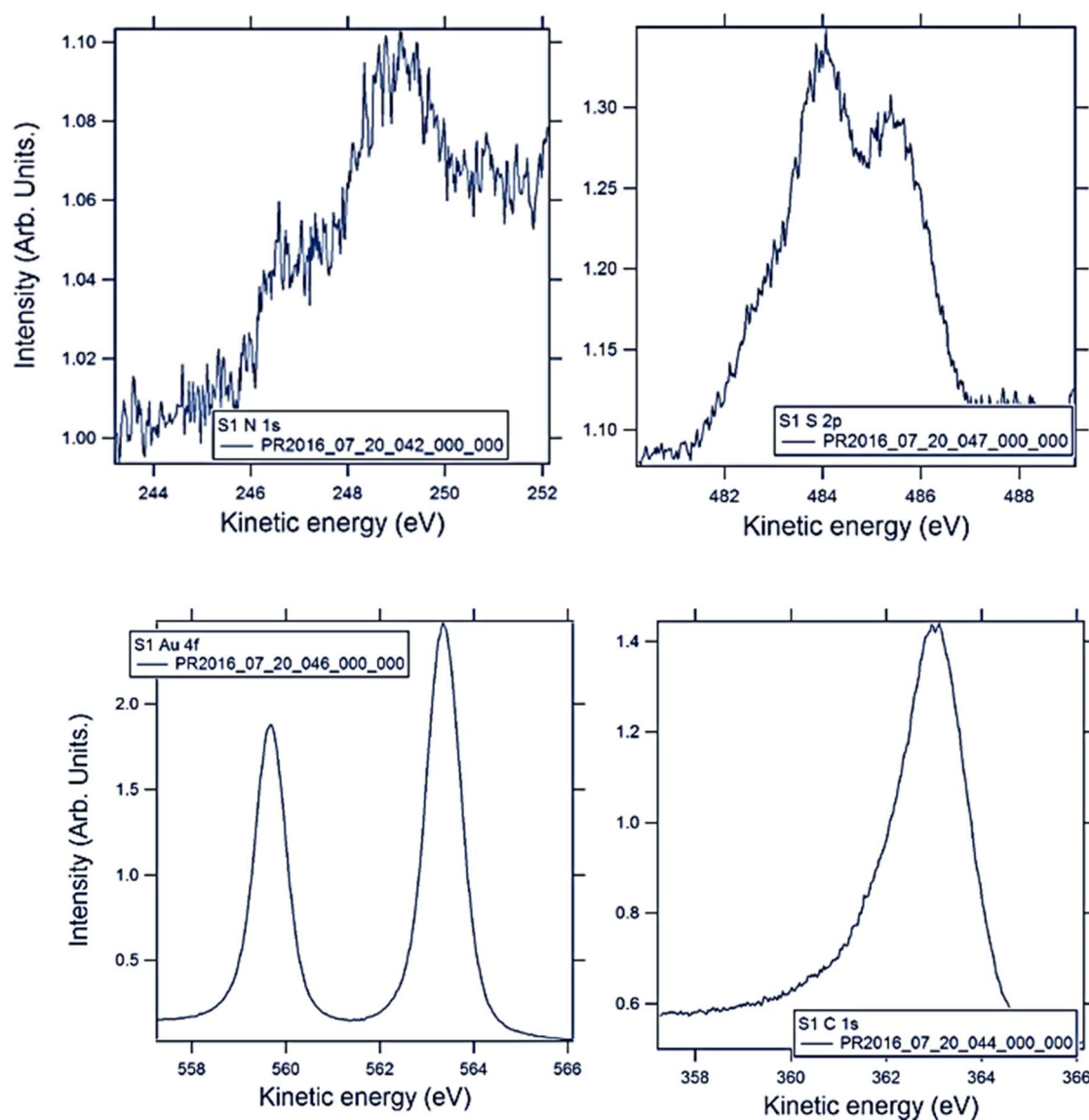


FIGURE 4.23: N 1s, S 2p and C 1s individual peaks of 4-mercaptobenzonitrile -SAMs attached via the thiol group to a Au layer

The S 2p spectrum consists of a dominant doublet. In agreement with experimental and theoretical data for other thiolates on gold surfaces, the S 2p peaks are assigned to bound and unbound sulphur groups, respectively^{73, 74}. The binding energy of a thiole molecule attached to the gold surface via the sulphur atom is expected to be lower than that of an unbound one, because the formation

of a 'covalent' bond is accompanied with charge transfer from the gold film to the sulphur atom.

The C 1s spectrum reveals always one maximum, also in the case of phenylethylthiol, where, based on literature^{69, 75}, three maxima were expected (the reason for this latter discrepancy has not been understood, yet). In general, all the tested SAMs evidenced the key point needed to ascertain the actual functionalization of the surface, i.e. the S 2p binding energies in line with those of a Au-S bond.

During these SPELEEM experiments, it has been observed that all the analysed layers are sensitive to soft X-ray radiation. In fact, as a result of the long-term exposure (higher than 30 min), changes in the spectrum have been observed. While this sensitivity did not affect the outcome of the presented measurements (each spectrum was acquired spanning different range of time and moving to a fresh zone every time), the mentioned changes clearly hint to a radiation-induced damage of the thiols molecules.

B. GI-XRD

Also GI-XRD have been attempted on the prepared SAMs. However, since the experiments were performed in standard atmosphere (i.e., not in UHV condition), no meaningful result have been obtained.

C. Conclusions

The core-level electronic structure of self-assembled thiols-layers on a gold substrate have been characterized by means of high-resolution SPELEEM analysis. The presence of all the peaks expected in the case of effective thiol-Au bond establishment indicates that the functionalization of the substrate had taken place, even though the technique is not able to give meaningful information on the degree of organization of the thiols on the considered gold surface. Long-term irradiation experiments on thiols layers revealed soft X-ray radiation-induced damage of the self-assembled monolayers.

4.7.1 OSSCs BINDING ON AU ELECTRODES SURFACE

A preliminary qualitative mechanical adhesion test has been carried out, trying to detach the crystal from the substrate (fixed onto a microscope glass) using a small spatula. The spatula was moved parallel to the microscope glass, trying to detach the crystal from the functionalized substrate via only tangential force (of course, in the limits of this manual procedure).

Under this test, not all the evaluated SAMs functionalizations provided a good adhesion of the crystal. Indeed 2 out of 5 systems functionalized with thiophenol lead to a detachment of the crystal from the electrode surface, leaving entirely the Au layer on PEN; 1 out of the 5 systems functionalized with phenylethylmercaptane lead to a detachment of the crystal from the functionalized electrode surface, again leaving entirely the Au layer on PEN. All the systems treated with 4-mercaptophenole and 4-mercaptobenzonitrile sustained successfully the first test. The same test has been carried out after two weeks. From these tests, it has been observed that the functionalizations with benzenethiole and 2-ethanethiole were not able to sustain an adhesion, while the other two SAMs withstood the test again, even though the functionalization with 4-mercaptophenol was less performing than that with 4-mercaptobenzonitrile (FIGURE 4.24). The general results of these tests are summarized in TABLE 4.

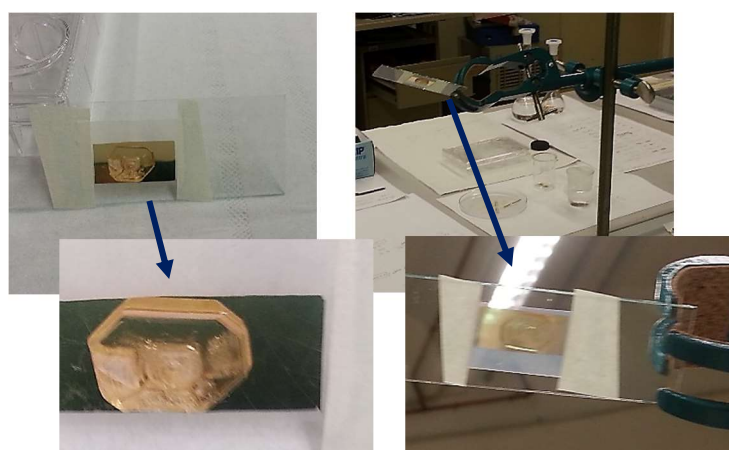


FIGURE 4.24: 4HCB single-crystal on the surface functionalized with 4-mercaptobenzonitrile. These images have been acquired after the second qualitative adhesion test.

EVALUATED THIOL	NUMBER OF EVALUATED SYSTEM	NUMBER OF CRYSTALS	NUMBER OF STABLE
		PASSING THE FIRST	SYSTEMS AFTER 2
		QUALITATIVE ADHESION TESTS	WEEKS
4-mercaptophenole	10	10	8 out of 10
4-mercaptobenzonitrile	10	10	10 out of 10
thiophenol	5	3	0 out of 3
phenylethylmercaptane	5	4	1 out of 4

TABLE 4: Results of realized qualitative adhesion test between self-standing crystals and functionalized electrodes.

During the second test some crystals have been broken due to an excessive force while trying to detach them from the electrode functionalized surface. It is worth mentioning that in all these cases Au layer was found on the crystal surface, suggesting in this way a stronger interaction between crystal-SAM-Au rather than Au-PEN. These results came at the end of the PhD project period. Therefore, it has not been possible to setup a quantitative adhesion test nor to optimize the functionalization of the electrode, which could result as an important point for the electrical contact between the semiconductor and the electrode. All these activities are programmed to be carried out as described in the **Chapter 5**. In any case, the devised method appeared to be rather effective for 4HCB, when the applied SAMs possess molecules able to establish H-bonds with the crystal molecules. This effectiveness appears to be much less marked when only π - π interactions are used the basis for the electrode-crystal adhesion.

BIBLIOGRAPHY

- ⁰¹ E. M. McCash: Surface Chemistry - Oxford University Press Inc. - New York - 2001;
- ⁰² D. Witt, R. Klajn, P. Barski and B. A. Grzybowski: Applications, Properties and Synthesis of ω -Functionalized n-Alkanethiols and Disulfides. The Building Blocks of Self-Assembled Monolayers - Curr. Org. Chem. - 8 - 1763÷1797 - 2004;
- ⁰³ B. Franklin, W. Brownrigg and M. Farish: Of the Stilling of Waves by means of Oil. Extracted from Sundry Letters between Benjamin Franklin, William Brownrigg and the Reverend Mr. Farish. - Philos. Trans. R. Soc. London – 64 - 445÷460 – 1774;
- ⁰⁴ A. Pockels: Surface tension- Nature - 43 - 437÷439 - 1891,
- ⁰⁵ I. Langmuir: The constitution and fundamental properties of solids and liquids. \$. Liquids - J. Am. Chem. Soc. – 39 -1848÷1906 - 1848,
- ⁰⁶ K. Blodgett: Monomolecular films of fatty acids on glass. - J. Am. Chem. Soc. – 56 – 495 – 1934;
- ⁰⁷ W. C. Bigelow, D. L. Pickett and W. A. Zism: Oleophobic monolayers. I. - J. Colloid Interface Sci. –1 - 513÷538 – 1946;
- ⁸ F. Schreiber: Structure and growth of selfassembling monolayers. - Prog. Surf. Sci.- 65 - 151÷256 – 2000;
- ⁹ K. D. Schierbaum, T. Weiss, E. U. Thoden van Velzen, J. F. J. Engbersen, D. N. Reinhoudt and W. Gopel: Molecular Recognition by Self- Assembled Monolayers of Cavitand Receptors. - Sci. – 265 - 1413÷1415 – 1994;
- ¹⁰ B.H. Huisman, R. P. H. Kooyman, F. C. J. M. van Veggel and D. N. Reinhoudt: Molecular recognition by self-assembled monolayers detected with surface plasmon resonance - Adv. Mater. - 8 - 561÷564 – 1996;
- ¹¹ D. J. Diaz, J. E. Hudson, G. D. Storrier, H. D. Abruna, N. Sauterajan and C. K. Ober: Lithographic Applications of Redox Probe Microscopy - Langmuir - 17 - 5932÷5938 -2001;

- ¹² C. Alain, M. Geissler, H. Schmid, B. Michel and E. Delamarche: Self-Assembled Monolayers of Eicosanethiol on Palladium and Their Use in Microcontact Printing – *Langmuir* – 18 - 2406÷2412 – 2002;
- ¹³ G. P. Lopez, H. A. Biebuyck, C. D. Frisbie and G. M. Whitesides: Imaging of features on surfaces by condensation figures - *Sci.* - 260 - 647÷652 – 1993;
- ¹⁴ S. Xu, S. Miller, P. E. Laibinis and G. Y. Liu: Fabrication of Nanometer Scale Patterns within Self-Assembled Monolayers by Nanografting - *Langmuir* – 15 - 7244÷7251 – 1999;
- ¹⁵ G. Y. Liu, S. Xu and Y. Qian: Nanofabrication of Self-Assembled Monolayers Using Scanning Probe Lithography - *Acc. Chem. Res.* - 33 - 457÷466 – 1999;
- ¹⁶ A. Ulman: An Introduction to Ultrathin Organic Films: From Langmuir--Blodgett to Self-Assembly - Academic Press - New York – 1991;
- ¹⁷ A. Ulman: Formation and Structure of Self-Assembled Monolayers - *Chem. Rev.* - 96 - 1533÷1554 -1996;
- ¹⁸ H. O. Finklea: *Electroanalytical Chemistry* - 19 - 109÷335 – 1996;
- ¹⁹ L. H. Dubois and R. G. Nuzzo: Synthesis, Structure, and Properties of Model Organic Surfaces - *Annu. Rev. Phys. Chem.* - 43 - 437÷463 – 1992;
- ²⁰ H. O. Finklea: *Encyclopedia of Analytical Chemistry* - Ed. R. A. Meyers – Wiley – 2000;
- ²¹ R. G. Nuzzo and D. L. Allara: Adsorption of bifunctional organic disulfides on gold surfaces - *J. Am. Chem. Soc.* – 105 - 4481÷4483 -1983;
- ²² Strong L. and Whitesides G. M., Structures of selfassembled monolayer films of organosulfur compounds adsorbed on gold single crystals: electron diffraction studies. *Langmuir*, 4, 546-558 (1988).
- ²³ C. D. Bain, J. Evall and G. M. Whitesides: Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solven - *J. Am. Chem. Soc.* – 111 – 7155÷7164 – 1989;

- ²⁴ P. E. Laibinis and G. M. Whitesides: Self-Assembled Monolayers of n-Alkanethiolates on Copper Are Barrier Films That Protect the Metal against Oxidation by Air - J. Am. Chem. Soc. – 114 - 9022÷9028 - 1992;
- ²⁵ J.M. Lehn: Supramolecular Chemistry – VCH – Weinheim- 1995;
- ²⁶ S. R. Hartshorn: Structural adhesives - Plenum Press - New York – 1986;
- ²⁷ L. Venkataraman, J. E. Klare, I. W. Tam, C. Nuckolls, M. S. Hybertsen and M. Steigerwald: Single-molecules circuits with well-defined molecular conductance – Nano Letters – 6 – 3 – 458÷462 – 2006;
- ²⁸ L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen and M. Steigerwald: Dependence of single-molecule junction conductance on molecular conformation – Nature Lett. - 442 – 904÷907 – 2006;
- ²⁹ Thomas Steiner : The Hydrogen Bond in the Solid State - Angew. Chem. Int. – 41 - 48 ÷ 76 - 2002;
- ³⁰ S.E. Kryachko and M. T. Nguyen : Hydrogen Bonding between Phenol and Acetonitrile, Hydrogen Bonding between Phenol and Acetonitrile - Phys. Chem. – 106 - 4267÷4271 – A – 2002;
- ³¹ A. Thote and R. B. Gupta: Hydrogen-bonding between a dichroic dye and a liquid crystal-forming molecule, for application to LCDs, Fluid Phase, Equilibria – 220 - 47÷55 – 2004;
- ³² A.R. Heiskanen, C.F. Spégel, N. Kostasheva, T. Ruzgas and J. Émneus: Monitoring of *Saccharomyces cerevisiae* cell proliferation on thiol-modified planar gold microelectrodes using impedance spectroscopy – Langmuir - 24 – 16 – 9066÷9073 – 2008;
- ³³ J. Kang, P.A. Rowntree: Gold film surface preparation for self-assembled monolayer studies - Langmuir - 23 – 509÷516 – 2007;
- ³⁴ L. M. Fischer, M. Tenje, A. R. Heiskanen, N. Masuda, J. Castillo, A. Bentien, J. Émneus, M. H. Jakobsen, A. Boisen: Gold cleaning methods for electrochemical detection applications - Microelectronic Engineering – 86 - 1282÷1285 – 2009;

- ³⁵ J. C. Hoogvliet, M. Dijksma, B. Kamp and W. P. van Bennekom: Gold Electrodes To Produce a Reproducible Surface Roughness for Self-Assembly - *Anal. Chem.* – 72 - 2016÷2021 – 2000;
- ³⁶ C. G. Worley and R. W. Linton: Removing sulfur from gold using ultraviolet/ozone cleaning - *J. Vac. Sci. Technol - A* 13(4) - 2281÷2284 – 2005;
- ³⁷ N. S. McIntyre, R. D. Davidson and T. L. Walzak: Uses of ultraviolet ozone for hydrocarbon removal: Applications to surface of complex composition or geometry - *Journal of Vacuum Science & Technology A Vacuum Surfaces and Films* – 9(3) – 1355÷1359 – 1991;
- ³⁸ M. J. Powers and T. J. Meyer: Medium and distance effects in optical and thermal electron transfer - *J. Amer Chem Soc* – 102 – 1289÷1297 - 1980;
- ³⁹ K. Kalyansundaram, J. Kiwi and M. Gratzel: Hydrogen Evolution from Water by Visible Light, a Homogeneous Three Component Test System for Redox Catalysis - *Helv. Chim. Acta* – 61 - 2720÷2730 – 1978;
- ⁴⁰ J. Kiwi and M. Grätzel: Hydrogen evolution from water induced by visible light mediated by redox catalysis - *Nature* - 281 - 657÷658 – 1979;
- ⁴¹ A. J. Bard and L. R. Faulkner: *Electrochemical Methods, Fundamentals and Applications* – John Wiley and Sons – New York – 1980;
- ⁴² D.D. MacDonald: *transient Techniques in Electrochemistry* – Plenum Press – New York – 1977;
- ⁴³ Z. Galus: *Fundamentals of Electrochemical Analysis* – John Wiley and sons – New York – 1977;
- ⁴⁴ T. Schmidt, S. Heun, J. Slezak, J. Diaz, K. Prince, G. Lilienkamp and E. Bauer: SPELEEM: combining LEEM and spectroscopic imaging - *Surf. Rev. Lett.* - 5 - 1287÷1296 – 1998;
- ⁴⁵ W. C. Marra, P. Eisenberger and A. Y. Cho: X-ray total-external-reflection–Bragg diffraction. A structural study of the GaAs-Al interface - *J. Appl. Phys.* – 50 - 6927 - 1979;
- ⁴⁶ K. N. Stoev and K. Sakura: Review on grazing incidence X-ray spectrometry and reflectometry - *Spectrochimica Acta - Part B* – 54 - 41÷82 - 1999;

- ⁴⁷ T. C. Huang and W. Parrish: Characterization of Single- and Multiple-Layer Films by X-Ray. Reflectometry - Adv. X-ray Anal. – 35 - 137÷142 – 1992;
- ⁴⁸ T. Ishida, S. Tsuneda, N. Nishida, M. Hara, H. Sasabe and W. Knoll: Surface-Conditioning Effect of Gold Substrates on Octadecanethiol Self-Assembled Monolayer Growth - Langmuir – 13 - 4638÷ 4643 -1997;
- ⁴⁹ N. S. McIntyre, R. D. Davidson, and T. L. Walzak R. Williston and M. Westcott A. Pekarsky: Uses of ultraviolet/ozone for hydrocarbon removal: Applications to surfaces of complex composition or geometry - J. Vac. Sci. Technol. – 9 - 1355÷1359 - 1991,
- ⁵⁰ C. G. Worley and R. W. Linton: Removing sulfur from gold using ultraviolet/ozone cleaning - J. Vac. Sci. Technol. - 13 - 2281÷2284 - 1995.
- ⁵¹ Szymanski S.D: March Plasma Systems – Concord – CA - 2007;
- ⁵³ A.R. Heiskanen, C.F. Spégel, N. Kostesha, T. Ruzgas, J. Émneus: Monitoring of *Saccharomyces cerevisiae* cell proliferation on thiol-modified planar gold microelectrodes using impedance spectroscopy - Langmuir - 24 – 16 - 9066÷9073 – 2008;
- ⁵⁴ C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesider and R. G Nuzzo: Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solven - *J. Am. Chem. Soc.* – 111 – 7155÷7164 – 1989;

- ⁵⁵ M. Kawasaki, T. Sato, T. Tanaka, and K. Takao: Controlled Layering of Two-Dimensional J-Aggregate of Anionic Cyanine Dye on Self-Assembled Cysteamine Monolayer on Au(111) - *Langmuir* - 16 - 5409÷5417 – 2000;
- ⁵⁶ R. Yamada, H. Wano, K. Uosaki: Effect of Temperature on Structure of the Self-Assembled Monolayer of Decanethiol on Au(111) Surface- *Langmuir* - 16 - 5523÷5525- 2000;
- ⁵⁷ C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo: Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold - *J. Am. Chem. Soc.* – 111 – 321÷335 – 1989;
- ⁵⁸ L. Sun, R. M. Crooks: Imaging of Defects Contained within *n*-Alkylthiol Monolayers by Combination of Underpotential Deposition and Scanning Tunneling Microscopy: Kinetics of Self-Assembly - *J. Electrochem. Soc.* – 138 - L23÷L25 – 1991;
- ⁵⁹ R. H. Terrill, T. A. Tanzer and P. W. Bohn: Surface Damage Characteristics of Self-Assembled Monolayers of Alkanethiols on Metal Surfaces -*Langmuir* - 14 – 845÷854 – 1998;
- ⁶⁰ C. E. D. Chidsey: Free Energy and Temperature Dependence of Electron Transfer at the Metal-Electrolyte Interface - *Science – Washington* - 251 – 835÷844 - 1991,
- ⁶¹ M. M. Rahman and M. N. Hasan: Compound Semiconductor Epitaxial Growth Techniques - *Int. J. Thin. Fil. Sci. Tec.* – 5 - 1 - 45÷49 – 2016;
- ⁶² J. Palisaitis and R. Vasiliauskas: Epitaxial growth of thin films - *Physics of Advanced Materials – Winter school* – 2008;
- ⁶³ R.W.Kelsall, I.Hamley and M.Geoghegan: Nano scale science and technology - *Wiley* - New York – 2005;
- ⁶⁴ K. Byrappa and T. Ohachi: *Crystal Growth Technology* – Springer - New York – 2003;
- ⁶⁵ E. Rosencher: *Optoelectronics* - Cambridge University Press - 2002;
- ⁶⁶ R.J. Malik and F.F.Y. Wang: III-V-Semiconductor Materials, Devices and Materials Processing. Theory and Practices - R.J. Malik – 7 - *North-Holland – Amsterdam* – 1989;

-
- ⁶⁷ G. K. Wertheim, S. B. DiCenzo, and S. E. Youngquist: Unit Charge on Supported Gold Clusters in Photoemission Final State - *Phys. Rev. Lett.* – 51 – 2310÷2313 - 1983,
- ⁶⁸ J.J. Pireaux, M. Liehr, P. A. Thiry, J. P. Delrue, R. Caudano: Electron spectroscopic characterization of oxygen adsorption on gold surfaces: II. Production of gold oxide in oxygen DC reactive sputtering - *Surf. Sci.* - 141 - 221÷232 -1984,
- ⁶⁹ A. J. Brad and L. R. Faulkner: *Electrochemical Methods: Fundamentals and Applications* – Wiley – New York – 2000;
- ⁷⁰ H. Kim and D. Kim: Effect of surface roughness of top cover layer on the efficiency of dye-sensitized solar cell - *Solar Energy* - 86 - 2049÷2055 – 2012;
- ⁷¹ A. Douillard, C. Hakme, L. David, I. Stevenson, G. Boiteux, G. Seytre, T. Kazmierczak, A. Galeski: Morphology and Texture Development of Uniaxially Stretched Poly(ethylene naphthalene-2,6-dicarboxylate) - *J. Appl. Polym. Sci.* – 103 - 395÷401 - 2007;
- ⁷² A. Locatelli, L. Aballe, T.O. Menteş, M. Kiskinova and E. Bauer: Photoemission electron microscopy with chemical sensitivity: SPELEEM methods and applications - *Surf. Interface Anal.* – 38 - 1554÷1557 -2006;
- ⁷³ A. Shaporenko, A. Terfort, M. Grunze and M. Zharnikov: X-ray spectroscopy characterization of self-assembled monolayers of nitrile-substituted oligo(phenylene ethynylene)s with variable chain length - *J. Electron Spectrosc. Related Phenom.* - 151 – 12÷24 – 2006;
- ⁷⁴ D.G. Castner, K. Hinds and D.W. Grainger: X-ray Photoelectron Spectroscopy Sulfur 2p Study of Organic Thiol and Disulfide Binding Interactions with Gold Surfaces - *Langmuir* - 12 – 5083÷5086 – 1996;
- ⁷⁵ K. Kummer, D. V. Vyalikh, G. Gavrilina and S. L. Molodtsov: High-resolution photoelectron spectroscopy of self-assembled mercaptohexanol monolayers on gold surfaces - *Journal of Electron Spectroscopy and Related Phenomena* - 163 - 59÷64 - 2008;

CHAPTER 5: Conclusions

5.1 CONCLUSIONS

Summarizing the overall work carried out, during these three years, the following main activities have been carried out:

1. Screening of different semiconductor structures able to provide single-crystals suitable for x-ray detection,
2. Optimization of the crystallization process to obtain crystals with suitable size and morphology,
3. Investigations over possible bonding procedures to physically promote the adhesion of free-standing single-crystals to the underlying electrodes.

Upon these activities a number of interesting results have been achieved and are presented hereafter.

In the first step of work, by growing different semiconductors from solutions in quasi-equilibrium conditions and with lab-scale methods, it was possible to identify those couple organic semiconductor/solvent able to provide the best organic semiconducting single crystals. Among all the grown single crystals, structures able to effectively detect X-rays have been selected in the frame of the i-Flexis project.

The second step of the work has allowed to properly tuning all the evaluated growth parameters in order to optimize the crystallization yield with respect to:

1. number of recovered single-crystals (in the present case the lower the number of recovered crystals, the better the result),
2. sizes of the crystals (in the present case the larger the size the better the result).

Experiments were focused on the two most representative semiconductors properly selected in the first part of the work, namely 4HCB - as a representative of platelet-like crystal - and NTI - as a representative of needle-shaped crystal. Moreover it has been demonstrated that, by changing the crystal growth parameters, it is also possible to properly tune the crystal surface morphology, obtaining extremely smooth surfaces. The obtained evidences suggest that an analogous approach could be successful to achieve the control over different organic semiconductor/solvent couple.

The last step of the work has allowed to test a possible way to effectively join the self-standing crystals to an underlying electrode. In particular, to achieve this result, the electrode has been functionalized with properly chosen self-assembled monolayers, able to establish non-covalent interactions with those pending at the single-crystal interface, that are structurally similar with SAMs themselves. Although the effectiveness of this approach has been tested only at qualitative level, first results in this sense are very promising and they prompt to a deeper investigation on the approach.

5.2 FUTURE PERSPECTIVES

Based on the promising first results of the adhesion process, the following steps are planned in order to set-up a possible reliable protocol to connect single-crystals to the electrodes:

1. Obtaining a good control over the functionalization of the electrode,
2. Characterization of the electrical transport taking place at the properly functionalized electrodes,
3. Definition of a quantitative protocol to define the adhesion entity of the physically adherent interfaces.

The first step of the planned work is particularly challenging since the real interface is characterized by roughness values that limit the application of the most part of the characterization techniques. Nevertheless, a comparison between the systems evaluated in

this work and a reference system (Au(111) single-crystal properly functionalized with a single layer of the selected thiols) could be beneficial to the purpose, via XPS measures. This is indeed the approach planned.

To carry on the second step of the planned work CV and EIS measures will be exploited.