

In situ studies of conjugated polymers by X-ray diffraction techniques

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Abstract

In this thesis conjugated materials are investigated, with a focus on (semi)conductive polymers and oligomers. These materials are promising candidates for use in organic electronics, such as thin-film organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVs). The aim is to elucidate structure-property relationships of active layers of conjugated organic thin films that influence device performance.

The structural investigation spans length scales from millimeters, corresponding to macroscopic device architecture, down to nanometers in the range of single crystalline domain sizes, that govern molecular stacking and crystalline order. Such complex structural information is essential for correlating multiscale ordering with device performance.

X-ray diffraction is a common technique for structural studies of thin films. However, conventional X-ray laboratory sources lack the brilliance to resolve these features at an advanced level. Therefore, this work is carried out at high-brilliance synchrotron facilities that enable high spatial and temporal resolution X-ray scattering and diffraction studies of active thin film layers. Even at synchrotron light facilities, small- and wide-angle X-ray scattering at conventional beamlines provide average device structures, while advanced nano-focused beamlines enable spatially resolved measurements and localized mappings across device cross-sections with nanometer precision.

Besides high-resolution measurements, in situ experimentation is a central part of the thesis. In situ annealing studies show how thermal treatment alters structural properties and its effect on electrical device performance. Understanding annealing dynamics and appropriate thermal budgets is beneficial for processing optimization and for developing robust fabrication protocols.

In addition to annealing, other external factors may also have an influence on the structural organization of the film. This work reveals how structural order is affected by an external electric field during film formation, highlighting possibilities for morphology control. The application of a permanent electric field to P3HT induces non-equilibrium aggregation, leading to reduced crystallinity, smaller crystallite size, and increased structural disorder. Such changes provide the advantages to tune morphology, including expanded interfacial area and enhanced nanoscale

heterogeneity. In contrast, an alternating electric field allows partial relaxation of polymer chains, resulting in a more equilibrium-like structure with preserved crystallinity.

Finally, in operando studies provide direct insights into the structure and electrical response, tracking voltage-induced structural alterations and lattice responses under working conditions.

The outcomes of this research include:

- In situ studies of conjugated polymer film formation reveal structural changes under an external electrical field. The quality of structural order and the size of crystalline domains can be modified during P3HT drop-casting. This effect is greater with a permanent electrical field than with an oscillating field. While the disordered morphology induced by a permanent field is unfavorable for charge transport in transistors, it can be advantageous for applications such as organic solar cells with increased interfacial area and nanoscale heterogeneity.
- The thermal protocol during annealing has a strong effect on structural order. In situ annealing studies show that a low thermal budget preserves and improves the microstructure of polymer-fullerene blends. In contrast, a P3HT:PCBM blend undergoes permanent, irreversible changes during the high thermal budget annealing with PCBM crystallization and phase separation. The structural order of PDOPT decreases until melted but recovers when returning to room temperature at a significantly enhanced level.
- X-ray nanobeam diffraction on quasi-freestanding P3HT films demonstrates the feasibility of high spatial resolution diffraction studies on organic thin films revealing local orientation variations. This method is ideal for the investigation of the local crystal structure of organic semiconductors while minimizing substrate induced contributions. Using an extremely focused X-ray beam (spot size approximately 150 nm), local variations in orientation and symmetry within the polymer network are directly detectable.

- Nanobeam grazing incidence diffraction (nanoGIXD) experiments revealed a strong gold reorientation and modifications of Au-polymer interfaces during device operation which can be detrimental for applications.
- In-operando nanoGIXD measurements revealed a significant anisotropy of the oligomer thin films, under source-drain applied voltages with strong structural variations for both in-plane and out-of-plane directions, including a +1.3 % tensile expansion of the π -stacking distance (d_{020}). The outcomes underline that high resolution X-ray diffraction techniques are excellent tools for spatially and temporally resolved studies of conjugated organic thin films. The results can support the device processing optimization and development of robust fabrication protocols.

Zusammenfassung

In dieser Arbeit werden konjugierte Materialien untersucht, mit Schwerpunkt auf (halb)leitenden Polymeren und Oligomeren. Diese Materialien sind vielversprechende Kandidaten für den Einsatz in der organischen Elektronik, etwa in organischen Dünnschicht-Feldeffekttransistoren (OFETs) und organischen Photovoltaikzellen (OPVs). Ziel ist es, Struktur-Eigenschafts-Beziehungen aktiver konjugierter organischer Dünnschichten aufzuklären, die die Leistung solcher Bauelemente beeinflussen.

Die strukturellen Untersuchungen erstrecken sich über Längenskalen von Millimetern, die der makroskopischen Bauteilarchitektur entsprechen, bis hin zu Nanometern im Bereich einzelner kristalliner Domänengrößen, die das molekulare Stapeln und die kristalline Ordnung bestimmen. Derartige komplexe Strukturinformationen sind unerlässlich, um die Ordnung mit der Bauelementleistung auf verschiedenen Größenskalen zu korrelieren.

Röntgenbeugung ist eine gängige Methode zur strukturellen Untersuchung von Dünnschichten. Herkömmliche Röntgenlaborquellen besitzen jedoch nicht die erforderliche Brillanz, um diese Merkmale aufzulösen. Daher wird diese Arbeit an hochbrillanten Synchrotronanlagen durchgeführt, die Röntgenstreuungs- und -beugungsstudien aktiver Dünnschichten mit hoher räumlicher und zeitlicher Auflösung ermöglichen. Auch an Synchrotronlichtquellen liefern konventionelle Messplätze mit Klein- und Weitwinkelröntgenstreuung lediglich gemittelte Strukturinformationen der Bauteile, während fortschrittliche, nanofokussierte Messplätze hochaufgelöste Messungen der lokalen Struktureigenschaften über Bauteilquerschnitte mit Nanometergenauigkeit ermöglichen.

Neben hochauflösenden Messungen ist die In-situ-Untersuchung der Materialien ein zentraler Bestandteil der Arbeit. In-situ-Annealing-Studien zeigen, wie thermische Behandlung strukturelle Eigenschaften der konjugierten Materialien verändert und wie sich dies auf die elektrische Leistung der Bauelemente auswirkt. Aus den Ergebnissen der Annealing-Studien lassen sich geeignete thermische Protokolle ableiten, die für die Herstellungsoptimierung vorteilhaft sind.

Neben Annealing können auch andere äußere Einflüsse die strukturelle Organisation der dünnen Filme beeinflussen. Diese Arbeit zeigt, wie die strukturelle Ordnung durch ein externes elektrisches Feld während der Filmbildung beeinflusst wird und zeigt Möglichkeiten zur Kontrolle der Film-Morphologie auf. Die Anwendung eines permanenten elektrischen Feldes auf P3HT induziert Aggregationen innerhalb des Films, die zu verringerter Kristallinität, kleineren Kristallitgrößen und reduzierter struktureller Ordnung führen. Solche externen Einflüsse bieten den Vorteil, die Film-Morphologie gezielt zu steuern, wie Vergrößerung der Oberfläche und verbesserte strukturelle Heterogenität auf Nanoskala. Im Gegensatz dazu erlaubt ein alternierendes elektrisches Feld die partielle Relaxation der Polymerketten, was zu einer gleichgewichtsähnlicheren Struktur mit erhaltener Kristallinität führt.

In-operando-Studien liefern direkte Einblicke in die Struktur und das elektrische Verhalten und verfolgen spannungsinduzierte strukturelle Änderungen unter Betriebsbedingungen.

Die Ergebnisse dieser Forschung umfassen:

- In-situ-Studien der konjugierten Polymerfilmbildung zeigen strukturelle Veränderungen unter einem externen elektrischen Feld. Die Qualität der strukturellen Ordnung und die Größe der kristallinen Domänen können während des P3HT-Filmbildung verändert werden. Dieser Effekt ist bei einem permanenten elektrischen Feld stärker als bei einem oszillierenden Feld. Während die durch ein permanentes Feld induzierte ungeordnete Morphologie für den Ladungstransport in Transistoren ungünstig ist, kann sie für Anwendungen wie organische Solarzellen durch eine vergrößerte Oberfläche und struktureller Heterogenität vorteilhaft sein.
- Das thermische Protokoll beim Annealing hat einen starken Einfluss auf die strukturelle Ordnung. In-situ-Annealing-Studien zeigen, dass ein niedriges thermisches Budget die Mikrostruktur von Polymer-Fulleren-Mischungen erhält und verbessert. Im Gegensatz dazu erfährt eine P3HT:PCBM-Mischung beim Annealing mit höherer Temperatur permanente, irreversible Veränderungen wie PCBM-Kristallisation und Phasenseparation. Die strukturelle Ordnung von PDOPT nimmt ab bis zur Schmelze, erholt sich jedoch beim Abkühlen auf Raumtemperatur auf einem deutlich erhöhten Niveau.

- Röntgen-Nanostrahl-Beugung an quasi-freistehenden P3HT-Filmen zeigt die Machbarkeit hochauflösender Beugungsstudien an organischen Dünnschichten und zeigt lokale Orientierungsvariationen auf. Diese Methode eignet sich ideal zur Untersuchung der lokalen Kristallstruktur organischer Halbleiter bei der ein substratinduzierter Beitrag minimal gehalten wird. Mit einem extrem fokussierten Röntgenstrahl (Spotgröße ca. 150 nm) sind lokale Variationen in Orientierung und Symmetrie innerhalb des Polymernetzwerks direkt detektierbar.
- Nanostrahl-Beugungsexperimente unter streifendem Einfall (nanoGIXD) an organischen Dünnschicht-Transistoren zeigen während des Betriebs eine starke Goldreorientierung und Modifikationen der Gold-Polymer-Grenzflächen, die für Anwendungen nachteilig sein können.
- In-operando-nanoGIXD-Messungen zeigen eine ausgeprägte Anisotropie der Oligomer-Filme in Dünnschichttransistorgeometrie unter angelegten Source-Drain-Spannungen, mit starken strukturellen Variationen sowohl in-plane als auch out-of-plane, einschließlich einer spannungsinduzierten Ausdehnung des π -Stapelabstands (d_{020}) um +1,3 %. Die Ergebnisse unterstreichen, dass hochauflösende Röntgenbeugungstechniken ausgezeichnete Werkzeuge für räumlich und zeitlich aufgelöste Studien konjugierter organischer Dünnschichten sind. Die Ergebnisse können die Prozessoptimierung der Bauelemente und die Entwicklung robuster Herstellungsprotokolle unterstützen.

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Symbols

Remarks regarding the typesetting: There are various typographical conventions differing from journal to journal and country to country. Throughout this thesis the symbols representing variables, physical quantities and physical constants are typeset in *italics*, whereas mathematical constants and functions, units as well as labels that do not represent physical quantities are upright. Vectors and matrices are represented by **boldface** letters; magnitudes of vectors are non-bold typeface.

Some symbols have multiple definitions. Their meaning should be clear from the context.

α, β, γ	angles between basis vectors of real lattice
α_c	critical angle of total external reflection
α_f	angle between scattered X-ray beam and sample surface
α_i	angle between incident X-ray beam and sample surface
α_t	angle between transmitted X-ray beam and sample surface
β	absorption part (imaginary part) of complex refractive index
δ	refractive part of complex refractive index
ζ	mixing parameter ($0 \leq \zeta \leq 1$)
2θ	scattering angle (angle between $\mathbf{k}_i$ and $\mathbf{k}_f$)
$2\theta_h$	horizontal component of scattering angle
$2\theta_v$	vertical component of scattering angle
λ	X-ray wavelength
Λ	penetration depth
μ	mobility; linear absorption coefficient
$\mu_{m, \text{air}}$	mass absorption coefficient of air
ν	X-ray frequency
ρ_e	electron density
ρ	mass density
σ	conductivity

ϕ	azimuthal angle in the $q_{\parallel}q_{\perp}$ -plane
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	basis vectors of crystallographic unit cell
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	basis vectors of reciprocal lattice
c	velocity of light in vacuum
C_{diel}	areal capacitance of gate dielectric
d	interplanar distance; film thickness
D	distance between sample and detector; diffusion coefficient
e	elementary charge
E	photon energy; electric field intensity
E_{g}	energy of band gap
f	atomic form factor
F	structure factor
F^*	complex conjugate of structure factor
$\mathbf{G}$	reciprocal lattice point vector
h	Planck's constant; height of X-ray beam
$\hbar$	reduced Planck's constant $\hbar = \frac{h}{2\pi}$
hkl	Miller indices of Bragg reflection
(hkl)	Miller indices of lattice plane
I	intensity of X-rays
I_0	intensity of incident X-ray beam
I_{SD}	source-drain current
$\mathbf{J}$	current density
$\mathbf{k}$	wave vector
k_{B}	Boltzmann constant
$\mathbf{k}_{\text{i}}$	wave vector of incoming X-ray beam
$\mathbf{k}_{\text{f}}$	wave vector of scattered X-ray beam
$\mathbf{k}_{\text{i,L}}$	wave vector of incoming X-ray beam in laboratory reference frame
$\mathbf{k}_{\text{f,L}}$	wave vector of scattered X-ray beam in laboratory reference frame

K	dimensionless constant
L	Lorentz factor; channel length
m	order of reflection
M	Molecular weight
M_n	number average molecular weight
M_w	weight average molecular weight
n	refractive index; charge carrier density
$\mathbf{p}$	momentum vector
P	polarization factor
p_x, p_z	pixel size in $\hat{\mathbf{x}}_d$ and $\hat{\mathbf{z}}_d$ direction, respectively
$\mathbf{q}$	scattering vector, wave vector transfer
$\hat{\mathbf{q}}_{x_L}, \hat{\mathbf{q}}_{y_L}, \hat{\mathbf{q}}_{z_L}$	coordinate system axes of reciprocal space in laboratory reference frame
$\hat{\mathbf{q}}_x, \hat{\mathbf{q}}_y, \hat{\mathbf{q}}_z$	coordinate system axes of reciprocal space in sample surface reference frame
$q_\perp$	out-of-plane component of scattering vector (normal to sample surface) in sample surface reference
$q_\parallel$	in-plane component of scattering vector (parallel to sample surface) in sample surface reference
$\mathbf{r}$	position vector
r_e	classical electron radius
$\mathbf{R}$	lattice vector
$\mathbf{R}_x$	rotation matrix around x -axis
$\mathbf{R}_x^{-1}$	inverse rotation matrix around x -axis
t	crystallite size, size of coherently scattering domains
T	temperature
$\mathbf{v}_d$	drift velocity
V	voltage

V_G	gate voltage
V_{SD}	source-drain voltage
V_T	threshold voltage
W	channel width
$\hat{x}_L, \hat{y}_L, \hat{z}_L$	coordinate system axes in laboratory reference frame
$\hat{x}_s, \hat{y}_s, \hat{z}_s$	coordinate system axes in sample surface reference frame
$\hat{x}_d, \hat{z}_d$	coordinate system axes of coordinate system related to the detector

1 Introduction

Conjugated polymers offer several advantages, including simple solution processing, low cost, mechanical flexibility, and the potential for chemical modification. These polymers are important for a wide range of applications in organic electronics, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), sensors and many more. To boost the performance of known conjugated polymers and to tailor novel materials with enhanced electrical properties, it is necessary to understand the underlying principles of charge transport in these materials.

A wide range of electrical devices is typically realized in thin-film geometries, and numerous parameters can influence the electrical performance of such devices, e.g. processing conditions (temperature, choice of solvent, pressure, coating method, external electrical or magnetic fields, etc.). A variation of these parameters can alter the morphology, structure and orientation of the thin-film device, which in turn affects the electrical properties of the material. Therefore, it is desirable to have precise control over the film fabrication conditions and to understand the relation between structural, orientational and electrical properties.

With the advent of nanobeam synchrotron facilities, measurements of unprecedented spatial resolution were made possible. In situ measurements allow for insight into structural development and changes during film fabrication or treatment.

Despite extensive structural and device studies on conjugated systems, several questions remain unresolved at the level addressed in this thesis. First, it is not established whether external electric fields applied during solution casting of P3HT can be exploited as a tool to tune crystalline order/disorder. Moreover, the role of field type (static vs. oscillating) is largely unclear. Second, the thermal-budget dependence of structural reversibility in P3HT and its bulk-heterojunction blends with PCBM and ICBA remains unclear, in particular whether beneficial annealing conditions can be separated from regimes that trigger irreversible phase separation or polymer melting. This has not been studied systematically by in situ GIXD. Third, although conventional diffraction has been widely applied to organic thin films, the local structural dynamics of operating, real-sized OFETs at the polymer channel and at the metal–polymer interfaces have remained largely inaccessible. Fourth, it is open

whether X-ray nanobeam diffraction can be successfully applied to locally probe quasi-free-standing organic films in transmission geometry that removes the substrate as a scattering background and grants direct access to a wide range of crystallite orientations. This information is inaccessible in conventional grazing incidence geometry due to averaged measurements caused by large beam dimensions. In particular, real-sized working OFETs have been characterized almost exclusively by ensemble-averaged diffraction or by ex situ microscopy, leaving the local response of the polymer channel and of the gold source–drain electrodes during device operation essentially unaddressed. Spatially resolved nanoGIXD scanning across the channel and over the electrode edges offers a capability to detect contact-region modifications, gold-electrode reorientation and Au–polymer interface changes that are washed out in the area-averaged signal.

The thesis is organized as follows. Chapter 2 introduces the concepts of organic electronic devices relevant to this work, including charge-carrier mobility, charge transport in conjugated thin films, the operating principles of thin-film OFETs, and the deposition and substrate-preparation techniques used here. Chapter 3 develops the X-ray methodology employed throughout this thesis: elastic scattering and Bragg diffraction, refraction at grazing incidence, X-ray reflectivity, two-dimensional grazing incidence X-ray diffraction including detector calibration and pixel-to- q conversion, the relevant synchrotron sources, and the treatment of radiation damage. Chapter 4 presents in situ GIXD studies of conjugated thin films under three external perturbations: first, drop-casting in static and oscillating electric fields (4.1), second, two-step thermal annealing of P3HT and of P3HT:PCBM and P3HT:ICBA blends (4.2), and third, the recrystallization behavior of PDOPT across its melting transition (4.3). Chapter 5 deals with X-ray nanobeam diffraction, demonstrating transmission nanoXRD on quasi-free-standing P3HT films (5.1), spatially resolved nanoGIXD of working P3HT OFETs and the resulting electrode-reorientation finding (5.2), and in operando nanoGIXD of oligomer OFETs revealing reversible and residual lattice strain under source–drain bias (5.3). Chapter 6 consolidates the structural conclusions across all studies, Chapter 7 provides a condensed summary, and Chapter 8 outlines an outlook for follow-up work, including device-relevant deposition control and extension of the nanobeam techniques to multilayer and flexible systems.

2 Concepts of organic electronic devices

2.1 General aspects of mobility

The charge carrier mobility μ is a measure of how quickly charge carriers (e.g. electrons, holes) can travel through a material. It is defined by the drift velocity $\mathbf{v}_d$ of the carriers under an applied electric field $\mathbf{E}$

$$\mu \mathbf{E} = \mathbf{v}_d . \quad (2.1)$$

The Einstein relation links the mobility to the diffusion coefficient D

$$\mu = \frac{eD}{k_B T} , \quad (2.2)$$

where e is the elementary charge, k_B is the Boltzmann constant and T the temperature.

Conductivity σ is a similar measure but includes the charge carrier density n and is related to mobility via

$$\sigma = en\mu \quad (2.3)$$

and relates the resulting current density $\mathbf{J}$ to the applied electric field $\mathbf{E}$:

$$\sigma \mathbf{E} = \mathbf{J} . \quad (2.4)$$

There are different experimental techniques to determine mobility, most of which measure it on a macroscopic scale (μm to mm). These methods make use of different physical effects.

The time-of-flight method measures the transient current through the channel between two electrodes as a function of time after the generation of charges near one of the electrodes using a laser [Kep60, LeB60, Cor07] or a voltage pulse [Wei09]. Mobility can be deduced from the observed transport times.

Another approach is the extraction of the mobility from the electrical characteristics of a field-effect transistor [Bra09]. The source-drain current I_{SD} is measured as a function of source-drain voltage V_{SD} at different gate voltages V_G . At low V_{SD} , the

source-drain current increases linearly (linear regime) and levels off and saturates at higher source-drain voltages (saturation regime).

Suffice it to mention at this point the equations for the source-drain current in the linear and saturation regimes. A more detailed discussion on the working principle of OFETs is given in Chapter 2.3.

Linear regime [Bra09]:

$$I_{\text{SD}} = \frac{W}{L} \mu C_{\text{diel}} \left(V_{\text{G}} - V_{\text{T}} - \frac{V_{\text{SD}}}{2} \right) V_{\text{SD}} \quad (2.5)$$

Saturation regime [Bra09]:

$$I_{\text{SD,sat}} = \frac{W}{2L} \mu C_{\text{diel}} (V_{\text{G}} - V_{\text{T}})^2 \quad (2.6)$$

where W is the channel width, L the channel length and C_{diel} the areal capacitance of the gate dielectric and V_{T} the threshold voltage.

Plotting $\sqrt{I_{\text{SD,sat}}}$ versus V_{G} allows for extraction of the mobility from the slope $s = \sqrt{\frac{W}{2L} \mu C_{\text{diel}}}$ of the resulting straight line.

In order to understand the origin and mechanisms of charge transport, it is necessary to take a closer look at the bonding nature and molecular structure, which are discussed in the following paragraph.

2.2 Charge transport in organic thin films

Organic semiconductors have several benefits over their inorganic counterparts, but they also have certain disadvantages. The most salient properties of organic and inorganic semiconductors are presented in the following paragraphs and are summarized as a comparison in Table 2.1.

Many differences in properties between organic and inorganic semiconductors originate from the different bonding nature. Inorganic semiconductors like silicon (Si), germanium (Ge) or gallium arsenide (GaAs) are covalently bonded and form a

lattice. Compared to other types of bonds, covalent bonds are strong (approximately 5 – 10 eV per bond), resulting in high hardness and rigidity as well as high melting temperatures. Consequently, processing inorganic semiconductors typically requires high temperature and vacuum processes.

Table 2.1: Comparison of properties of inorganic and organic semiconductors

Inorganic semiconductors	Organic semiconductors
• covalent bonds • hard, rigid • high melting temperatures • expensive processing involving vacuum and high temperature • crystalline, periodic structure • band structure • strong electronic delocalization • high mobility • good stability	• van der Waals bonded • softer, mechanically flexible • lower melting temperature • cheap solution-based processing at room temperature • poor crystallinity, twisting and bending • no bands but HOMO and LUMO • weaker delocalization • lower mobility • environmental stability and degradation can be an issue • chemical functionalization

Electronic states in such crystalline solids can be described by a band model. The orbitals of individual atoms combine to form molecular orbitals, which are split into bonding and antibonding levels. The number of these energy levels is proportional to the number of atoms. Due to the large number of atoms ($\sim 10^{23}$), the energy levels are so densely distributed that they can be treated as continuous energy bands. These bands are separated by band gaps, which is a result of the Schrödinger equation for a spatially periodic potential of the form $V(r) \propto -\frac{e^2}{r}$. An example of the 1D case is shown in Figure 2.1.

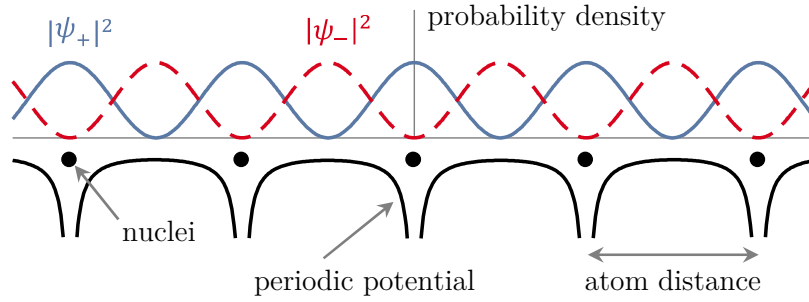


Figure 2.1: Periodic potential of a crystalline material (redrawn according to [Kit06]).

The bands are filled with electrons according to the Fermi-Dirac distribution obeying Pauli's exclusion principle. For charge transport, only the bands nearest to the Fermi level are of interest. The valence band is the highest populated band and is below the Fermi level. The conduction band is the lowest empty band above the Fermi level. Depending on the size of the band gap, materials can be classified into metals (Fermi level in conduction band), dielectrics (Fermi level in band gap and $E_g \gg k_B T$) and semiconductors (Fermi level in band gap and $E_g \gtrsim k_B T$).

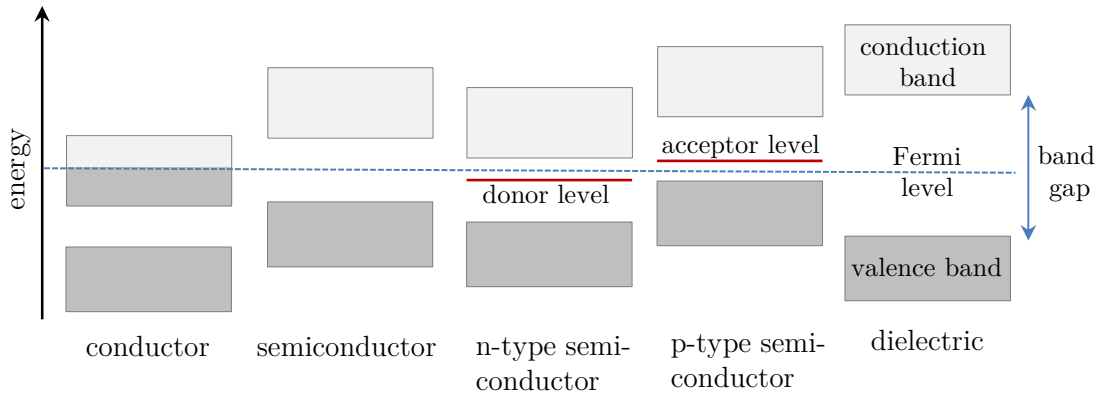


Figure 2.2: Simplified model of energy bands and band gap for metal (conductor), semiconductor, n- and p-doped semiconductor and insulator (dielectric)

Conduction can only occur in partially filled bands. In a fully occupied valence band, electrons are immobile. Valence electrons must be lifted to the (mostly) empty conduction band where there are sufficient empty states to move. For every electron that is transferred to the conduction band, a hole remains in the valence band. These

holes can move within the valence band and contribute to conduction. Metals are conductors because they have a partially filled band, where the electrons are delocalized and mobile. In dielectrics, valence and conduction bands are separated by a band gap that is much larger than the thermal energy, $E_g \gg k_B T$. Therefore, electrons cannot be transferred from the valence band to the conduction band and the material is electrically insulating. The band gap of SiO_2 , for example, is 9 eV which is large compared to $k_B T \approx 25 \text{ meV}$ at room temperature. The band gap in semiconductors, on the other hand, is smaller; Si, for example, has a band gap of only 1.11 eV [Kit06]. At the absolute zero temperature, there will be no intrinsic conduction. At rising temperatures, electrons are thermally excited from the valence band to the conduction band and allow for conduction.

The electrical properties of semiconductors can be significantly altered by the introduction of impurities or dopants. The additional dopant levels reduce the effective band gap and enable conduction even at room temperature. Doped silicon is a popular substrate for thin-film transistors as it can readily serve as a gate and a thermally grown SiO_2 layer can act as a dielectric layer. Remaining disadvantages of silicon substrates are the inflexibility and rigidity that make them unattractive for flexible electronic applications. There is a trend towards all-polymer devices (see, for example, [Gar94, Mat99, Kim15]). However, silicon is still used as a standard substrate for many applications.

In contrast to the strongly covalently bonded inorganic semiconductors, organic semiconductors are composed of carbon-based molecules which are bound together by much weaker van der Waals interactions ($\sim 0.1 \text{ eV}$ per bond). As a consequence, organic semiconductors have lower melting temperatures and are softer. Most organic semiconductors are usually not crystalline but semi-crystalline or even amorphous (see Figure 3.3). This is due to the large size of the molecules. Long molecule chains that are composed of repeating monomer units are termed polymers, which is derived from Greek πολῦ (many, much) and μέρος (part). Due to the length of the molecules, they tend to be flexible and kink, twist and fold, and the chains are often entangled. This is an obstacle to crystallization. Since a band model can be applied only to materials that form a periodic potential, in other words, materials that crystallize well, it can, to some limited extent, be applied only to some smaller and short molecules that feature a high degree of crystallinity [Bäs12]. In general, charge

transport in organic semiconductors is very different from inorganic semiconductors. One can distinguish intermolecular and intramolecular charge transport for which different models exist. Intramolecular transport refers to charge transport along one and the same molecule. This requires a closer look at the molecular structure. The common key feature of organic semiconductors is conjugation, i.e. alternation of double and single carbon-carbon bonds (see Figure 2.4). The concept of orbitals and orbital hybridization and charge transport was discussed in my Master thesis [Gro11] and parts of it are included in this chapter. It explains how conjugated bonds are formed. Orbitals represent the probability of finding electrons in a specific location around the nucleus of an atom. Mathematically, they are described by the electronic wave functions which are solutions of Schrödinger's equation. Covalent bonds between two atoms are formed by orbital overlaps. Bonds that are formed by the overlap of two orbitals along their axes, or in other words in head-to-head fashion, are named σ -bonds. The orbitals involved may have any shape, e.g. they can be s-type, p-type or hybridized orbitals. Due to the maximum overlap, σ -bonds are strongest. In π -bonds, the overlap between two (mostly p-type) orbitals occurs in a side-to-side fashion. Compared to σ -bonds, the degree of overlap in π -bonds is smaller, resulting in a weaker bonding strength. A carbon-carbon double bond is composed of a σ -bond from two sp^2 -hybridized orbitals and a π -bond from two p-orbitals, whereas a carbon-carbon single bond consists of a single σ -bond.

In a system with alternating double and single bonds, the regularly arranged p-orbitals (see Figure 2.3) overlap with each other and bridge the intermediate σ -bond, resulting in delocalization of the π -electrons throughout the entire conjugated chain. The extent of delocalization along the chain is defined as conjugation length. It can be interrupted inter alia by kinks and twists of the molecular chain.

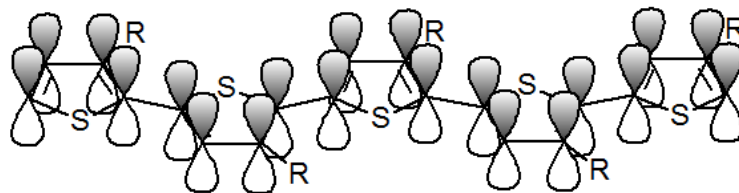


Figure 2.3: Illustration of p-orbitals in a conjugated P3AT molecule (adopted from [Gro11]). R represents the alkyl-side chains.

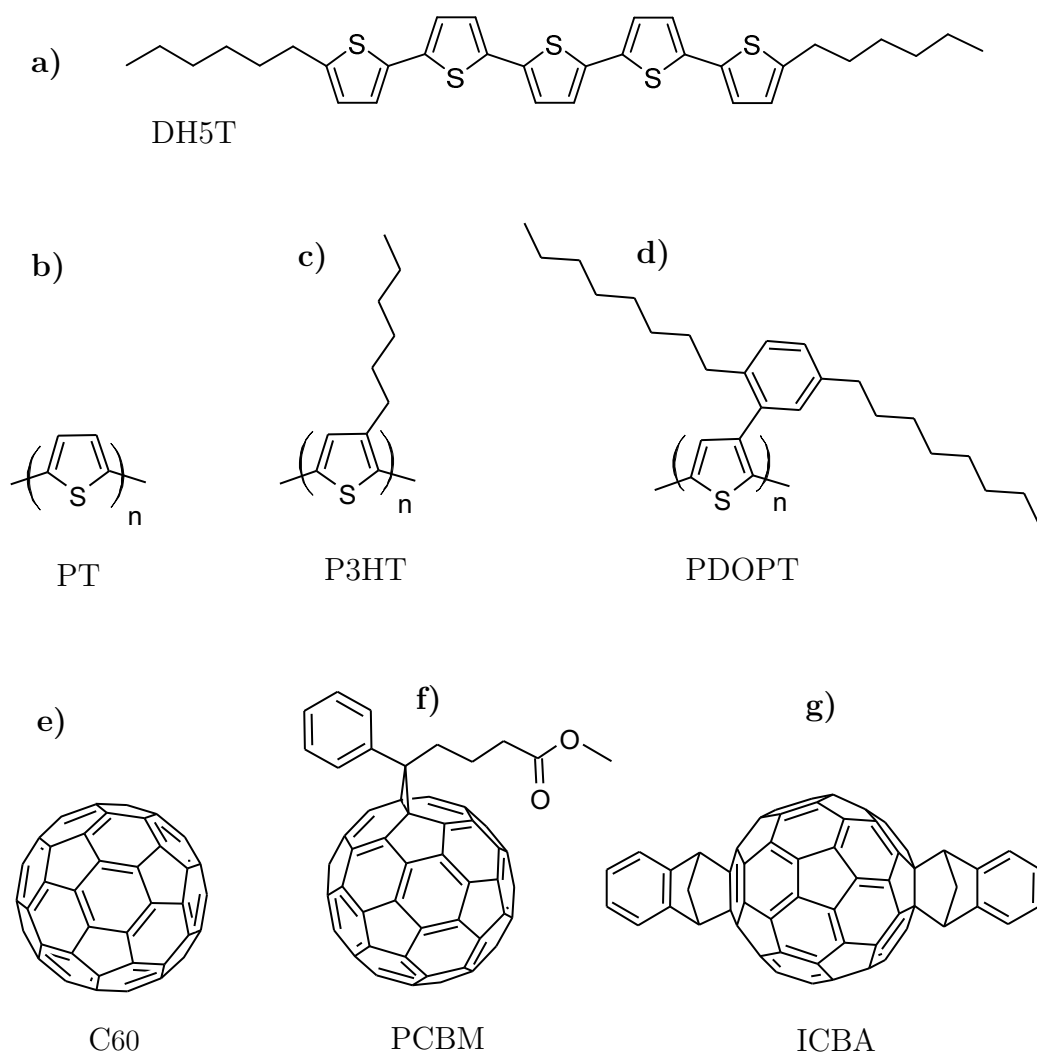


Figure 2.4: Selected organic semiconductors and fullerenes (drawn using the ACD/ChemSketch software [Che26]):

- (a) α,α' -dihexyl-quinquethiophene (DH5T)
- (b) polythiophene (PT)
- (c) poly(3-hexylthiophene-2,5-diyl) (P3HT)
- (d) poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT)
- (e) C60 fullerene and its derivatives
- (f) phenyl-C61-butyric acid methyl ester (PCBM)
- (g) indene-C60 bisadduct (ICBA)

As mentioned earlier, charge transport in organic semiconductors is very different from inorganic ones. However, there are certain analogies. Instead of bands, molecules form molecular orbitals as shown above. The highest occupied orbital (HOMO) is the analogue to the valence band and the lowest unoccupied orbital (LUMO) is the analogue to the conduction band.

Charge transport along the conjugated chain can be explained by polaron formation. It is faster than interchain transport which is the bottleneck in charge transport. For intermolecular charge transport, hopping transport is a common model.

Other than in crystalline materials, the charge carriers are not entirely delocalized. In fact, they occupy localized states and move between these states either by tunneling or by phonon-assisted hopping depending on the barrier shape between the sites, thermal energy and spatial separation of the sites [Bly05]. The carriers can cross the barrier and hop to a neighboring site if they can acquire sufficient energy by phonon absorption. This model of nearest-neighbor hopping was proposed by Miller and Abrahams [Mil60]. The relation between conductivity and temperature is given by [Mor99]

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_A}{k_B T}\right), \quad (2.7)$$

where σ_0 is a constant and E_A is the activation energy.

The variable range hopping model was first introduced by Mott [Mot69]. This model also considers hopping between sites other than only the nearest neighbors. The conductivity resulting from the calculation of the most probable hopping distance is obtained by [Mor99]:

$$\sigma = \sigma_0(T) \cdot \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right), \quad (2.8)$$

$\sigma_0(T)$ has only a weak dependency on temperature and T_0 is a constant. Equation (2.8) holds for three-dimensional conduction. The denominator in the exponential function has to be adjusted for the two- and one-dimensional cases. With d as the dimensionality of the charge transport ($d = 1, 2, 3$) it yields

$$\sigma = \sigma_0(T) \cdot \exp \left(- \left(\frac{T_0}{T} \right)^{\frac{1}{d+1}} \right). \quad (2.9)$$

The hopping conductivity increases with temperature because of an increased number of phonons. At zero temperature, there are no phonons available to assist the hopping.

Besides Mott’s approach, there are many other approaches to describe the conductivity for hopping processes. Most of them include a dependency of the form

$$\ln(\sigma) \propto - \frac{1}{T^{\text{const}}}, \quad (2.10)$$

where $0 < \text{const} < 1$.

Scattering at defects and grain boundaries leads to a reduction of mobility and conductivity.

Molecules containing conjugated rings tend to stack in a face-to-face fashion; this is often referred to as π -stacking. It was attributed to an overlap of the p-orbitals, but in a non-covalent manner. Martinez and Iverson [Mar12] favor the π -system polarization model proposed by Hunter and Sanders [Hun90] to explain π -interactions. π -stacking plays an important role in intermolecular charge transport as this is where hopping transport occurs between the molecules.

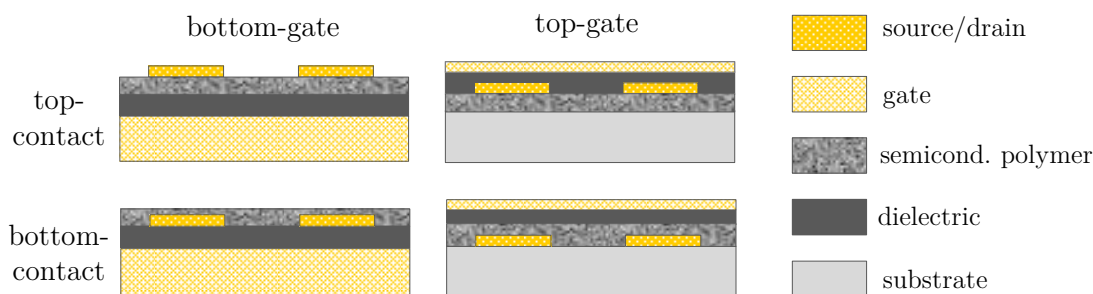


Figure 2.5: Common organic thin film field-effect transistor geometries with different stacking sequences of the semiconducting polymer, electrodes, dielectric layer and substrate.

2.3 Thin-film OFETs

Field-effect transistors are among the most popular applications for organic semiconductors. In a field-effect transistor, the current flow through the active channel between the source and drain electrode is controlled by a third gate electrode. Common organic transistor geometries are shown in Figure 2.5. The polarity and magnitude of the gate bias lead to accumulation or depletion of charges near the gate/dielectric interface.

2.4 Device fabrication techniques

Many applications of organic electronics are based on thin films, among them thin-film transistors and OLEDs. The great advantage of semiconducting polymers is their solution processability. This is usually achieved by attachment of side chains to the backbone chain. In the case of P3HT, hexyl side chains are attached to the thiophene backbone chain (compare Figure 2.4 (a) and (b)) which renders it soluble. Side chains, however, can affect structure formation and film morphology.

2.4.1 Polymer film deposition

Solution-based thin film preparation techniques include spin coating, drop casting, dip coating, doctor blading, inkjet printing, spray coating and roll-to-roll printing.

Film thickness and roughness of organic films depend very much on the processing conditions. In general, spin-coated films are smoother, more homogeneous and thinner than films that are fabricated by drop casting. However, Salammal and co-workers demonstrated, that it is possible to obtain rather thin and flat films with enhanced crystallinity from drop casting low-concentration polymer solutions under low-temperature conditions [Sal12b].

2.4.2 Electrode deposition

Common techniques for electrode deposition are sputtering and thermal evaporation. The deposition method of the electrodes must be suitable for the device geometry. While thermal evaporation of electrodes directly onto the substrate works well in bottom-contact geometry, it is not suitable for top-contact deposition as the elevated temperatures during the thermal evaporation process would damage the polymer layer. In this case, sputtering is the preferred technique.

2.4.3 Substrate cleaning

Prior to film deposition, the substrates are cleaned in an ultrasonic bath with different cleaning steps [Gro11, Sal12]: first, in a 2 % solution of Hellmanex (Hellma GmbH & Co. KG) and distilled water, second, in 2-propanol and last with acetone. The duration of each cleaning step is approximately 20 minutes. After each step, the substrates were thoroughly rinsed with distilled water and finally dried in an air stream.

3 X-ray characterization methods

3.1 Basics of X-ray scattering

3.1.1 Momentum transfer and elastic scattering

X-rays are electromagnetic waves covering wavelengths in the range similar to atomic distances of about 0.1 Å to 100 Å. When X-rays hit matter, their electromagnetic interaction, mainly with the atoms' electrons, can lead to energy and/or momentum exchanges, engendering scattering and absorption phenomena.

The energy of X-rays, and electromagnetic waves in general, is quantized with the quantum being called photon. Its energy E is related to its frequency ν or wavelength λ through

$$E = h\nu = \frac{hc}{\lambda}, \quad (3.1)$$

where h is Planck's constant and c the speed of light in vacuum. Photon energies of X-rays are usually given in units of electronvolts (eV) or kiloelectronvolts (keV).

Due to the wave-particle duality, X-rays can behave like rest-massless particles to which a momentum can be assigned. A comparison of equation (3.1) with the relativistic energy-momentum relation for rest-massless particles

$$E = pc \quad (3.2)$$

yields for the magnitude of the momentum of a photon

$$p = \frac{h}{\lambda}. \quad (3.3)$$

As the momentum is a vector, it is necessary to include the propagation direction of the photon which can be written as

$$\mathbf{p} = \hbar \mathbf{k}, \quad (3.4)$$

where $\hbar = \frac{h}{2\pi}$ is the reduced Planck's constant and $\mathbf{k}$ the wave vector with a magnitude of $|\mathbf{k}| = \frac{2\pi}{\lambda}$ and pointing in the wave's propagation direction.

For elastic scattering, there is no energy transfer; hence, the incident and scattered photons have the same energy. From equations (3.1) to (3.4) it is clear that the wavelength is conserved and the magnitudes of the incoming and scattered wave vectors are equal:

$$k \equiv |\mathbf{k}_f| = |\mathbf{k}_i| = \frac{2\pi}{\lambda}. \quad (3.5)$$

Parameters referring to the incoming wave are indexed with i, and parameters referring to the scattered wave are denoted by index f.

As the name already implies, the momentum transfer is the difference between the scattered and incident wave vector,

$$\mathbf{p}_f - \mathbf{p}_i = \hbar(\mathbf{k}_f - \mathbf{k}_i) = \hbar\mathbf{q}. \quad (3.6)$$

The wave vector transfer or scattering vector $\mathbf{q}$ is defined as

$$\mathbf{q} \equiv \mathbf{k}_f - \mathbf{k}_i. \quad (3.7)$$

The scattering angle between the incoming and the scattered wave is conventionally denoted by 2θ (see Figure 3.1). Simple trigonometric considerations lead to the relation

$$q = 2k \sin(\theta). \quad (3.8)$$

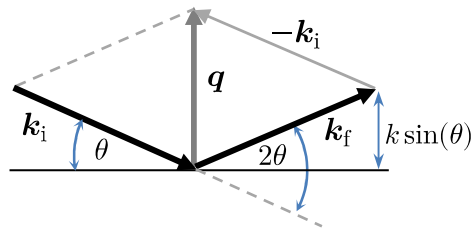


Figure 3.1: Relationship between incident and scattered wave vectors ($\mathbf{k}_i$ and $\mathbf{k}_f$) and scattering vector $\mathbf{q}$.

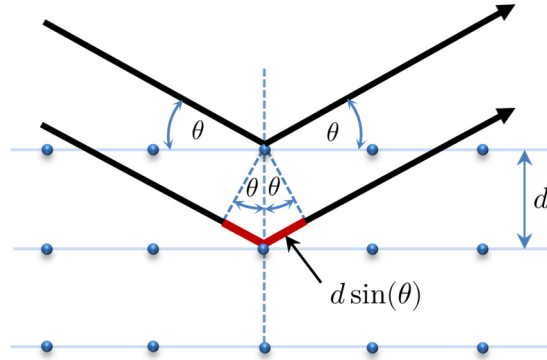


Figure 3.2: Illustration of Bragg's law. X-rays are reflected from lattice planes. Constructive interference occurs when the path difference (red lines) is an integer multiple of the wavelength.

3.1.2 Bragg's law

X-rays scattered from matter interact with each other and interfere. When they are scattered from regular structures, e.g. crystals, constructive or destructive interference can be observed as X-rays undergo a phase shift when passing through the material. An easy approach to obtain the position of diffraction maxima in angular space was proposed by William Lawrence Bragg [Bra13]. He assumed that the atoms of crystals were arranged in planes from which the X-rays were reflected (see Figure 3.2). Constructive interference from a set of planes with a distance d occurs when the path difference (marked in red in Figure 3.2) of the reflected rays is an integer multiple of the wavelength. Bragg's law reads

$$m\lambda = 2d \cdot \sin(\theta_B) \quad (3.9)$$

where m is an integer number and represents the order of reflection, d is the interplanar distance, and θ_B is the scattering angle under which constructive interference can be observed, also known as Bragg angle.

A higher reflection order corresponds to a first order reflection from lattice planes with smaller d -spacing; that is to say, the m^{th} reflection of lattice planes with interplanar distances d is located at the same angle as the first order reflection of planes with a spacing of d/m . Therefore, Bragg's law can be written as

$$\lambda = 2d_{hkl} \cdot \sin(\theta_B), \quad (3.10)$$

where h, k, l are the Miller indices that are used to address particular sets of planes. The reader should be careful not to confuse the Miller index k with the magnitude $k = \frac{2\pi}{\lambda}$ of the wave vector. Unfortunately, the notation is ambiguous; however, this is the common convention. The meaning of k should be clear from the context. Miller indices are integer numbers.

3.1.3 Crystals and reciprocal space

For the analysis of X-ray diffraction experiments, it is often more convenient to work in reciprocal space rather than real space. This requires a general understanding of the concept of crystal structures because diffraction patterns basically represent the crystal structure in reciprocal space. That is to say, a diffraction pattern is essentially the Fourier transform of the crystal. The description of crystal structures in real and reciprocal spaces is briefly introduced in the following paragraphs.

A crystal structure can be described by the repetition of a group of atoms or molecules (basis) at periodically arranged points (lattice). Crystals feature long range order, which does not exist in amorphous materials. Most conjugated polymers are semi-crystalline with crystallites being embedded in an amorphous matrix (see Figure 3.3).

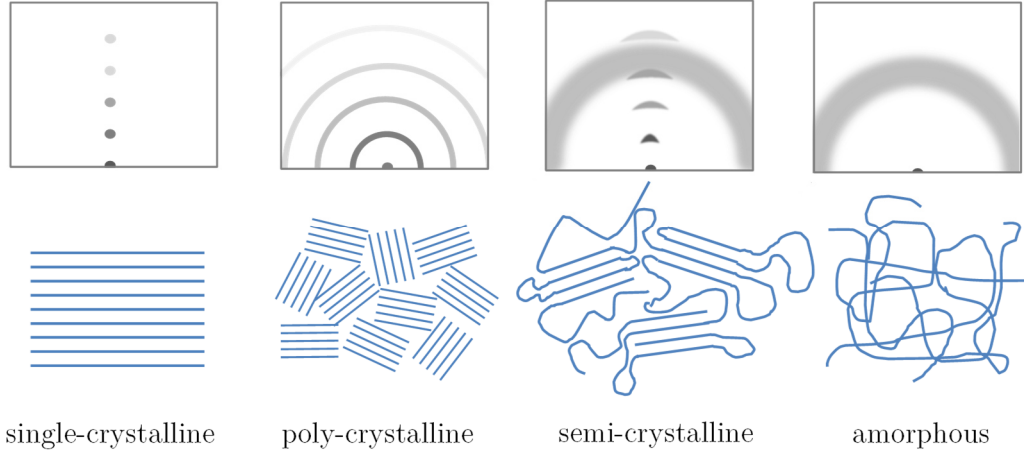


Figure 3.3: Molecular arrangement for single-crystalline, poly-crystalline, semi-crystalline and amorphous material (bottom row) and schematic representation of the corresponding 2-dimensional grazing incidence diffraction patterns (top row). For simplicity, only the diffraction peaks originating from one set of lattice planes and the contribution of the amorphous part (broad halo) are included.

The smallest repeating unit of a crystal is called unit cell and is characterized by its three basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. Alternatively, the three basis vectors can be represented by six lattice constants a , b , c , α , β , and γ which are the magnitudes of the basis vectors and their angles with respect to each other ($\alpha = \angle(\mathbf{b}, \mathbf{c})$; $\beta = \angle(\mathbf{c}, \mathbf{a})$; $\gamma = \angle(\mathbf{a}, \mathbf{b})$).

Each lattice point can be located by a lattice vector $\mathbf{R}$ which is a linear combination of the three basis vectors

$$\mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, \quad (3.11)$$

where u , v , and w are integer numbers.

The reciprocal lattice is the Fourier transform of the real space lattice. Its basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are defined as

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad (3.12)$$

The normalization of 2π is conventionally used in solid state physics. Certain communities, for example, crystallographers, prefer a normalization of 1. Throughout this thesis, the factor 2π is consistently included.

Any reciprocal lattice point is given by a reciprocal lattice vector $\mathbf{G}_{hkl}$:

$$\mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*. \quad (3.13)$$

Bragg's law in equation (3.10) is equivalent to the Laue condition which states that constructive interference occurs when the wave vector transfer $\mathbf{q}$ is equal to a reciprocal lattice vector $\mathbf{G}_{hkl}$:

$$\mathbf{G}_{hkl} = \mathbf{q}. \quad (3.14)$$

A graphical representation of the diffraction condition is the Ewald sphere, which is illustrated in Figure 3.4 for the 2-dimensional case.

The distance between two adjacent parallel lattice planes with Miller indices (hkl) is

$$d_{hkl} = \frac{2\pi}{G_{hkl}}. \quad (3.15)$$

Therefore, the Bragg equation takes the following form in the reciprocal space:

$$q = \frac{2\pi}{d_{hkl}}. \quad (3.16)$$

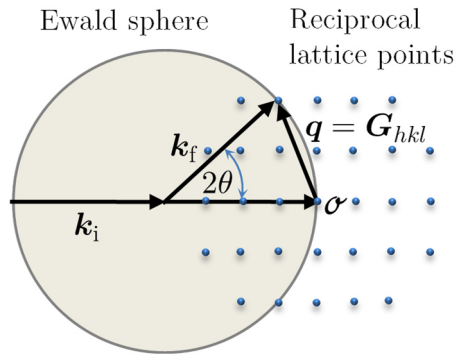


Figure 3.4: Ewald construction. For simplicity, it is shown in 2 dimensions. The radius of the Ewald sphere (in 2 dimensions more correctly “Ewald circle”) is $k = \frac{2\pi}{\lambda}$. Scattering vectors that point to reciprocal lattice points on the surface of the Ewald sphere satisfy the diffraction condition.

3.1.4 Scattered intensity

Bragg's law provides information about possible diffraction conditions and considers only the crystal lattice. However, X-rays are not scattered from the lattice, which is merely a mathematical construct. In fact, X-rays are scattered from atoms and molecules, i.e. the basis, and the intensity depends on their scattering potential and their arrangement within the unit cell. Therefore, the intensity of a reflection is determined, inter alia, by the structure factor [Als11, DeJ16]

$$F_{\text{crystal}} = \sum_{\text{unit cell}} f_j(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}_j) \sum_{\text{lattice}} \exp(i\mathbf{q} \cdot \mathbf{R}_n), \quad (3.17)$$

where $\mathbf{R}_n$ are the lattice vectors, $\mathbf{r}_j$ the atomic positions in the unit cell and $f_j(\mathbf{q})$ the respective atomic form factors:

$$f_j(\mathbf{q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}. \quad (3.18)$$

The scattered intensity is proportional to the square of the structure factor

$$I \propto |F|^2 = F \cdot F^*. \quad (3.19)$$

Besides the structure factor, there are several other factors that affect the measured intensity, among them the polarization factor, the Lorentz factor, sample absorption, air scattering, or shadows from the experimental setup.

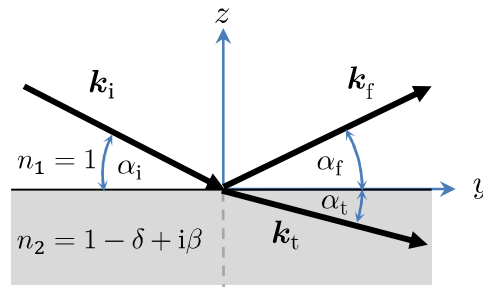


Figure 3.5: Illustration of Snell's law with definitions of angles

3.2 Refraction

Similar to visible light, X-rays are refracted at interfaces between different media, which is described by Snell's law of refraction

$$n_1 \cos(\alpha_i) = n_2 \cos(\alpha_t), \quad (3.20)$$

where n_1, n_2 are the refractive indices of the two media, α_i is the angle between the incident wave and the interface, and α_t is the angle between the transmitted wave and the interface. While the refractive index for visible light is a real number greater than unity, the refractive index for X-rays is expressed as a complex number [Als11],

$$n = 1 - \delta + i\beta, \quad (3.21)$$

with

$$\delta = \frac{\rho_e r_e \lambda^2}{2\pi}, \quad (3.22)$$

where ρ_e is the electron density and r_e the classical electron radius, and

$$\beta = \frac{\mu \lambda}{4\pi}. \quad (3.23)$$

The parameter β controls absorption as it contains the linear absorption coefficient μ .

Since δ is several orders of magnitudes smaller than unity, the real part of n is only slightly smaller than 1. As a consequence, X-rays are deflected only very weakly by refraction.

When X-rays impinge from vacuum ($n = 1$) or air ($n \approx 1$) on a sample, which is often true for X-ray measurements on thin films, the critical angle of total external reflection α_c follows from Snell's law (equation (3.20)) by setting $\alpha_t = 0$, approximating $\cos(\alpha) \approx 1 - \frac{\alpha^2}{2}$, and neglecting absorption $\beta \approx 0$. This yields

$$\alpha_c \approx \sqrt{2\delta} \quad (3.24)$$

for the critical angle.

The penetration depth Λ is defined as the distance after which the intensity of the X-rays is attenuated to a fraction of $\frac{1}{e}$ of the initial intensity. Lambert-Beer's law of attenuation

$$I = I_0 \exp(-\mu x) \quad (3.25)$$

would yield for the penetration depth

$$\Lambda_{\text{LB}} = \frac{\sin(\alpha_i)}{\mu}. \quad (3.26)$$

It provides acceptable results at incident angles above the critical angle but fails in the small angle region where the incident angle is smaller than the critical angle $\alpha_i < \alpha_c$ (see Figure 3.6). For the latter region, the correct description is a plane wave propagating parallel to the surface and being exponentially attenuated with increasing depth. This is obtained by including the absorption term $\beta > 0$, which yields a complex number for α_t :

$$\alpha_t = \sqrt{\alpha_i^2 - \alpha_c^2 + 2i\beta} = \text{Re}(\alpha_t) + i \cdot \text{Im}(\alpha_t). \quad (3.27)$$

The penetration depth for small incidence angles can then be written as [Bir06, Als11]

$$\Lambda = \frac{\lambda}{4\pi \cdot \text{Im}(\alpha_t)}. \quad (3.28)$$

Figure 3.7 illustrates the penetration depths for materials used in this thesis, i.e. P3HT, Si and Au, for two different photon energies.

Below the critical angle the penetration depth is not equal to 0 but in the range of a few nanometers because the evanescent wave penetrates into the material with exponential decay.

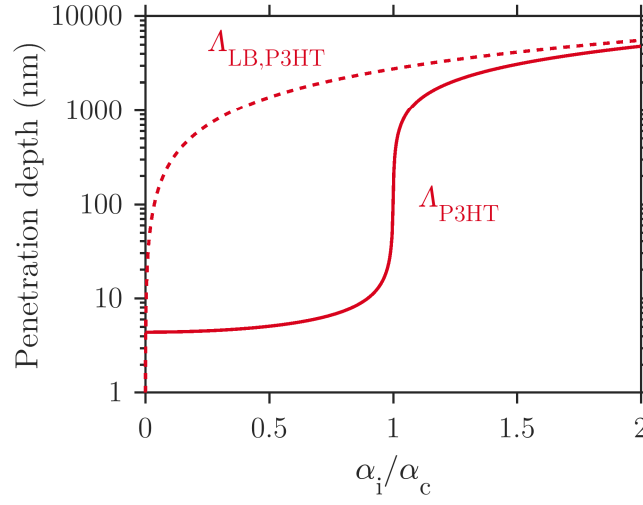


Figure 3.6: Penetration depth for P3HT calculated by Lambert-Beer's law (equation (3.26), dashed line) and calculated by equation (3.28) (solid line) at 12.38 keV Lambert-Beer's law fails in the small angle regime.

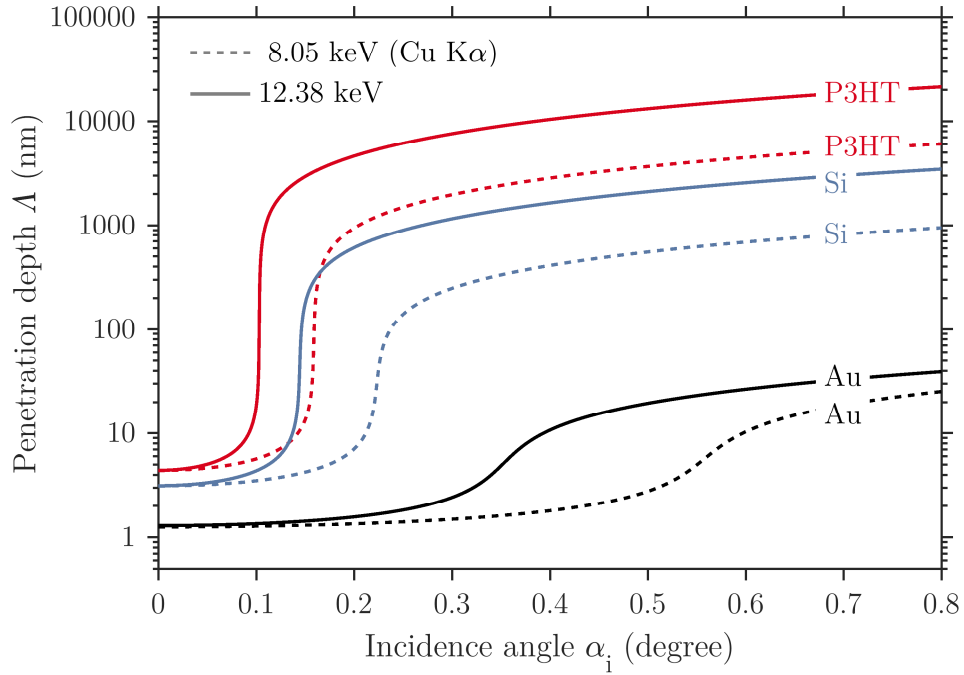


Figure 3.7: Comparison of penetration depths calculated for P3HT, Si and Au at 8.05 keV (Cu K_{α} -radiation) and 12.38 keV

3.3 X-ray reflectivity

Specular X-ray reflectivity, where the angle of incidence is equal to the exit angle of the reflected beam and thus $\mathbf{q}$ parallel to the surface normal, is sensitive to electron density variations perpendicular to the sample surface. It provides information about layer thicknesses and interface roughness. It is applicable for the measurements of film thicknesses ranging from a few nanometers to a few hundred nanometers. The reflectivity determined for an ideally flat, infinitely thick sample is known as Fresnel reflectivity. The reflection and transmission coefficients r and t represent the amplitude ratios of the reflected and transmitted waves and the incident wave. They are obtained from Snell's law (Equation (3.20)) and Maxwell's equations, which dictate the boundary conditions for the electromagnetic wave at the interface. As they depend on polarization they must be derived for each, σ - and π -polarization. However, in the small-angle region the deviations are negligible; therefore, it is sufficient to consider only the σ -polarized case, which yields [Bir06, Als11]:

$$r = \frac{k_{i,z} - k_{t,z}}{k_{i,z} + k_{t,z}} \approx \frac{\alpha_i - \alpha_t}{\alpha_i + \alpha_t} \quad (3.29)$$

$$t = \frac{2k_{i,z}}{k_{i,z} + k_{t,z}} \approx \frac{2\alpha_i}{\alpha_i + \alpha_t} \quad (3.30)$$

with the complex angle α_t according to Equation (3.27). The reflected intensity is readily obtained by $R_F = |r|^2 = r \cdot r^*$.

Organic semiconductors are commonly used in thin-film geometry such as thin-film transistors (see Figure 2.5). In terms of reflectivity calculations, the substrates, often glass or silicon, are usually much thicker than the polymer film and are assumed to be infinitely thick. The incoming X-ray beam is partially reflected at the film surface (Figure 3.8). The transmitted portion of the beam is in turn reflected and transmitted at the substrate and film interfaces until finally escaping from the film. The reflected waves will interfere resulting in intensity maxima when the path difference is a multiple of the wavelength, which yields

$$m\lambda = 2d \cdot \sin(\alpha_t), \quad (3.31)$$

where d is the film thickness. In the small angle approximation $\sin(\alpha_t)$ can be replaced by Equation (3.27). When absorption is neglected, we obtain

$$(m + \Delta m)\lambda = 2d\sqrt{a_m^2 - \alpha_c^2}. \quad (3.32)$$

This relation is also known as the modified Bragg equation. Δm is 0 for maxima and $\frac{1}{2}$ for minima. The equations above hold for the case where the film is optically denser than the substrate, i.e. the refractive index $n_{\text{film}} > n_{\text{substrate}}$. On reflection from an optically denser substrate, $n_{\text{film}} < n_{\text{substrate}}$, the reflected wave has an additional phase shift of π . As a result, the relations for minima and maxima are reversed [Kru05] and m has to be replaced by $+\frac{1}{2}$. The oscillations that can be observed in the reflectivity curve are referred to as Kiessig oscillations [Kie31a, Kie31b].

The contrast in electron densities of the different materials determines the perceptibility of the Kiessig oscillations. As it is clear from Equation (3.32), the spacing of the Kiessig maxima is related to the film thickness. In reciprocal space, similar to Equation (3.16), the distance Δq between two subsequent Kiessig maxima (or minima) is inversely proportional to the film thickness d :

$$\Delta q = \frac{2\pi}{d} \quad (3.33)$$

This relation can be used for a quick estimate of the film thickness, which can then be used as an input parameter for fitting procedures. The maxima will be closer together for a thicker film. If the film is too thick, usually more than a few hundred nm, the fringes get too close to each other and cannot be resolved anymore due to limited angular instrumental resolution.

The reflection coefficient for a thin film is obtained by summing the individual amplitudes considering the reflection and transmission coefficients and including the respective phase factors [Als11]:

$$r_{\text{thin film}} = \frac{r_{01} + r_{12}p^2}{1 + r_{01}r_{12}p^2} \quad (3.34)$$

with the phase factor $p = \exp(i2k_1 \sin(\alpha_1))$, where k_1 is the magnitude of the transmitted wave vector according to Figure 3.8. Again, the reflected intensity is the square of the reflection coefficient, $R_{\text{thin film}} = |r_{\text{thin film}}|^2$.

In organic electronics, there is often more than one layer involved. Thin-film transistors (see Figure 2.5), for example, include the semiconducting polymer film, electrodes, and the dielectric layer. The reflectivity of such multilayer systems can be

computed in a recursive fashion as proposed by Parratt [Par54]. Various computer programs for reflectivity fitting, for example, XOP/IMD [Win98], make use of such recursive algorithms.

The reflectivity determinations above were assuming ideally flat surfaces and interfaces. In reality, there are small, random thickness variations. This film roughness causes diffuse scattering, resulting in decreased reflected intensity and less pronounced Kiessig fringes. For very rough surfaces, the fringes cannot be resolved anymore, and therefore thickness determination becomes impossible.

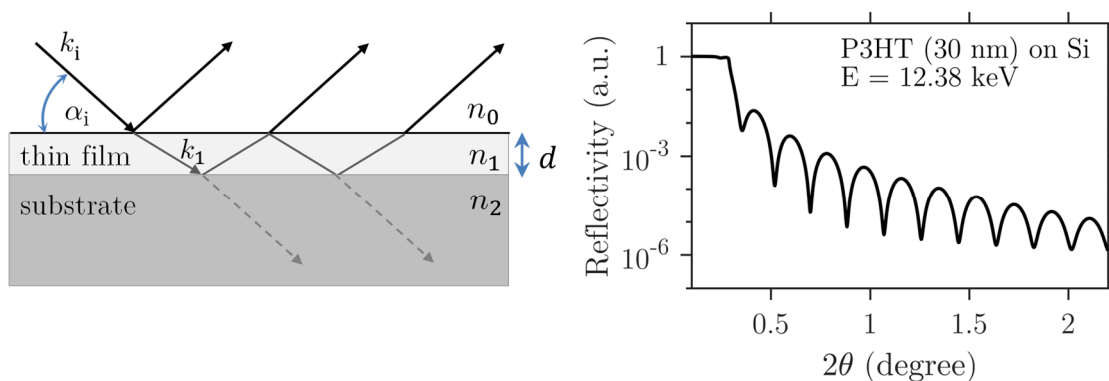


Figure 3.8: Reflectivity from a thin film. Multiple reflections from the substrate contribute to the reflected intensity (left). Constructive and destructive interference lead to Kiessig fringes (right). The reflectivity was calculated for a 30 nm thick P3HT layer ($(\text{C}_{10}\text{H}_{14}\text{S})_n$, $\rho = 1.1 \text{ g/cm}^3$) at a photon energy of 12.38 keV.

3.4 Two-dimensional grazing incidence X-ray diffraction from organic thin films

As shown in paragraph 3.2, the penetration depth of X-rays strongly decreases for small angles below the critical angle. For this reason, grazing incidence X-ray diffraction (GIXD) is a tool well suited for the structural characterization of thin films and surfaces or interfaces. The incidence angle, and thus the penetration depth, is kept small, close to the critical angle, resulting in reduced background signals

originating from the substrate. At the same time, the exposed area is rather large as the beam footprint f on the sample (see Figure 3.9) increases with a smaller incident angle according to

$$f = \frac{h}{\sin(\alpha_i)}. \quad (3.35)$$

This enhances the diffraction signal of the thin film. Here, h is the height of the incident X-ray beam.

The scattering geometry of GIXD is illustrated in Figure 3.12(a). Two-dimensional detectors cover a large area in reciprocal space and allow for fast data collection without the need for time-consuming scanning while preserving sensitive samples from additional exposure (see Chapter 3.5 for more details on radiation damage).

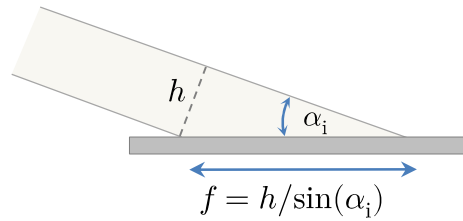


Figure 3.9: Geometry of beam footprint on sample

3.4.1 Detector calibration

The beam center on the detector as well as the sample-to-detector distance D can be obtained from the powder diffraction pattern of a known reference material. Suitable reference materials for GIXD are silicon powder or silver behenate powder [Hua93, Bla95, Bla00].

The center of the beam is extracted by determining the center of the diffraction rings. As the lattice constants and the wavelength λ are known, D can be calculated using Bragg's law. X-ray data analysis programs (e.g., FIT2D [Ham97, Ham98]) allow for refinement of the calibration by fitting the diffraction rings.

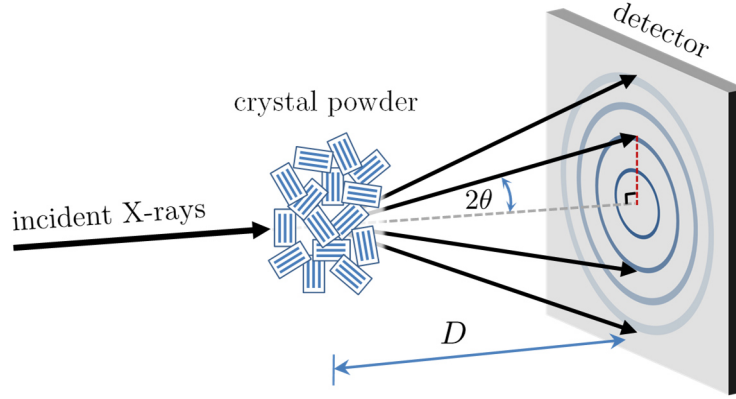


Figure 3.10: Schematic of sample-to-detector distance determination by powder diffraction of a crystal powder with known lattice constants.

Detectors that are mounted on a diffractometer arm and can perform angular movements in 2θ direction can be calibrated without a calibrant by performing a scan in horizontal $2\theta_h$ and vertical $2\theta_v$ direction, respectively, and recording the direct beam position on the detector.

It is evident from Figure 3.11 that the sample-to-detector distance D is the adjacent side to the vertical angle $2\theta_v$ and is related to it through

$$D = \frac{\Delta z_d \cdot p_z}{\tan(2\theta_v)}, \quad (3.36)$$

where $\Delta z_d = z_{d,1} - z_{d,0}$ with $z_{d,1}$ being the coordinate of the direct beam on the detector at a detector tilt of $2\theta_v$, $z_{d,0}$ is the position of the beam center without detector tilt and p_z the pixel size in z -direction.

The equation for the horizontal direction is obtained analogously:

$$D = \frac{\Delta x_d \cdot p_x}{\tan(2\theta_h)}, \quad (3.37)$$

where $\Delta x_d = x_{d,1} - x_{d,0}$ with $2\theta_h$ being the horizontal detector tilt and $x_{d,0}$, $x_{d,1}$ the coordinates of the beam position and p_x the pixel size in x -direction, respectively.

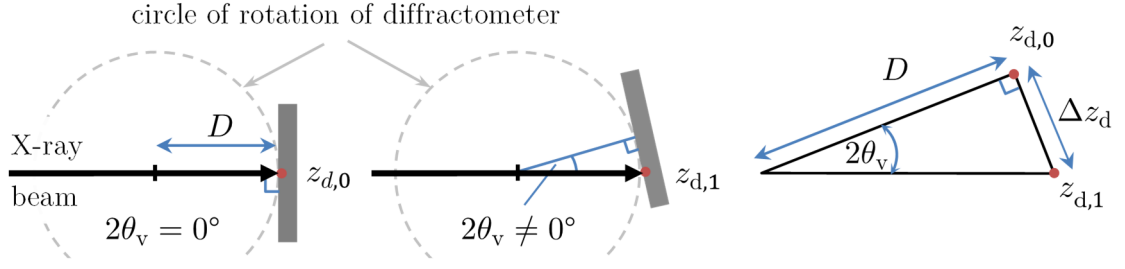


Figure 3.11: Schematic of sample-to-detector distance determination by moving the detector and monitoring the direct beam position.

3.4.2 Conversion from real to reciprocal space (pixel to $\mathbf{q}$)

For the description of the scattering vector, it is expedient to introduce three Cartesian coordinate systems as reference frames: the laboratory frame and the sample surface reference frame, each of which has its associated reciprocal space coordinate system [Bir06, Bre08]. Additionally, the two-dimensional detector coordinate system is defined. The designation of the basis vectors that span the respective coordinate system is summarized in Table 3.1.

Table 3.1: Summary of the basis vectors of the reference systems

Reference frame	real space	reciprocal space
laboratory	$\hat{\mathbf{x}}_L, \hat{\mathbf{y}}_L, \hat{\mathbf{z}}_L$	$\hat{\mathbf{q}}_{x_L}, \hat{\mathbf{q}}_{y_L}, \hat{\mathbf{q}}_{z_L}$
sample substrate	$\hat{\mathbf{x}}_s, \hat{\mathbf{y}}_s, \hat{\mathbf{z}}_s$	$\hat{\mathbf{q}}_x, \hat{\mathbf{q}}_y, \hat{\mathbf{q}}_z$
detector	$\hat{\mathbf{x}}_d, \hat{\mathbf{z}}_d$	---

Figure 3.12 (a) and (b) show the GIXD scattering geometry in the surface reference frame and in the laboratory reference frame (c). For the conversion of the detector pixels into reciprocal space, the scattering vector $\mathbf{q}$ is parameterized in the laboratory reference frame.

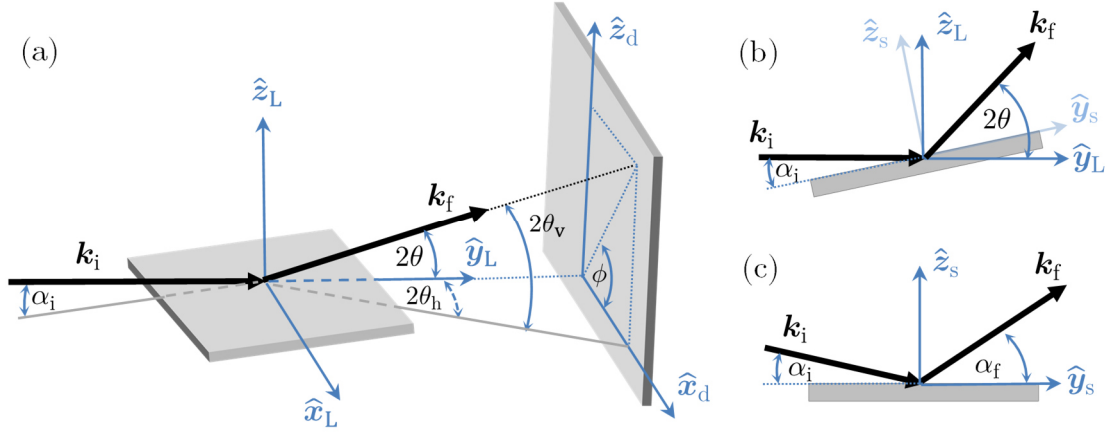


Figure 3.12: Scattering geometry with definition of angles for grazing incidence X-ray diffraction (GIXD) in sample laboratory reference frame seen in (a) three-dimensional view and (b) side view. (c) Side view in sample surface reference frame.

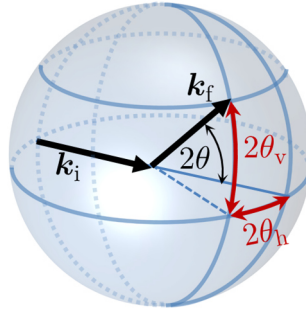


Figure 3.13: Decomposition of scattering angle 2θ into horizontal ($2\theta_h$) and vertical ($2\theta_v$) components

As depicted in Figure 3.13, the scattering angle $2\theta = \angle(\mathbf{k}_i, \mathbf{k}_f)$ can be decomposed into a horizontal component $2\theta_h$ in the $\mathbf{x}_L \mathbf{y}_L$ -plane and a vertical component $2\theta_v$ through the following relation:

$$\cos(2\theta) = \cos(2\theta_v) \cdot \cos(2\theta_h) \quad (3.38)$$

The wave vectors $\mathbf{k}_{i,L}$ and $\mathbf{k}_{f,L}$ can be expressed in the laboratory reference frame as

$$\mathbf{k}_{i,L} = k \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \mathbf{k}_{f,L} = k \begin{pmatrix} \cos(2\theta_v) \sin(2\theta_h) \\ \cos(2\theta_v) \cos(2\theta_h) \\ \sin(2\theta_v) \end{pmatrix} \quad (3.39)$$

The scattering vector $\mathbf{q}_L$ is then given by

$$\mathbf{q}_L = \mathbf{k}_{f,L} - \mathbf{k}_{i,L} = k \begin{pmatrix} \cos(2\theta_v) \sin(2\theta_h) \\ \cos(2\theta_v) \cos(2\theta_h) - 1 \\ \sin(2\theta_v) \end{pmatrix} \quad (3.40)$$

In the GIXD setup at synchrotrons, the sample is usually tilted to form the incidence angle α_i between the incoming X-ray beam and the sample surface as shown in Figure 3.12. The transformation from the laboratory reference frame into the sample surface reference frame is achieved by a rotation of the coordinate system around the x_L -axis by the angle α_i :

$$\mathbf{q} = \mathbf{R}_x(\alpha_i) \cdot \mathbf{q}_L, \quad (3.41)$$

where $\mathbf{R}_x(\alpha_i)$ is the rotation matrix around the x_L -axis

$$\mathbf{R}_x(\alpha_i) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\alpha_i) & \sin(\alpha_i) \\ 0 & -\sin(\alpha_i) & \cos(\alpha_i) \end{pmatrix} \quad (3.42)$$

The components of the scattering vector in the sample reference frame are given by

$$q_{x,s} = k \cos(2\theta_v) \sin(2\theta_h) \quad (3.43)$$

$$q_{y,s} = k [\cos(\alpha_i) (\cos(2\theta_v) \cos(2\theta_h) - 1) + \sin(\alpha_i) \sin(2\theta_v)] \quad (3.44)$$

$$q_{z,s} = k [\sin(\alpha_i) (1 - \cos(2\theta_v) \cos(2\theta_h)) + \cos(\alpha_i) \sin(2\theta_v)] \quad (3.45)$$

The angles $2\theta_v$ and $2\theta_h$ can be expressed in terms of sample-to-detector distance D and detector pixel coordinates x_d and z_d

$$2\theta_h = \arctan\left(\frac{x_d \cdot p_x}{D}\right) \quad (3.46)$$

$$2\theta_v = \arctan\left(\frac{z_d \cdot p_z}{D / \cos(2\theta_h)}\right), \quad (3.47)$$

where p_x and p_z are the pixel sizes in the $\hat{\mathbf{x}}_d$ and $\hat{\mathbf{z}}_d$ direction, respectively.

Two-dimensional GIXD data are typically presented by plotting the perpendicular component $q_\perp$ of the scattering vector versus the parallel component $q_\parallel$, where

$$q_{\parallel} = \sqrt{q_x^2 + q_y^2}, \quad (3.48)$$

$$q_{\perp} = q_z \quad (3.49)$$

Crystallites in thin films often have a preferential orientation with respect to the substrate surface and random in-plane orientation, resulting in a cylindrical symmetry with $\hat{\mathbf{q}}_z$ being the cylinder axis, called the axis of rotation hereafter (see Figure 3.14 and Figure 3.15). This is the so-called fiber texture.

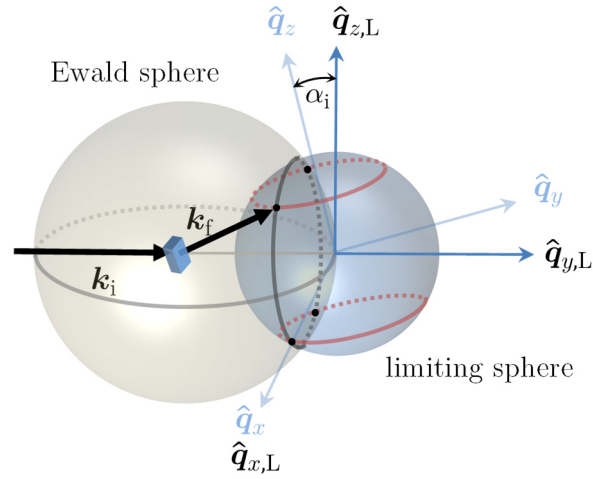


Figure 3.14: Diffraction geometry of cylindrical symmetric samples (adapted from [Str09a]). Reciprocal lattice vectors form rings on the sphere which is referred to as limiting or resolution sphere (blue sphere, radius $\frac{2\pi}{d_{\text{limit}}}$) in reciprocal space. In positions where this ring intersects the Ewald sphere (grey sphere, radius $\frac{2\pi}{\lambda}$) the Bragg condition is fulfilled (black dots). In GIXD geometry, reflections close to the rotation axis $\mathbf{q}_z$ will never intersect the Ewald sphere; this is the “blind region”.

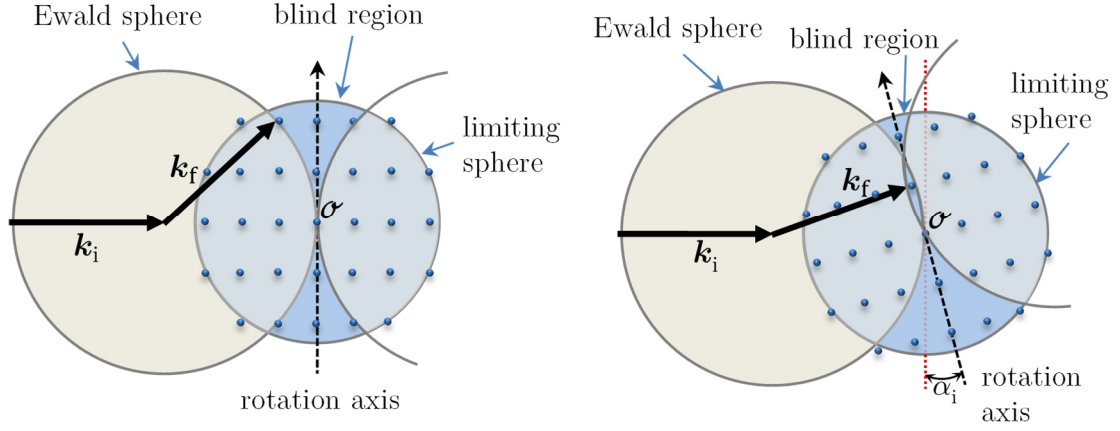


Figure 3.15: 2D cross-section of Ewald sphere and limiting sphere. Blind regions are shaded blue. They depend on the incidence angle α_i .

Bragg's law is fulfilled whenever a reciprocal lattice point intersects the Ewald sphere. The Ewald sphere has a radius of $r_{\text{Ewald}} = k = \frac{2\pi}{\lambda}$. It is evident that the theoretical diffraction limit is $r_{\text{limit,theo}} = 2k$, as only lattice points within this distance can fulfil Bragg's law. In practice, the resolution limit is usually lower, i.e., the radius of the limiting sphere $r_{\text{limit}} \leq 2k$ due to detector resolution and decreased scattered intensity at higher angles. The smallest lattice spacing that can be detected is $d_{\text{limit}} = \frac{2\pi}{r_{\text{limit}}}$.

Figures 3.14 and 3.15 show the full sphere in reciprocal space. In GIXD, we usually observe only the Northern hemisphere because a thick substrate and/or the sample holder introduces a horizon as it absorbs the X-ray beam and does not allow it to transmit. In the case of transparent substrates, for example, silicon nitride membranes, it will be possible to detect the Southern hemisphere as well.

Due to the curvature of the Ewald sphere, there is a "blind region" close to the axis of rotation (blue shaded wedges in Figure 3.15). This region cannot be detected in GIXD geometry where the incidence angle is small. The border of the blind region is the surface of the Ewald sphere, which can be parameterized in the laboratory system by [Bre08]:

$$q_{x,L}^2 + (q_{y,L} + k)^2 + q_{z,L}^2 = k^2. \quad (3.50)$$

The components of $\mathbf{q}_L$ are obtained by a rotation around the x_L -axis

$$\mathbf{q}_L = \mathbf{R}_x^{-1}(\alpha_i) \cdot \mathbf{q} \quad (3.51)$$

which yields

$$q_{x,L} = q_x \quad (3.52)$$

$$q_{y,L} = q_y \cos(\alpha_i) - q_z \sin(\alpha_i) \quad (3.53)$$

$$q_{z,L} = q_y \sin(\alpha_i) + q_z \cos(\alpha_i) \quad (3.54)$$

Inserting equations (3.52) to (3.54) into (3.50) one obtains

$$q_x^2 + (q_y + k \cos(\alpha_i))^2 + (q_z - k \sin(\alpha_i))^2 = k^2. \quad (3.55)$$

The resulting sphere is centered at $(0, -k \cos(\alpha_i), k \sin(\alpha_i))$.

For the aforementioned case of cylindrical symmetry, the equation for the bordering circles on the reciprocal space map $q_\perp$ versus $q_\parallel$ can be written as

$$(q_\parallel \pm k \cos(\alpha_i))^2 + (q_\perp - k \sin(\alpha_i))^2 = k^2. \quad (3.56)$$

Due to the transformation from detector pixels to q , the resulting $q_\parallel q_\perp$ -map is distorted and is no longer gridded. A way to obtain a gridded q -map is to start from a regularly gridded $q_\parallel q_\perp$ -map and then use the inverse mapping to obtain a scattered pixel map in real space. The points of the obtained pixel map do not coincide with the original detector grid, but their corresponding intensity can be evaluated by means of interpolation.

The reverse mapping from a $q_\parallel q_\perp$ -map with predefined equidistant spacing to detector pixels was published by Stribeck and Nöchel [Str09, Str09a] for fiber diffraction and can be applied for thin films measured in GIXD geometry, for example, thin polymer films with random in-plane orientation, i.e., fiber texture, alike. The detector coordinates x_d and z_d are expressed as function of $q_\parallel$ and $q_\perp$:

$$z_d(q_{\parallel}, q_{\perp}) = \frac{2\lambda D q}{4\pi - \frac{\lambda^2 q^2}{2\pi}} \cdot \frac{\frac{q_{\perp}}{q} - \frac{\lambda q}{4\pi} \sin(\alpha_i)}{\cos(\alpha_i)} \quad (3.57)$$

and

$$x_d(q_{\parallel}, q_{\perp}) = \frac{2\lambda D q}{4\pi - \frac{\lambda^2 q^2}{2\pi}} \left[1 - \frac{\lambda^2 q^2}{16\pi^2} - \left(\frac{\frac{q_{\perp}}{q} - \frac{\lambda q}{4\pi} \sin(\alpha_i)}{\cos(\alpha_i)} \right)^2 \right]^{\frac{1}{2}}. \quad (3.58)$$

The reader should be aware that in their publication [Str09, Str09a] the authors follow the crystallographic convention for the definition of the scattering vector: $\mathbf{s} = \frac{\mathbf{q}}{2\pi}$.

Figure 3.16 demonstrates the distortion of the detector grid after transformation from real space (pixels) to reciprocal space (q) which leaves the blind region in the center. The extent of this region depends on the incident angle α_i . An exact out-of-plane profile at $q_{\parallel} = 0$ is not accessible in grazing incidence geometry. It can be accessed only in the specular condition (see, for example, [Bak10]).

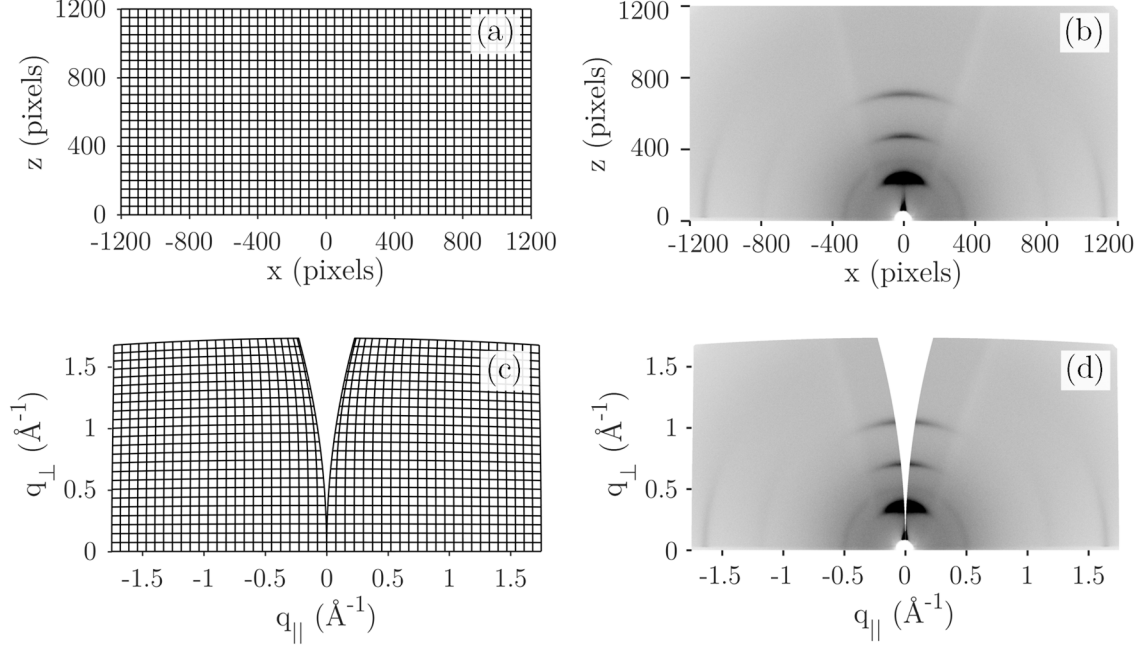


Figure 3.16: Detector grid in (a) real space mapped to (c) reciprocal space for grazing incidence diffraction conditions ($\alpha_i = 0.13^\circ$) and corresponding example of P3HT diffraction patterns measured at DELTA, BL9 in (b) pixels, and (c) in reciprocal space.

Information that can be extracted from grazing incidence diffraction patterns includes lattice spacings, preferred orientations, degree of crystallinity, crystallite sizes, and strain.

Lattice spacings can be determined from the Bragg peak positions by Equation (3.16): $q = 2\pi/d_{hkl}$.

The finite size of coherently scattering domains (crystallite sizes) leads to a broadening of the diffraction peak. It can be extracted from the full width at half maximum (FWHM) by applying the Scherrer equation [Sch18]:

$$t_{hkl} = \frac{K\lambda}{\Delta(2\theta)_{\text{FWHM}} \cdot \cos(\theta_{hkl})}, \quad (3.59)$$

where t is the crystallite size and K is a dimensionless constant that depends on the crystallite shape. It has a value of about 0.9. $\Delta(2\theta)_{\text{FWHM}}$ is the peak width in radian. In reciprocal space Scherrer's equation reads [Smi09]:

$$t_{hkl} = \frac{2\pi K}{\Delta q_{hkl}}. \quad (3.60)$$

One has to be aware that besides crystallite size, also lattice microstrain and instrumental effects contribute to a broadening of the peak, namely beam divergence, beam bandwidth, and the footprint size [Smi09]. The measured peak broadening is a convolution of the signal originating from the crystallites and the instrumental profile.

3.4.3 X-ray Sources and properties of X-rays

Typical laboratory sources are X-ray tubes which produce a spectrum that consists of the continuous spectrum of bremsstrahlung with superimposed characteristic lines that are specific to the target material. The maximum X-ray energy is ruled by the acceleration voltage $E_{\text{max}} = V_{\text{acc}} \cdot e$. X-rays produced by X-ray tubes are unpolarized, and the intensity is rather limited. Organic materials are carbon based and have low atomic numbers (carbon: $Z = 6$) and are therefore weak scatterers. In addition, in thin films the scattering volume is very small. As a result, scattering experiments performed with X-ray tubes have poor counting statistics and take very long, or it might even be impossible to resolve the diffraction pattern at all.

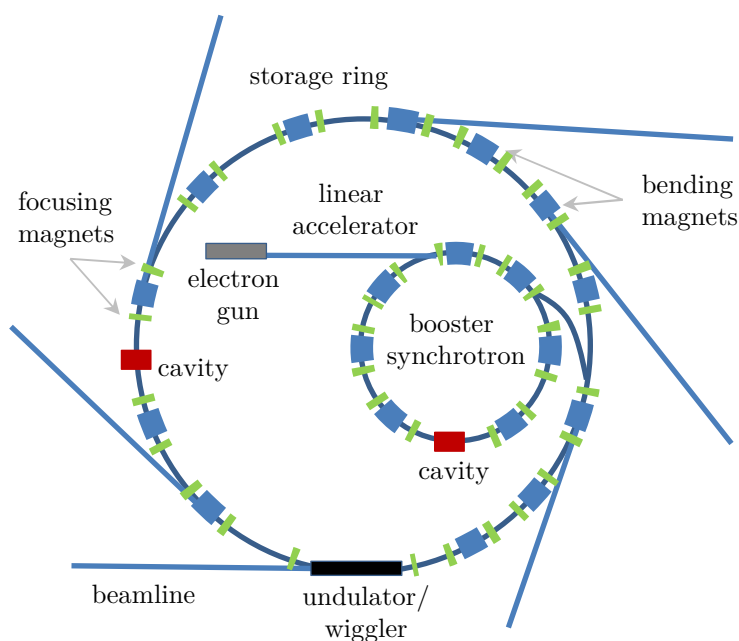


Figure 3.17: Schematic representation of a synchrotron showing the most essential components: electron gun, linear accelerator, booster synchrotron, storage ring, cavities, bending and focusing magnets, insertion devices (undulator/wiggler) and beamlines.

Synchrotron light sources are excellent sources of highly intense X-rays. Historically, synchrotron light was a by-product of particle accelerators that were used primarily for research in particle physics. Nowadays, synchrotrons are particle accelerators that are dedicated to production of X-rays. Basic components of a synchrotron include an

electron gun for electron production, a linear accelerator for pre-acceleration, a circular booster synchrotron for further acceleration, and a storage ring where electrons circulate to produce X-rays. The electrons are accelerated by cavities through synchronized high-frequency electromagnetic waves. Dipolar bending magnets guide the electrons on a circular orbit. Quadrupole and possibly sextupole magnets keep the electron beam focused. X-rays are emitted when the electrons are radially accelerated, that is in the bending magnets. The X-rays are guided to beamlines where they can be used for experiments. Special insertion devices, namely wigglers and undulators, are used to increase the photon flux. A periodic arrangement of magnets with alternating polarity forces the passing electron beam on a wave-shaped trajectory, hence the names undulator and wiggler. At each oscillation the electron beam emits X-rays, resulting in a highly intense X-ray beam. In summary, synchrotron radiation has the following properties:

- high intensity (faster experiments, better photon statistics)
- broad, continuous spectrum (energy can be selected by a monochromator)
- highly collimated
- high degree of polarization (in horizontal orbit plane)
- pulsed time structure (electron bunches)

Beamline BL9 at DELTA, Dortmund, Germany [DEL16]

The Dortmunder Elektronenspeicherring-Anlage (DELTA) is a comparatively small synchrotron with a storage ring circumference of 50.4 m. Electrons are accelerated to an energy up to 1.5 GeV. The synchrotron does not run in a top-up mode; the current in the storage ring typically ranges from 120 mA down to 60 mA, which has to be accounted for in the data evaluation. A superconductive asymmetric wiggler serves as an insertion device for beamline BL9. The monochromatic energy is extracted by a silicon (311) double crystal monochromator and can be selected in a range of 7 to 27 keV. The beamline is equipped with a 6-circle diffractometer (Huber). Diffraction patterns can be recorded with a MAR345 2-dimensional image plate detector (pixel size $100 \times 100 \mu\text{m}^2$, diameter of image plate 3450 pixels), or alternatively a smaller 2-dimensional Pilatus 100K ($172 \mu\text{m}^2$ pixel size, 487×195 pixels). Sample alignment

and X-ray reflectivity measurements are preferentially done with the NaI point detector, or alternatively by selecting a small region of interest on the Pilatus detector. However, the point detector and the Pilatus detector cannot be used simultaneously, as the detector arm of the diffractometer allows only for one detector to be mounted at a time.

Beamline ID13 at ESRF, Grenoble, France [ESR26]

The storage ring of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, has a circumference of 844 m and a ring current of 200 mA; it does not run in top-up mode. Electrons are accelerated up to 6 GeV. The nano-branch of beamline ID13 is equipped with silicon compound refractive lenses that allow for focusing hard X-rays to 100 nm dimensions [Sch13]. The available photon energy range is 7 – 30 keV. Diffraction images can be recorded with a 2-dimensional FReLoN detector ($\sim 50\text{ }\mu\text{m}$ pixel size, 2048×2048 pixels). An optical microscope which is aligned to the X-ray beam position in the center of rotation of the diffractometer and a photodiode are available for sample alignment. The nano-focus setup requires the aperture pinhole to be close to the sample. This restricts the sample width to roughly 5 mm. The setup is usually used in transmission geometry where the sample is mounted in a vertical position. For grazing incidence geometry, the sample is rotated around its vertical axis to form the incidence angle.

Beamline P03 at PETRA III, Hamburg, Germany [Pet26]

PETRA III at the DESY is a high-brilliance synchrotron light source situated in Hamburg. Its storage ring has a circumference of 2304 m; it runs at 120 mA ring current and at 6 GeV electron energy. Unlike the ESRF and DELTA it operates in top-up mode, maintaining a nearly constant ring current by frequently injecting small amounts of electrons into the storage ring. Beamline P03 at PETRA III is a micro- and nanofocus beamline that offers small- and wide-angle X-ray scattering in grazing as well as transmission geometry in the range of 12 – 20 keV. The beam can be focused down to $250 \times 350\text{ nm}^2$ by Kirkpatrick–Baez mirrors (JTEC). The beamline is equipped with a CCD-based Photonic Science area detector with a pixel size of $62 \times 62\text{ }\mu\text{m}^2$ and a total array size of 2940×2940 pixels to record the scattered intensity. Due to high brilliance and small beam size this beamline is well suited for in situ measurements with high spatial resolution.

3.5 Radiation Damage

X-ray-based characterization techniques are often considered as non-destructive investigation methods because it is possible to gain information about the inner structure of a sample without permanent alteration, for example, cutting it. However, this is not generally true. X-rays are ionizing radiation and can cause severe damage to the exposed material. Especially organic materials are prone to radiation damage [Vas16]. High beam intensity comes at the cost of strong damage in the form of breaking bonds, secession of side chains [Hol09] and chemical modification.

The ALARA principle (**A**s **L**ow **A**s **R**easonably **A**chievable) known from radiation protection should be applied to organic materials for X-ray measurements at high beam intensities to minimize radiation damage. The exposure time should be kept as short as possible and as long as necessary to record reasonable intensity. It is also advisable to perform the experiment under inert atmosphere. The energy of hard X-rays is higher than the binding energy of O₂ molecules, and that can dissociate and form highly reactive ozone [Wei88] which can chemically alter the sample. However, this might not always be possible to keep the sample in a cell with inert atmosphere during the experiment. Especially in nanobeam experiments, space is very restricted (aperture distance ~ 5 mm). In addition to space limitation, any sample cell for inert atmosphere requires some sort of windows to keep it hermetically sealed, yet transparent for X-ray. At very low scattered signal from the sample, the absorption of the chamber windows can be a crucial factor and might not be tolerable.

4 Conjugated polymer thin films under external perturbation

4.1 External electric field

The structural order of conjugated materials is of crucial importance for their application in electrical devices as it has a strong influence on the electrical performance. This chapter will investigate the impact of externally applied electric fields during polymer film fabrication on polymer alignment and crystallinity of P3HT thin films, which is a widely studied conjugated polymer. Conjugated polymers like P3HT are composed of chains with alternating single and double bonds (see Figure 2.4), which allow electrons to move more freely along the thiophene backbone chains. In contrast to short molecules, for long polymer chains usually only a fraction of the molecules form ordered crystalline domains, which are embedded in an amorphous matrix. Charge transport through the amorphous matrix via hopping is the bottleneck [Sir99]. Overall, the conductivity depends on how well the polymer chains are organized and oriented. When these chains align and pack in an ordered, crystalline fashion, charge carriers can travel more efficiently, improving the overall electrical performance of devices such as organic field effect transistors and photovoltaic cells.

Shabi et al. demonstrated that low-temperature drop casting of P3AT yields a higher degree of edge-on orientation, which they attribute to a slower solvent evaporation rate [Sal12, Sal12b]. Bagui and Kumar Iyer reported enhancement of crystallinity and an alignment effect of the polymer when subjected to an external electrical field [Bag11] which they assigned to polarization. The dipole moment of P3HT is approximately 1.0 to 1.6 D because of the electronegative sulfur. Alignment of P3HT fibers was also observed by Mas-Torrent when applying an AC voltage during the preparation directly to electrodes on which the film was drop cast [Mas04].

Slow evaporation at low temperatures allows for more time for the polymer chains to arrange in a favorable configuration and more time for the electric field to act on the polymer. Therefore, the question arises whether it is possible to enhance crystallinity and to promote electric field-assisted alignment by low-temperature casting under an external field. To answer this question, polymer films were cast at low temperature

under an external electrical field and investigated using X-ray diffraction and X-ray reflectivity.

Experimental details: rr-P3HT was provided by the Macromolecular Chemistry Group of Prof. Scherf (University of Wuppertal). Regioregularity was $> 99\%$ and the molecular weight of $M_w = 40\,000$ g/mol. The P3HT was dissolved in chloroform at low concentrations 0.4 mg/ml and 0.08 mg/ml. Silicon substrates (Silchem, (100)-orientation, n-type phosphor doped, 300 nm thermally grown SiO₂ layer) were cut into 10×10 mm² sized substrates with a wafer saw and cleaned according to the protocol mentioned in Chapter 2.4.3.

The samples were prepared in a custom-designed chamber which is equipped with a plate capacitor (see Figure 4.1 and Figure 4.2) that can be driven with a voltage up to ± 3 kV (Heinzinger high-voltage desktop power supply, LNC 3000-10 pos and LNC 3000-10 neg). A motorized syringe allows for automatic deposition of the polymer solution onto the substrate. With a custom-made switch box, the voltage could be alternated between positive and negative voltage applied to the capacitor plates at a frequency provided by a function generator (Aim-TTi TG315). The distance between the capacitor plates measured 13 mm. The electrical field of a plate capacitor is given by $E = \frac{U}{d}$, where U is the voltage applied to the plates and d is the distance between them. The chamber and the sample stage that holds the capacitor plates were designed using the software Autodesk Inventor and constructed in the mechanical workshop at the University of Siegen.

The samples were drop-cast at low temperature under a lateral external electric field according to the following protocol: First, the substrate was placed in the chamber between the capacitor plates. The chamber was flushed with nitrogen for inert atmosphere and then placed in the freezer at $-30\text{ }^\circ\text{C}$ for one hour to reach thermal equilibrium. Then, the external electric field was switched on, and the substrate was covered with polymer solution using the motor-controlled syringe. The substrate was left to dry in the freezer for one hour at low temperature and under applied electric field. After drying, the chamber was removed from the freezer and kept at room temperature to warm up for 1.5 hours. As a final step, the samples were annealed under nitrogen at $185\text{ }^\circ\text{C}$ for 1 hour to further enhance crystallinity. Table 4.1 summarizes the parameters for sample fabrication.

Table 4.1: Summary of samples prepared under external electric field

Material	Concentration (mg/ml)	Voltage (kV)	Frequency (kHz)
P3HT	0.4	-	-
P3HT	0.4	3	-
P3HT	0.4	3	2
P3HT	0.8	-	-
P3HT	0.8	3	-
P3HT	0.8	3	2

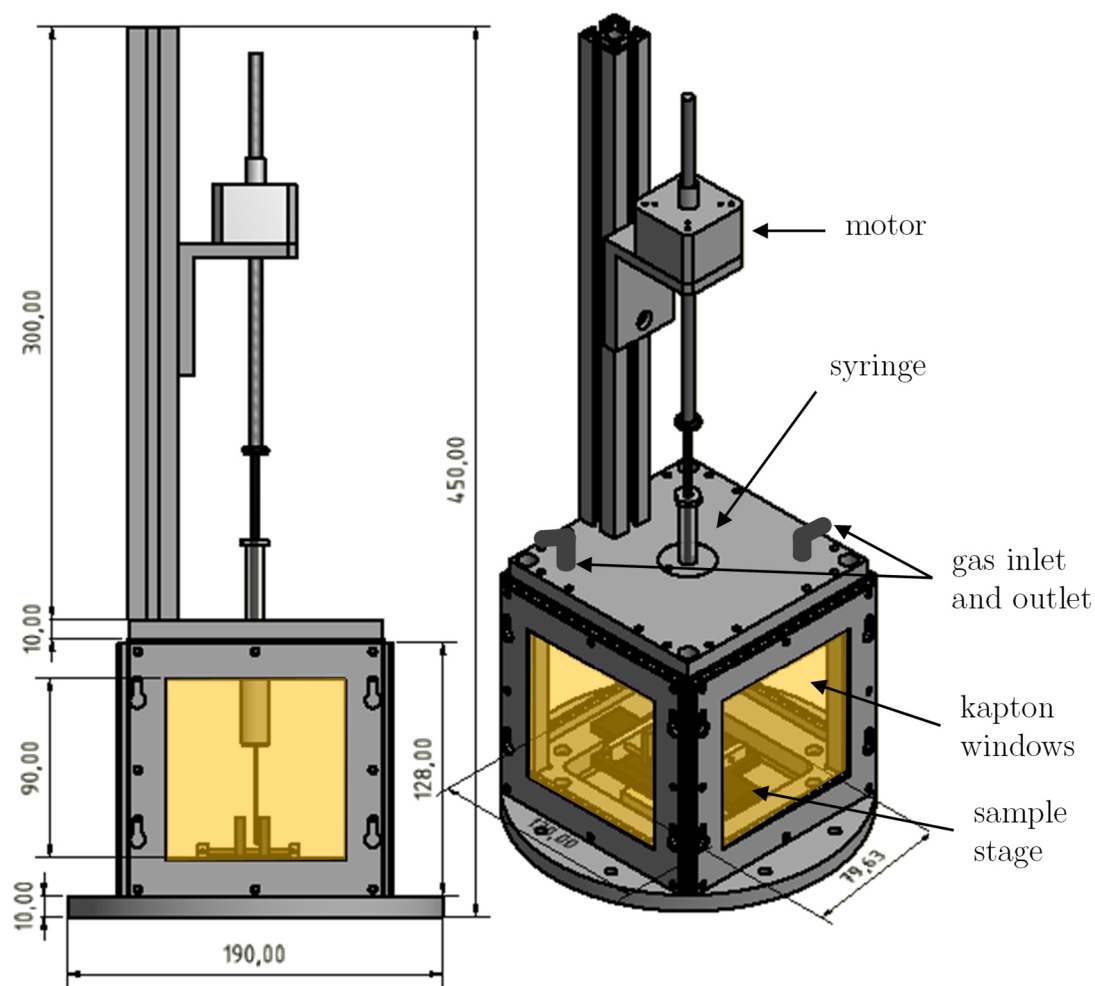


Figure 4.1: Custom-designed chamber for sample preparation under external electrical field, designed using the CAD software Autodesk Inventor [Aut26]

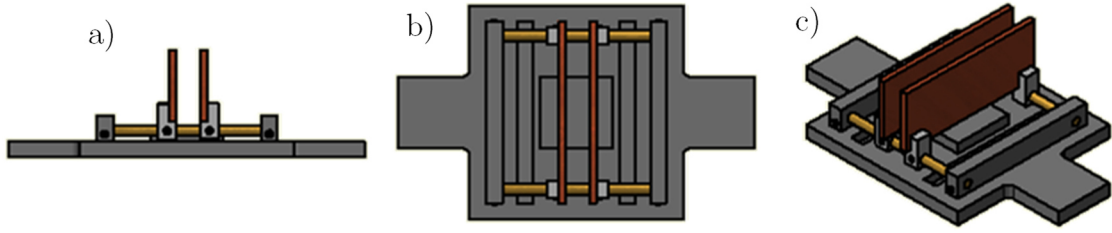


Figure 4.2: Detailed view of sample stage (gray) with adjustable capacitor plates (brown) side view a), top view b), and isometric view c), designed using the CAD software Autodesk Inventor [Aut26]

X-ray measurements were performed ex situ at the beamline BL9 at the DELTA synchrotron in Dortmund, Germany. The photon energy was 12.38 keV, which corresponds to a wavelength of $\lambda = \frac{h \cdot c}{E} = 1 \text{ \AA}$. The samples were measured in the directions both parallel to and perpendicular to the electric field that had been applied during film preparation. The measurements included X-ray reflectivity and diffraction measurements.

In the reflectivity curves shown in Figure 4.3, no Kiessig fringes can be observed. The spacing of the fringes is inversely proportional to the film thickness (see equation (3.33)). A large film thickness, which is typical for drop-cast films, results in extremely closely spaced fringes, beyond the resolution limit. Additionally, roughness dampens the XRR curves, which can also obscure the fringes. The strongest alterations are observed under constant electric field. The intensity reduction in reflectivity suggests a roughness increase which is strongest for the constant field (blue curve) and less pronounced for the alternating field (black curve). The reference film fabricated without external electric field seems to have the smoothest surface. The trends are reproducible for the two different concentrations and for different directions on the samples (parallel and perpendicular to the electric field direction).

Roughness increase under external electrical field has also been observed for P3HT:PCBM blends by [Ma11] and is an advantage for organic photovoltaic devices as it provides a larger surface area for the contacts.

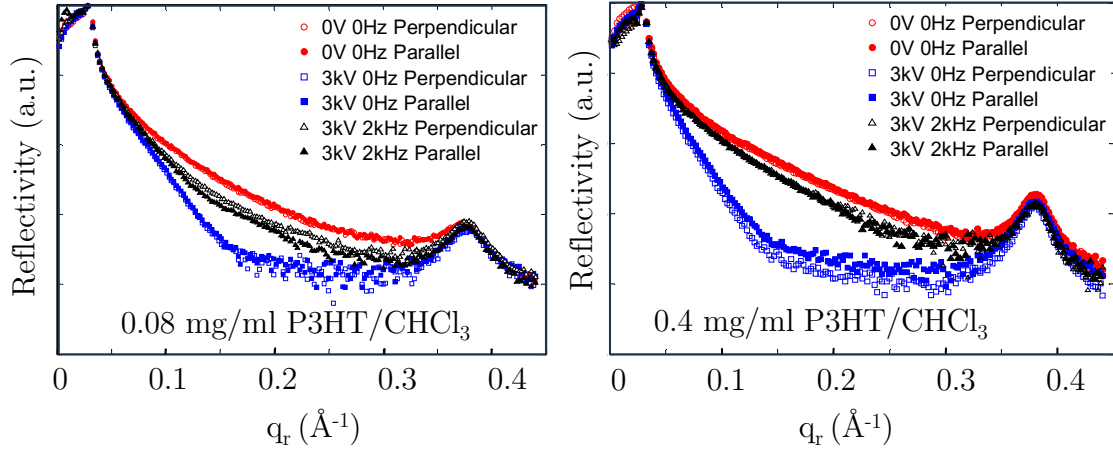


Figure 4.3: XRR profiles for P3HT samples drop cast from P3HT under no field (red), constant E-field (blue) and alternating E-field (black), measured parallel and perpendicular to the direction of the external electrical field.

The analysis of the (100) Bragg peak of P3HT (Figure 4.4) confirms the finding that the strongest alteration occurs for permanent electric field. It provides clear evidence that the presence of a permanent electric field during film fabrication significantly alters the microstructure of the polymer. The pronounced reduction in peak intensity (more than 40 %) and the increase in peak width FWHM (approximately 20%) suggest a decrease in crystalline order and a reduction in coherent crystallite size. This behavior contrasts with that of both the reference sample and the alternating-field case, which exhibit comparable peak widths and only minor variations in amplitude, suggesting that the permanent electrical field induces a fundamentally different structural perturbation.

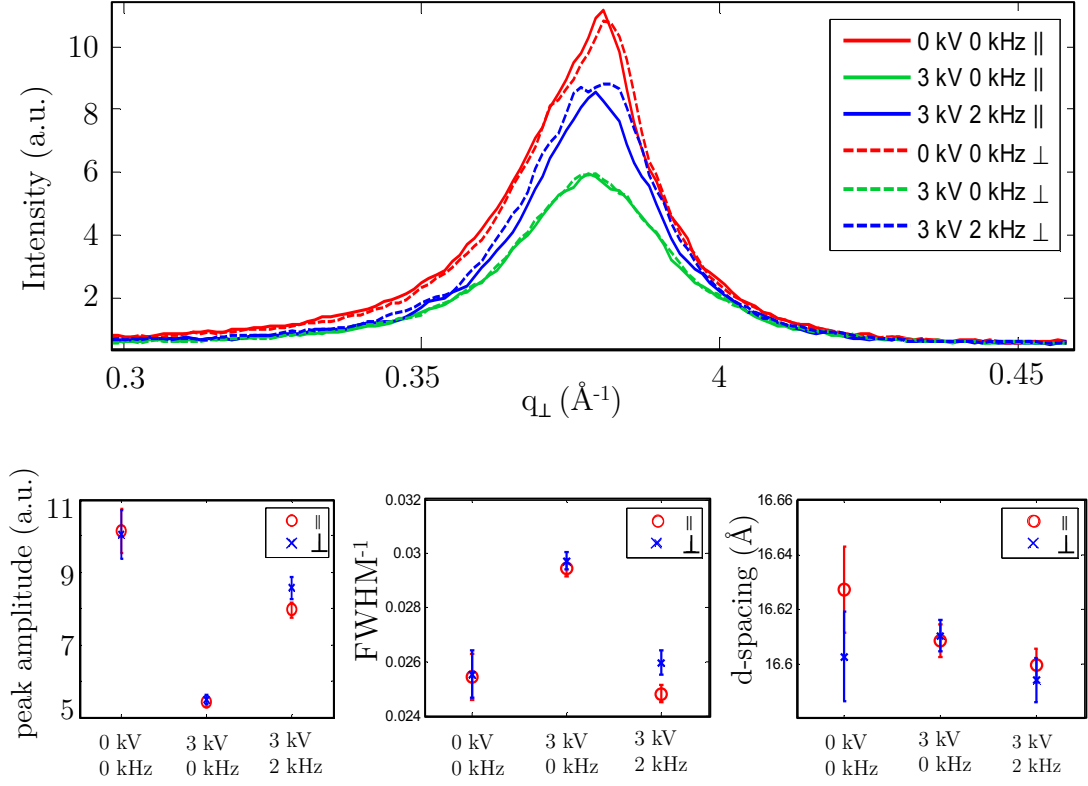


Figure 4.4: (100) diffraction peak measured at specular condition ($\alpha_i = \frac{2\theta_B}{2}$) (top) for P3HT film cast from 0.4 mg/ml solution at different external electric fields. no field (red), constant field (green) and alternating field (blue). Peak amplitudes, FWHM and d-spacings are shown in the three graphs below.

The underlying physical mechanism can be attributed to field-induced non-equilibrium assembly during solvent evaporation. Applying a constant electric field, P3HT chains in solution are under continuous polarization. This promotes aggregation and kinetically trapped configurations. Instead of allowing chains to reorganize into well-ordered lamellar stacks during slow solvent evaporation, the field drives the formation of disordered aggregates with limited long-range order. These aggregates act as imperfect nucleation centers, leading to smaller crystallites and increased structural disorder. This is directly reflected in the broadened (100) peak and reduced diffraction intensity.

In contrast, an alternating electric field does not provide a constant driving force for polarization. The periodic reversal of the field allows partial relaxation of the polymer chains, enabling more equilibrium-like self-assembly and thus preserving crystallinity closer to the reference case without external perturbation. This highlights that continuous directional force, rather than the mere presence of an electric field, is responsible for disrupting the structural order.

Additionally, the permanent field can induce local concentration gradients and electrophoretic effects in solution, leading to spatially heterogeneous deposition. Such inhomogeneities further limit crystal growth and promote a distribution of domain sizes, contributing to peak broadening. At the molecular level, the competition between π - π -stacking interactions and field-induced dipolar interactions results in hindered packing, where chains are unable to adopt optimal lamellar arrangements.

Studies on P3HT have demonstrated that the polymer readily forms aggregates in solution, which strongly influence film morphology and crystallinity upon deposition [Hua08]. Similarly, A. Salleo and co-workers showed that slight variations in processing conditions can shift the balance between ordered crystallization and disordered aggregation, with a direct impact on electronic properties [Nor13]. These studies support the interpretation that external perturbations, such as a constant electric field, can drive the system into less ordered, kinetically trapped states with reduced crystalline coherence.

4.2 Role of annealing of P3HT and BHJ blends

While subjecting P3HT to an external electric field during film casting in the previous chapter did not yield improvements in crystallinity, annealing is a known method to enhance crystallinity in polymer films [Jos09, Sal12]. At elevated temperatures the polymer chains become more mobile, allowing them to rearrange and combine to form larger, more ordered crystalline domains, which can improve charge transport.

P3HT and BHJ blends are of great interest for potential OPV applications and are widely studied. This chapter focuses on the correlation of their structure and electrical conductivity during a 2-step annealing process to elucidate ideal conditions for enhanced device properties. In a first heating cycle, the samples are heated stepwise to an elevated temperature below the melting temperature and going back to room temperature. In the subsequent second heating cycle, the film is heated to a temperature above the melting point of the polymer before returning back to room temperature.

Experimental details: rr-P3HT was purchased from Sigma Aldrich. The molecular weight is $M_n \approx 60\,000$ g/mol, $M_w/M_n \leq 2.5$ and the regioregularity $> 98\%$. The nominal melting is $230\text{ }^\circ\text{C}$. The fullerene derivatives PCBM₆₀ (purity $> 99.5\%$) and ICBA (purity $> 99\%$) were purchased from Solenne BV. All materials were used as received. Pure P3HT and blends were prepared in toluene at a concentration of 5 mg/ml and a selected ratio of 1:1 according to Table 4.2.

Table 4.2 Overview of solution parameters for P3HT and BHJ solutions

Material	Ratio	Solvent	Concentration (mg/ml)
pure P3HT	-	toluene	5
P3HT:PCBM	1:1	toluene	5
P3HT:ICBA	1:1	toluene	5

To correlate the structural and electrical properties, prototype conductive test beds were fabricated. Gold electrodes, approximately 80 nm in thickness, were thermally evaporated onto glass substrates measuring $18 \times 18 \text{ mm}^2$. For better adhesion a 5 nm chromium layer was first thermally evaporated onto the substrate. Chromium acts as an adhesion promoter, reducing delamination of the electrodes. The channel length was 2 mm to ensure that the X-ray beam ($1 \text{ mm} \times 0.2 \text{ mm}$ in the horizontal and vertical directions) would illuminate only the active channel area. Then, the polymer and blends were drop-cast onto the channels of the pre-fabricated test beds.

Grazing incidence X-ray diffraction measurements were performed at beamline BL9 at the DELTA synchrotron in Dortmund (Germany) at a photon energy of 13 keV. The sample was placed on a Linkam HFSX350-GI heating stage with a flush-mounted heating block for grazing incidence experiments [Lin16]. A fixed voltage was applied to source and drain electrodes using a Keithley sourcemeter, simultaneously recording the source-drain current response. This allows for the detection of any nonlinearities or switching behavior in electrical conductivity, which is relevant to electronic applications. Figure 4.5 shows a schematic of the measurement setup.

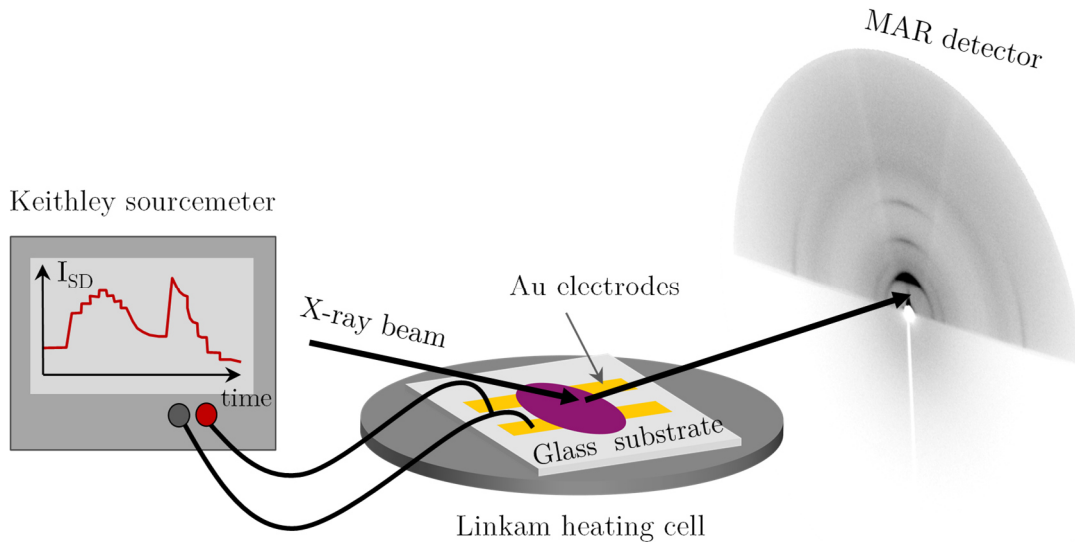


Figure 4.5: Schematic representation of the experimental annealing setup for in situ annealing with simultaneous electrical measurements. The sample is placed on a Linkam heating cell with a flush-mounted heating block that is suitable for grazing incidence X-ray experiments.

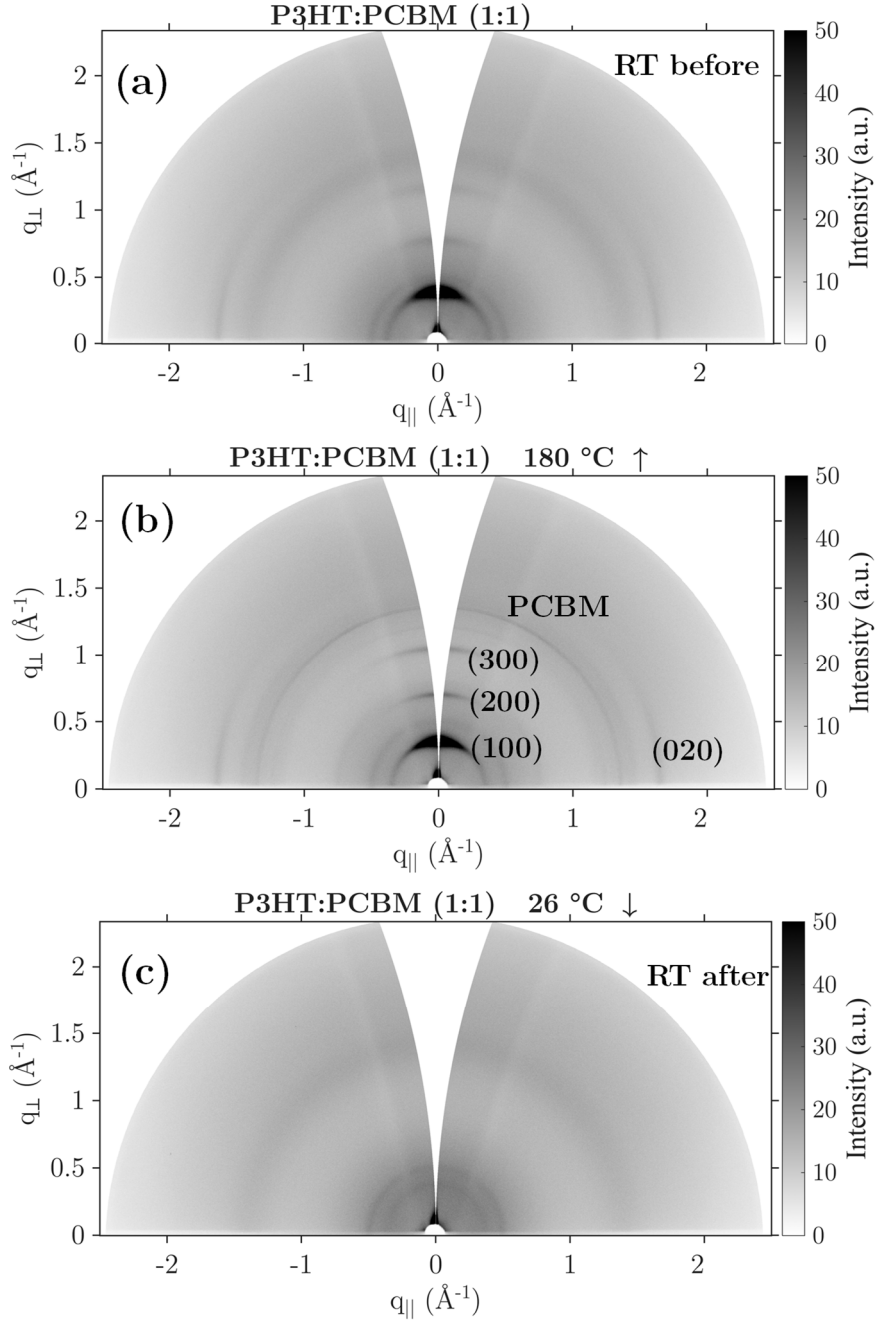


Figure 4.6: 2-dimensional diffraction patterns of P3HT:PCBM blend (1:1). Pure P3HT and P3HT:ICBA diffraction patterns are attached in the appendix.

P3HT usually adapts a monoclinic or orthorhombic unit cell with $a \approx 1.6$ nm, b and $c \approx 0.78$ nm and $\gamma \approx 86 - 90^\circ$ [Xie11]. The initial 2D-pattern shown in Figure 4.6 exhibits typical features of P3HT with dominating edge-on orientation as reflected by (h00) peaks in out-of-plane direction and the (020) peak related to π - π in-plane. The broader halo is attributed to the fullerene derivative.

The corresponding line profiles extracted from the 2D-GIXD patterns are presented in Figure 4.7 for out-of-plane direction and Figure 4.8. for in-plane direction for pure P3HT, P3HT:ICBA, and P3HT:PCBM (ratio 1:1) for the two heating cycles. Figure 4.9 focuses on the behavior of the (100) and (020) P3HT peaks for the pure polymer and the mixtures.

The heating protocol involved the following steps:

First cycle: RT $\rightarrow$ 70 °C $\rightarrow$ 80 °C $\rightarrow$ 90 °C $\rightarrow$ 100 °C $\rightarrow$ 90 °C $\rightarrow$ 80 °C $\rightarrow$ 70 °C $\rightarrow$ RT

Second cycle: RT $\rightarrow$ 150 °C $\rightarrow$ 180 °C $\rightarrow$ 200 °C $\rightarrow$ 220 °C $\rightarrow$ 250 °C $\rightarrow$ RT

The first annealing cycle improves polymer microstructure, whereas the fullerene-based amorphous halo remains almost unchanged.

In the second heating cycle, starting at 180 °C the line profiles of P3HT:PCBM develop a discrete crystallization feature in the q-range associated with PCBM aggregates (Figure 4.7 and 4.8, right), accompanied by sharpening of the P3HT (100) reflection. This trend is clearly visible when monitoring the (100) peak of P3HT shown in Figure 4.9, left. The corresponding P3HT:ICBA profile (Figure 4.7 and 4.8, middle) shows no equivalent peak emergence: the broad amorphous fullerene halo sharpens only marginally and remains the dominant fullerene-derivative feature even after the high-temperature step. P3HT:ICBA preserves the finely intermixed donor–acceptor morphology, which is favorable for charge separation in OPVs up to higher temperatures, whereas the morphology of P3HT:PCBM is coarsening. Its small mixed domains transform into larger, purer phases, which are less favorable for photovoltaic devices.

The two fullerene-based acceptors used in this work are not structurally equivalent and differ in their thermal response. PCBM is a single-addition C₆₀ derivative with a well-defined chemical structure, whereas ICBA is a bis-adduct of indene to C₆₀ (see Figure 2.4) and exists as a mixture of regio- and stereoisomers. The isomeric

heterogeneity of ICBA hinders long-range packing. ICBA is reported in the literature to crystallize much less readily than PCBM under identical annealing conditions [Zha10], which supports the observed findings. The in situ GIXD data presented here are consistent with this picture.

After applying a high thermal budget (250 °C) above the melting temperature, the film undergoes irreversible microstructural alterations without recovery of the peaks back at room temperature (Figure 4.6).

These microstructural changes were correlated with the current for both heating cycles. For the first cycle, the current increases in an almost linear and reversible fashion with temperature for the blends. For the second heating cycle after initial short enhancement the current degrades dramatically (Figure 4.10).

According to the desired properties for device application, the thermal protocol should be chosen with care. To enhance the blend microstructure while avoiding pronounced phase separation, the acceptor material and the thermal annealing protocol should be carefully selected. If PCBM crystallization is to be avoided, the annealing temperature should be kept in the linear regime and not exceed 150 °C.

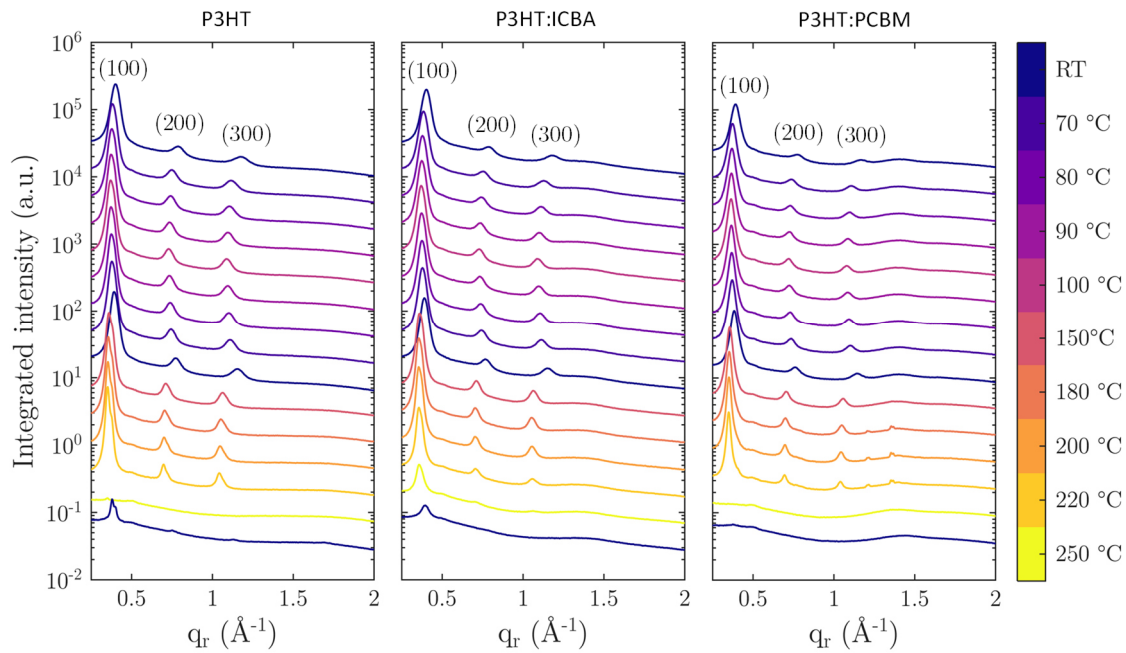


Figure 4.7: Out-of-plane line profiles pure P3HT (left), P3HT:ICBA (middle) and P3HT:PCBM (right) at different during the temperature cycles

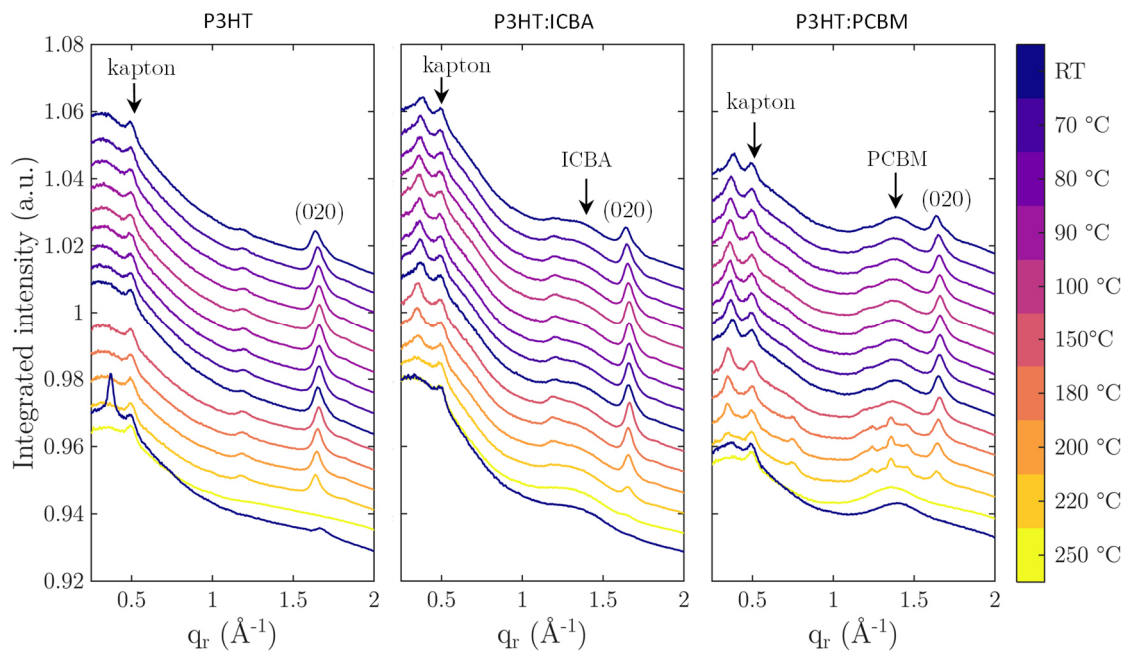


Figure 4.8: In-plane line profiles pure P3HT (left), P3HT:ICBA (middle) and P3HT:PCBM (right) at different during the temperature cycles

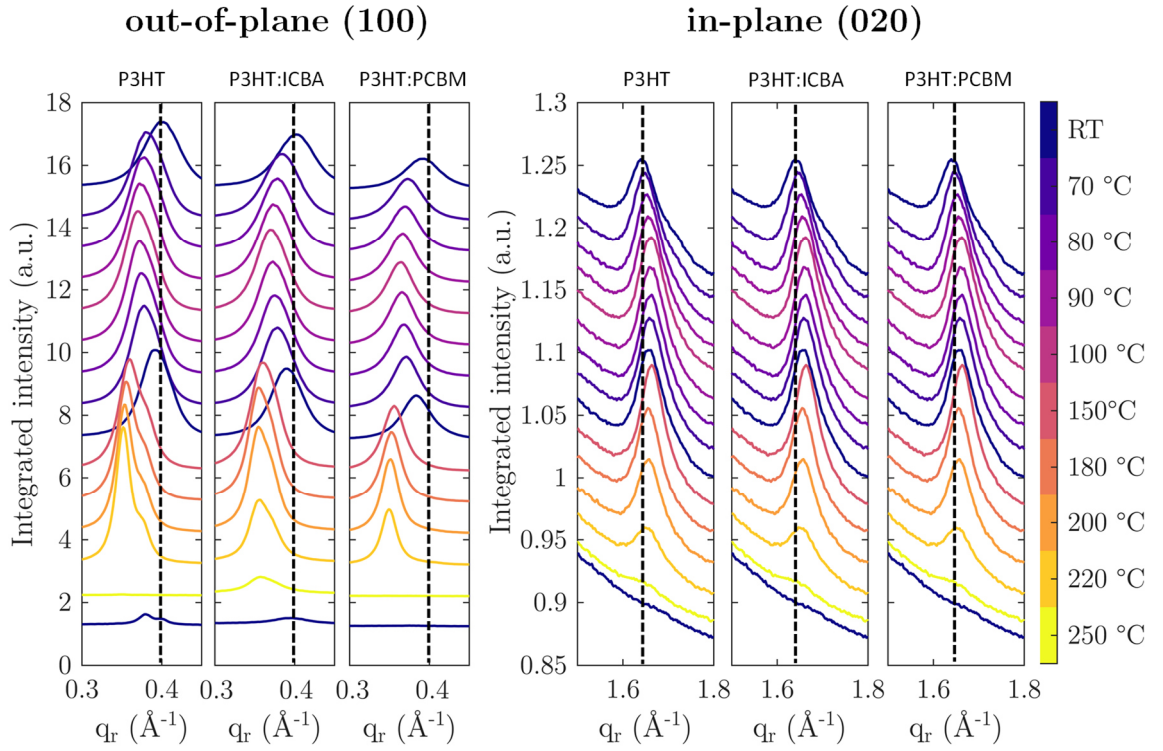


Figure 4.9: Out-of-plane line profiles of P3HT (100) peak measured for pure P3HT and blends (left) and in-plane P3HT (020) peak (right) during the temperature cycles

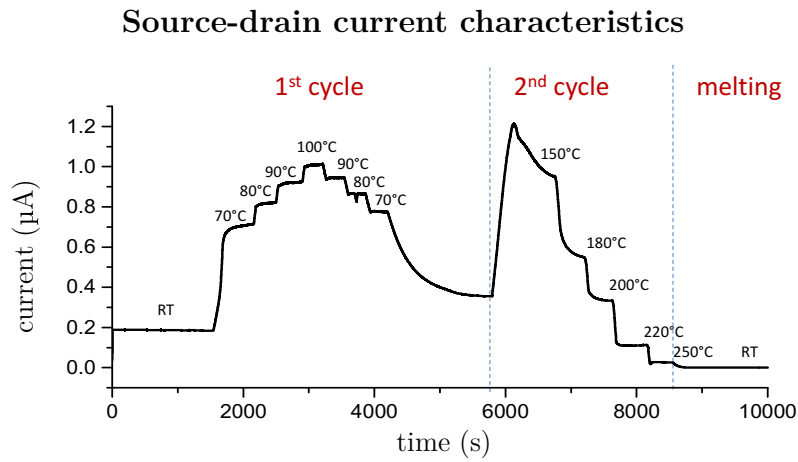


Figure 4.10: Typical current response for P3HT:fullerene derivative blends (in this case P3HT:PCBM) during annealing. The first cycle remains in a linear regime. In the second cycle, near 150 °C there is a break down in current. See also Figure A.2.4.

4.3 PEDOPT recrystallization

Conjugated polymers typically exhibit a semicrystalline structure with crystallites embedded in an amorphous matrix when prepared as a thin film from solution. In particular, the self-seeding approach allows for the controlled growth of the single crystals. This is achieved by heating the polymer film (or solution) to the seeding temperature close to the melting temperature. Due to polydispersity and the dependence of the melting temperature on the molecular weight, the higher molecular weight fraction remains solid/crystalline acting as nucleation seeds, while the other fraction is melted. Depending on the material, this is followed by quenching. Then the sample is heated to the crystallization temperature. Depending on the parameters (film thickness, temperatures, time, etc.), the resulting crystals can vary strongly in shape, size and quality. In this context there are still the open questions of whether grown crystals are truly single crystalline and which structural changes take place during the growth. To address these questions, we investigated conjugated poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT) by means of GIXD during the melting and recrystallization processes.

Experimental details: A solution from poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT), $M_w=2.7 \times 10^4$ g/mol, PDI=1.86, was prepared in p-xylene at a concentration of 3 mg/ml. PDOPT films were prepared by drop casting the solution onto silicon wafers at room temperature. The film was heated up to 130 °C while tracing GIXD patterns that were recorded at DELTA BL9 (Dortmund, Germany) with the same setup used in the previous chapter.

In order to monitor time resolved changes, diffraction patterns were acquired during melting and recrystallization (see Figure 4.11). The melting process of PDOPT is investigated in the range of 70 °C to 130 °C. The sample is heated to 70 °C at a fast rate (20 °C/min). The heating rate is then reduced to 1 °C/min and diffraction images (exposure time 60 s each) are taken every 2 °C. The recrystallization process is monitored at a cooling rate of 5 °C/min. During the X-ray measurement the temperature was kept constant.

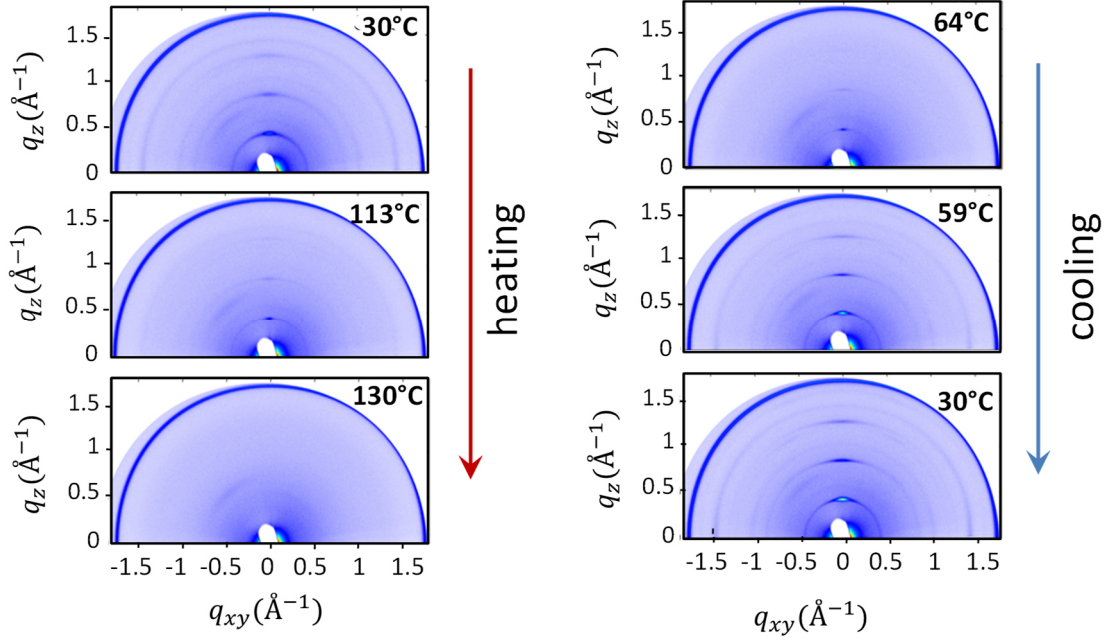


Figure 4.11: Melting and recrystallization of PDOPT monitored with GIXD at DELTA.

A pronounced enhancement of the structural peaks has been found after thermal treatment. The diffraction peaks gradually decrease and vanish at temperatures in the range of the melting point. At a temperature of 130 °C, the film is completely melted, and there are no more diffraction peaks to be detected. Upon cooling the sample down, the diffraction peaks are recovering. It can be noticed that compared to the initial state, the diffraction peaks have gained in intensity, indicating a higher degree of crystallinity and improved orientation.

Compared to regioregular P3HT, PDOPT has received considerably less structural attention. The currently accepted crystallographic model is an orthorhombic unit cell with parameters $a \approx 29.1 \text{ \AA}$, $b \approx 10.5 \text{ \AA}$, $c \approx 7.7 \text{ \AA}$ as determined by Hamidi-Sakr et al. [Ham16] from electron-diffraction analysis of epitaxially oriented PDOPT films. The large a -axis corresponds to the lamellar stacking direction and yields a (100) d-spacing of $d_{100} \approx 2.9 \text{ nm}$, almost twice the spacing d_{100} reported for P3HT [Xie11], reflecting the bulky 2,5-dioctylphenyl side groups. A defining structural feature distinguishing PDOPT from alkyl-substituted polythiophenes is the absence of π - π -stacking between thiophene backbones. Melting and recrystallization of PDOPT

have been independently reported by Keheze et al. [Keh17] using optical spectroscopy; the present in situ GIXD measurements complement that work by tracking the same thermal transitions in reciprocal space.

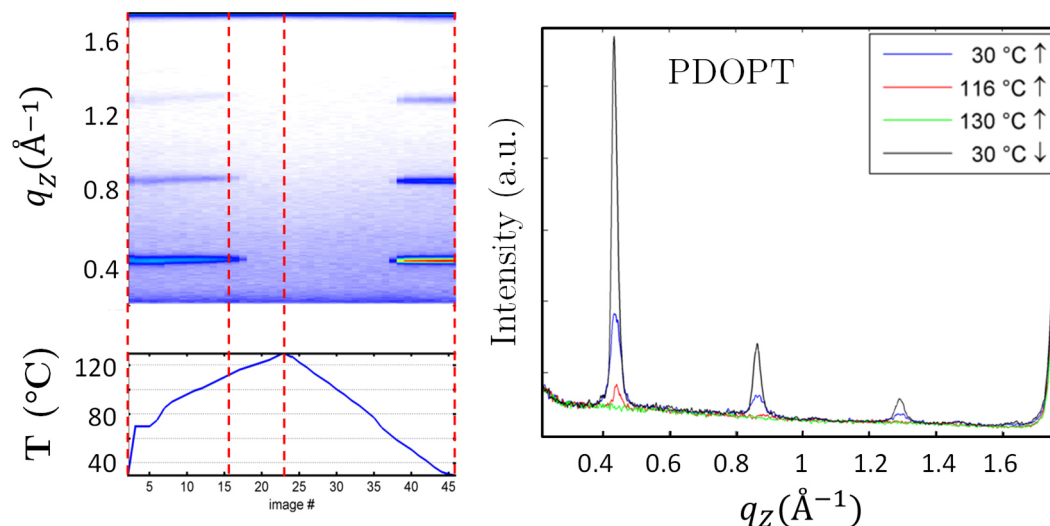


Figure 4.12: 2D representation of out-of-plane line profiles (left top) and temperature (left bottom), out-of-plane line profiles at the selected temperatures (right)

5 X-ray nanobeam diffraction

The previous chapters were dealing with device alterations due to treatment during fabrication and post-processing treatment as seen by conventional GIXD. The large size of the X-ray beam did not allow for more detailed spatially resolved measurements on a small scale, as the measured signal is averaged over a large area. Therefore, the OFET substrate discussed previously had a large channel length of one to two millimeters to ensure that the X-ray beam illuminated only the polymer channel. Commercially available OFET test chips with pre-patterned electrodes (see, for example, [Oss16, Fra26]), that are widely used for mobility characterization of newly synthesized materials, have much smaller channel lengths of a few to a few tens of micrometers. With the advent of nano-focused synchrotron beams, it has become possible to study such devices on a small scale. The following chapters are devoted to local structural investigations of P3HT thin film by X-ray nanobeam

diffraction. First, the transmission XRD of quasi-free-standing organic films with nanobeam will be discussed in Chapter 5.1.

The effect of an external electrical field was shown earlier in Chapter 4.1. The electric field was produced by a plate capacitor in non-contact mode. Chapter 5.2 is focused on the effect of an electric field in contact mode; that is a voltage directly applied to the source/drain electrodes of an OFET device.

Finally, in Chapter 5.3, scanning X-ray nano-diffraction for in-operando monitoring of structural changes in OFETs is employed. The advantages of this cutting-edge technique allow for real-time observation of structural changes during device operation.

5.1 Transmission XRD of P3HT with nanobeam

Grazing incidence X-ray diffraction is a powerful method for thin film analysis. By variation of the incidence angle, it reveals depth-resolved information about the inner structure (peak position), crystallite size (peak width), and orientational distributions (intensity distribution). However, when it comes to spatial resolution, this method is stretched to its limits. Due to the shallow incidence angle, the footprint of typical μm -sized beams can reach the dimensions of the entire sample length or even longer, resulting in averaged information. Additionally, there is only limited access to the orientational distribution of the in-plane Bragg peaks, in particular the (020) peak of P3HT, which is associated with the π - π -stacking and plays an important role in charge transport.

In order to overcome these limitations, the diffraction experiment is performed in transmission geometry similar to transmission electron microscopy (TEM). This requires transparent substrates. Quasi-free-standing polymer films were cast on silicon grids with a few nm thin silicon nitride membranes and probed with an X-ray nanobeam (see Figure 5.1). The 3D orientational distribution of microcrystallites can be obtained by making snapshots of diffraction patterns taken at different inclination angles χ .

Information on the complete orientation distribution of microcrystallites can be determined by pole figure measurements where random intensity distribution can be distinguished from clustering of poles along preferential directions [Koc98]. This technique was developed for bulky materials and thick films and adapted to uniaxially aligned thin films in reflection geometry. Further progress in quantification of crystallite alignment in thin films was achieved by combination of GIXD and specular X-ray diffraction patterns [Bak10]. Such a combination allows for obtaining complete pole figures for out-of-plane reflexes. However, in a specular reflection mode, in-plane orientations cannot be determined. Transmission geometry can be adapted for thin film characterization where both in- and out-of-plane orientational distributions can be simultaneously analyzed. Moreover, by using an X-ray nanobeam, the alignment of crystallites can be locally probed. This technique is demonstrated using P3HT thin films as a model system.

Experimental details: Thin poly(3-hexylthiophene) (P3HT, see Figure 5.1 (e) for molecular structure) films were spin cast from a 5 mg/ml solution in chloroform on Si TEM grids (3 mm in diameter) which include several rectangular windows ($2\text{ mm} \times 50\text{ }\mu\text{m}$) covered with 15 nm thick Si_3N_4 membranes (Dune Sciences, Inc.) as seen in Figure 5.1 (a). The different windows on one substrate are referred to as channels hereafter. The thickness of the polymer film is thick with respect to the Si_3N_4 membranes; hence the films are considered as “quasi-free-standing”.

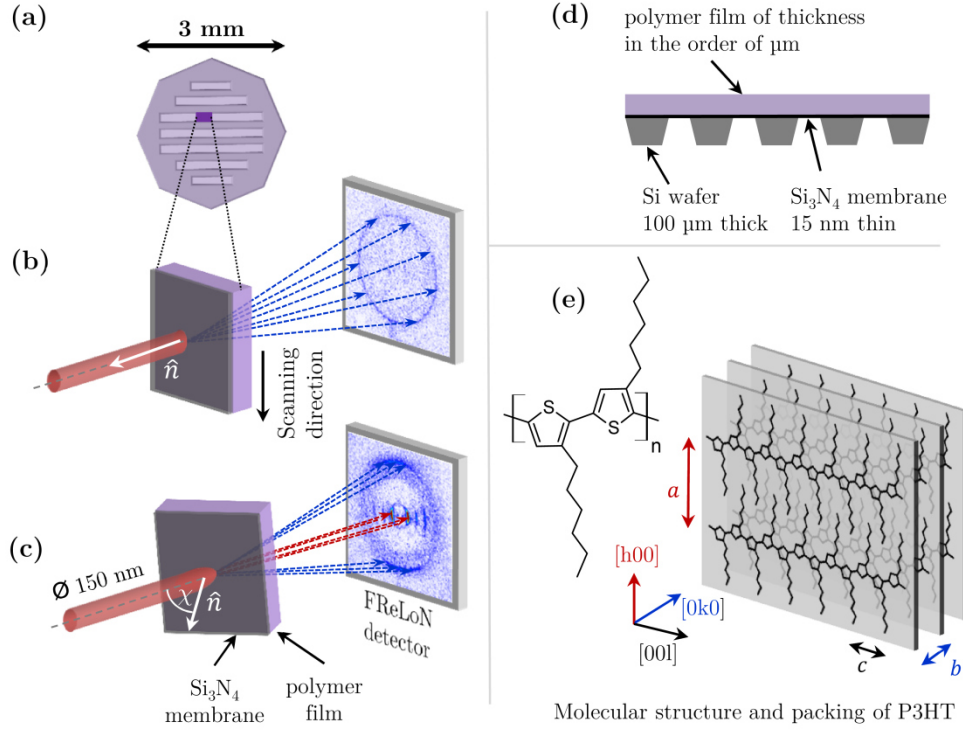


Figure 5.1: (a) Sample with rectangular windows. Schematic representation of transmission setup for X-ray beam striking under (b) normal and (c) under oblique angle χ (d) Cross sectional side view of sample: silicon wafer with windows is covered with a 15 nm thin Si₃N₄ membrane that supports the polymer film. (e) Molecular structure and packing of P3HT

The experimental setup of nanobeam studies in X-ray transmission geometry is shown in Figure 5.1 (b) and (c). In the first case (Figure 5.1(b)), X-rays strike the sample normal to the thin film surface (inclination angle $\chi = 0^\circ$). The diffraction pattern shows a well-defined Debye-Scherrer ring with the peak position at $q_{(020)} = 1.6 \text{ \AA}^{-1}$ where the (020) planes are associated with the π - π conjugated network of P3HT. Such a pattern corresponds to in-plane randomly distributed nanocrystals. In the second case (Figure 5.1(c)), taken under an oblique inclination angle χ with respect to the sample normal, an orientational anisotropy of the crystalline domains within the thin film becomes visible. Here, two strong intensity poles arise instead of the initially uniformly distributed (020) ring.

Additionally, strong diffraction signals appear at smaller q -values ($q_{(100)} = 0.36 \text{ \AA}^{-1}$) corresponding to planes associated with a stacking of $17.5 \text{ \AA}$ in the direction of alkyl side chains.

Measuring quasi-free-standing thin films in transmission geometry instead of traditional GIXD of thin films on thick Si substrates will provide access to the complete map of orientational distributions, which can be achieved by variation of the inclination angle χ . Using a nanobeam enables us to resolve orientational features on the smallest scale. It was shown that local alignment on nanoscale is essentially affecting device performance [Fis12].

Nanoscale X-ray transmission studies were conducted using a 150 nm beam at the ID 13 nano-focus beamline at the ESRF (Grenoble, France). The experiment was performed at an energy of 15.25 keV and an incident flux of $3 \cdot 10^9 \text{ photons/s}$. Diffraction patterns were collected with a large-area FReLoN (**F**ast-**R**eadout **L**ow **N**oise) camera with 2048×2048 pixels ($50 \times 50 \text{ }\mu\text{m}^2$ pixel size, binning 4×4 pixels). Nano-meshes with 6 snapshots at four different inclination angles χ (0° , 25° , 50° and 75° with respect to the sample surface normal) were collected by scanning the sample with a step size of 200 nm in direction perpendicular to the projection of the striking X-ray beam on the film surface. The exposure time was optimized to minimize radiation damage while obtaining sufficiently high intensity diffraction patterns. Thin films were measured under ambient conditions with an optimal exposure time of 5 seconds with respect to radiation damage and signal intensity.

Diffraction patterns were measured in transmission geometry with the X-ray beam impinging normal to the sample surface ($\chi = 0^\circ$) through to highly inclined ($\chi = 75^\circ$) geometries as seen in Figure 5.2. For the case of normal incidence (Figure 5.2 a), a single exposure reveals a ring-like diffraction pattern for crystalline domains satisfying the Bragg conditions at $\theta_{(020)}$. Due to the nano-dimensions of the probing beam as well as nano-sized P3HT crystallites embedded in an amorphous matrix, the diffraction pattern is similar to the one from dilute systems where intensity fluctuations along the ring can be resolved [Woc09, Kur13]. X-ray cross correlation analysis can be adapted to probe local symmetries on the smallest scale [Gut14, Kur15]. However, it does not provide information about out-of-plane orientation.

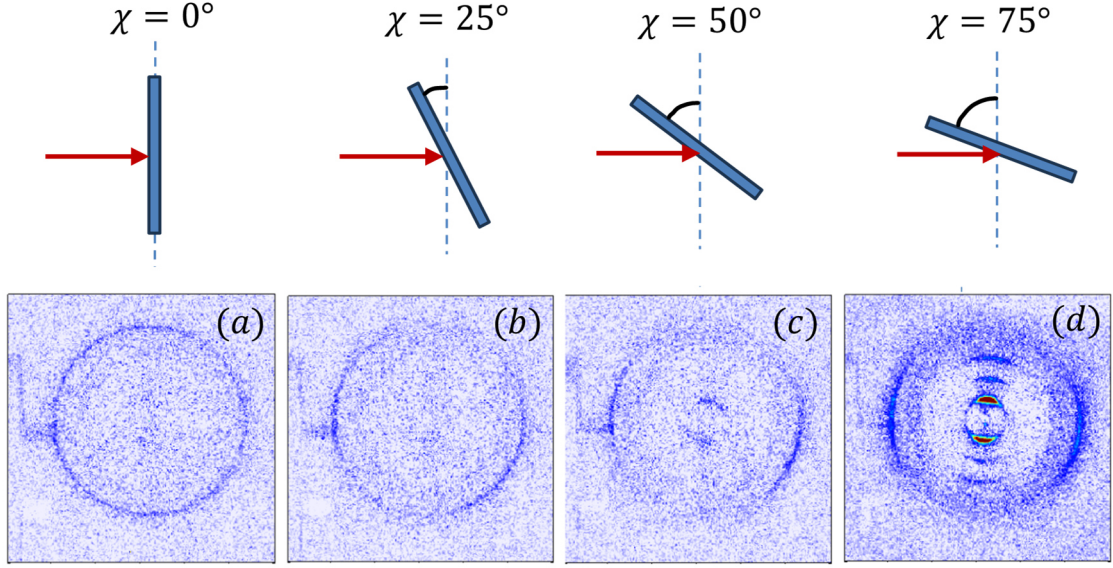


Figure 5.2: Diffraction patterns of single snapshots at normal (a) and different inclination angles $\chi=25^\circ$ (b), $\chi=50^\circ$ (c) and $\chi=75^\circ$ (d)

Figure 5.2 (d) shows a highly textured pattern in contrast to the nearly homogeneous distribution in Figure 5.2 (a). In this case, diffraction features are very similar to the ones conventionally measured by GIXD, confirming preferential orientations of nanocrystals. This indicates a strong domination of edge-on orientation, similar to numerous GIXD studies [Sir99, Kim06, Por11]. In this geometry, information about in-plane orientation is very limited.

Diffraction patterns measured at different incidence angles can be combined to reconstruct a three-dimensional reciprocal space map as seen in Figure 5.3, which includes full information about in-plane and out-of-plane distributions. It is obvious that small angular steps in χ during the measurements will improve the resolution.

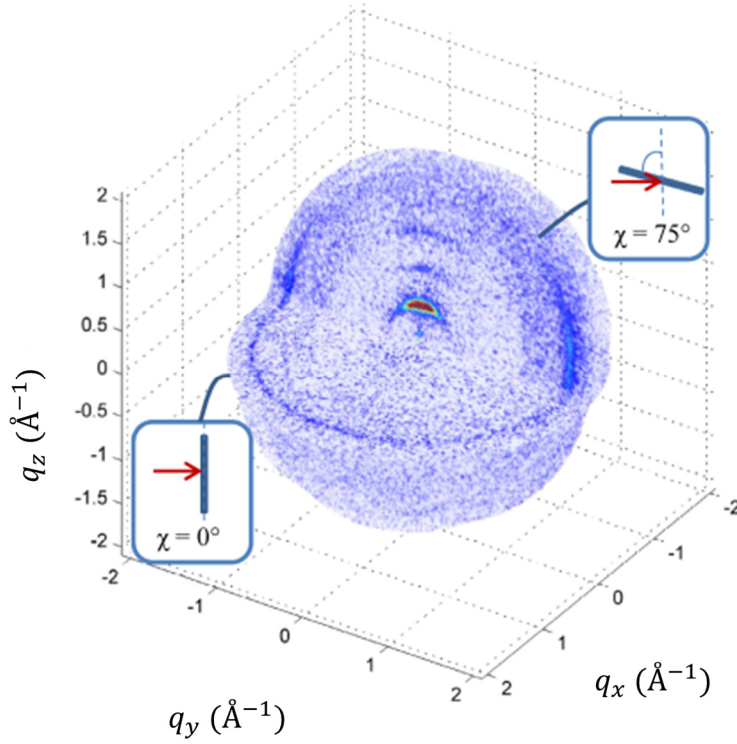


Figure 5.3: Reconstructed 3D reciprocal space map

The intensity peak at $q_{r,(020)} = 1.6 \text{ \AA}^{-1}$ corresponds to a uniform in-plane distribution of nanocrystals. Here we do not detect any preferential in-plane orientation of the π - π stacked lamellae. It is noteworthy that this information cannot be obtained from traditional grazing incidence experiments.

With increasing inclination angle χ , orientational features start to dominate. Already at $\chi = 25^\circ$ inclination intensity re-distribution is detectable and further increases for the higher inclination angles. Finally, it results in two well-defined intensity poles at $\phi = 90^\circ$ and $\phi = 180^\circ$ with favorable edge-on orientation of the (020) reflection. In addition to the (020) reflection, one can monitor the orientational distribution at $q_{r,(100)} = 0.36 \text{ \AA}^{-1}$ which is associated with the stacking of alkyl side chains. It ranges from no intensity at $\chi = 0^\circ$ to highly intense peaks at higher inclination angles for the (100) planes, confirming the preferential edge-on orientation.

When comparing the diffraction patterns taken at highly inclined geometry, we observe a shift in the azimuthal distribution which is very small for different positions within the same channel but more pronounced between different channels of the same sample (see Figure 5.4). This can be attributed to local variations in orientation.

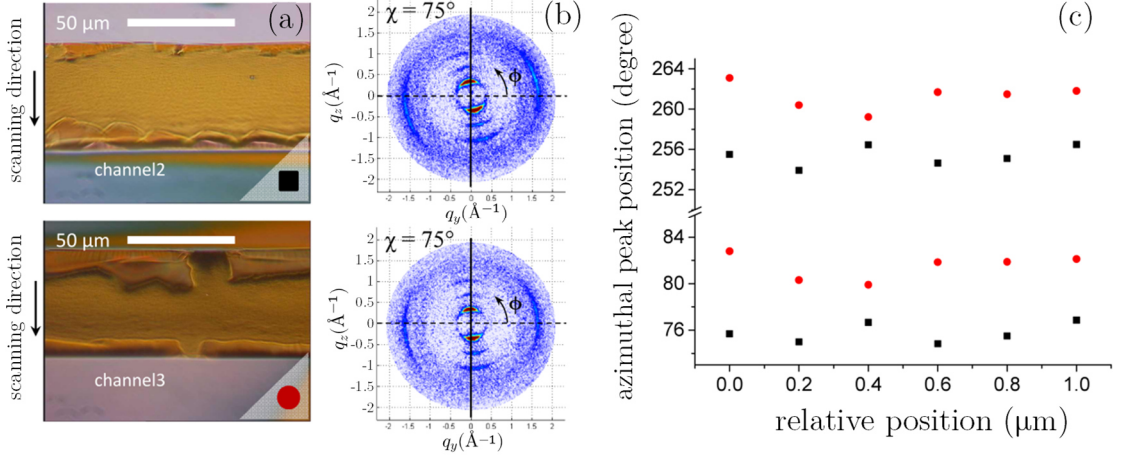


Figure 5.4: (a) Optical microscopy images of P3HT films and (b) corresponding diffraction patterns at the inclination angle $\chi = 75^\circ$ on two different channels of the same sample. (c) Azimuthal peak positions at $q_r = 0.36 \text{ \AA}^{-1}$ for vertical scan with 200 nm step size (black squares on channel 2 and red circles on channel 3)

To conclude, it was demonstrated that X-ray transmission experiments are feasible on quasi freestanding organic thin films. The diffraction pattern measured in transmission geometry provides complete information about the π - π conjugated network, which is hardly accessible by conventional X-ray techniques. Moreover, single snapshots taken at different inclination angles with X-ray nanobeam allow for reconstructing local orientational distribution and azimuthal tilt. A particular advantage of nanobeam is to detect local variations in in-plane orientation distribution as seen in Figure 5.4(c). The beam footprint on the sample increases with increasing tilt angles χ ; therefore, the obtained diffraction patterns include information averaged over the exposed volume. Using an X-ray nanobeam reduces averaging and allows for higher spatial resolution that is not accessible with traditional μm beam sizes and we are able to resolve local changes in orientations.

5.2 Local scale structural changes of working devices

Since the discovery of conductive and semiconducting polymers, the interest in organic electronics has risen sharply. Many new materials have been synthesized and need to be tested for their electrical performance. Commercially available OFET substrates with pre-patterned electrodes facilitate the device fabrication process, which is basically reduced to film preparation. As device stability is crucial for applications, it is important to be aware of possible alterations that might occur during device operation. However, studies on the behavior of functioning OFET devices on the local scale and their electrode-polymer interfaces are lacking. The nano-sized X-ray beam grants access to spatially resolved monitoring of the structural behavior across the P3HT polymer channel and the source and drain gold electrodes. In this subchapter, real-sized OFETs are examined with nanoGIXD for local structural changes during ongoing operation. The results have been published in the journal *Nanoscale* [Gro20].

Experimental details: For the OFET samples, commercially available OFET chips (Fraunhofer Institute for Photonic Microsystems) carrying 16 transistors with interdigitated source/drain gold contacts and channel lengths in the range of 10 to 20 μm were cut with a wafer saw into smaller chips (3.2 to 5.4 mm in size). By using the bottom-contact geometry, initial gold diffusion during electrode deposition into the conducting polymer channel is avoided as the electrodes are prepared first and then the polymer film is cast. Electrically non-conductive aluminum oxide sample supports were prepared with gold contacts by screen printing. The individual chips were glued onto a sample support with holder and the small source and drain electrodes ($0.5 \times 0.5 \text{ mm}^2$) of the chips were wire bonded to the larger gold contacts on the sample support. Copper wires for connections to the Keithley sourcemeter were soldered to the gold contacts on the sample support. The sample support was glued to a brass pin that was screwed to a matching socket in the goniometer. The semiconducting polymer layers were drop-cast from solutions of P3HT in chloroform (concentration 2 mg/ml) onto the OFET substrates. OFETs were powered with a Keithley 2612A sourcemeter and source-drain voltages were varied from 0 V to 100 V.

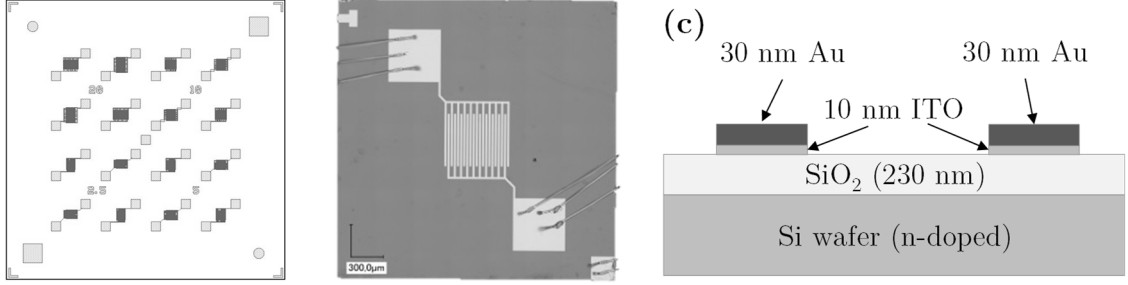


Figure 5.5: (a) Electrode layout of Fraunhofer test chips with 16 individual OFET devices (adopted from [Fra16]), (b) optical micrograph of single OFET device with interdigitated source and drain electrodes and (c) cross-sectional view of layered structure of the OFET test chip.

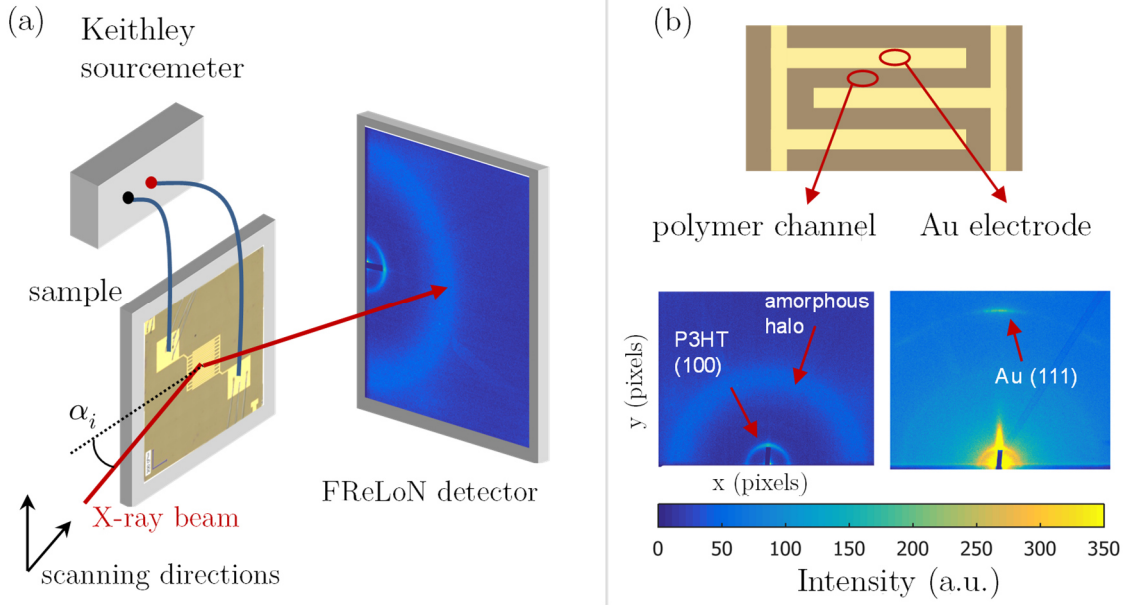


Figure 5.6: (a) Schematic representation of nano-GIXD setup with the sample in vertical position and (b) typical diffraction patterns at polymer channel and electrode position.

The nanoGIXD experiment, which is schematically shown in Figure 5.6, was conducted at the nanofocus end-station of beamline ID13 at ESRF, Grenoble, France. The photon energy was 14.9 keV (wavelength $\lambda = 0.83 \text{ \AA}$). The monochromatic X-

ray beam was focused to a spot size of $180 \times 180 \text{ nm}^2$ by silicon compound refractive lenses [Sch13]. The incoming flux at the sample position was around 1×10^{10} photons/s. The diffraction images were recorded with a FReLoN detector with 2048×2048 pixels and a pixel size of $50 \times 50 \text{ }\mu\text{m}^2$ in a 2×2 binning mode. Short exposure times (typically 1 s per image) were chosen to minimize radiation damage to the samples.

The samples were mounted in a vertical scattering geometry (cf. Figure 5.6) and illuminated with a fixed incident angle of $\alpha_i = 0.2^\circ$ to illuminate the polymer film, whilst minimizing reflection from the underlying substrate. This resulted in a beam footprint on the sample along the beam direction of $\frac{h_{\text{beam}}}{\sin(\alpha_i)} = 52 \text{ }\mu\text{m}$ (where h_{beam} is the height of the beam), which defines the lateral resolution. The resolution normal to the electrodes is given by the width of the beam, $w_{\text{beam}} = 0.18 \text{ }\mu\text{m}$. The sample was scanned in both the directions parallel and normal to the electrode digits. The scanning geometry is shown in Figure 5.7. The scan step sizes were calculated to be $0.2 \text{ }\mu\text{m}$ in x-direction and $57 \text{ }\mu\text{m}$ in y-direction covering a total area of $60 \times 286 \text{ }\mu\text{m}^2$.

Gold crystallizes in a face centered cubic (fcc) structure with a lattice parameter of $a = 4.078 \text{ }\text{\AA}$. The first few reflection positions are calculated by [Ref16] and summarized for reference in Table 5.1

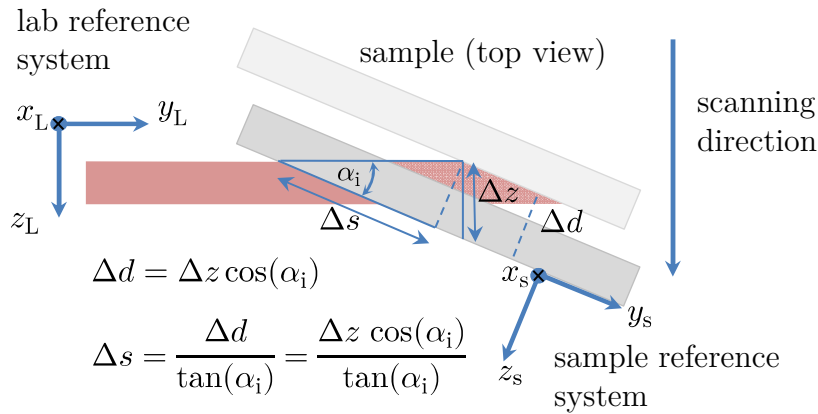


Figure 5.7: Mesh scanning in grazing incidence geometry (top view). A small motor movement in z_L -direction results in a large displacement Δs in y -direction on the sample surface.

Table 5.1: Calculated Bragg reflections and corresponding lattice spacings for Au [Ref16]

hkl	q ($\text{\AA}^{-1}$)	d ($\text{\AA}$)
111	2.6687	2.3544
200	3.0815	2.0390
220	4.3579	1.4418
311	5.1101	1.2296
222	5.3373	1.1772
400	6.1630	1.0195

Figure 5.6 (b) shows a single diffraction pattern of the polymer channel where the strong P3HT (100) reflection at $q = 0.39 \text{ \AA}^{-1}$ and its weaker higher orders which are related to the hexyl side chain stacking as well as the amorphous halo at $q = 1.65 \text{ \AA}^{-1}$ are visible. At the electrode position, this pattern is superimposed by the strong signal of the gold as seen in Figure 5.6 (b) with the Au (111) peak at $q = 2.66 \text{ \AA}^{-1}$.

The spatially resolved nanoGIXD mappings of the pristine OFET device show little variation of the diffraction patterns within the polymer channel regions and electrode regions, respectively, with well-defined borders (see Figure 5.8). Application of a source-drain voltage V_{SD} leads to irreversible changes as shown by the nanoGIXD mappings that were done at $V_{SD} = 10 \text{ V}$, 50 V and 100 V with stronger variations of the diffraction patterns and less defined electrode-polymer interfaces.

The different behavior of the two electrodes becomes even more obvious when looking at the orientation factor of the Au (111) Bragg reflection.

Throughout the scan, different features are observed in the diffraction patterns as shown in Figure 5.10. Especially the Au (111) reflection changes significantly after application of the source-drain voltage. Initially, the Au (111) reflection is arc-shaped with its maximum intensity in the out-of-plane direction at $q_{\perp} = 0$, indicating a certain degree of orientation of the gold. After applying the source-drain voltage, the top Au electrode remains ordered while the Au (111) reflection in the area of the

bottom electrode exhibits powder rings corresponding to random orientation. Herman's orientation factor can be used to quantify the degree of orientation for each single diffraction pattern according to [Her46]

$$f = \frac{1}{2}(3\langle\cos^2(\phi)\rangle - 1) \quad (5.1)$$

where

$$\langle\cos^2(\phi)\rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2(\phi) \sin(\phi) d\phi}{\int_0^{\pi/2} I(\phi) \sin(\phi) d\phi} \quad (5.2)$$

For data analysis, the integral in Equation (5.2) is approximated by the sum:

$$\langle\cos^2(\phi)\rangle = \frac{\sum_{\phi=0}^{\pi/2} I(\phi) \cos^2(\phi) \sin(\phi)}{\sum_{\phi=0}^{\pi/2} I(\phi) \sin(\phi)} \quad (5.3)$$

An f -value of $f = 1$ corresponds to complete orientation along the reference direction, $f = -0.5$ indicates an orientation perpendicular to it. For completely random orientation, the f vanishes. Due to experimental constraints, the integration region is restricted nearly to an angular range of $\pi/4$.

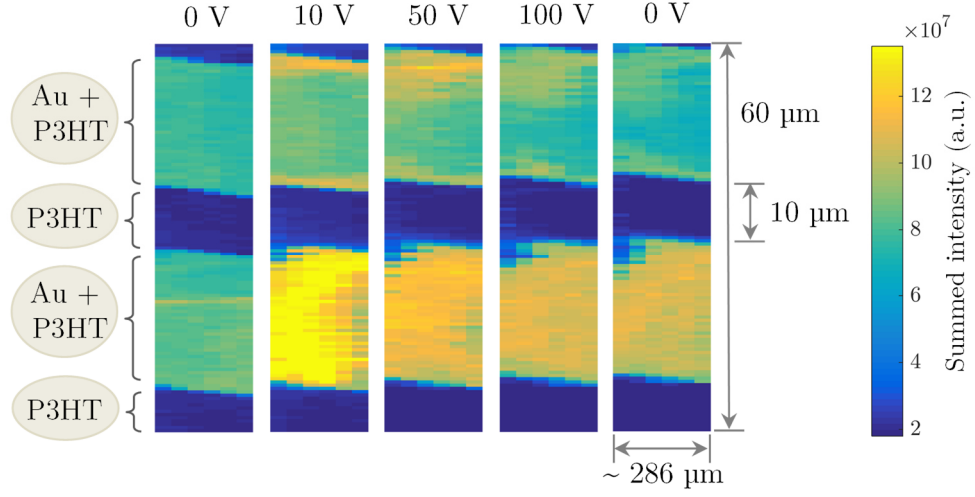


Figure 5.8: Diffracted intensity mapping for different source-drain voltages. Each pixel corresponds to the total intensity of a whole diffraction pattern at the particular position.

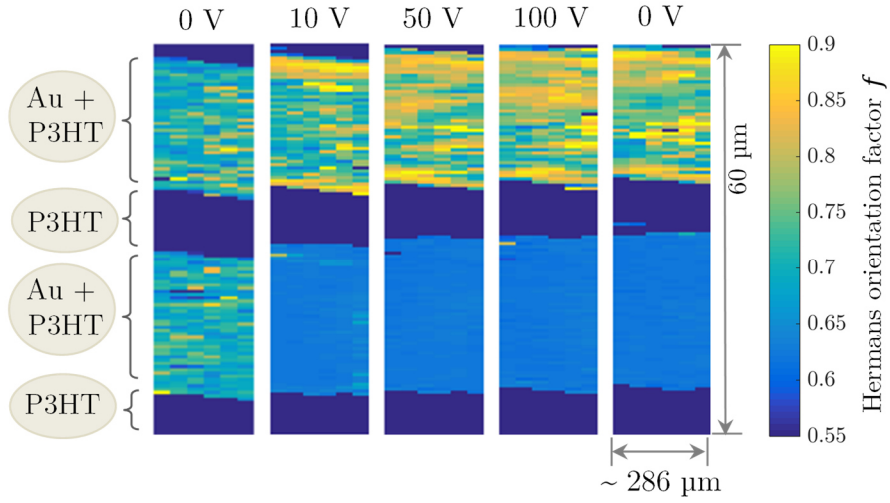


Figure 5.9: Mapping of Hermans' orientation factor calculated for the Au (100) reflection according to Equation (5.1).

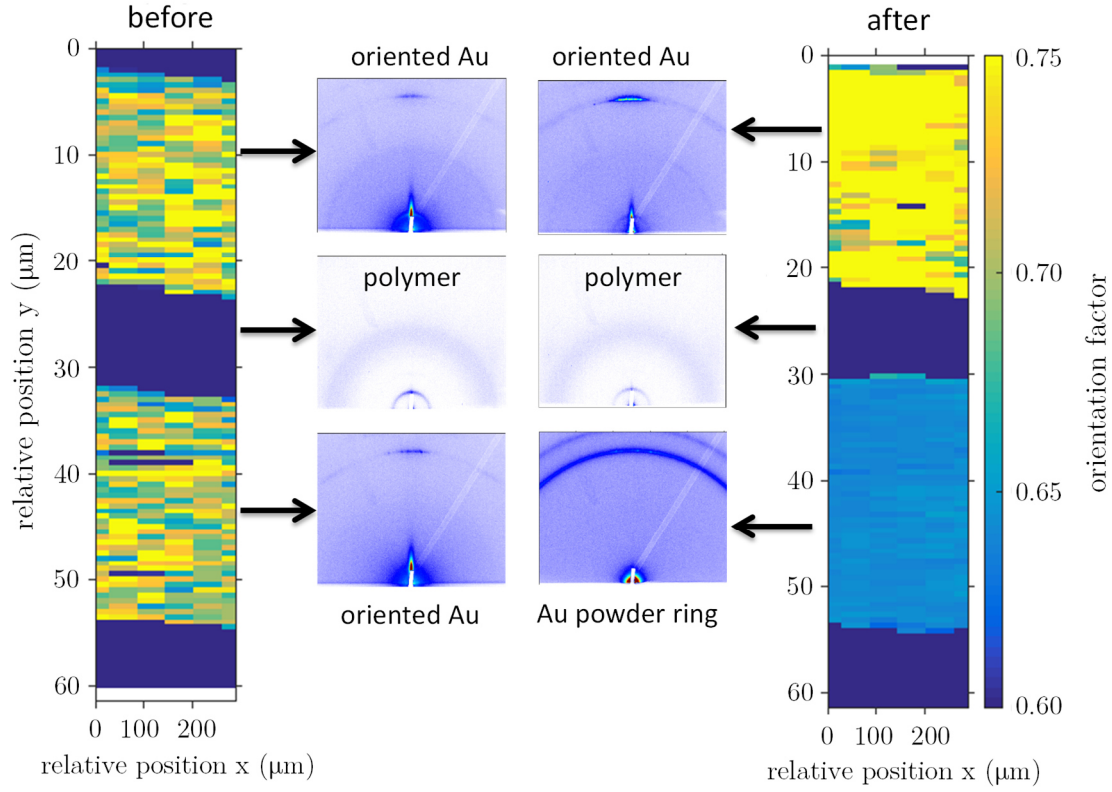


Figure 5.10: Mapping of orientation factor for Au (111) before and after application of source-drain voltage (left and right) and single diffraction patterns on electrodes (top and bottom) and in polymer channel (middle)

The highest degree of out-of-plane orientation found is $f = 0.8$. The factor f would be equal to 1 in the case of total orientation. A completely disordered system is represented by the condition $f = 0.6$ (Figure 5.10). The Au patterns of both electrodes are initially highly oriented, with a dominating local variation in the f -factor in the range from $f = 0.7$ to $f = 0.75$.

Both top and bottom electrodes provide similar features with sharp Au-polymer interfaces. However, for the working OFET device the situation is different: on the one hand, the top electrode preserves its features of the preferential orientation; however, the bottom electrode changes dramatically. For this electrode, now all diffraction patterns reveal powder-like features instead of the oriented intensity spots.

The Au-polymer interfaces also behave differently for both electrodes. Interestingly, the top one maintains its sharp, well-defined interface, whereas the bottom one shows strong modifications for the working device.

The different behavior of both electrodes could be caused by inhomogeneities and defects at the metal/organic interface resulting in high resistivity and leading to local heating.

To conclude, it is demonstrated that by nanoGIXD it is possible to monitor structural changes in real-size working OFET devices. A strong gold reorientation and modifications of Au-polymer interfaces during device operation was observed, which can be detrimental for applications and should be considered in future device engineering.

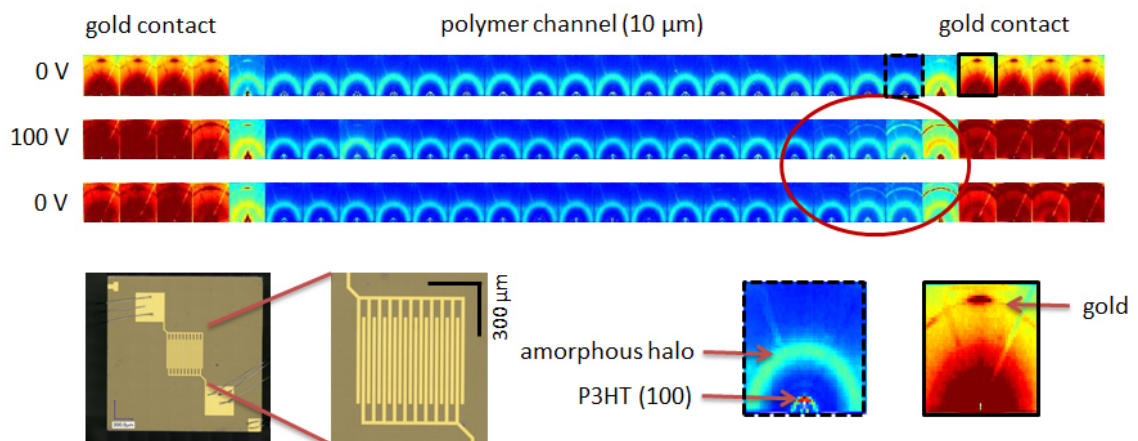


Figure 5.11: Spatially resolved GIXD patterns over a P3HT OFET channel before, during, and after applying 100 V to the source-drain electrodes. The red circle represents the area where gold has diffused into the polymer. Left down: commercially available OFET substrates with 10 μm channel length

5.3 In operando studies of OFETs on nanoscale

In the previous chapter the OFETs were used with fixed wire bonded electrical connections, which limits the flexibility in sample replacement. To address these limitations, a compact in-operando setup was designed and developed to enable simultaneous electrical and structural characterization of OFET devices. The setup allows for precise positioning of individual transistors within the measurement stage at nanofocus beamlines, while source and drain electrodes are electrically connected to external measurement electronics via adjustable gold pins as contacts.

The integration of NanoGIXD into this compact configuration provides a powerful tool for probing voltage-induced structural changes in oligothiophene thin films. The use of a high-energy synchrotron beam (16.98 keV) combined with a large-area detector enables reciprocal-space coverage extending up to approximately $3 \text{ \AA}^{-1}$ in both in-plane and out-of-plane directions, allowing simultaneous investigation of molecular packing parallel and perpendicular to the device surface. The grazing incidence geometry ensures surface sensitivity while maintaining penetration through the active layer. The results of this study were published in [Gri25] and adapted in this chapter.

Experimental details: DH5T thin films were thermally evaporated onto prefabricated OFET test chips from Ossila. The test chips carried 20 single channel gold electrode pairs on silicon substrate with channel lengths of $15 \text{ }\mu\text{m}$. As for the previous studies, a Keithley sourcemeter 2612A was used for electrical measurements. The gate voltage was kept at -10 V , while the source-drain voltage was scanned in the range of -10 to 10 V .

X-ray diffraction measurements of the working DH5T oligothiophene thin-film transistors were carried out at the nanofocus endstation of the P03 beamline at PETRA III, Hamburg, Germany. A monochromatic X-ray beam with a photon energy of 16.98 keV was focused to approximately 300 nm^2 using Kirkpatrick–Baez mirrors (JTEC). The samples were measured in grazing incidence geometry, allowing for controlled penetration depth and enhanced surface sensitivity. Diffraction patterns were recorded using a CCD-based Photonic Science area detector with a pixel size of $62 \times 62 \text{ }\mu\text{m}^2$ and a total array size of 2940×2940 pixels, positioned at a sample-to-detector distance of 317 mm .

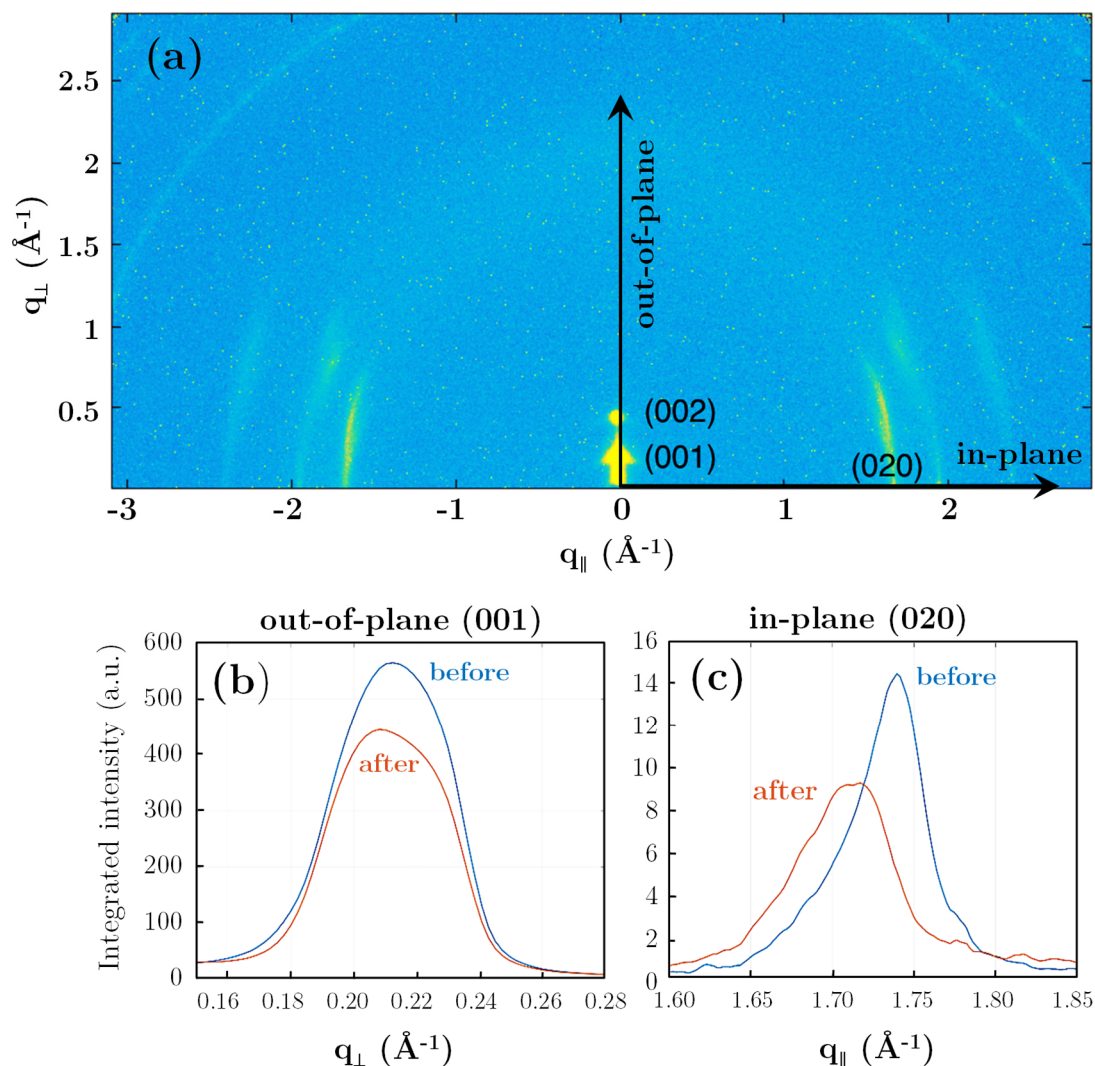


Figure 5.12: (a) nanoGIXD pattern of the thiophene-based oligomer DH5T; (b) out-of-plane (001) line profile before (blue) and after the working cycle (red); (c) in-plane (020) line profile before (blue) and after working cycle (red)

The nanoGIXD pattern of DH5T-based oligomer presented in Figure 5.12 (a) can be indexed to a monoclinic unit cell, in which the molecules adopt a tilted orientation relative to a fully upright alignment along the π - π -stacking direction. The multilayer structure exhibits a well-defined surface morphology, characterized by molecular monolayer terraces with an average thickness of approximately 89 nm. For the

subsequent structural analysis, the (001) and (020) diffraction peaks were selected, corresponding to the long molecular axis and the π - π -stacking direction, respectively. In both crystallographic directions, the initial line profiles (blue) were systematically compared with the profiles obtained after device operation cycles under applied voltages of -2 V, -5 V, and -10 V (Figure 5.12(b) and (c)).

The in-plane line profiles revealed pronounced structural changes in the π - π -stacking direction, including an expansion of the (020) interplanar spacing accompanied by a noticeable broadening of the full width at half maximum (FWHM) (Figure 5.12(c)). It is important to note that dedicated control measurements excluded the possibility of radiation-induced damage, confirming that the observed structural modifications are not caused by X-ray exposure. In contrast, the out-of-plane diffraction peak remained largely stable following device operation. No measurable variation in interplanar spacing was detected, and only marginal broadening of the peak was observed (Figure 5.12(b)). These results indicate that the structural changes induced during device operation predominantly affect the in-plane molecular packing, while the out-of-plane ordering remains comparatively robust.

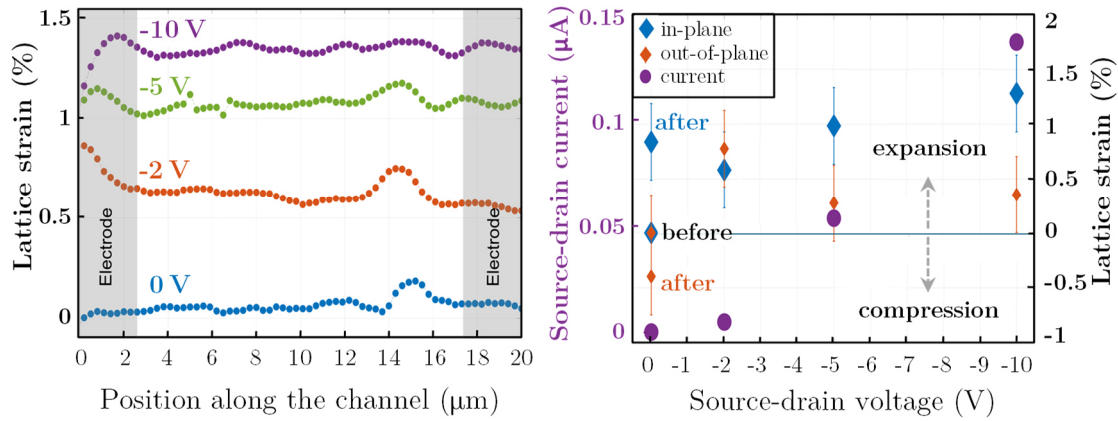


Figure 5.13 left: Lattice strain for (020) in-plane peak along the measured channel in a pristine state (blue curve) and under the applied source-drain voltages of -2 , -5 and -10 V (red, green and magenta curves, respectively); right: Lattice strain provoked by externally applied V_{SD} voltage for in-plane (blue) and out-of-plane (red) directions before the voltage, during and after the voltage was released.

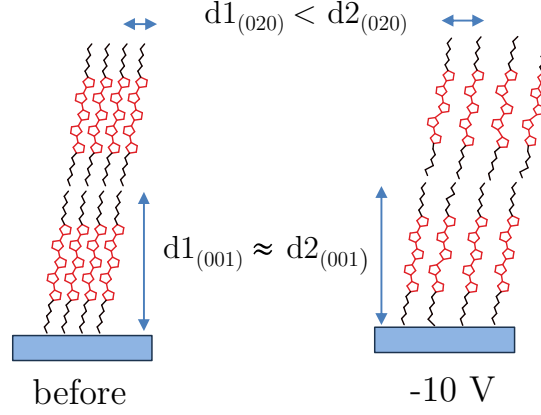


Figure 5.14: Model of molecular stacking under working conditions for DH5T OFET

A more comprehensive understanding of the device behavior can be obtained by analyzing the spatially resolved lattice strain at each applied voltage step, including contributions from both the electrodes and the transistor channel with high spatial resolution. It is noteworthy that the experimentally measured deviations in the d-spacing exceed the values previously shown for the channel region alone. These variations are summarized together with the corresponding error bars (Figure 5.13). A schematic representation illustrates the molecular arrangement of DH5T in the initial state and under the highest applied source–drain voltage ($V_{SD} = -10$ V), highlighting the structural response in both in-plane and out-of-plane directions. A direct comparison of lattice strain in these two crystallographic directions at different applied V_{SD} voltages, while maintaining a constant gate voltage ($V_G = -10$ V), reveals a clear trend. Initially, the system remains unstrained in both directions prior to voltage application. With increasing V_{SD} , a systematic expansion of the in-plane π - π -stacking is observed (schematically illustrated in Figure 5.14). The lattice response at each applied voltage step can be directly correlated with the corresponding current–voltage characteristics of the OFET, demonstrating the strong coupling between structural evolution and electrical performance.

In general, the out-of-plane direction exhibits higher structural stability, showing only minor variations at all applied voltages and after device operation. In contrast, the π - π -stacking in the in-plane direction is significantly more sensitive to electrical bias,

displaying a monotonic increase in tensile strain with increasing voltage. A maximum strain of approximately 1.3 % is reached at $V_{SD} = -10$ V. These structural changes are partially irreversible after completion of the device cycle, with a residual tensile strain of approximately 1 % remaining in the π - π -stacking direction. These findings further indicate that reducing the applied operating voltages is beneficial for maintaining structural integrity and improving device reliability, which is consistent with ongoing efforts aimed at lowering the power consumption of OFET devices.

The compact in-operando configuration offers several key advantages for studying structure–property relationships in organic electronic devices. First, it enables the acquisition of diffraction patterns under applied electrical bias, capturing structural rearrangements that cannot be observed under equilibrium conditions. Second, the setup allows systematic comparison of structural states before, during, and after voltage application, providing insight into reversible and irreversible structural processes. Third, the use of short acquisition times balances the need for sufficient diffraction intensity with the minimization of radiation-induced damage, ensuring reliable structural analysis. The implementation of this approach at a nanofocus synchrotron beamline further enhances its capability to resolve nanoscale structural variations across device channels.

Overall, the development of a compact in operando OFET characterization platform represents a significant methodological advancement, enabling direct investigation of the interplay between electrical operation and microstructural evolution in organic semiconductor devices. This approach provides a robust foundation for studying nanoscale structural dynamics and improving the design and reliability of next-generation organic electronic systems.

6 Conclusions

External perturbation by external electrical field

In situ studies of conjugated film formation demonstrated that external electrical fields significantly influence structural evolution during P3HT drop-casting. The presence of an applied electric field negatively affects the quality of structural order, leading to substantial modifications in crystalline domain size. This influence was found to be more pronounced under a permanent electrical field compared to an oscillating field, highlighting the sensitivity of polymer self-assembly to external perturbations.

In situ annealing: different behavior for different thermal budgets

The applied thermal protocol during annealing was shown to have a decisive impact on structural order and phase behavior. In situ annealing studies revealed that low thermal budgets preserve and improve the microstructure of polymer blends. In contrast, high thermal budget annealing induces irreversible structural changes in P3HT:PCBM blends, including PCBM crystallization and phase separation upon exceeding melting temperatures. For PDOPT, structural order decreases significantly upon heating but recovers after cooling to room temperature, reaching an enhanced level compared to the initial state.

Structural properties of quasi free-standing films in transmission

X-ray nanobeam diffraction studies on quasi free-standing P3HT films demonstrated the feasibility of high spatial resolution transmission measurements on organic thin films. This approach enables direct observation of local variations in crystal orientation and symmetry significantly reduces substrate related interference, providing new insights into the intrinsic structural organization of polymer networks at the nanoscale.

Local properties of P3HT working devices with NanoGIXD

Nanobeam grazing incidence diffraction measurements enabled spatially resolved characterization of structural changes within operating devices. These experiments revealed local structural heterogeneities and interfacial modifications, particularly at electrode–polymer interfaces. Structural changes directly affect charge transport

behavior and can be detrimental to device performance, emphasizing the importance of nanoscale structural control for reliable device performance.

In operando studies of DH5T OFETs on nanoscale

In operando nanoGIXD measurements revealed pronounced structural anisotropy in oligomer thin films under applied source–drain voltages. Significant structural variations were observed in both in-plane and out-of-plane directions during device operation, providing direct insight into nanoscale structural dynamics governing OFET functionality under realistic working conditions.

7 Summary

The results presented in this thesis demonstrate that the structural organization of conjugated organic materials is highly sensitive to external stimuli, including electrical fields, thermal treatment, and device operation conditions. External perturbations during film formation were shown to significantly alter crystalline domain size and structural order, particularly under permanent electric fields. Furthermore, systematic in situ annealing studies revealed that the applied thermal budget critically determines the reversibility and stability of microstructural evolution, with low thermal budgets improving blend morphology while high thermal budgets induce irreversible phase separation and crystallization effects.

A direct link between structural dynamics and electrical behavior was established through nanoscale diffraction experiments, which revealed electrode reorientation and interface modifications during device operation. These findings highlight the importance of structural stability at metal–polymer interfaces for reliable device performance. In addition, the use of nanobeam X-ray diffraction in transmission geometry enabled high-resolution investigation of quasi free-standing films, providing unique access to intrinsic structural properties independent of substrate effects. Finally, in operando nanoscale diffraction measurements demonstrated pronounced structural anisotropy and dynamic structural rearrangements in organic semiconductor devices under applied voltage bias. Together, these results provide a comprehensive understanding of the structure–property–function relationships governing organic thin films and devices, bridging the gap between materials processing, nanoscale structure, and device operation.

8 Outlook

The findings of this thesis open several promising directions for future research in the field of organic semiconductor thin films and devices. A key challenge remains the controlled manipulation of structural order during film formation under external perturbations. Future work could focus on optimizing electric-field-assisted deposition techniques to tailor crystalline domain orientation and improve charge transport pathways in functional devices.

Further systematic investigations of thermal protocols with precisely controlled heating and cooling rates could enable improved stability and reproducibility of polymer blend morphologies. In particular, combining in situ structural characterization with complementary spectroscopic or electrical measurements would allow deeper insight into kinetic processes governing phase separation and crystallization dynamics.

The demonstrated capability of nanobeam X-ray diffraction on quasi free-standing films suggests strong potential for studying intrinsic structural behavior in a wide range of organic and hybrid materials systems. Extending this methodology to multilayer structures, heterojunctions, and flexible substrates could provide valuable insights relevant to emerging applications in modern organic electronics.

Moreover, the observed structural changes at metal–polymer interfaces during device operation highlight the need for improved electrode design and interface engineering. Future studies may explore alternative electrode materials, surface treatments, or interfacial layers to enhance structural stability and mitigate degradation effects under electrical bias.

Finally, the implementation of in operando nanoscale diffraction techniques represents a powerful tool for investigating real-time structural dynamics in working devices. Expanding these approaches to more complex device architectures, including high-performance organic field-effect transistors and organic photovoltaic systems, will further advance the understanding of functional processes under realistic operating conditions. Such developments are expected to contribute significantly to the rational design of next-generation organic electronic devices with improved efficiency, stability, and reliability.

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Appendix

A.1 Peak functions

Gaussian:

$$f_G(x) = y_0 + A \frac{\sqrt{4\ln(2)}}{\sqrt{\pi} \cdot w} \cdot \exp\left(-\frac{4\ln(2)}{w^2}(x - x_c)^2\right) \quad (\text{A.1})$$

where A is the area, y_0 the offset, w the full width at half maximum (FWHM) and x_c the center of the peak.

Lorentzian:

$$f_L(x) = y_0 + A \frac{2}{\pi} \cdot \frac{w}{4(x - x_c)^2 + w^2} \quad (\text{A.2})$$

with the same parameter meanings as for the Gaussian.

The Pseudo-Voigt profile is a linear combination of a Gaussian and Lorentzian of the form:

$$f_{\text{PVG}}(x) = y_0 + A \left[\eta \cdot \frac{2}{\pi} \cdot \frac{w}{4(x - x_c)^2 + w^2} + (1 - \eta) \cdot \frac{\sqrt{4\ln(2)}}{\sqrt{\pi} \cdot w} \cdot \exp\left(-\frac{4\ln(2)}{w^2}(x - x_c)^2\right) \right] \quad (\text{A.3})$$

where the mixing parameter η is in the range of with $0 < \eta < 1$.

The peak height H is obtained by computing $H = f(x_c)$.

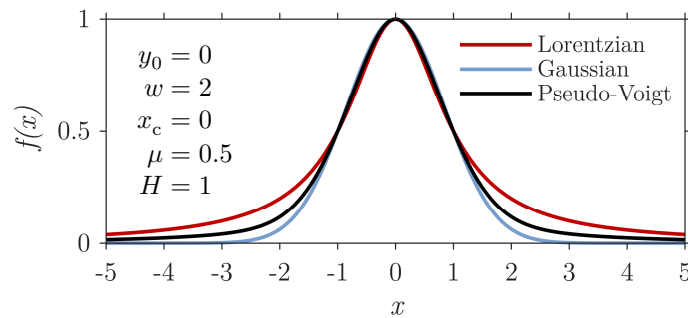


Figure A.1.1: Comparison of peak functions: Gaussian (blue), Lorentzian (red) and pseudo-Voigt (black)

A.2 Supplementary material for annealing of P3HT and BHJ blends

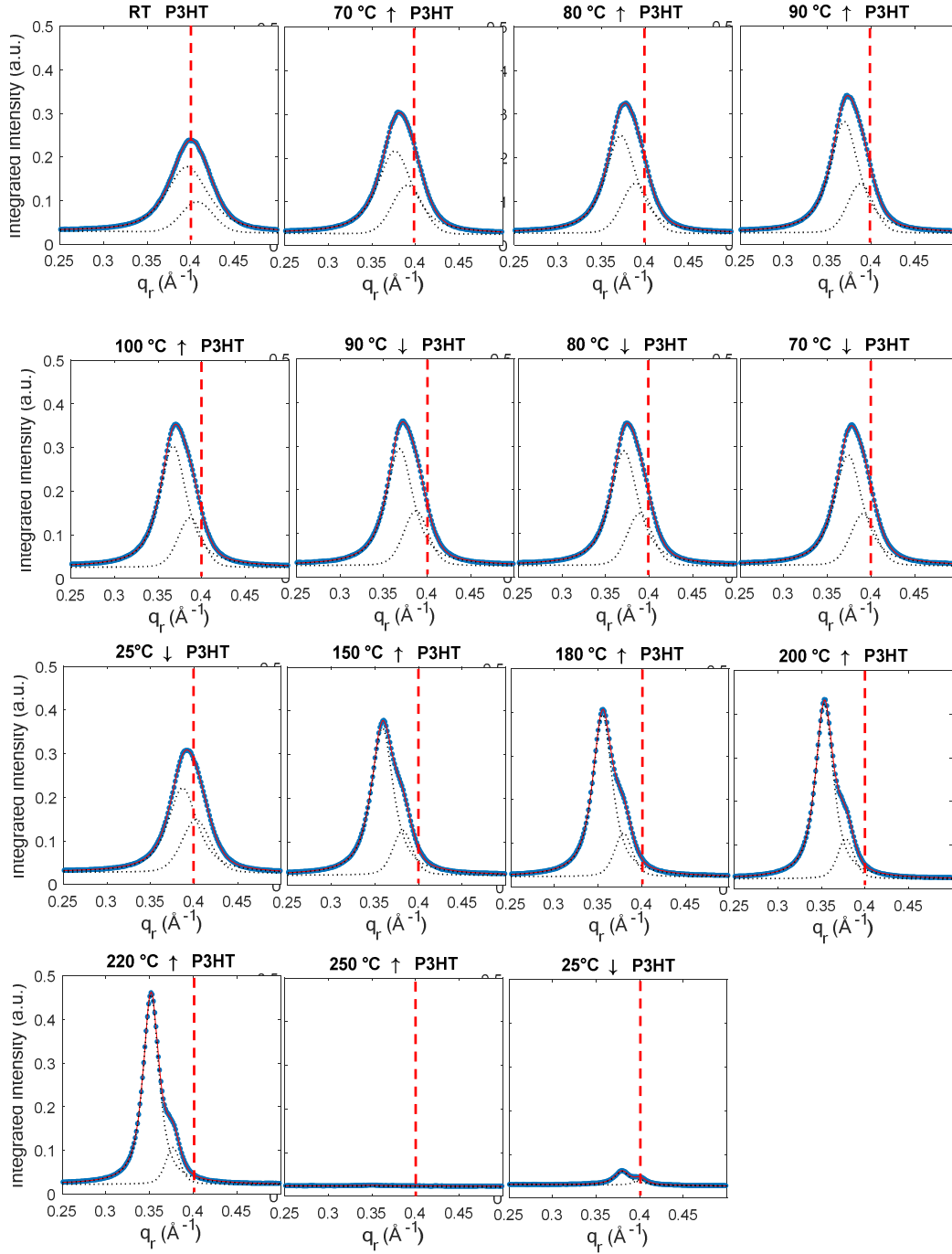


Figure A.2.1: Out-of-plane line profiles of (100) diffraction peak for pure P3HT and respective double peak pseudo-Voigt fit during 2-step temperature cycle.

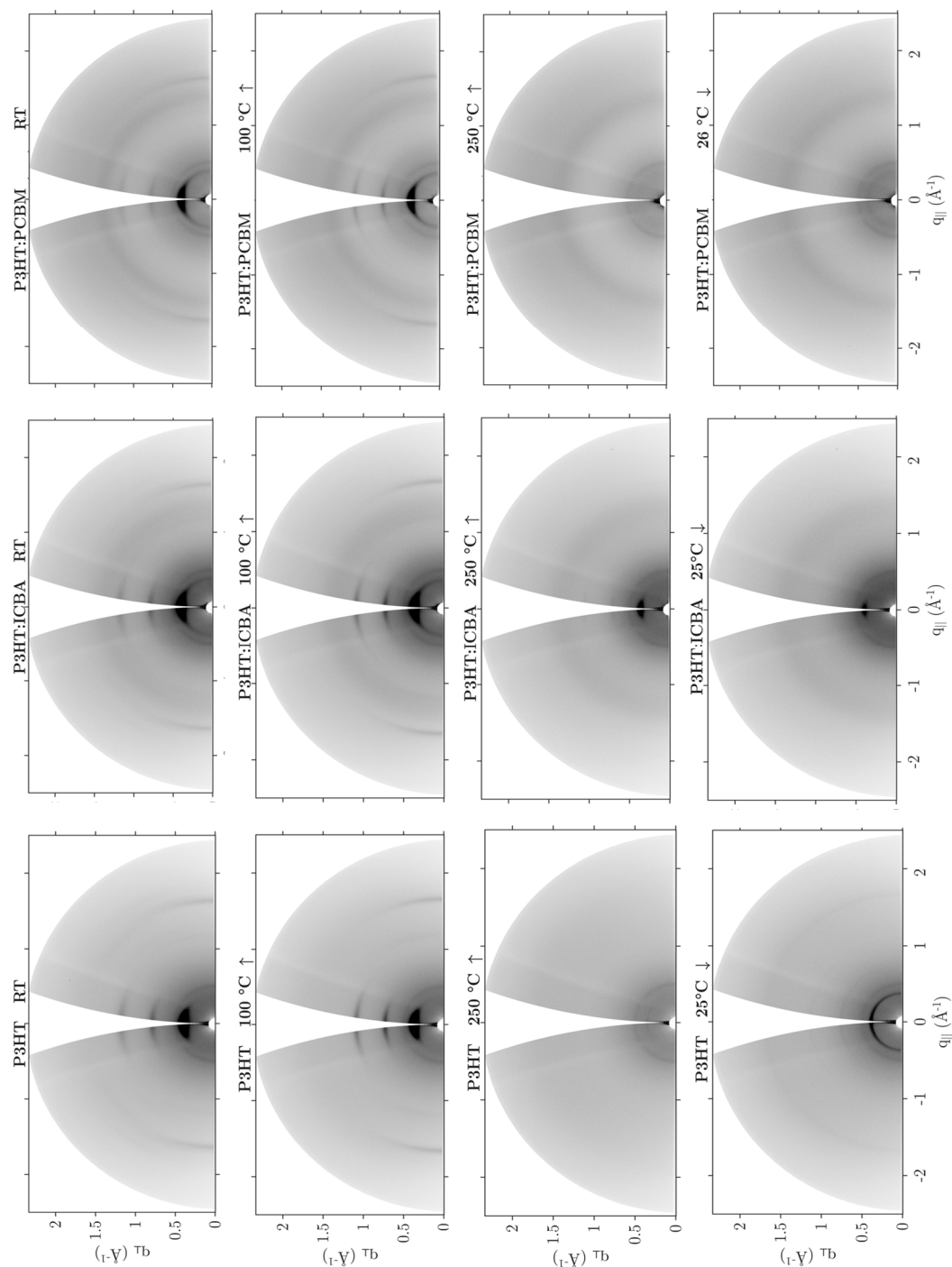


Figure A.2.2: 2D diffraction patterns of P3HT (bottom row), P3HT:ICBA (middle row) and P3HT:PCBM top row for selected temperatures during the annealing cycles: from left to right: initial room temperature, 100 °C, 250 °C, final room temperature.

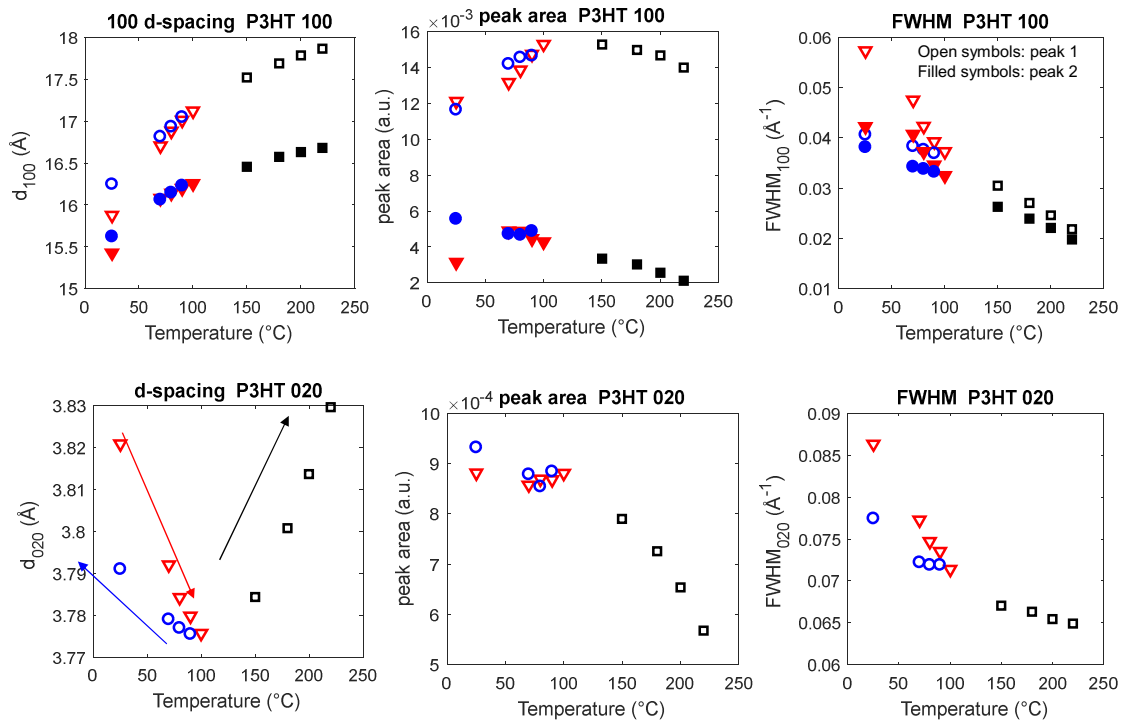


Figure A.2.3: P3HT peak positions of (100) and (020) reflection as function of temperature (left) and integrated peak intensity as function of temperature.

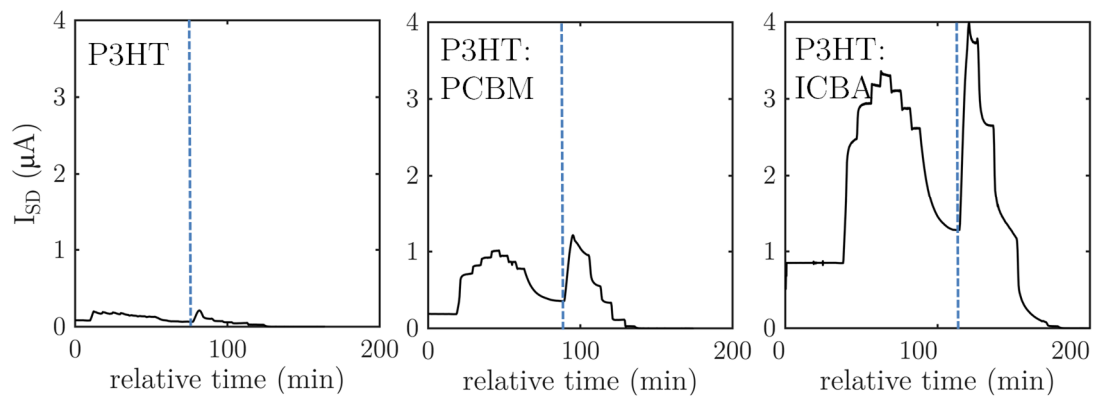


Figure A.2.4: Source-drain current during the heating cycle for pure P3HT, P3HT:PCBM and P3HT:ICBA (1:1) blends. The vertical dashed line indicates the beginning of the second heating cycle

A.3 Physical constants

Table A.3.1: Physical constants [Moh25]

symbol		value	unit
c	speed of light in vacuum	299 792 458	m/s
h	Planck's constant	$6.626\,070\,15 \cdot 10^{-34}$	J · s
		$4.135\,667\,696 \cdot 10^{-15}$	eV · s
$\hbar$	reduced Planck's constant $\hbar = h/2\pi$	$1.054\,571\,817 \cdot 10^{-34}$	J · s
e	elementary charge	$1.602\,176\,634 \cdot 10^{-19}$	C
k_B	Boltzmann constant	$1.380\,649 \cdot 10^{-23}$	J/K
N_A	Avogadro constant	$6.022\,140\,76 \cdot 10^{23}$	mol ⁻¹
r_e	classical electron radius	$2.817\,940\,320\,5(13) \cdot 10^{-15}$	m

A.4 Material properties

Table A.4.1: Mass densities of selected materials that are relevant in organic electronics

Material	Mass density ρ (g/cm ³)	Reference
P3HT	1.33	[GIS15]
	1.1	[New12], [Mac12], [Kon13]
PCBM	1.3 - 1.5	[Mac12]
Si	2.3290	(near RT) [Wik16]
	2.3296	[RSC16]
	2.328	[Hös00]
Au	19.3	[CXRO16], [Hen93]

Table A.4.2: Refractive index and critical angles of P3HT, Si and Au for selected photon energies [CXRO16, Hen93]. The critical angle α_c is calculated according to equation (3.24).

Energy (eV)	Material	ρ (g/cm ³)	δ	β	α_c (deg)
8050 (Cu K α)	P3HT	1.1	$3.837 \cdot 10^{-6}$	$2.757 \cdot 10^{-8}$	0.159
	Si	2.33	$7.577 \cdot 10^{-6}$	$1.726 \cdot 10^{-7}$	0.223
	Au	19.3	$4.712 \cdot 10^{-5}$	$4.848 \cdot 10^{-6}$	0.556
12380	P3HT	1.1	$1.618 \cdot 10^{-6}$	$5.144 \cdot 10^{-9}$	0.103
	Si	2.33	$3.178 \cdot 10^{-6}$	$3.156 \cdot 10^{-8}$	0.144
	Au	19.3	$1.878 \cdot 10^{-5}$	$2.541 \cdot 10^{-6}$	0.351
14900	P3HT	1.1	$1.116 \cdot 10^{-6}$	$2.509 \cdot 10^{-9}$	0.086
	Si	2.33	$2.189 \cdot 10^{-6}$	$1.506 \cdot 10^{-8}$	0.120
	Au	19.3	$1.362 \cdot 10^{-5}$	$2.069 \cdot 10^{-6}$	0.299
15000	P3HT	1.1	$1.101 \cdot 10^{-6}$	$2.445 \cdot 10^{-9}$	0.085
	Si	2.33	$2.159 \cdot 10^{-6}$	$1.466 \cdot 10^{-8}$	0.119
	Au	19.3	$1.348 \cdot 10^{-5}$	$2.021 \cdot 10^{-6}$	0.297
20000	P3HT	1.1	$6.188 \cdot 10^{-7}$	$8.235 \cdot 10^{-10}$	0.064
	Si	2.33	$1.211 \cdot 10^{-6}$	$4.592 \cdot 10^{-9}$	0.089
	Au	19.3	$7.952 \cdot 10^{-6}$	$7.265 \cdot 10^{-7}$	0.228

Table A.4.3: Field-effect transistor mobilities for selected organic and inorganic semiconductors

Material	Mobility μ (cm ² /Vs)	Reference
P3HT	0.01 – 0.1	[Kla06] page 114
	0.2	[Wan03]
	0.05 - 0.1	[Sir99]
PQT	0.05 – 0.12	[Kla06] page 114
	0.07 – 0.12	[Ong04]
c-Si	1430 – 1448	[Hul99] page 430
a-Si	10	[LeC70]
	~1	[Kla06] page 108

Table A.4.4: linear absorption coefficient for air at selected photon energies [Hen93, CXRO16]. The composition of air is estimated to be 78 % nitrogen, 21 % oxygen, 1 % argon and the density 0.0012 g/cm³ at 20 °C.

Energy (eV)	β	μ_{air} (1/m)
8050	$1.6092 \cdot 10^{-11}$	1.3139
12380	$2.8638 \cdot 10^{-12}$	0.3593
15000	$1.3488 \cdot 10^{-12}$	0.2051
18000	$6.7718 \cdot 10^{-13}$	0.1235
20000	$4.6382 \cdot 10^{-13}$	0.0940

Table A.4.5: Selected solvents for solutions processing materials

	formula	MW	boiling point (°C)	melting point (°C)	Density (g/ml)	dielectric constant	dipole mo- ment (D)
chloroform	CHCl ₃	119.38	61.2	-63.5	1.498	4.81	1.04
toluene	C ₇ H ₈	92.14	110.6	-93	0.867	2.38	0.37
p-xylene	C ₈ H ₁₀	106.17	138.3	13.3	0.861	2.27	0
o-DCB		147	180	-17	1.306		2.5

A.5 Detector specifications

Table A.5.1: Detector specifications

	Mythen	Perkin Elmer Digital X-ray Flat Panel detector	MAR345 Image plate detector	FReLoN 4M	PILATUS 100K
Material	Silicon	amorphous silicon			
Energy range		20 keV – 15 MeV	4 – 100 keV		4.5 – 36 keV
Pixel number	1x1280	2048 x 2048	diameter 345 mm	2048 x 2048	195 x 487
pixel size	500 μm x 8 mm	200 x 200 μm^2	100 x 100 μm^2	$\sim 50 \mu\text{m}$	172 x 172 μm^2
pixel depth/ dynamic range	18 bit	16 bit			20 bit
noise					
read-out time /fps	250 μs	up to 30 fps (2 x binning)	96 s (total cycle 108 s)		2.3 ms
Max. count rate	1 MHz	max. 65000 cps	max. ~ 60000 cps		2×10^6 X- ray/sec

Abbreviations

AFM	atomic force microscopy
a-Si	amorphous silicon
a.u.	arbitrary units
BESSY	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung
BHJ	bulk heterojunction
CAD	computer-aided design
c-Si	crystalline silicon
DH5T	α,α' -dihexyl-quinquethiophene
DCB	dichlorobenzene
DELTA	Dortmunder Elektronenspeicherring-Anlage
DESY	Deutsches Elektronen-Synchrotron
DFT	density functional theory
ED	electron diffraction
ESRF	European Synchrotron Radiation Facility
FWHM	full width at half maximum
ICBA	indene-C60 bisadduct
GISAXS	grazing incidence small angle scattering
GIWAXS	grazing incidence wide angle scattering
GIXD	grazing incidence X-ray diffraction
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MTR	multiple trap and release
OFET	organic field-effect transistor
OLED	organic light-emitting diode
OPV	organic photovoltaics
P3HT	poly(3-hexylthiophene)

PBTTT	poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene)
PCBM	phenyl-C61-butyric acid methyl ester
PDI	polydispersity index
PDOPT	poly(3-(2,5-dioctylphenyl)thiophene)
PETRA	Positron-Elektron-Tandem-Ring-Anlage
PTB7	polythieno[3,4-b]-thiophene-co-benzodithiophene
PTFE	polytetrafluoroethylene, also known as Teflon
PV	photovoltaics
rr	regioregular
rra	regiorandom
SAXS	small angle scattering
SC	semiconductor
SEM	scanning electron microscopy
SOLEIL	Source optimisée de lumière d'énergie intermédiaire du LURE (LURE: Laboratoire d'utilisation du rayonnement électromagnétique)
TEM	transmission electron microscopy
TFT	thin film transistor
VRH	variable range hopping
WAXS	wide angle scattering
XCCA	X-ray cross-correlation analysis
XPS	X-ray photoelectron spectroscopy
XRR	X-ray reflectivity

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