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**DEVELOPMENT OF ADVANCED ATOMIC FORCE MICROSCOPY METHODS
FOR NANOSCALE SEMICONDUCTOR CHARACTERIZATION**

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Abstract

This thesis investigates electronic processes in disordered semiconductors, focusing on amorphous oxides and organic materials. We developed quantitative, spatially-resolved methods to establish a direct link between microscopic electronic disorder and macroscopic device performance.

We established a quantitative KPFM spectroscopy technique for metal - insulator - semiconductor (MIS) structures of finite thickness. Applying an analytical solution of the non-linear Poisson equation to IGZO thin-film transistors, we locally extracted key density of states (DOS) parameters. The method yielded a conduction band-tail width of $E_t = (44.4 \pm 0.1)$ meV. Furthermore, the approach demonstrated that the X-ray irradiation shifts the threshold voltage by accumulating static charge in the gate dielectric, leaving the semiconductor DOS unchanged.

We analyzed the spatial resolution limits of organic optobioelectronic interfaces, based on H₂Pc/PTCDI heterojunctions, using photovoltage and photoelectrochemical current microscopies. The spatial confinement of the optoelectronic excitation correlates directly with the effective carrier diffusion length (λ_d), which we measured as $\lambda_d = (1.5 \pm 0.1)$ μm for the bare junction. We showed that incorporating PEDOT:PSS enhances charge carrier lifetime and mobility, increasing λ_d to (7.0 ± 0.3) μm . Photoelectrochemical mapping confirmed micrometer-scale resolution ($\sigma_e = (6.5 \pm 0.9)$ μm) in an aqueous environment.

To fully address spatial disorder and its effect on charge transport in two dimensions, this work introduces Lateral Electrostatic Force Microscopy (L-EFM) to overcome the limitation of conventional AFM methods in sensing in-plane electric fields. L-EFM provides quantitative mapping, a crucial capability for understanding charge transport and stability in complex device architectures. A calibration procedure using a parallel-plate capacitor enables the conversion of the torsional signal into absolute field values. We validated L-EFM on doped silicon p-n junctions, providing quantitative in-plane field maps. The technique reliably measures lateral electric fields in electrically floating structures, a scenario where conventional KPFM cannot operate, thus extending our diagnostic capabilities to insulating and complex systems.

These developments provide essential new routes for microscopic diagnosis and optimization, establishing a robust framework to enhance the stability, efficiency, and predictability of disordered electronic devices.

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1 Introduction

1.1 Objectives and approach

The motivation behind this work is to understand how microscopic disorder and local electrostatics determine the electronic behaviour of semiconductors. In amorphous oxides and molecular materials, the lack of long-range order leads to spatial fluctuations in potential and to broad distributions of localized states, which affect charge injection, transport, and recombination. These effects are difficult to describe within the traditional models developed for crystalline systems, where a single band structure can represent the entire material.

Most electrical and optical characterization methods average over large areas and therefore cannot capture the microscopic inhomogeneities that dominate in disordered systems. To obtain a complete picture, it is necessary to probe the local electronic structure and to relate it quantitatively to the macroscopic device response. Scanning probe techniques, and in particular atomic force microscopy, provide an effective route to this goal. Their ability to map local potentials and charges with nanometric resolution makes them a unique tool to investigate how microscopic variations translate into functional behaviour.

However, the potential measured by AFM-based electrical methods does not directly correspond to the Fermi level or to the work function of the material. It reflects a complex balance between band bending, trapped charge, and capacitive coupling between tip, sample, and cantilever. For this reason, a quantitative interpretation of the measurements requires a physical model that describes the electrostatic interaction in realistic device geometries.

The approach followed in this thesis is to combine experimental developments in scanning probe microscopy with analytical modeling of the electrostatic problem. This allows transforming qualitative maps of potential into quantitative information on local electronic parameters such as band-tail width, trap density, and charge distribution. The same framework can be extended to different semiconductor systems, providing a unified description of local electronic phenomena in materials where disorder plays a dominant role.

Research objectives

The goal of this thesis is to improve the use of AFM-based electrical techniques for the study of disordered semiconductors. We want to show that local measurements, combined with suitable modeling, can provide quantitative information—such as the width of band tails, the density of traps, or the distribution of charges—that cannot be obtained from macroscopic methods.

- **Chapter 3** deals with amorphous oxide semiconductors. The aim is to demonstrate that KPFM spectroscopy can be used not only to visualize local potential variations, but to extract quantitative parameters of the band-tail density of states. By applying the method to IGZO thin films and devices, we show that it is possible to separate intrinsic electronic disorder from extrinsic trapping processes and to obtain values that are consistent with independent spectroscopic measurements.
- **Chapter 4** focuses on organic semiconductors. The objective here is to use AFM-based local probes to quantify fundamental charge transport parameters, namely the carrier mobility and the recombination time. By combining high-resolution potential mapping with time-resolved measurements, we demonstrate how nanoscale disorder and interfacial traps affect both the dynamics and the spatial distribution of charge carriers in molecular films.
- **Chapter 5** presents the development of lateral-EFM. This new method makes it possible to measure the in-plane component of the electric field, which is not accessible with conventional EFM. Together with the experimental setup, we introduce the mathematical framework needed to interpret the results. The technique is then validated on model structures and devices.

After this general introduction, the thesis moves directly to the presentation of the original experimental and methodological contributions, which constitute its central focus.

1.2 Semiconductors and electronic devices

Semiconductors are the basis of modern electronic technologies. Their main characteristic is the ability to modulate the material conductivity when subjected to external factors such as doping, applied electric fields, or light. Unlike metals, which always have high and almost fixed conductivity, semiconductors can be tuned to cover a very wide range. Thanks to this property, they can be used in many different devices, including integrated circuits, light-emitting diodes,

solar cells, and sensors. This flexibility makes them essential for active components, where the electrical response must be controlled in a precise way.

From a structural point of view, semiconductors can be divided into crystalline and amorphous. Crystalline semiconductors have a periodic atomic arrangement that leads to well-defined electronic bands, and charge transport can be described within band theory, with defects considered as small perturbations[1]. Amorphous semiconductors lack long-range order, and the resulting structural disorder introduces localized states within the bandgap, commonly referred to as band tails [2, 3]. These states play a central role in limiting carrier mobility and in determining the electrical and optical response of the material. At the same time, amorphous phases can be processed at low temperatures and deposited on large areas, which makes them attractive for applications where scalability and compatibility with flexible substrates are required [4].

In amorphous semiconductors the lack of long-range order causes a broadening of the band edges and the appearance of electronic states inside the gap. These states are spatially localized and are usually referred to as band tails [2]. A useful way to describe the situation is through the concept of a mobility edge, i.e. an energy threshold that separates localized states from extended ones (Figure 1.1). States below this threshold contribute little to conduction and carriers can move only by thermally activated hopping. Above the mobility edge, instead, charge transport is delocalized and follows a band-like mechanism. The position of the Fermi level with respect to the mobility edge therefore determines whether the material behaves as an insulator or as a conductor. Besides the intrinsic tail states generated by disorder, amorphous materials also contain defect-related states, for example due to structural irregularities or compositional fluctuations [3]. These additional states can act as traps or recombination centers, and their occupation is known to change under electrical stress, with direct consequences on the stability and performances of devices.

The way semiconductors are used in technology depends directly on their electronic structure. Crystalline materials like silicon or GaAs give the best performance in logic and power devices because they offer high carrier mobility and well-defined band edges. Amorphous semiconductors work differently. Their mobility is low, but they can be processed at low temperature and on large areas. This means they can be integrated on glass or plastic substrates and are therefore the base of thin-film transistors for displays, X-ray detectors, or flexible circuits [4, 5]. The drawback is that the presence of localized states and defects strongly affects device behavior. For example, in oxide TFTs they are responsible for threshold voltage shifts under bias stress and for changes in subthreshold slope. In practice, this sets the limit for stability and long-term reliability. Understanding how these microscopic states connect to macroscopic performance is therefore essential, not only for well-established large-area electronics but also for new fields like transparent and bio-integrated devices [6, 7].

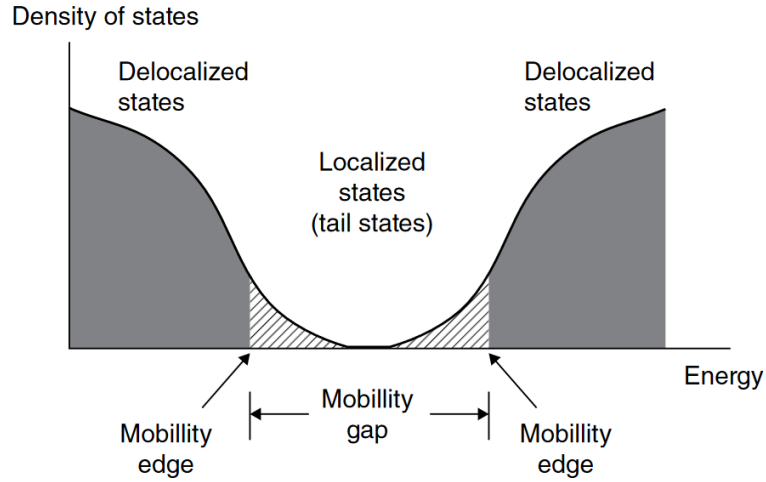


Figure 1.1: Electronic density of states in amorphous semiconductors. The mobility edge divides the localized states (also called tail states) from the delocalized states.[3]

The presence of localized states and defects described above is not uniform across the material. Their density and energetic distribution can vary locally depending on microstructure, stoichiometry, or processing conditions [8, 9]. In thin-film devices, where the active region is often only a few tens of nanometers thick, such microscopic variations can have a strong impact on the overall electrical behavior. Conventional characterization methods, such as current–voltage measurements or optical spectroscopy, average over large areas and cannot resolve this level of detail. As a consequence, they can’t distinguish whether a measured instability originates from a uniform bulk effect or from local effects. This limitation is particularly critical in disordered semiconductors and in organic or oxide thin films, where the electronic response is strongly affected by spatial inhomogeneities. For these reasons, there is a growing interest in experimental approaches that can directly access the local potential landscape and map the distribution of electric fields inside devices [10–12]. Establishing this connection between microscopic properties and macroscopic performance is now considered essential to understand transport, stability, and degradation mechanisms in modern thin-film electronics.

1.3 Amorphous semiconductors

Amorphous semiconductors represent a broad class of materials that can be processed at low temperature and deposited over large areas. In contrast to crystalline semiconductors, where band transport dominates, in the amorphous phase carrier motion is governed by localized states. This results in lower mobilities and stability, but also in easier processing and compatibility with unconventional substrates. Two material families stand out in this context: amorphous metal oxides, exemplified by IGZO, and organic semiconductors. Both have been

investigated as active layers in thin-film devices and both are now considered for emerging applications where conventional crystalline semiconductors cannot be employed.

1.3.1 Indium Gallium Zinc Oxide

Among amorphous oxide semiconductors, indium–gallium–zinc oxide (IGZO) is by far the most studied material and has become one of the first choices for large-area thin-film electronics. Since its first demonstration as an active channel material in 2004 by Nomura et al. [4], IGZO has gained attention because it combines several features that are normally difficult to obtain in the same material: optical transparency, relatively high carrier mobility, and low-temperature deposition by sputtering. The origin of these properties lies in the electronic structure of post-transition metal oxides, where transport is mediated by the overlap of cation s-orbitals. This mechanism is much less sensitive to disorder than the p- or d-orbitals typically involved in conventional semiconductors, and it explains why IGZO can sustain mobilities in the range of 5–20 cm²/Vs even in the amorphous phase [13].

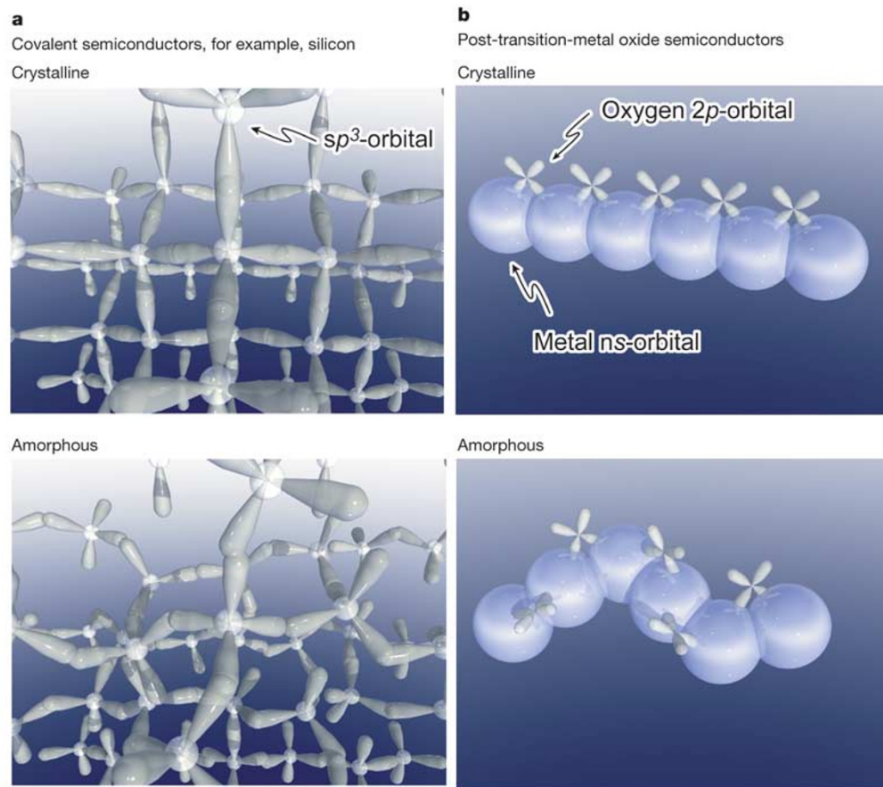


Figure 1.2: Schematic drawing of orbitals and consequent transport paths for (a) covalent semiconductors and (b) amorphous oxide semiconductors composed by post-transitionmetal cations. [4]

The higher mobility of IGZO compared to covalent amorphous semiconductors comes from

the type of orbitals that carry the current. In silicon and similar materials, conduction relies on directional sp^3 orbitals. When long-range order is lost in the amorphous phase these orbitals no longer overlap efficiently, so transport becomes strongly limited. In oxide semiconductors like IGZO the situation is different. Here the conduction band is built from the isotropic ns orbitals of indium, gallium and zinc. These orbitals can still overlap even without crystalline order, so carriers remain more delocalized and mobilities stay relatively high (Figure 1.2) [4–6, 13]. This explains why IGZO thin-film transistors can reach mobilities an order of magnitude higher than hydrogenated amorphous silicon, while keeping the advantages of amorphous processing.

IGZO has a bandgap of about 3 eV, thus it is transparent in the visible range and can be used in displays, imaging devices, and transparent circuits. The fact that it is amorphous means it can be deposited uniformly on large substrates and even on flexible ones. This avoids the typical grain boundary problems of polycrystalline silicon, which limit uniformity and mobility. Another advantage is that IGZO devices remain stable in air and can be processed with standard photolithography. For these reasons IGZO has quickly been adopted in industry, and today it is found in commercial products such as high-resolution LCD and OLED displays [5].

Despite these advantages, IGZO transistors often suffer from instabilities when a gate bias is applied for long times. Typical effects are threshold voltage shifts, hysteresis in the transfer curve, and variations in the subthreshold slope [14]. These problems are connected to localized states close to the conduction band edge. Oxygen vacancies are considered the main intrinsic defects: depending on their charge state they may behave as shallow donors, form deep traps, or change the shape of the conduction band tails [15, 16]. Their role is still not fully clear, since the formation energy strongly depends on the oxygen content, the exact stoichiometry, and also on the presence of hydrogen or other impurities. On top of that, inhomogeneities introduced during deposition or annealing can broaden the density of states even more and further reduce device stability.

Experiments show that the conduction band tail in IGZO can be described by an exponential distribution of the density of states,

$$g(E) = N_0 \exp\left(-\frac{E_c - E}{E_t}\right)$$

where E_c is the conduction band edge, E_t is the characteristic band-tail energy (typically a few tens of meV), and N_0 is the effective density of states at the band edge [17, 18]. These localized states control both steady-state transport and the response under electrical stress, and therefore have a strong impact on long-term reliability. For this reason, an accurate determination of the DOS is essential to optimize device performance and to understand degradation

mechanisms. IGZO is therefore an excellent test case for advanced microscopic techniques that aim to resolve electronic properties at the local scale.

1.3.2 Organic semiconductors

Organic semiconductors are the other main class of materials considered in this thesis. Their electronic transport is very different from oxides such as IGZO: instead of extended conduction bands, charges move by hopping between localized π -orbitals of conjugated molecules. This makes carrier motion intrinsically slower and strongly affected by molecular packing and energetic disorder [19, 20]. Nevertheless, organics bring in features that are unique: they can be processed at low temperature, deposited on flexible or even biological substrates, and their chemical structure can be tailored to tune absorption and energy levels [21].

Small molecules like phthalocyanines (H_2Pc) or perylene-diimides (PTCDI) are widely used as p- and n-type semiconductors [22], and will be central in Chapter 4. Other examples include the polymer P3HT and fullerene derivatives such as PCBM, which became standard in organic solar cells and were also applied to neuronal stimulation [23, 24]. Conducting polymers like PEDOT:PSS are instead employed as transparent contacts or interlayers, combining high conductivity with mechanical softness [25]. These examples illustrate how different classes of organic semiconductors can be combined to realize devices with functions that cannot be achieved with rigid inorganic oxides.

From a general perspective, organic semiconductors offer a very different set of properties compared to oxides. They can be deposited at low temperature, even from solution, and this makes them suitable for large-area coatings on plastic or soft substrates. Their mechanical softness and chemical tunability also make them compatible with biological environments, where rigid inorganics usually cannot operate [19, 20]. The same features, however, come with evident drawbacks: oxygen and humidity accelerate degradation, while disorder and trapping strongly affect reproducibility. For this reason organics are not meant to replace high-mobility inorganic semiconductors, but rather to open a complementary path for devices that need flexibility or direct bio-integration.

Organic semiconductors first became relevant with thin-film transistors and OLEDs, which opened the field of plastic electronics and flexible displays [26, 27]. At the same time they were investigated in photovoltaics, where blends like P3HT:PCBM became model systems to look at charge separation and collection [28]. More recently their use moved into bioelectronics, where the soft mechanical properties and the ability to conduct both ions and electrons make them suitable for direct contact with living tissue [29]. Examples include heterojunctions like H_2Pc /PTCDI and polymer systems such as P3HT:PCBM, both explored for optical stimulation of neurons and retinal cells [23, 24]. These cases show how materials originally developed for

solar cells or displays are now tested as functional interfaces in biology.

Despite these achievements, organic semiconductors still face important limitations. Instability under oxygen and humidity, strong energetic disorder, and low carrier mobilities remain the main bottlenecks for reproducible device operation [19, 28]. For optoelectronic and bioelectronic applications an additional problem is spatial resolution: once charges are generated in the organic layer they can diffuse over micrometer distances, blurring the localization of the excitation. This aspect is particularly critical when aiming at single-cell stimulation or high-resolution mapping, where the length scale of interest is only a few micrometers. Understanding how molecular structure, morphology, and interface engineering control carrier diffusion is therefore essential. In the following chapters we will use microscopic techniques to address this point, focusing on model heterojunctions such as H₂Pc/PTCDI that allow a direct link between the electronic properties of organics and their performance in optobioelectronic devices.

1.3.3 Motivation for the study of amorphous semiconductors

Amorphous semiconductors are central to several technology sectors where large-area fabrication, mechanical flexibility, and optical transparency are required. Amorphous oxide semiconductors, and in particular IGZO, have become the backbone of thin-film transistors used in display backplanes, x-ray imaging panels, and emerging transparent sensor platforms [4, 30, 31]. Their compatibility with low-temperature deposition on glass or plastic substrates allowed the production of high-resolution and lightweight displays on industrial scale.

In parallel, organic semiconductors became commercially available through applications such as organic light-emitting diodes (OLEDs), flexible circuits, and thin-film sensors. Moreover, they are now actively explored for bioelectronic interfaces where their mechanical softness and chemical versatility provide unique advantages [19, 20]. These developments show that amorphous and molecular semiconductors are not limited to fundamental research, but already enable large-scale technologies and open new directions beyond conventional electronics.

Despite these achievements, the practical deployment of amorphous semiconductors is still limited by critical challenges. In amorphous oxides such as IGZO, device performance is affected by threshold voltage shifts, bias-stress instabilities, and sensitivity to ionizing radiation, all of which compromise the long-term reliability required for display backplanes and for electronic systems operating in harsh environments [7, 14]. These issues are directly linked to localized band-tail states and to the interaction of carriers with structural and chemical disorder. In organic semiconductors, the main obstacles arise from energetic disorder, which limits reproducibility and device lifetime, and from the diffusion–recombination of photoex-

cited carriers, which restricts the spatial resolution achievable in optoelectronic and bioelectronic interfaces [19, 32]. These limitations represent not only a scientific challenge but also a technological bottleneck for the integration of organics in advanced sensing and biomedical platforms.

Addressing these challenges requires experimental approaches that can directly connect microscopic electronic disorder to macroscopic device operation. Standard characterization methods provide averaged values but cannot resolve the local variations that often dominate transport and stability. Developing quantitative local probe techniques, capable of mapping the electronic structure with nanometric resolution, is therefore essential for both fundamental understanding and for guiding the optimization of device performance. The present thesis is motivated by this need and explores how scanning probe methods can be advanced to provide reliable microscopic insight into disordered semiconductors.

1.4 Characterization of amorphous semiconductors

Before introducing the different characterization techniques, it is useful to define the scope of this section. The discussion is limited to methods that provide information on the electronic structure of semiconductors, including energy levels, charge distribution, and potential landscapes. Structural or chemical characterization is not considered here, as it lies outside the objectives of this work. Techniques that rely on long-range crystalline order, such as X-ray or electron diffraction and angle-resolved photoemission spectroscopy (ARPES), are only mentioned for reference. They represent the standard approach to study band structure in crystalline semiconductors, but lose direct applicability in amorphous and molecular materials, where electronic states are localized and no clear band dispersion is defined.

1.4.1 Macroscopic characterization

Electrical measurements Transfer characteristics of IGZO thin-film transistors are usually analyzed to extract mobility, subthreshold slope and threshold voltage. The shape of the I–V curve itself already reflects the presence of localized states at the band edge. Nomura et al. showed that bias stress produces large shifts of the threshold, a clear fingerprint of charge trapping in tail states [4]. Hsieh et al. used the dependence of the drain current on gate voltage to fit an exponential density of states with characteristic energies of a few tens of meV, directly linking the slope of the transfer curve to the band-tail width [17]. Vogt et al. instead emphasized that an exponential tail alone is not sufficient, and that a Gaussian distribution of deeper states has to be added to capture hysteresis and bias-stress behavior [18]. These examples illustrate how standard transistor measurements are consistently used to back-extract

density-of-states parameters. At the same time, all the values obtained are averaged over the whole channel and cannot resolve spatial variations or interfacial effects. Electrical measurements on organic thin-film transistors are widely used to assess charge transport in disordered π -conjugated systems. From the slope of the transfer curve in the linear regime, one extracts the effective mobility, which typically spans several orders of magnitude depending on molecular packing and trap density. Horowitz et al. discussed how trap-limited conduction leads to a gate-voltage dependent mobility, reflecting the exponential distribution of localized states in the band tails [27]. Podzorov et al. investigated single-crystal organic transistors and showed that even in highly ordered systems, shallow traps dominate the subthreshold slope and threshold voltage stability [33]. More recently, Salleo et al. demonstrated that analysis of transfer curves under bias stress reveals the progressive filling of localized states, linking macroscopic hysteresis to microscopic disorder [34].

Capacitance–voltage (C–V) profiling is a widely used macroscopic technique to assess the density of states in amorphous oxide semiconductors. Deviations from the ideal MOS capacitor response are interpreted in terms of localized states that participate in charge storage. Lee et al. demonstrated that multifrequency C–V characteristics of a-IGZO TFTs allow the extraction of subgap states by distinguishing fast band-tail states from slower, deeper traps [35]. Yu et al. performed temperature-dependent C–V measurements and showed that the extracted DOS is dominated by exponential tails, with characteristic energies consistent with values obtained from electrical transport [15]. More recently, Wang et al. simplified the DOS extraction procedure by developing a single-scan C–V method, enabling routine estimation of tail and deep-state densities in IGZO TFTs [36]. These works highlight the utility of C–V analysis for quantifying DOS parameters in amorphous oxides, while also emphasizing that the values obtained represent averages over the device area and remain strongly influenced by dielectric quality and processing conditions. CV methods have also been employed to investigate trap states and charge accumulation in organic thin-film transistors (OTFTs). In pentacene devices, frequency-dependent capacitance reveals slow trapping processes at the dielectric/semiconductor interface, which directly affect hysteresis and threshold voltage stability [37]. Sangeeth et al. investigated pentacene OTFTs with different dielectric interfaces and demonstrated that the C–V response can be modeled in terms of interface traps [38]. A further example is provided by Scheinert et al., who combined current–voltage and C–V data to extract trap distributions in pentacene transistors with modified gate oxides, highlighting how dielectric surface treatment strongly influences interfacial state density [39].

Hall effect measurements provide a direct method to determine carrier density, mobility, and carrier type from the transverse voltage induced under a magnetic field, independently of device geometry and contact resistance. In crystalline semiconductors they represent the reference method for transport characterization. In amorphous oxide semiconductors such as

IGZO, measurable Hall voltages can often be obtained despite structural disorder [5, 40]. Reported Hall mobilities in optimized oxides reach values comparable to the field-effect mobility, indicating that a fraction of the carriers participates in extended band-like transport. In organic semiconductors, by contrast, the Hall voltage is typically extremely small or even undetectable because transport occurs via thermally activated hopping between localized states; a measurable Hall effect has been observed only in highly ordered single-crystal or high-mobility polymer systems, where coherent transport extends over several molecules [41, 42]. Overall, Hall effect measurements remain a fundamental macroscopic probe for crystalline and highly conductive amorphous semiconductors, but they lose applicability as disorder increases.

Optical spectroscopy Optical spectroscopy has been extensively applied to amorphous oxide semiconductors to probe bandgap and subgap states. Absorption measurements reveal the wide bandgap of IGZO, typically above 3 eV, and the exponential Urbach tail. Photocurrent spectroscopy is particularly effective in quantifying the conduction-band tail: Hsieh et al. analyzed the spectral response of a-IGZO TFTs and fitted the subgap photocurrent with an exponential distribution of states, extracting characteristic energies of a few tens of meV [17]. Jeon et al. compared photocurrent data with capacitance profiling, showing that a consistent picture emerges only when both exponential tails and Gaussian deep states are considered in the DOS [31]. More recent works have confirmed that optical methods, despite their macroscopic nature, can provide DOS parameters in good agreement with electrical characterization [15]. However, as in the case of C–V, the extracted parameters represent averages over large device areas and remain influenced by processing conditions and oxygen content and annealing [43].

As for amorphous oxides, optical techniques are also a central macroscopic probe for organic semiconductors, providing access to their electronic and excitonic structure. Steady-state absorption and photoluminescence spectra define the optical gap and confirm the excitonic nature of the primary photoexcitations in conjugated materials. Photocurrent action spectroscopy, in direct analogy to subgap absorption studies in oxides, is used to determine interfacial energetics and the efficiency of exciton dissociation in donor–acceptor blends [44]. Transient photovoltage and transient absorption measurements further resolve carrier lifetimes and recombination pathways, parameters that play the same role as band-tail widths in oxides by setting the operational limits of the devices. Noriega et al. connected gate-voltage dependent mobility to an exponential distribution of states in polymer semiconductors, showing how energetic disorder inferred from transport can also be rationalized in terms of optical observables [45]. In bioelectronic applications, Rivnay et al. emphasized that optical probes capture photoinduced polarization and charge dynamics at the interface with biological media [29]. In all cases, the extracted parameters are averaged over the device, so local heterogeneity—molecular packing, phase separation, interfacial disorder—remains hidden, exactly as in

the case of amorphous oxides.

Among the spectroscopic methods employed to probe the electronic structure, photoelectron spectroscopies occupy a central role, as they provide direct access to the energy distribution of occupied states and, through inverse or hard X-ray variants, to the bulk electronic structure. Ultraviolet and X-ray photoelectron spectroscopy allow one to determine fundamental quantities such as the work function, the ionization energy, and the alignment of energy levels at interfaces. These measurements enable the quantitative determination of level offsets that control charge injection, exciton dissociation, and carrier separation in devices based on semiconducting thin films [46, 47]. In amorphous oxide semiconductors, XPS and hard X-ray photoelectron spectroscopy (HAXPES) have been extensively employed to identify the electronic states associated with oxygen vacancies and to quantify their role as donors or trap centers. They also provide information on Fermi level pinning, subgap states, and interfacial dipoles at semiconductor–dielectric or semiconductor–metal interfaces. In the case of IGZO and related oxides, depth-resolved photoemission measurements have revealed how oxygen stoichiometry and post-deposition annealing control the energetic position of defect states and the band alignment with contact materials [48, 49]. In molecular semiconductors, photoelectron spectroscopy provides a direct probe of the HOMO–LUMO alignment across donor–acceptor heterojunctions. The resulting energy-level diagrams are essential to understand the separation of photogenerated excitons and the formation of interfacial charge-transfer states that dominate the optoelectronic response [50]. Combined with transport and optical data, these techniques establish the energetic framework necessary for a quantitative interpretation of charge generation, transport, and recombination processes in both inorganic and organic semiconductors. In disordered or amorphous semiconductors, photoelectron spectroscopies provide only partial insight into the electronic structure, as the absence of long-range order suppresses the band dispersion and blurs the distinction between extended and localized states. Nevertheless, these techniques remain fundamental to determine the absolute position of the electronic levels and the nature of the occupied states.

Limitations of macroscopic approaches and motivation for local probes Macroscopic techniques, both electrical and optical, have been crucial to establish the fundamental picture of disorder in amorphous semiconductors. In amorphous oxides, transfer curve analysis, capacitance–voltage profiling, and photocurrent spectroscopy consistently point to exponential band tails and deep defect states as the origin of bias instabilities and threshold shifts. In organic semiconductors, electrical transistor measurements and optical spectroscopies have clarified the excitonic nature of the gap, the role of energetic disorder, and the impact of interfacial traps on device performance. However, in all cases the extracted parameters represent averages over large device areas. Local variations in morphology, composition, or defect den-

sity are intrinsically lost, even though they often govern device operation and stability. This mismatch between the microscopic origin of the phenomena and the macroscopic character of the probes motivates the use of spatially resolved methods. Scanning probe microscopy techniques, such as Kelvin probe force microscopy (KPFM) and electrostatic force microscopy (EFM), provide direct access to local potentials and electric fields with nanometric resolution, thereby complementing the macroscopic characterization and enabling a deeper understanding of amorphous semiconductors.

1.4.2 Microscopic characterization

The microscopic characterization of semiconductors aims to uncover how local variations shape their electronic behaviour. Macroscopic measurements such as current–voltage curves, capacitance spectroscopy or optical absorption tell only an average story, which works well for crystalline materials where defects are few and act as small perturbations. In amorphous and molecular systems this picture breaks down. Their intrinsic structural disorder gives rise to strong local changes in electrostatic potential, trap density and carrier mobility. These fluctuations define the density of states near the band edges and ultimately control charge transport and recombination. In amorphous oxides like IGZO, differences in stoichiometry or in the number of oxygen vacancies can generate potential variations of several hundred meV over nanometric distances, producing localized tail states and non-uniform conductivity [4, 51]. Organic thin films behave in a similar way: the orientation and packing of π -conjugated molecules introduce local energetic disorder that affects injection barriers and transport pathways [52, 53]. To understand these materials, one has to connect structure and electronic function at the same spatial scale. Techniques able to resolve morphology, potential and opto-electronic response locally have therefore become essential to study semiconductors beyond the crystalline limit.

Electron microscopies represent the most established approach for resolving the structural and chemical landscape of semiconductors at the nanometric scale. Scanning electron microscopy provides morphological and compositional contrast through the detection of secondary and backscattered electrons, while transmission electron microscopy reveals the arrangement of atoms, grain boundaries, and defect clusters. In amorphous oxides such as IGZO, high-resolution transmission imaging and electron energy-loss spectroscopy have been used to identify nanometric variations in stoichiometry and oxygen vacancy concentration, linking structural disorder to changes in conductivity and threshold voltage [4, 51]. Similar methods have been applied to hybrid and organic thin films to visualize molecular packing, interface morphology, and domain purity in donor–acceptor blends, revealing correlations between microstructure and charge-transport anisotropy [54, 55]. Although electron microscopies pro-

vide unmatched structural information, they offer limited sensitivity to local electrostatic potentials or defect states, and must therefore be complemented by techniques capable of directly probing the electronic landscape.

To complement the structural information provided by electron microscopies, optical methods have been developed to probe how local structure affects photoinduced electronic processes. These approaches rely on the spatial modulation of illumination and the detection of the resulting photocurrent or photovoltage, enabling the mapping of charge generation and recombination with micrometric precision. Scanning photocurrent microscopy is one of the most established techniques in this class. By scanning a focused laser beam across an operating device, it reveals spatial variations in carrier collection and identifies regions dominated by traps or internal electric fields. In lateral organic heterojunctions, Lombardo and co-workers used this method to visualize the extension of depletion regions and the position of built-in junctions, showing how bias and illumination reshape the internal field distribution [56]. Similar optical mapping approaches have been applied to amorphous oxide semiconductors, where scanning internal photoemission microscopy allowed Shiojima and colleagues to resolve the spatial distribution of Schottky barriers at Au/a-IGZO contacts, highlighting the inhomogeneous electronic structure at metal–oxide interfaces [57]. These optical microscopies bridge the gap between structural and electronic characterization by linking local morphology to optoelectronic response. However, their spatial resolution is limited by optical diffraction, and the measured signal is often averaged over the optical absorption depth. Quantitative access to the local potential and trapped charge therefore requires the use of scanning probe microscopies, which are discussed in the following section.

1.5 Scanning probe microscopies to investigate semiconductors

The introduction of scanning probe microscopies completely changed how semiconductors can be studied. When the first tunnelling microscopes appeared in the early eighties, followed a few years later by the atomic force microscope, it suddenly became possible to look at surfaces with nanometric and even atomic precision. What was revolutionary was not only the resolution but also the idea that a single sharp probe could measure almost any kind of physical signal, simply by changing the way it interacts with the sample. Depending on how the tip is driven and what is detected, the same setup can sense forces, capacitance, local potentials or even light scattering. Unlike electron microscopes, which need vacuum and conductive samples, these instruments work in air or liquid and can probe real devices even in operando. This makes them especially useful for materials that are partly insulating or too fragile for

conventional microscopy. In semiconductors they fill the space between structural and electrical characterization: topography shows how grains, domains or interfaces are arranged, while electrical modes reveal how charges move or get trapped. Over time, a whole family of techniques has evolved from the same idea, each focusing on a different aspect of the local electronic landscape. Conductive AFM, scanning capacitance microscopy, Kelvin probe force microscopy and optical near-field methods all share the same basic principle but tell a different part of the story.

1.5.1 Conductive atomic force microscopy

Among scanning probe techniques, conductive atomic force microscopy (C-AFM) extends AFM from pure morphology to local electrical read-out by using a conductive tip under bias to record the current flowing through the tip-sample junction during scanning. The concept took shape in the mid-1990s and was quickly applied to thin dielectrics and semiconductor films, where it enabled nanoscale maps of leakage paths and breakdown precursors that macroscopic current-voltage measurements cannot resolve [58]. This shift established C-AFM as a standard route to correlate structure and transport at the nanometric scale in semiconductor research. Today C-AFM is routinely used to acquire simultaneous maps of topography and current with nanometric resolution, and to perform site-specific I - V spectroscopy from classical oxides to emerging low-dimensional semiconductors. Recent studies demonstrate how C-AFM reveals local conduction mechanisms, Schottky barrier variations and defect-assisted transport in technologically relevant materials such as polymer blends and transition metal dichalcogenides [59, 60].

In conductive AFM the current collected by the tip originates from different transport regimes depending on the material and on the local electric field. In thin dielectric layers the dominant mechanism is tunnelling through the barrier, while in semiconducting or molecular films current can arise from hopping between localized states or from space-charge-limited conduction. The possibility to acquire current maps while controlling the applied bias allows identifying conduction paths, defect-related leakage, and regions where the local electric field is enhanced [61].

C-AFM has been extensively applied to oxides and semiconductor thin films to investigate leakage behaviour and dielectric breakdown. Early studies on silicon dioxide demonstrated the formation of conductive spots associated with local degradation, revealing the microscopic origin of breakdown in gate dielectrics [58]. Similar experiments have been performed on amorphous oxide semiconductors, where local variations in current directly trace grain-boundary conduction and trap-assisted transport. In organic semiconductors the same approach has been used to visualize percolation networks and to relate current distribution to molecular or-

dering and phase separation [59]. More recently, C-AFM has been applied to two-dimensional materials and van der Waals heterostructures, providing nanoscale insight into contact resistance, defect-mediated tunnelling and interface quality [60].

Because the tip acts as a nanoscale electrode, local current–voltage curves can be recorded at specific positions on the surface. From these data it is possible to extract parameters such as barrier height, series resistance or local carrier injection behaviour. Despite limitations related to the high electric field at the tip apex and possible local modifications of the material, C-AFM remains one of the most direct and versatile tools to correlate nanoscale structure and electrical functionality in semiconductor materials.

The high sensitivity of C-AFM to local conduction makes it particularly powerful for studying failure mechanisms and inhomogeneities in thin semiconductor and dielectric layers. However, its operation relies on charge injection and on the formation of a conductive path between tip and sample, which limits its use to materials with finite conductivity. In cases where charge accumulation and capacitive coupling play a dominant role, different approaches are required. Scanning capacitance microscopy was developed to address this regime, allowing the detection of local variations in capacitance and carrier concentration without the need for a direct current path.

1.5.2 Scanning capacitance microscopy

Scanning capacitance microscopy (SCM) was developed as an extension of atomic force microscopy to measure local variations in capacitance and carrier concentration with nanometric resolution. In contrast to conductive AFM, which detects the current flowing through the tip–sample junction, SCM senses changes in the capacitance between a conductive tip and the sample surface under an applied bias. The method relies on the formation of a metal – insulator – semiconductor structure, where an AC voltage modulates the depletion region of the semiconductor, producing a measurable variation in capacitance. The signal, proportional to the derivative of capacitance with respect to the bias voltage, is detected with a high-frequency circuit integrated into the AFM electronics [62].

This approach enables the mapping of dopant concentration and polarity at the nanoscale, allowing direct visualization of p–n junctions, depletion layers and electrically active defects. Compared to conventional capacitance–voltage measurements, SCM provides spatially resolved information on the electrical activity of dopants, as well as local variations of dielectric constant and trapped charge. These capabilities have made SCM a reference technique for two-dimensional dopant profiling and process control in microelectronics [63, 64]. More recently, it has been applied to polycrystalline and amorphous semiconductors, where capacitance contrast reveals inhomogeneities in charge accumulation and interface states that cannot

be captured by macroscopic electrical characterization [65].

Beyond crystalline silicon, SCM has been successfully applied to wide-bandgap semiconductors and to emerging thin-film technologies. In gallium nitride and silicon carbide devices it has been used to study local variations of carrier density and surface charge induced by processing or irradiation [66, 67]. In polycrystalline and amorphous oxides, including indium–gallium–zinc oxide and related materials, SCM contrast reveals inhomogeneous charge accumulation and trap densities at grain boundaries, which strongly influence device stability. Similar concepts have been extended to organic semiconductors, where the modulation of local capacitance provides indirect information on charge storage and dielectric response in multilayer heterostructures [68].

Due to its sensitivity to subsurface charge distribution, SCM is also exploited in the development of advanced dielectric stacks and gate oxides. It can identify local variations in permittivity, trapped charge or interface states that alter the effective capacitance of a device. These applications make SCM complementary to conductive and Kelvin probe force microscopy, forming together a coherent set of techniques capable of probing charge transport, electrostatics and doping with nanometric resolution [62, 65].

The detailed investigation of local capacitance variations provides valuable insights into the electronic landscape of amorphous semiconductors. To further deepen the understanding of surface and interface phenomena that govern device behavior, it becomes essential to explore complementary techniques capable of mapping electrostatic potential with comparable spatial precision. This naturally leads to the study of Kelvin Probe Force Microscopy, whose capabilities will be considered in the following section.

1.5.3 Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM) extends atomic force microscopy to the quantitative measurement of local electrostatic potentials and surface work functions. The technique detects the contact potential difference between a conductive tip and the sample through an AC modulation of the tip–sample bias, allowing reconstruction of the surface potential landscape with nanometric resolution [69]. Unlike current- or capacitance-based methods, KPFM probes the equilibrium electrostatic state, providing absolute energy calibration and direct comparison across different materials [12]. While SCM or EFM give indirect information on charge storage or carrier modulation, KPFM measures directly the local vacuum level and band bending, accessing the potential landscape that controls charge transport.

Initially developed for conductive and crystalline materials, Kelvin probe force microscopy soon became a key tool for semiconductors, mapping local variations in potential associated with doping, interface states, or trapped charge. On crystalline silicon, it has been used

to image p - n junctions and work function variations across device cross-sections with sub-10 nm accuracy, complementing capacitance-voltage profiling and spreading resistance microscopy [70, 71]. In wide-bandgap semiconductors such as GaN and SiC, KPFM has resolved potential fluctuations caused by interface charge, irradiation damage, and spontaneous polarization, clarifying their role in threshold instability and leakage currents [72].

In amorphous and polycrystalline oxides, the absence of long-range order produces a complex electrostatic landscape dominated by localized defects and traps. KPFM provides direct microscopic access to this disorder, correlating potential fluctuations with microstructure [69]. Measurements on amorphous oxide semiconductors revealed nanoscale potential inhomogeneities linked to oxygen vacancy distribution and interfacial charge [73]. Spectroscopic KPFM, based on potential-voltage curves, enables quantitative extraction of the density of states, band-tail width, and flat-band potential, providing a microscopic complement to macroscopic electrical and optical techniques [74]. Similar approaches have been extended to other disordered systems, including hydrogenated amorphous silicon and high- k dielectrics, to investigate metastable defects, bias stress, and radiation damage [75].

KPFM has also been widely used in organic and hybrid semiconductors. In donor-acceptor heterojunctions, illumination-dependent KPFM maps visualize charge separation and carrier diffusion, revealing the built-in potential gradients that drive photocurrent generation [76]. In organic thin-film transistors, KPFM under bias exposes contact-induced doping, trap filling, and local variations of surface potential related to molecular packing and morphology [77]. The introduction of time-resolved and pump-probe KPFM further allows the detection of transient photovoltage components with distinct dynamics, providing direct access to recombination and transport kinetics [78–80].

From a methodological point of view, the lateral resolution depends on the effective tip-sample capacitance geometry and typically reaches a few tens of nanometers in air or below 10 nm in vacuum. However, the long-range nature of electrostatic forces requires careful modeling of the tip-sample interaction, especially in heterogeneous materials or on rough surfaces. Operation mode (amplitude - modulated or frequency - modulated) and environmental conditions strongly affect the contrast and reliability of the measurements, demanding critical evaluation of possible artifacts and topographic cross-talk.

Within this thesis, KPFM is employed as the central platform to probe local electronic properties in different classes of disordered semiconductors. Under both dark and illuminated conditions, surface potential maps are correlated with charge transport and photoresponse in oxide and organic thin films. Quantitative analysis, supported by electrostatic modeling, allows determination of local band bending, trap distributions, and the physical limits of spatial resolution in lateral device geometries. KPFM thus bridges microscopic electrostatics and macroscopic electrical behavior, providing a consistent framework to understand how struc-

tural disorder and interfacial energetics define the functionality of modern semiconductor devices.

1.5.4 Hybrid and advanced AFM-based techniques

Among the most advanced implementations, atomic - resolution AFM represents the ultimate limit of spatial resolution in scanning probe microscopy. By operating in ultra-high vacuum and using frequency-modulation detection, it enables direct imaging of individual atoms, chemical bonds, and surface reconstructions on crystalline surfaces [81]. Although such experiments are limited to well-ordered materials, they provide essential benchmarks for understanding surface relaxation, defect formation, and adsorption geometries that influence electronic states in amorphous or polycrystalline thin films.

Beyond structural imaging, a broad class of hybrid AFM techniques has emerged, coupling the mechanical probe with optical or photothermal excitation to access complementary contrasts. Scattering-type scanning near-field optical microscopy (s-SNOM) combines an AFM tip with a focused infrared or visible beam to detect the scattered near-field, achieving spatial resolutions down to tens of nanometers beyond the diffraction limit. The detected amplitude and phase encode the local dielectric function and optical absorption, enabling nanoscale mapping of plasmonic, phononic, or excitonic resonances in semiconductor and hybrid materials [82, 83]. In amorphous and nanocrystalline oxides, such approaches have been applied to visualize dielectric inhomogeneities and carrier localization, while in organic semiconductors they resolve phase segregation and local optical response.

A related approach is tip-enhanced Raman spectroscopy (TERS), which exploits the plasmonic field enhancement at a metallic tip to amplify the Raman scattering signal from the sample. TERS provides molecular vibrational contrast with nanometric resolution, revealing the correlation between local packing, chemical structure, and electronic heterogeneity within organic semiconductors and donor-acceptor heterojunctions [84, 85]. In oxide semiconductors, near-field Raman methods have been employed to identify strain fields, nonstoichiometric domains, and the vibrational signatures of oxygen vacancies.

Other optical hybrids include photothermal-induced resonance AFM (PTIR) and related photothermal detection modes, which measure local thermal expansion following optical absorption to obtain infrared spectra at the nanoscale [86]. These methods have been exploited to map phase composition and carrier generation pathways in polymer:fullerene blends and organic photovoltaics, linking nanoscale morphology to optoelectronic performance.

Together, these advanced modalities bridge structural, chemical, and electronic characterization, enabling multimodal correlation between nanoscale morphology, charge localization, and optical activity in complex disordered semiconductors.

1.6 Summary and outlook

The characterization of amorphous and hybrid semiconductors relies on a combination of structural, electrical, and spectroscopic techniques that probe different length scales and physical quantities. Electron microscopies such as SEM and TEM provide direct access to morphology, stoichiometry, and defect organization, revealing how compositional disorder and nanostructure correlate with transport and stability.

Scanning probe microscopies extend this understanding to the local electrical scale. Conductive AFM and SCM visualize current paths, capacitance variations, and dopant distributions, while KPFM maps the surface potential and electronic landscape with sub-100 nm resolution, identifying trapped charges, interface dipoles, and contact effects. Hybrid implementations integrating optical or vibrational contrasts, such as s-SNOM, TERS, or PTIR, further connect molecular structure and optical response, bridging the gap between morphology and function.

Complementary macroscopic techniques provide averaged but quantitative information on the electronic structure and transport. Photoelectron spectroscopies determine the absolute energy levels, work function, and band alignment, enabling comparison across materials and device stacks. Electrical and optical measurements such as I-V, C-V, Hall effect, and optical absorption characterize carrier type, mobility, density of states, and recombination dynamics under operating conditions.

Together, these approaches establish a coherent framework to link microscopic organization and macroscopic behavior. Their integration reveals how structural disorder, interfaces, and electrostatic inhomogeneity control charge injection, trapping, and transport in amorphous oxides and organic semiconductors. This multiscale characterization provides the experimental foundation for the quantitative analysis and device-level modeling developed in the following chapters.

To conclude this overview of advanced characterization methods for semiconductors, Figure 1.3 provides a comparative summary of the physical information accessible through the most relevant electrical, optical, and scanning probe techniques. Each method probes a specific subset of microscopic parameters, ranging from morphological and compositional properties to local electrical and dynamical responses. The blue color scale distinguishes between direct and indirect observables, emphasizing how complementary measurements are required to achieve a complete understanding of the electronic landscape of disordered semiconductors. Scanning probe microscopies, in particular, uniquely bridge nanoscale morphology with electrical functionality, while optical and electrical spectroscopies provide averaged quantities that are essential for device-level interpretation. The combined use of these approaches en-

AFM (Topography)	D								●
c-AFM	I		I	D				I	●
KPFM		D	D		I			I	●
SCM			I		D	D			●
TERS	I						D		●
PV/PC Microscopy	I	I	I	D	I			D	●
I-V			I	D	I				●
C-V			I		I	D		I	●
Hall effect				D	I				●
PC spectroscopy (EQE)				I				I	●
SEM	D							I	●
XPS		I			I		D		●

Morphology / roughness
Surface potential
Charge / electric field
Conductivity / transport
Doping profile
Dielectric response
Composition / structure
Carrier dynamics

● Local (<1μm) ● Microscale (~1-10μm) ● Macroscopic (>10μm)

Figure 1.3: Comparative matrix of characterization techniques and the type of physical information they provide. Each cell indicates whether a given quantity is directly (D, dark blue) or indirectly (I, light blue) accessible by the corresponding technique. The table highlights the complementarity between scanning probe, optical, and electrical methods in mapping morphology, potential, charge, and dynamic processes in semiconductor materials.

ables a multiscale correlation between structure, energetics, and charge transport phenomena, which is fundamental for both inorganic and organic systems.

2 Methods

2.1 Atomic Force Microscopy

Atomic Force Microscopy is a high-resolution, non-optical technique that allows accurate and nondestructive measurement of several material features, such as topographical, electrical and magnetical properties.[87, 88] The basic operation principle of a standard AFM system involves a sharp tip mounted at the end of a flexible cantilever. The motion along the three axes is controlled by piezoelectric ceramic scanners. When the tip is approached on the surface, at a distance of approximately 0.1-20 nm, information of sample properties can be studied from the interaction between the tip and the sample surface which induce the deflection of the flexible cantilever. This process is tracked through a laser shone on the back-side coating of the cantilever and recollected on a position-sensitive photodetector(PSPD). Practically, a PSPD is a photodetector divided in four quadrants which allows to measure the amount of lateral and vertical deflection of the laser beam with respect to its center position.[87] While the AFM tip moves above features of different height, a feedback loop controls the z-scanner to maintain a constant distance from the surface.

The dimension of the tip is usually around 10-20 nm at the apex, which is one order of magnitude higher than atomic dimensions. Thus, the potential energy of the tip can be approximated with Lennard-Jones potential for two atoms [89]

$$U_{LJ}(r) = U_0 \left[-2 \left(\frac{r_0}{r} \right)^6 + \left(\frac{r_0}{r} \right)^{12} \right] \quad (2.1)$$

where r_0 is the average interatomic distance. Depending on the tip-sample distance r the interaction can be either attractive or repulsive, enabling different AFM techniques. When the tip is positioned at a distance such that van der Waals and long-range electrostatic forces are prevalent, the forces are attractive and the system operates in non-contact mode (NC-AFM). In this configuration, the cantilever is oscillated near its mechanical resonance by a piezo actuator. When the tip approaches the sample surface, the interaction shifts its resonance frequency and phase, changing the oscillation amplitude. The z-feedback changes the height

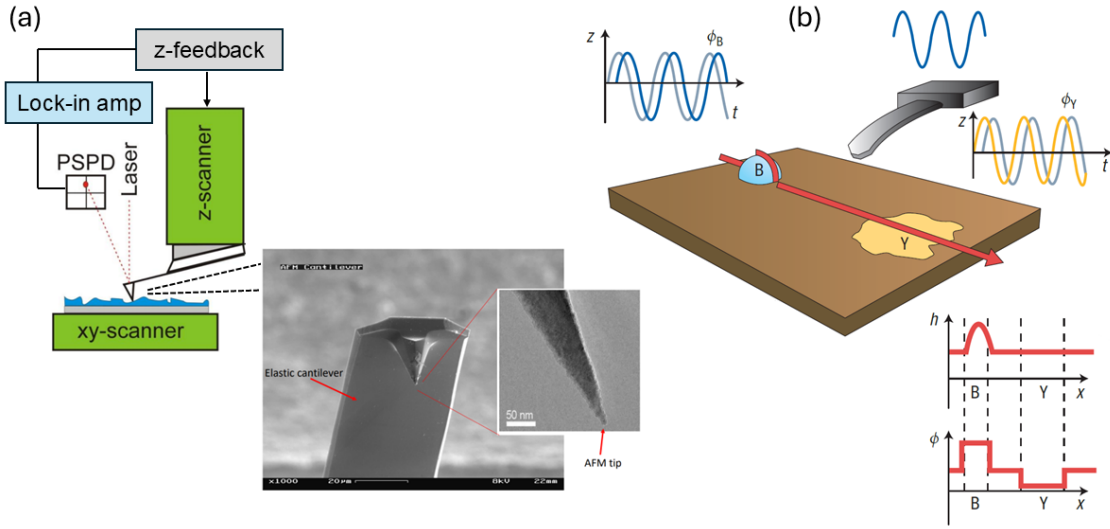


Figure 2.1: Atomic Force Microscopy. (a) AFM operational schematic. The inset shows an SEM image of the cantilever and tip of a standard AFM probe. (b) Working principle of non-contact AFM. Surface height changes (blue area) affect amplitude and phase, while phase contrast reveals compositional changes (yellow area). [90]

to bring the cantilever oscillation amplitude back to the setpoint amplitude. Non-contact AFM is ideal to study soft and fragile sample in a non-destructive way, as the tip never goes in real contact with the surface. Furthermore, NC-AFM is fundamental for the measurement of electrostatic forces via capacitive coupling, enabling more advanced techniques such as Electrostatic Force Microscopy (EFM) and Kelvin Probe Force Microscopy (KPFM) which are discussed below.

2.1.1 Electrostatic Force Microscopy

Electrostatic Force Microscopy (EFM) is the standard AFM technique used to probe electrostatic interactions between the tip and the sample. It is a variant of non-contact AFM, as the tip does not physically go in contact with the surface during measurement. Unlike conventional AFM probes, which are typically fabricated from undoped silicon, EFM requires tips coated with a conductive metal layer—commonly gold, iridium, or platinum—to enable capacitive coupling with the surface.

To understand signal generation in EFM it is fundamental to consider the electrostatic interaction between a biased AFM tip and the surface. This interaction arises from the capacitive coupling of the two bodies and the total capacitance $C(z)$ is dependent on the distance

between tip and sample. When an external voltage is applied, an electrostatic force arises along the vertical axis. In EFM the potential applied on the tip is the sum of a DC and AC components at frequency ω

$$V(t) = V_{DC} + V_{AC} \cos(\omega t) \quad (2.2)$$

The force acting on the cantilever can be calculated as

$$F_{el}(t) = \frac{1}{2} \frac{dC}{dz} V(t)^2 \quad (2.3)$$

$$F_{el}(t) = \frac{1}{2} \frac{dC}{dz} [(V_{DC} - V_{CPD}) + V_{AC} \cos(\omega t)]^2 \quad (2.4)$$

Here we inserted the contribution of the contact potential difference V_{CPD} inside the equation of the force. The CPD arises from a difference in work function between the AFM tip and the sample surface. When two materials with different work function are electrically connected, electrons redistribute to align Fermi levels. As a consequence, a potential difference builds up which is given by $eV_{CPD} = \phi_{tip} - \phi_{sample}$, where ϕ_{tip} and ϕ_{sample} are the work function of tip and sample respectively and e the electron charge. In electrostatic force microscopy this potential modifies the net voltage and must be accounted for to properly interpret force response.[69]

Expanding equation 2.4 we can obtain all the contributions of electrostatic force

$$F_{el} = F_{DC} + F_{\omega} + F_{2\omega} \quad (2.5)$$

$$\begin{aligned} F_{el} = & \frac{dC}{dz} \left[\frac{1}{2} (V_{DC} - V_{CPD})^2 + \frac{V_{AC}^2}{2} \right] + \\ & + \frac{dC}{dz} (V_{DC} - V_{CPD}) V_{AC} \cos(\omega t) + \\ & - \frac{1}{4} \frac{dC}{dz} V_{AC}^2 \cos(2\omega t) \end{aligned} \quad (2.6)$$

Equation 2.6 shows that the electrostatic response amplitude can be divided in three terms: one constant, one at frequency ω and the last at frequency 2ω . The ω term also depends on the contact potential difference and is nullified when $V_{DC} = V_{CPD}$.

Many EFM variants exist and they can be broadly categorized into two main families: Amplitude Modulation (AM) and Frequency Modulation (FM) techniques. In AM-EFM, the cantilever is driven at a fixed frequency—typically much lower than the resonance one—and the electrostatic interaction between the biased tip and the sample causes changes in the oscillation amplitude which are detected using a lock-in amplifier. AM-based approaches are generally easier to implement and interpret qualitatively, making them widely used for mapping

surface charges and dielectric properties. However, they suffer from lower force sensitivity and spatial resolution due to the convolution of topographical and electrostatic signals. In contrast, FM-EFM techniques monitor the shift in the resonance frequency of the cantilever, which results from the gradient of the electrostatic force acting between the tip and the sample. This approach provides enhanced sensitivity and enables more quantitative analysis.[69, 88]

Equation 2.6 describes how AM-EFM works: the cantilever's oscillation amplitude at frequency ω changes in function of the electrical forces acting on the tip and the amplitude value is proportional to the total force. The second harmonic signal, at frequency 2ω does not have any dependence on CPD potential and can be used to extract the capacitance gradient.

However, EFM is not a fully quantitative technique as the signal depends not only on the local electrostatic force, but also on the capacitance gradient. This is strongly influenced by tip-sample distance. To overcome this limitation, Kelvin Probe Force Microscopy (KPFM) introduces an active feedback mechanism that compensates the electrostatic force, enabling quantitative mapping of the contact potential difference.

2.1.2 Kelvin Probe Force Microscopy

Kelvin Probe Force Microscopy (KPFM) is an atomic force microscopy technique that enables quantitative mapping of the local surface potential with nanometric resolution. Its operation is based on the measurement of the contact potential difference (CPD) between the AFM tip and the sample surface. The physical phenomenon behind KPFM measurements is illustrated in figure 2.2. In the absence of electrical contact, the tip and the sample maintain their respective work functions (ϕ_t and ϕ_s) and Fermi levels ($E_{F,t}$ and $E_{F,s}$). When brought into electrical contact, charges redistribute until the Fermi levels align, generating an electrostatic potential difference across the tip-sample gap. This potential difference, defined as

$$eV_{CPD} = \phi_t - \phi_s \quad (2.7)$$

represents the voltage that must be applied to cancel the electrostatic force between tip and sample.

In KPFM, an AC modulation is applied to the tip, and the resulting electrostatic force contains a component oscillating at the modulation frequency ω . A feedback loop continuously adjusts the DC bias applied to the tip (V_{DC}) until this AC force component is nullified. When the condition $V_{DC} = V_{CPD}$ is met, the electrostatic interaction is fully compensated and the applied bias corresponds directly to the local contact potential difference.

Compared to conventional Electrostatic Force Microscopy (EFM), where the signal depends on the tip-sample distance as $F_{el} \propto C''(z)V^2$, KPFM eliminates this dependence by actively

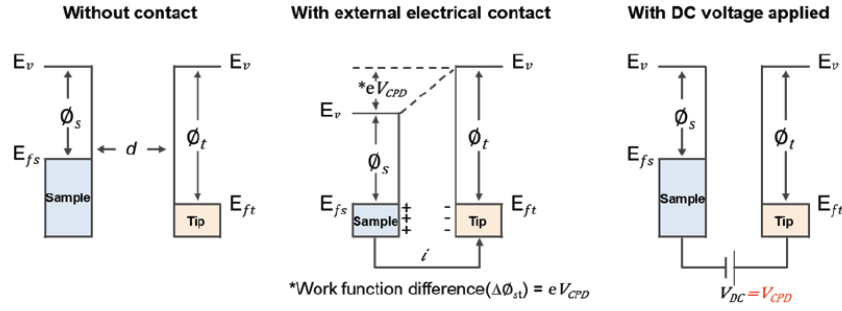


Figure 2.2: Schematic energy diagrams illustrating the working principle of Kelvin Probe Force Microscopy. Left: isolated tip and sample with different work functions. Center: charge redistribution upon electrical contact, leading to the definition of the contact potential difference (V_{CPD}). Right: application of a DC voltage compensates the CPD and nullifies the electrostatic interaction. Image adapted from Park Systems.

nullifying the force at the modulation frequency. This allows for a truly quantitative mapping of the surface potential, independent of the tip–sample spacing.

Thanks to this principle, KPFM has become a powerful tool to investigate semiconductors and electronic devices. It provides absolute values of surface potential, and when combined with external perturbations such as optical illumination or gate biasing, it gives direct access to phenomena such as carrier diffusion, recombination dynamics, and density of states at the nanoscale [10, 12, 91].

KPFM on Thin-Film Transistors

KPFM was employed to investigate the electronic properties of amorphous oxide thin-film transistors (TFTs). The measurements were carried out using a Park Systems NX-10 Atomic Force Microscope (AFM) operated in amplitude modulation mode. The cantilevers were NSC36 probes (MikroMasch), made of n-type silicon with a chromium/gold coating, with a nominal spring constant of 2 N/m and a resonance frequency of about 130 kHz.

In order to perform electrical measurements simultaneously with AFM imaging, we built a homemade probestation integrated into the Park NX-10 system. This custom setup allowed stable contacting of the source, drain, and gate electrodes of the transistors while keeping the device accessible to the AFM tip, enabling combined topographic and surface potential mapping under controlled electrical biasing.

The source electrode of the transistor was grounded, while controlled voltages were applied to the gate and drain electrodes using a Keysight B2911A Source Measurement Unit (SMU). Depending on the applied gate bias, the semiconductor channel was driven either into depletion, where it behaves as a dielectric and the gate field penetrates through the semi-

conductor, or into accumulation, where mobile carriers screen the gate field and the channel behaves as a conductor.

The surface potential measured by KPFM (V_{KPFM}) was recorded as a function of the applied gate voltage, producing spectroscopy curves that capture the transition from depletion to accumulation. These curves are directly influenced by the distribution of localized states in the amorphous semiconductor, which determines how carriers accumulate or deplete under an external field.

To extract quantitative information, the experimental $V_{\text{KPFM}}-V_G$ curves were analyzed with an analytical model based on the Poisson equation for a metal–insulator–semiconductor junction with exponential band tails. Fitting the data provided key density-of-states parameters such as the band tail width, doping density, and flat-band potential.

KPFM on Organic Heterojunctions

For the measurements on organic heterojunctions we used the same AFM setup and cantilevers described in the previous section. In this case, the key component was the optical excitation system, which was entirely designed and assembled in our laboratory.

A Thorlabs L520P50 laser diode ($\lambda = 520$ nm) was employed as light source and driven by a dedicated current controller. The beam was collimated and guided through a lens tube containing a set of focusing optics and a $2\ \mu\text{m}$ pinhole, producing a Gaussian spot of about $2.6\ \mu\text{m}$ on the sample surface. The light intensity was modulated at 720 Hz, matching the frequency range of maximum device response.

The complete optical system, including the lens tube and the custom sample holder, was integrated with the AFM to allow simultaneous scanning and optical excitation from below. Figure 2.3 (a) shows the optical layout, including the laser diode, the protection circuit, the focusing lenses, and the $2\ \mu\text{m}$ pinhole used to define the spot size. Figure 2.3 (b) reports photographs of the actual setup: the image on the left shows a top view highlighting the optical tube, while the image on the right shows a side view of the sample holder mounted inside the AFM.

This configuration enabled us to map the surface photovoltage generated locally at the illuminated spot of the heterojunction. By scanning the AFM tip, we obtained simultaneous morphology and surface potential maps, which were later analyzed to extract the spatial profile of photogenerated carriers and the effective carrier diffusion length.

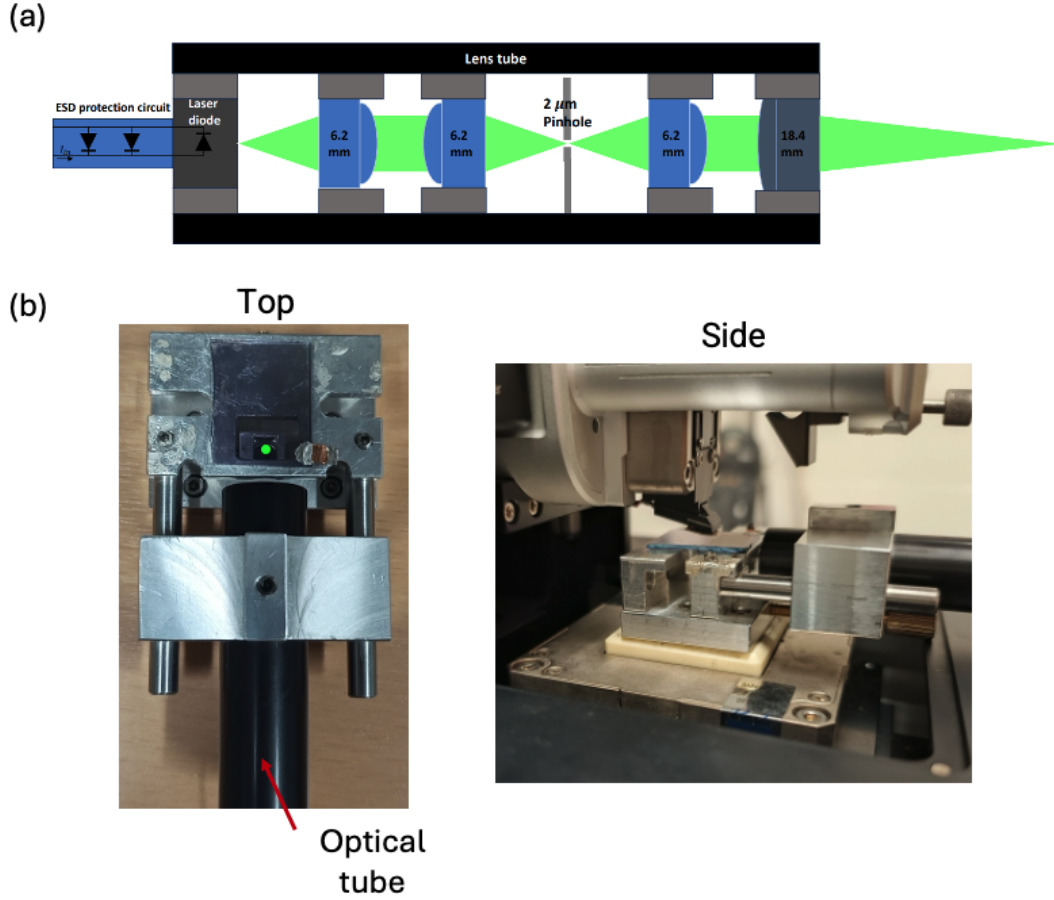


Figure 2.3: Optical excitation setup for KPFM on organic heterojunctions. (a) Optical layout of the homemade lens tube with laser diode, protection circuit, focusing lenses, and 2 μm pinhole. (b) Photographs of the experimental setup integrated with the AFM: top view highlighting the optical tube (left) and side view showing the custom sample holder mounted in the AFM (right).

2.1.3 Lateral Electrostatic Force Microscopy

AFM setup and detection

Lateral EFM measurements were performed with a commercial atomic force microscope (Park Systems NX10). The microscope was operated in standard topography mode with simultaneous acquisition of the lateral electrostatic signal, so that morphology and torsional response were recorded in a single scan.

The torsional deflection of the cantilever was detected with the built-in four-quadrant optical beam deflection system. The left-right photodiode difference was routed to an external lock-in amplifier (MFLI, Zurich Instruments), which demodulated the signal at the drive frequency. The modulation frequency was set to 17 kHz, sufficiently far from the flexural resonances of the cantilever to avoid mechanical cross-talk.

The detection bandwidth was controlled by adjusting the lock-in time constant in the range 100 μs to 10 ms, depending on scan speed and resolution requirements, with a 24 dB/octave roll-off. This configuration allowed optimizing the trade-off between noise reduction and temporal response.

To investigate the dependence of the torsional response on tip-sample separation, we performed amplitude-distance spectroscopies in which the tip was approached and retracted vertically while recording the lateral EFM amplitude. These measurements enabled a direct evaluation of the Z -dependence of the signal under controlled conditions.

Cantilevers

Two types of conductive silicon cantilevers were employed for the lateral EFM experiments. The first set consisted of long probes from Nanosensors with a nominal length of 225 μm and coated with Pt/Ir, providing stable conductivity and high torsional sensitivity. The second set were NSC36 probes (MikroMasch) coated with Au, with a nominal spring constant of about 2 N/m and a resonance frequency of approximately 130 kHz.

No significant differences were observed in the measured lateral EFM signal when switching between Pt/Ir- and Au-coated probes, indicating that the response is robust with respect to the specific cantilever type.

A direct calibration of the torsional channel into absolute force units was not performed. Instead, the quantitative scaling of the lateral response was obtained through the capacitor-based calibration procedure described in Chapter 5, which directly links the measured lock-in amplitude to the electric field.

Electrical excitation and suppression of vertical forces

The electrical excitation for lateral EFM was provided by the internal electronics of the AFM, which applied a sinusoidal modulation at 17 kHz superimposed to the DC bias on the tip.

In amplitude-modulation both vertical and lateral electrostatic forces oscillate at the same frequency. This is not an intrinsic limitation, but becomes critical when the vertical component is much larger than the lateral one, since even a small cross-talk can dominate the torsional signal. To mitigate this effect, all measurements were performed on flat samples, reducing coupling with the topography. In addition, the Kelvin probe feedback was kept active during the scans to continuously compensate the local contact potential difference. This procedure strongly attenuates the vertical contribution, allowing the lateral response to be isolated.

As an additional control, in selected experiments the sample was rotated by 90° with respect to the cantilever torsional axis. In this configuration the in-plane electric field is orthogonal to the torsional motion and the lateral EFM signal vanishes, confirming the selectivity of

the method.

2.2 DC electrical characterization

The DC characterization of field-effect devices is based on the analysis of transfer curves, in which the drain current (I_{DS}) is measured as a function of the gate voltage (V_{GS}) at a fixed drain bias (V_{DS}). This experiment determines how effectively the gate modulates the channel conductivity, and it provides access to the main figures of merit of the device.

In the linear regime, for small drain voltages, the current is described by

$$I_{DS} = \mu_{FE} C_i \frac{W}{L} (V_{GS} - V_{th}) V_{DS} \quad (2.8)$$

where μ_{FE} is the field-effect mobility, C_i the capacitance per unit area of the gate dielectric, W and L the channel width and length, and V_{th} the threshold voltage. The mobility can be extracted from the slope of the transfer curve in this regime:

$$\mu_{FE} = \frac{L}{W C_i V_{DS}} \frac{\partial I_{DS}}{\partial V_{GS}} \quad (2.9)$$

The threshold voltage is determined through the extrapolation method, by extending the linear portion of the transfer curve to its intercept with the V_{GS} -axis. This parameter identifies the minimum gate bias required to form a conductive channel.

The subthreshold slope (SS) is obtained from the steepness of the transfer curve in the subthreshold region:

$$SS = \left(\frac{\partial \log_{10} I_{DS}}{\partial V_{GS}} \right)^{-1} \quad (2.10)$$

It quantifies the switching efficiency of the device and is directly linked to the density of interfacial and gap states.

For the devices investigated in this thesis, DC measurements are essential to connect device-level performance with microscopic material properties. The field-effect mobility reflects the impact of disorder and localization phenomena on charge transport. The threshold voltage is a sensitive probe of trapped charges at interfaces or within the bulk, which often determine the onset of conduction. The subthreshold slope directly relates to the density of trap states in the band gap, a critical quantity in disordered semiconductors.

By systematically extracting these parameters, DC measurements provide a quantitative framework to evaluate charge transport, stability, and the role of defect states in the investigated material systems.

2.3 Optical characterization

2.3.1 Transient measurements

We measured the device dynamics by recording transient photovoltage signals under pulsed illumination, as schematically shown in Figure 2.4. A function generator drove a green LED ($\lambda = 530$ nm), operated in pulsed mode to generate square light pulses with $50 \mu\text{s}$ duration and sharp rise/fall edges. We collimated the beam and aligned it to uniformly illuminate the active area of the device, ensuring reproducible excitation conditions. We used a second metal electrode on top of the device, separated by a thin dielectric layer. This electrode couples capacitively to the underlying structure and allows us to measure the photovoltage in a capacitive way. The voltage was monitored with a digital oscilloscope in high-impedance mode. To minimize external interference, we used shielded cables, short electrical connections, and a grounded faraday cage.

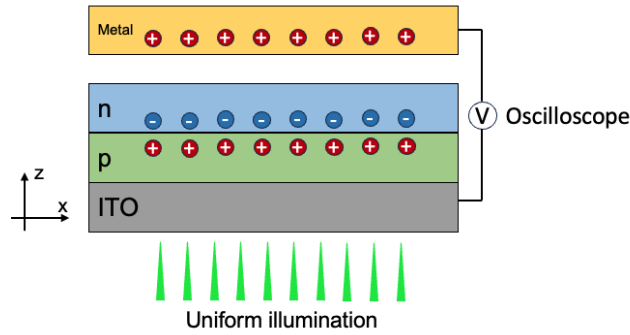


Figure 2.4: Schematic representation of the transient photovoltage measurement. The p–n junction is uniformly illuminated from the ITO side, and the open-circuit photovoltage is monitored directly at a second metal contact with a digital oscilloscope.

We evaluated the device response by analyzing the decay of the photovoltage after the light pulse was switched off. The transient traces were processed by averaging over several illumination cycles to improve the signal-to-noise ratio. We then fitted the averaged decay curves using

$$V(t) = \frac{V_0}{1 + t/\tau_{\text{rec}}} \quad (2.11)$$

where V_0 is the photovoltage amplitude at the beginning of the decay and τ_{rec} is the effective recombination lifetime. This expression follows from the assumption of bimolecular recombination, which represents the dominant process in disordered organic semiconductors. [32, 92]

2.3.2 Photocurrent spectroscopy

Photocurrent spectroscopy relies on the absorption of photons in the semiconductor. When light with photon energy above the bandgap is incident on the device, it creates electron–hole pairs in the active layer. These photogenerated carriers are separated by the built-in electric fields of the device and contribute to a measurable photocurrent under bias. At photon energies below the bandgap, absorption occurs through localized states that extend into the gap, resulting in a weaker but still detectable photocurrent. By monitoring the photocurrent as a function of photon energy, one can therefore probe both the absorption onset, which reflects the optical bandgap, and the exponential tail, which corresponds to the density of localized states. Measurements were performed inside a Nextron probe station with micromanipulators for stable electrical contact and a light-tight enclosure to suppress ambient illumination. A xenon arc lamp coupled to a monochromator provided monochromatic excitation with spectral resolution better than 2 nm. Order-sorting filters blocked higher-order harmonics to guarantee spectral purity.

During acquisition, the devices were biased at constant drain-source voltage and fixed gate potential. We amplified the photocurrent with a low-noise current amplifier (Femto DLPCA-200) and demodulated the signal using a lock-in amplifier (Stanford Research SR844). A mechanical chopper defined the modulation frequency for the lock-in detection.

To calibrate the photon flux at each wavelength, we used a silicon photodiode with a known spectral responsivity. From these measurements we obtained the photon flux $\Phi_\gamma(E)$, which allowed us to normalize the device response. The external quantum efficiency was calculated as

$$\text{EQE}(E) = \frac{I_{\text{ph}}(E)/q}{\Phi_\gamma(E)}$$

where $I_{\text{ph}}(E)$ is the photocurrent and q the elementary charge.

In the sub-bandgap region, the absorption coefficient of amorphous semiconductors follows an exponential dependence with a characteristic energy E_t , which reflects the band-tail distribution.[93] Because the photocurrent is directly proportional to the absorbed photon flux, the EQE follows the same exponential behavior. When plotting $\text{EQE}(E)$ as a function of photon energy, the sub-bandgap portion of the spectrum shows an exponential tail, whose slope provides a direct measure of the characteristic band-tail energy E_t .

The optical bandgap was determined in a complementary way. After identifying the region of steep increase in the EQE spectrum, we extrapolated the rising edge to the baseline to obtain the threshold energy corresponding to the optical bandgap. This procedure, combined with the tail-slope analysis, ensures that both parameters are consistently extracted from the same set of measurements under identical biasing and optical conditions.

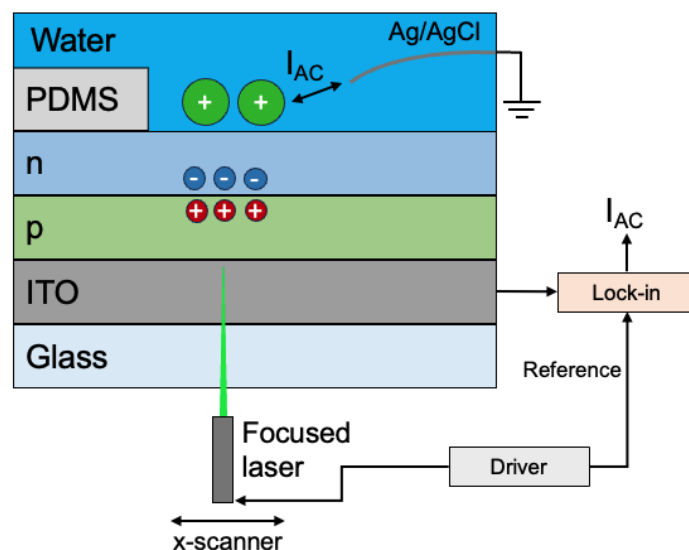


Figure 2.5: Schematic of the photocurrent microscopy setup.

2.3.3 Photocurrent mapping

Figure 2.5 illustrates the working principle of the photocurrent microscope. The device is built on a transparent glass substrate coated with an ITO electrode, on top of which a pn-junction is deposited. The laser source, the same employed in KPFM measurements, is focused through the transparent substrate onto the active layer. When the junction is illuminated, photons generate electron-hole pairs that are separated by the internal fields of the semiconductor. These carriers drive charge transfer reactions at the interface with the electrolyte, producing a local photoelectrochemical current that flows into the solution and is collected by the Ag/AgCl reference electrode.

Because the laser is modulated in intensity, the resulting signal is an alternating photocurrent I_{AC} . This configuration allows lock-in detection, which extracts the part of the current that is strictly correlated with the light excitation and filters out background contributions. In this way, the signal directly reflects the local photoelectrochemical activity of the illuminated region.

A characteristic feature of this technique is its sensitivity to the presence of dielectric or insulating overlayers. When the semiconductor surface is covered by a material such as PDMS, the electrolyte cannot reach the junction and interfacial charge transfer is suppressed. In those regions the photocurrent is strongly reduced or absent, while exposed semiconductor areas generate a clear response. This intrinsic mechanism provides the imaging contrast, with active regions appearing bright and passivated regions remaining dark.

Imaging is obtained by scanning the laser beam across the device with a motorized XY

stage (PIL-511). The sample remains fixed in the electrolyte to avoid liquid disturbances, while the laser spot is displaced with micrometer precision over the surface. At each position the photocurrent is recorded, and the collection of these data points yields a two-dimensional map of the photoelectrochemical activity. In this way, the method provides a direct link between the microscopic structure of the device and its local functional response under optical excitation.

2.4 Device fabrication

All devices investigated in this thesis were fabricated within collaborating laboratories. I did not directly participate in the fabrication processes; however, the relevant methods are summarized here to provide the necessary context for the device architectures and for the characterization results discussed in the following chapters.

2.4.1 Photolithography and Processing

The device architectures studied in this thesis were structured by means of standard photolithography, which enabled the reproducible definition of electrodes, dielectric layers, and channel regions with micrometric resolution (Fig. 2.6a). The technique relies on the use of a photosensitive resist, a polymer whose chemical solubility is modified by exposure to ultraviolet (UV) radiation through a patterned mask. In this way, the mask design is transferred onto the resist, which acts as a temporary stencil for subsequent deposition or etching steps.

The process began with careful substrate cleaning. Contaminants and organic residues can compromise adhesion and film uniformity, so substrates were first sonicated in acetone and isopropanol, and subsequently exposed to oxygen plasma to remove residual hydrocarbons and increase surface energy. For organic heterojunction devices, where delamination in aqueous environments is a concern, the ITO electrodes were further functionalized by vapor-phase silanization with octyltriethoxysilane (OTS) to improve interfacial adhesion. [94]

A uniform layer of photoresist was then deposited by spin coating and soft-baked to evaporate residual solvent and stabilize the film (schematically illustrated in Fig. 2.6b). The resist-coated substrate was aligned with a photomask and exposed to UV light at 365 nm; exposure locally modified resist solubility so that, after development, only the selected regions remained protected, forming a patterned mask with well-defined edges.

The patterned resist acted either as a sacrificial layer for lift-off or as a protection mask during dry etching. In lift-off, metallic films such as molybdenum were deposited by sputtering onto the patterned resist, and subsequent resist stripping left the contacts with the desired geometry. When structuring dielectric or semiconductor layers, the patterned resist protected

the underlying material during reactive ion etching, enabling selective removal of the exposed regions.

Photolithography was also combined with solution processing. Polymeric layers such as PEDOT:PSS were deposited by spin coating, with GOPS added as a cross-linker to increase robustness in aqueous environments;^[95] the films were then annealed at 140°C to complete cross-linking and improve adhesion. For oxide semiconductor devices, post-deposition annealing at 180°C in air was used to activate IGZO and stabilize electrical performance.

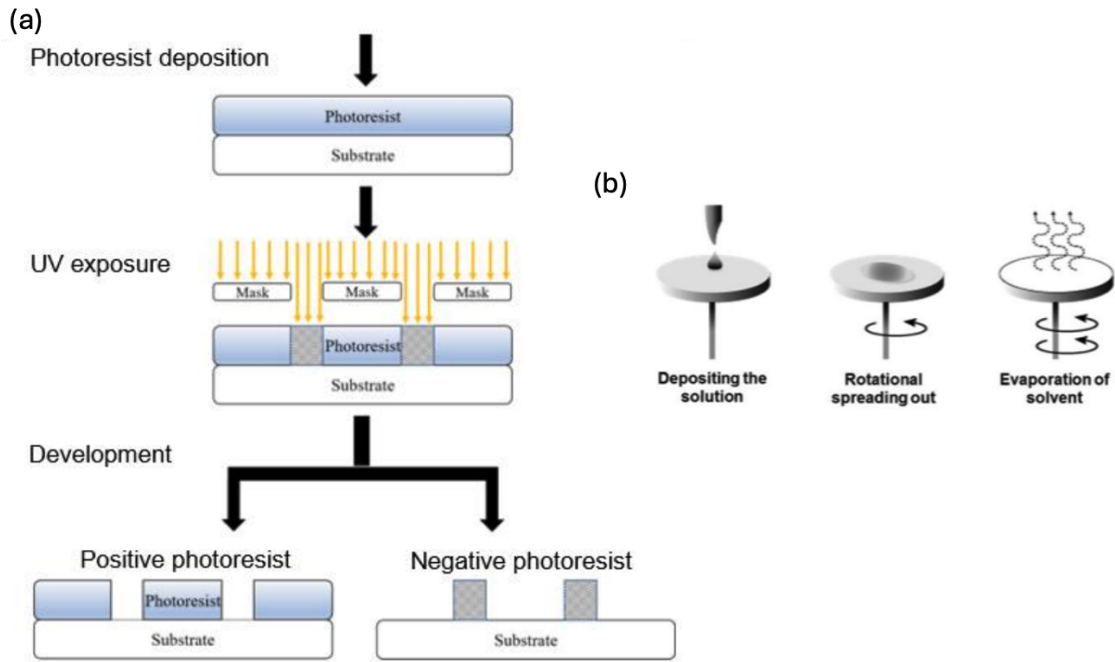


Figure 2.6: (a) Schematic of the photolithography flow: photoresist deposition, UV exposure through a mask, development, and the resulting patterns for positive vs. negative resists. (b) Spin-coating stages for resist deposition: dispensing, radial spreading during rotation, and solvent evaporation.

After defining the device geometry by photolithography, the functional layers were deposited by physical vapor deposition and atomic layer deposition.

2.4.2 Physical Vapor Deposition (PVD)

Physical vapor deposition techniques were employed to grow both inorganic and organic thin films used in the devices investigated in this thesis. In general, PVD relies on the physical transformation of a solid into vapor under high vacuum and its subsequent condensation onto a substrate. This approach enables precise control over film thickness and composition, while minimizing contamination from the ambient atmosphere. Among the various PVD approaches, magnetron sputtering and thermal evaporation were adopted.

In the case of oxide thin-film transistors, magnetron sputtering was used to deposit both the semiconducting and metallic layers. In this technique, a low-pressure argon plasma is ignited inside the deposition chamber. Positively charged argon ions are accelerated towards the target material, transferring their momentum and ejecting atoms or clusters from the surface. These species travel through the vacuum and condense on the substrate, forming a thin film. Magnetron assistance enhances the plasma density and stabilizes the discharge, improving deposition rates and uniformity. Sputtering is particularly suited for amorphous oxide semiconductors such as indium–gallium–zinc oxide (IGZO), where it provides dense and homogeneous films with reproducible stoichiometry.[4] In this work, a 60 nm thick IGZO layer was deposited using a target with composition ratio In:Ga:Zn = 2.5:1.2:1. After growth, the films were thermally annealed to activate the semiconductor and improve electrical performance. The same sputtering process was also employed to deposit molybdenum electrodes with thicknesses of 60 nm, chosen for their good adhesion, low resistivity, and compatibility with standard photolithographic processing.

For organic heterojunction devices, thermal evaporation in high vacuum was employed to deposit small-molecule semiconductors such as metal-free phthalocyanine (H_2Pc) and perylene-tetracarboxylic diimide (PTCDI). The deposition took place at a base pressure below 10^{-6} mbar to minimize contamination and ensure high film purity. The materials were sublimated from resistively heated crucibles and condensed on the cooled substrates. Deposition rates were precisely controlled in the range of 0.5 Å/s for H_2Pc and 5–6 Å/s for PTCDI, as monitored by a quartz crystal microbalance, ensuring homogeneous films with well-defined thickness. Bilayer heterojunctions were prepared with 30 nm of each material, for a total active thickness of 60 nm. The high vacuum conditions were essential to preserve the molecular structure and to prevent thermal degradation, which is a critical requirement for achieving reproducible optoelectronic properties in organic devices.

2.4.3 Atomic Layer Deposition (ALD)

Atomic layer deposition was employed for the growth of the dielectric stack in thin-film transistors. This technique is based on self-limiting surface reactions that proceed in a cyclic manner, enabling precise control of film thickness with sub-nanometer accuracy and excellent uniformity over large areas. In this work, thermal ALD was used to deposit a multilayer dielectric composed of 80 nm of Ta_2O_5 and 20 nm of Al_2O_3 .

The choice of this stack was motivated by multiple factors. First, Ta_2O_5 and Al_2O_3 provide a high dielectric constant and stable interfaces with IGZO, ensuring reliable gate insulation and good electrostatic control of the channel. In addition, tantalum-based oxides efficiently absorb ionizing radiation thanks to the high atomic number of Ta ($Z=73$). This property makes Ta_2O_5

particularly suitable for thin-film transistors designed for X-ray detection, since the dielectric not only acts as a gate insulator but also contributes to the device response under irradiation conditions. [96]

3 Accurate determination of band tail properties in amorphous semiconductor thin film with Kelvin probe force microscopy

3.1 Introduction

Amorphous semiconductors are fundamental for large area electronic devices, such as active matrices in detectors or displays. The disordered structure of the amorphous phase causes the formation of localized states at the edges of the valence and conduction bands, called band tails. Such band tails are of fundamental importance for the transport properties of the material since they act as trapping states for carriers[97]. An important technological aim is the downscaling of amorphous semiconductor device dimensions, where local border effects become increasingly relevant. In such a situation, band-tails and general density of states (DOS) properties have to be understood as local properties that are influenced by local variations in the microstructure, chemical composition, or electrostatic charge trapping. However, most techniques that assess DOS properties rely on macroscopic probes and quantify average material properties. Examples are spectroscopic methods that measure absorption or photocurrent generation as well as electrical methods based on capacitance or transistor measurements and modeling [35, 36, 98–101]. Instead, a microscopic technique that could reveal DOS properties with nanometric resolution on working microstructured semiconductor thin-film devices is highly wanted to improve device understanding and optimization.

Kelvin Probe Force Microscopy (KPFM) is an advanced atomic force microscopy technique that can measure electrical properties of a sample with high resolution and precision, including the density of states [10, 11, 102, 103]. With KPFM, one measures the contact potential difference between the tip and the sample [91]. This quantity is related to the amount of charge injected into the surface layer [104]. However, the relationship is complex because of band bending and non-uniform charge distribution [12]. Despite these issues, KPFM has been successfully applied to study different phenomena in amorphous semiconductors [105–107].

Examples are the measurement of the surface potential in thin-film transistors (TFTs) [108, 109] or the determination of the DOS in ultrathin semiconducting layers where band bending is not relevant [110, 111]. For semiconducting layers of finite thickness, the interpretation of KPFM measurements requires the solution of the non-linear Poisson equation to describe band bending correctly [112]. So far, a possible numerical solution was only described by Germs et al. in their study on amorphous oxide semiconductors, where they proposed an iterative procedure to approximate the DOS for these materials [40]. Despite this progress, a reliable analytical model to derive the DOS from KPFM measurements in amorphous semiconductors with a finite layer thickness is not available.

One of the most promising amorphous semiconductors is Indium–Gallium–Zinc Oxide (IGZO), as it can be easily deposited by sputtering and presents a mobility of the order of $10 \text{ cm}^2/\text{Vs}$, which is ten times higher than amorphous silicon [5]. IGZO has a reduced band tail width with respect to a-Si, and this finding is related to the increased mobility [6]. Band tails in IGZO can be modeled as exponentials described by two parameters: the band tail width and the oxygen vacancy doping density. This assumption is confirmed by experimental studies [15, 97, 98]. In addition to its high mobility, IGZO is characterized by a larger bandgap than a-Si, causing a low off-state current and a high transparency. These properties make IGZO an ideal material for use in transparent electronics such as flexible displays and sensors [5]. Investigations of the DOS properties of IGZO have been performed by several groups, employing a wide range of techniques [6, 15, 98].

The aim of this study is to achieve reliable local measurements of the amorphous band tail in IGZO using Kelvin Probe Force Microscopy (KPFM). We analyze KPFM spectroscopy data with a model based on the solution of the non-linear Poisson equation for the metal – insulator – semiconductor (MIS) junction. The model is analytical and allows for a direct fit of the experimental data, providing values for the relevant DOS parameters, such as the band tail width E_t , the doping density N_D , and the flat band potential V_{FB} . We validate the accuracy of our method by comparing it to photocurrent spectroscopy measurements. We further demonstrate the value of our method by analyzing the effect of ionizing radiation on DOS properties.

3.2 MIS model for IGZO thin film transistors

The standard configuration for KPFM experiments on thin-film semiconductor devices is depicted in Fig. 3.1(a). The KPFM tip is operated above the exposed semiconducting thin film. The source and drain electrodes contact the semiconducting layer, and a field effect is exerted by the gate electrode, separated from the semiconductor by a thin dielectric layer. The source

is connected to the ground, while potentials V_D and V_G applied to the drain and the gate are controlled by a source measurement unit. The KPFM experiment probes the local surface morphology of the semiconducting channel and measures the local surface voltage, V_{KPFM} . Depending on the applied gate voltage, two limiting cases of the surface voltage have to be considered: In depletion, the channel is void of carriers and behaves as a dielectric; the electric field of the gate penetrates without screening the semiconductor and interacts with the KPFM tip. The surface voltage varies with the applied gate voltage. In contrast, in accumulation, the semiconducting layer behaves as a conductor, and its carriers screen the gate field. Accordingly, surface voltage is constant. KPFM spectroscopy experiments that aim at probing the DOS of the semiconductor, characterize the surface voltage as a function of the gate voltage while the transition from depletion to accumulation occurs.

In order to derive a quantitative model for KPFM spectroscopy on the semiconducting thin film, we consider the schematic energy diagram of the MIS junction during the interaction with the Atomic Force Microscope (AFM) tip as shown in Fig. 3.1(b). All relevant energetic parameters are indicated in the diagram. We distinguish two cases: first, the flat band condition that is drawn in gray lines. Second, the depletion condition is highlighted with black lines. The solid lines refer to energy levels, while the dashed lines stand for vacuum levels. The Fermi level in the semiconductor is given by the grounded source electrode and is colored red in the diagram. The application of a voltage to the gate produces band bending inside the semiconductor. This effect is quantified with the potential $\phi(x)$, which expresses the shift of vacuum level in the semiconductor with respect to the flat band condition. The spatial coordinate of $\phi(x)$ starts at the external interface $\phi(x=0)=\phi_0$ and ends at the interface with the gate dielectric $\phi(x=t)=\phi_t$. Here, t denotes the thickness of the semiconducting layer. Other important parameters in the diagram regard the drop in vacuum level across the gate dielectric V_{ox} and the work functions of the gate and source electrodes, Φ_g and Φ_s , respectively. Additional offsets in vacuum level occur at interfaces due to static trapped charges or interfacial dipoles. They are denoted as ϕ_{ds} and ϕ_{dg} and refer to the interfaces source/semiconductor and gate/dielectric, respectively. Finally, the diagram includes the AFM probe interacting electrostatically with the MIS junction. The potential V_{KPFM} is controlled by the KPFM feedback loop targeting the absence of electrostatic forces between the tip and the sample. Accordingly, there is no electric field between the tip and the semiconductor surface, and the vacuum level of the AFM tip aligns with the semiconductor interface. The measured V_{KPFM} thus reports on changes in vacuum level at the external semiconductor interface occurring when the gate voltage is changed [12].

Based on the energy diagram, we derive the quantitative model for the KPFM experiment in two steps. First, we develop the relation for the potential $\phi(x)$ describing band bending in an amorphous semiconductor of finite thickness. Second, we identify how the experimental

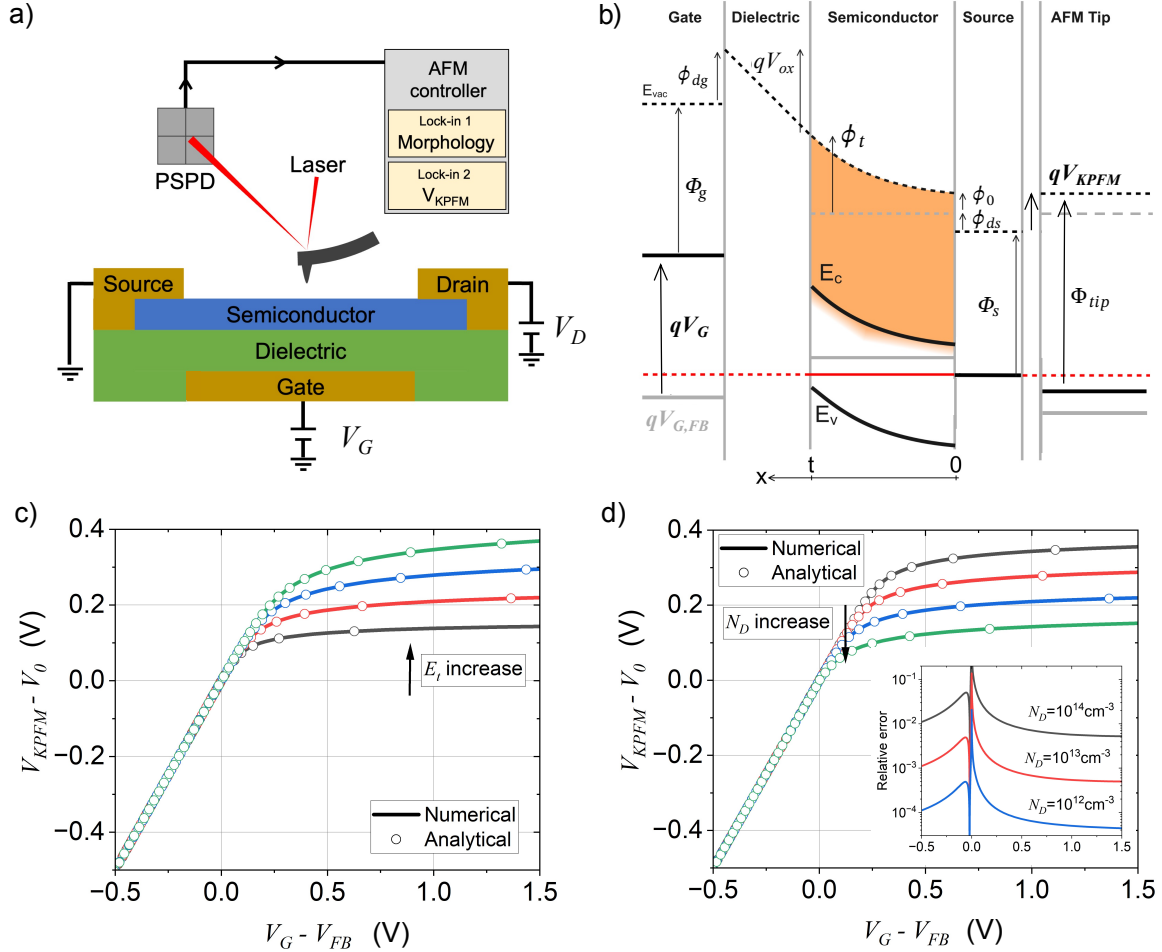


Figure 3.1: KPFM spectroscopy and model. (a) Schematic of the Kelvin Probe Force Microscopy experiment performed on working thin-film transistors. In the KPFM spectroscopy experiments, the tip potential is measured while the transistor gate voltage is varied. (b) Schematic band diagram of the metal-insulator-semiconductor junction interacting with the AFM tip. The gray color corresponds to the flat band condition. The energy levels in depletion are depicted in black. The semiconductor is grounded through the source. The AFM tip is interacting with the semiconductor. (c) and (d) Simulated KPFM spectroscopy measurements for different values of E_t and N_D .

observables V_{KPFM} and V_G are linked to the parameters entering the potential function $\phi(x)$. We note that we do not distinguish for KPFM experiments between trap states or conducting states, as both contribute to local charge accumulation and, hence, contribute to changes in KPFM surface potential. Accordingly, the model also fully includes Fermi-level pinning effects occurring at semiconductor interfaces.

Band bending occurs due to the buildup of local space charge $\rho(x)$ in the semiconductor. For an n -doped amorphous semiconductor, we can write

$$\rho(x) = q_0 N_D \left[1 - \exp\left(\frac{\phi(x)}{E_t}\right) \right] \quad (3.1)$$

where E_t describes the exponential band tail, $\text{DOS}(E) \propto \exp(E/E_t)$ [6, 113], N_D introduces the concentration of n -type doping sites, and q_0 refers to the unit charge. Equation (3.1) is derived from the solution of the Fermi–Dirac integral under the zero-temperature assumption. The finite temperatures can be accounted for as a temperature dependent shift in the flat band voltage. The equation for $\phi(x)$ is then defined by combining (3.1) with the Poisson equation,

$$\frac{d^2\phi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0} \quad (3.2)$$

The resulting differential equation requires two boundary conditions to provide a unique solution for $\phi(x)$. Following our KPFM experiment, we consider the external semiconductor interface at $x=0$, where we nullify the electric field and measure the local surface potential. Accordingly, we set $\phi(x=0)=\phi_0$ and $\phi'(x=0)=0$. For these boundary conditions, we obtain an analytical solution for the condition $\phi(x=0) \gg E_t$,

$$\phi(x) = E_t \ln \left\{ \exp\left(\frac{\phi_0}{E_t}\right) \left[\tan^2\left(\frac{x}{\lambda}\sqrt{2} \exp\left(\frac{\phi_0}{2E_t}\right)\right) + 1 \right] \right\} \quad (3.3)$$

where $\lambda = \sqrt{\frac{E_t \varepsilon \varepsilon_0}{q_0^2 N_D}}$ describes a characteristic length scale of the semiconductor. The solution describes the band bending occurring when negative carriers accumulate in the channel and strongly screen the gate field, and it depends explicitly on the DOS parameters. Below, we compare the analytical solution with the complete numerical one and show that it is, in many situations, also a good approximation to describe KPFM experiments in the depletion regime.

In the second part of our derivation, we link the potential function $\phi(x)$ to the experimental observables V_G and V_{KPFM} . Key to this are the function values at the external and internal semiconductor interfaces: $\phi(x=0)=\phi_0$ and $\phi(x=t)=\phi_t$, respectively. When a potential is applied to the gate, the vacuum level and the conduction band edge are shifted, and due to the finite thickness of the semiconductor, a residual of the gate electric field can reach the

external semiconductor interface. The resulting shift in the conduction band is ϕ_0 , and it is directly related to the voltage V_{KPFM} measured at the AFM tip in the KPFM experiment. A direct measurement of ϕ_0 is difficult as different offsets contribute to V_{KPFM} , such as the work function of the AFM-tip, the possible dipole layer forming at the semiconductor interface, and amplifier offsets in the KPFM signal acquisition. Accordingly, we introduce the Kelvin probe surface voltage measured in flat band conditions, $V_{\text{KPFM,FB}}$, and obtain

$$\phi_0 = V_{\text{KPFM}} - V_{\text{KPFM,FB}} \quad (3.4)$$

Next, we consider the semiconductor interface with the gate dielectric and derive the relation that links the surface voltage ϕ_t to the gate voltage V_G . Following the energy diagram in Fig. 3.1(b), we find

$$qV_G = qV_{G,\text{FB}} + \phi_t + qV_{\text{ox}} \quad (3.5)$$

where $V_{G,\text{FB}}$ is the flat band voltage and V_{ox} is the potential drop over the gate dielectric, which is given by $V_{\text{ox}} = \sigma/c_{\text{ox}}$. The capacitance of the gate dielectric c_{ox} is a constant, and the surface charge density in the semiconducting channel σ can be directly computed from the potential function $\phi(x)$ (see the supplementary material). Note that Eq. (3.3) allows us to express both ϕ_t and σ as a function of ϕ_0 . Accordingly, the combination of Eqs. (3.3)–(3.5) provides an analytical expression for V_G as a function of V_{KPFM} .

Figures 3.1(c) and 3.1(d) show the simulated V_{KPFM} vs. V_G curves for different combinations of DOS parameters. At negative gate voltages, when the channel is in depletion, a linear relation with a unitary slope is observed as the gate field passes through the semiconductor. Instead, toward positive gate voltages, the curve flattens and reaches a plateau. V_{KPFM} becomes independent of V_G as the gate field is fully screened in the semiconducting channel. Figure 3.1(c) demonstrates how the parameter E_t , describing the width of the conduction band tail, strongly impacts the shape of the curves. Wider band tails (larger E_t) cause a wider transition from full depletion to full accumulation and, hence, a reduced curvature of the V_{KPFM} vs. V_G curve. Accordingly, the plateau is reached at higher KPFM voltages. In contrast, the parameter describing the dopant concentration N_D has a different effect, as shown in Fig. 3.1(d). The shape of the V_{KPFM} vs. V_G curve is not altered with N_D , but higher values cause a shift of the curve to lower values of V_{KPFM} . Due to the high dopant concentration, more charge carriers are in the channel at flat band potential and full screening of the gate field occurs already at smaller shifts in the vacuum level. The two graphs also show excellent agreement between the numerical and approximated analytical solutions for the tested combinations of DOS parameters. Interestingly, for a wide range of DOS parameters, the analytical solution turns out to be also a good approximation in depletion condition even though the condition

$\phi \gg E_t$ is no longer valid. The relative error of the approximate analytical solution is largest in flat band condition and increases at higher doping concentrations N_D .

The simulations show that the band tail width E_t can be determined from experimental data as it directly impacts the shape of the V_{KPFM} vs. V_G curves. In contrast, the doping density N_D is not uniquely determined by the curve. Changes in N_D only translate the curve, and variations in the flat band offset parameters $V_{G,\text{FB}}$ and $V_{\text{KPFM,FB}}$ have the same effect. In order to determine N_D , additional data need to be considered, and here, we describe two possible approaches: First, flat band voltage $V_{G,\text{FB}}$ can also be measured with alternative techniques, such as capacitance measurements. Subsequently, also $V_{\text{KPFM,FB}}$ and N_D can be obtained from the data. However, capacitance measurements are not always feasible, and border effects in small transistor channels can make their interpretation difficult. Therefore, we follow a second approach that aims at determining $V_{\text{KPFM,FB}}$ with additional KPFM measurements done on the source electrode. Following the energy diagram in Fig. 3.1(b), one can write $V_{\text{KPFM,FB}} = V_{\text{KPFM,s}} + \phi_{ds}$. Here, ϕ_{ds} is the barrier that charge carriers have to overcome when injection or extraction occurs from the semiconducting channel. As transport in optimized TFTs is not limited by contact effects, as shown experimentally, we can assume that $\phi_{ds} < k_B T$ and exploit this assumption in the determination of $V_{\text{KPFM,FB}}$ and, subsequently, N_D . The measurement of $V_{\text{KPFM,s}}$ is easily achieved in the same experiment, as it is enough to enlarge the scanning area to include part of the source electrodes.

3.3 Expertimental determination of band-tail properties on IGZO TFT

To test our model, we perform KPFM experiments on indium–gallium–zinc oxide (IGZO) thin film transistors with a 60nm thick semiconducting layer and a dielectric composed of 80nm of Ta_2O_5 and 20nm of Al_2O_3 . The source and drain contacts are made of molybdenum, as is the gate electrode. The channel has a geometry of $W = 320\mu\text{m}$ and $L = 20\mu\text{m}$. The optical microscope image of the device is reported in Fig. 3.2(a). In this device, the gate is placed below the channel while the source and drain electrodes are deposited on top, as reported in Fig. 3.2(a). Figure 3.2(b) shows the transfer characteristics of the device. We measured a mobility of $(7.3 \pm 0.2) \text{ cm}^2/\text{Vs}$ and a subthreshold slope of $(0.12 \pm 0.02) \text{ V/decade}$. Microscopic images of the channel as obtained by KPFM in amplitude modulation mode are shown in Figs. 3.2(c) and 3.2(e). In the height map, one clearly recognizes the channel and the source and drain electrodes. The V_{KPFM} map was obtained with $V_G = -2.7\text{V}$ and $V_D = 0.1\text{V}$. Accordingly, the channel shows a negative potential, confirming the penetration of the gate field and the absence of charge carriers. In Fig. 3.2(d), we report both the V_{KPFM} and the height pro-

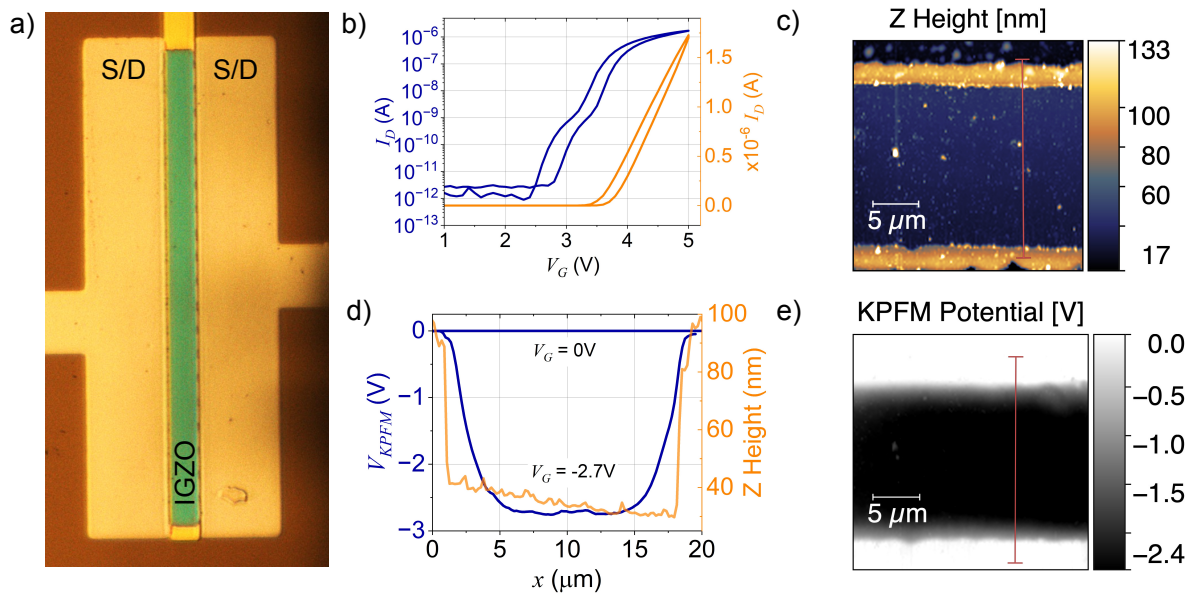


Figure 3.2: (a) Optical microscope image of an a-IGZO thin film transistor with channel geometry of $320 \times 20 \mu\text{m}^2$. The source and drain electrodes are deposited on the top of the device, while the gate is under the semiconducting channel. (b) Transfer characteristics in log scale (blue) and linear scale (orange). (c) AFM height map of the channel. (d) KPFM potential and morphology profiles of the sample along the indicated line. (e) KPFM potential map of the channel at $V_G = -2.7\text{V}$.

file along the red line in Figs. 3.2(c) and 3.2(e). For comparison, the KPFM base line obtained at $V_G = 0V$ is also shown in the profile. The KPFM data show that close to the contacts, electrostatic interactions with the source electrodes limit the measurements, but inside the channel, a flat and constant potential is measured.

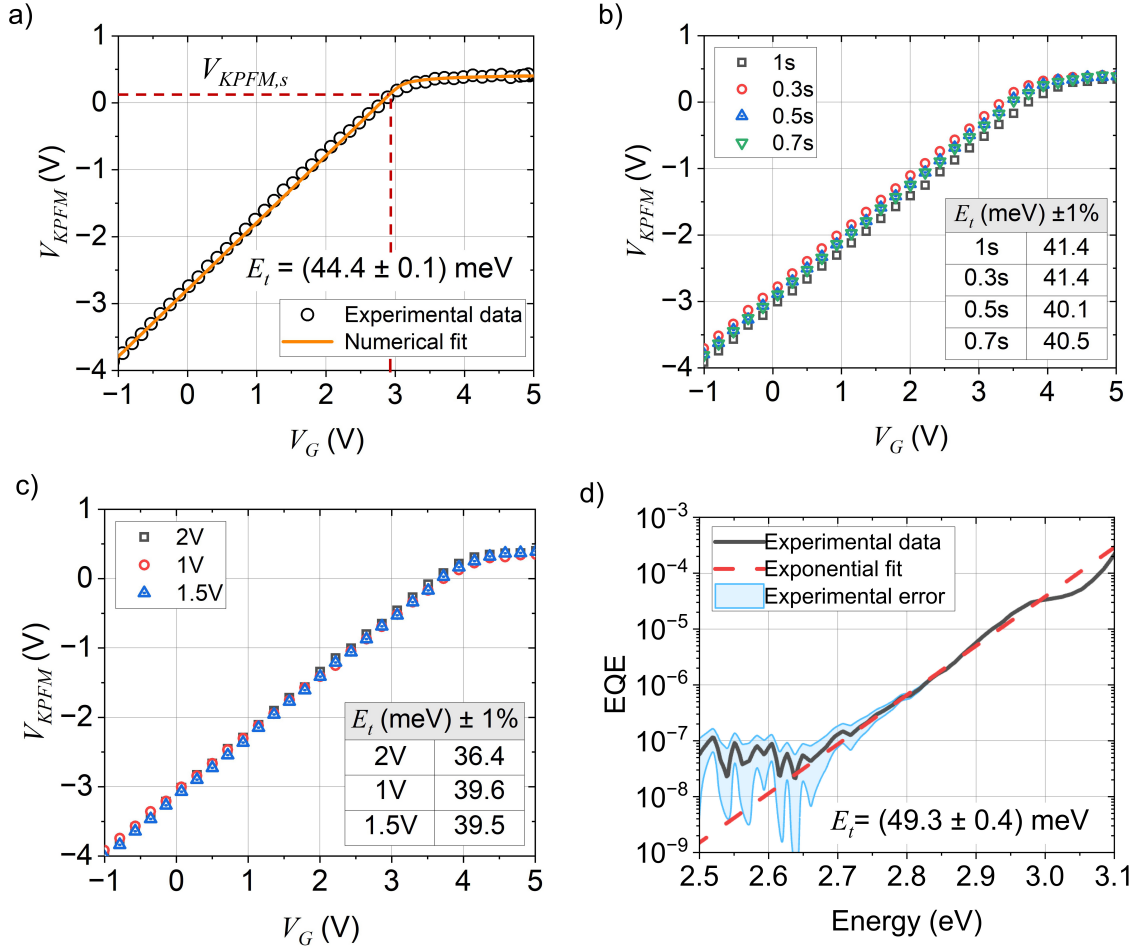


Figure 3.3: KPFM spectroscopy and fit to the model. (a) Experimental V_{KPFM} vs. V_G curve and fit with extracted E_t . The red dashed line shows the KPFM potential measured on the source electrode and allows extraction of the flat band potential. (b) KPFM curves for different sweep times and fixed AC driving voltage with fitted E_t (inset). (c) KPFM curves for different AC driving voltages and fixed sweep time of 1s with fitted E_t (inset). (d) Photocurrent EQE spectrum measured on the IGZO thin film transistor; the band tail width is obtained by a linear fit in the interval 2.7–3.0 eV.

Next, we continue with KPFM spectroscopic measurements done at a single position in the center of the channel to determine the IGZO's DOS parameters. Figure 3.3(a) shows the measurement of V_{KPFM} obtained in the channel while the gate voltage V_G was swept from -1V to 5V. On the source electrode, we obtain a constant value of $V_{KPFM,s} = 0.02V$, and the value

is indicated in the plot to mark the flat band potential condition at $V_{G,FB} = (2.8 \pm 0.2) V$. With this condition, the model fits well and uniquely to the experimental data, yielding a band tail width $E_t = (44.4 \pm 0.1) meV$ and a doping density of $N_D = (1.4 \pm 0.6) \times 10^{12} cm^{-3}$. The values are stable, and variations of experimental parameters, such as KPFM tip bias amplitude V_{AC} or sweep time, do not have a significant impact on the obtained values, as shown in Figs. 3.3(b) and 3.3(c). In this regard, the stability toward variations in V_{AC} also confirms that the contact potential difference (CPD) interpretation of KPFM measurements in semiconductors is correct and the linear response is maintained [12].

The extracted DOS parameters can be compared to values obtained with different, not microscopic, techniques, as done in Table 3.1. Our estimates of band tail width E_t and doping density N_D are lower than values found in the literature with capacitance measurements. We note that differences in the fabrication protocol of the IGZO film might explain such variations [114]. In particular, the amount of oxygen vacancy density strongly depends on the conditions during semiconductor deposition and annealing. For instance, a reduced number of oxygen vacancies are expected in a more crystalline IGZO sample [16]. To provide an alternative characterization of the conduction band tail in the tested transistor structures, we conduct photocurrent spectroscopy experiments. Figure 3.3(d) reports the external quantum efficiency (EQE) in photocurrent measured at different photonic excitation energies. A linear dependence is observed on the logarithmic plot and fits an exponential with a characteristic energy of $E_t^{(PC)} = (49.3 \pm 0.4) meV$. This finding is in excellent agreement with the KPFM value. A slightly higher value from photocurrent spectroscopy is expected due to the contribution of the valence band tail.

3.4 Use-case: measurement of X radiation-induced damage in IGZO thin film transistors

Finally, we demonstrate the relevance of our technique for understanding TFT stability and degradation. An example is the x-ray induced radiation damage causing a shift to negative voltages [7]. Such an effect is critical for different radiation related applications, such as the degradation of active-matrix detector backplanes or the sensitivity of microelectronic dosimeters. Despite this relevance, two basic mechanisms can potentially explain the negative shift. On the one hand, one can assume that ionizing radiation impinges on the semiconductor and causes the generation of oxygen vacancies acting as additional doping sites. Consequently, more carriers are in the channel at flat band potential, and a more negative gate voltage is needed to switch-off the channel. On the other hand, ionizing radiation is known to cause positive space-charge build-up in wide band-gap oxide dielectrics. The reason is that the x-

ray generated hole and electron carriers behave differently in these dielectrics. Electrons are mobile and ultimately exit from the dielectric into conductive contact. Hole charges, instead, are trapped and continue to accumulate with increasing exposure doses. The generated positive space charge causes a potential offset in the gate dielectric and shifts the flat band potential to negative values.

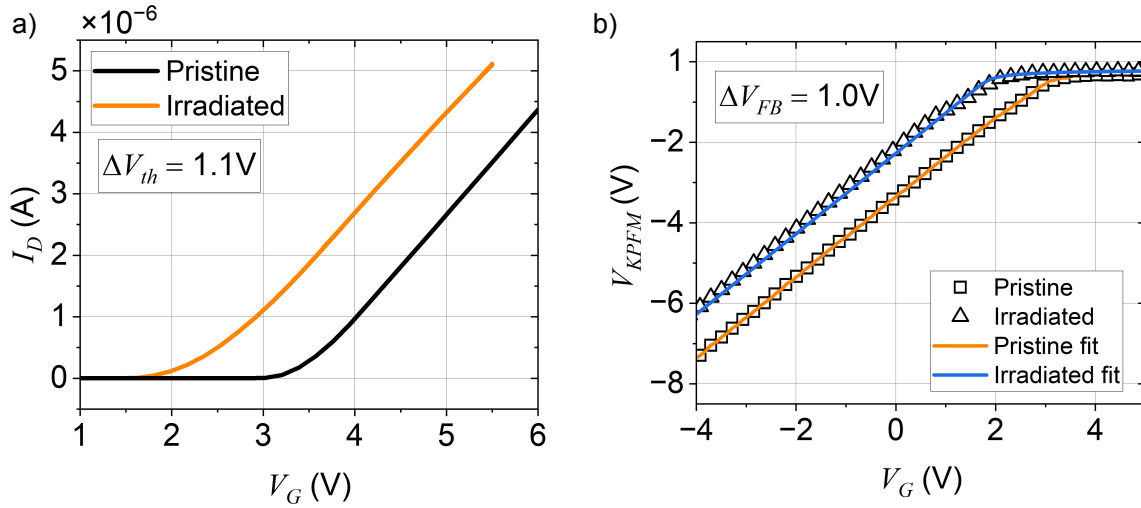


Figure 3.4: Investigation of x-ray radiation damage in IGZO TFT. (a) Transfer characteristics before and after exposure to x-ray radiation (400 mGy at energy corresponding to the Mo-K α peak, $E = 17.5\text{keV}$). (b) KPFM spectroscopy performed in the center of the channel before and after radiation exposure. Solid lines: fit to the developed KPFM model.

To decipher which of the two possible causes is relevant, we perform KPFM experiments on TFTs before and after exposure to a total dose of 400mGy. The transfer characteristics of the device, reported in Fig. 3.4(a), in the pristine and irradiated conditions show a clear shift in threshold of $\Delta V_{th} = (-1.10 \pm 0.01)\text{V}$. The corresponding KPFM spectroscopy measurements are shown in Fig. 3.4(b) together with the fits to our model. The extracted parameters are reported in Table 3.2. We note that both N_D and E_t are not modified during the exposition, while the flat band potential V_{FB} is reduced. The shift is $\Delta V_{FB} = (-1.0 \pm 0.2)\text{V}$, which is coherent with the measured shift in the threshold voltage. We can conclude that the DOS parameters are not modified by x-ray irradiation; therefore, the effect of x-rays in our device is to generate positive charges in the gate dielectric.

3.5 Conclusions

We have developed an analytical model to describe Kelvin Probe Force Microscopy (KPFM) spectroscopy on amorphous semiconductor thin films of finite thickness. The approach is

Experiment	Type	N_D (cm⁻³)	E_t (meV)
This work	KPFM	$(1.1 \pm 0.6) \times 10^{12}$	44.4 ± 0.1
Tsuji et al.	CV	1.2×10^{17}	80
Jeon et al.	Simulated	5×10^{16}	67
This work	Photocurrent	—	49.3 ± 0.4

Table 3.1: Comparison of DOS parameters extracted from both this work and the literature with different experimental techniques.

Parameter	Pristine	Irradiated
N_D ($\times 10^{12}$ cm ⁻³)	1.4 ± 0.6	1.5 ± 0.6
E_t (meV)	44.4 ± 0.1	45.8 ± 0.2
V_{FB} (V)	2.8 ± 0.1	1.8 ± 0.1

Table 3.2: Comparison of density of state parameters before and after x-ray irradiation.

based on the solution of the Poisson equation for a metal–insulator–semiconductor junction under the influence of the AFM tip, and allows the extraction of band tail width, doping density, and flat band potential from local KPFM measurements.

Application to indium–gallium–zinc oxide (IGZO) thin-film transistors provided $E_t = 44.4 \pm 0.1$ meV, $N_D = (1.1 \pm 0.6) \times 10^{12}$ cm⁻³, and $V_{FB} = 2.8 \pm 0.1$ V. These results are in good agreement with photocurrent spectroscopy, which yielded $E_t = 49.3 \pm 0.4$ meV.

The method was further employed to investigate the effects of X-ray irradiation (400 mGy at 17.5 keV) on the same devices. A shift in V_{FB} from 2.8 ± 0.1 V to 1.8 ± 0.1 V was observed, consistent with the presence of static charge in the gate dielectric. The band tail width and doping density were unchanged within experimental uncertainty.

The developed methodology is applicable to a broad range of semiconductor materials and device architectures. It enables quantitative and spatially resolved mapping of DOS parameters, and offers a powerful tool for studying local electronic properties and degradation mechanisms in thin-film electronics.

3.6 Supplementary material

Full derivation of MIS junction model with exponential DOS interacting with KPFM tip

Figure 3.1(b) shows a scheme of the energy levels of relevance for the MIS junction and the AFM tip. Energy levels at flat band potential are drawn in grey while we use black to depict

energy levels in depletion. The diagram visualizes all parameters that are of relevance for our model. We split the derivation into two parts. First, we investigate in detail the band-bending occurring in the semiconductor. Second, we relate the band bending to the experimental observables, that is the gate voltage V_G and the KPFM voltage V_{KPFM} . Here we derive the model for an n -type semiconductor.

3.6.1 Band bending in a semiconductor with exponential DOS

The amount of band bending in the semiconductor is quantified by the function $\phi(x)$, which determines the shift of the vacuum level in the semiconductor starting from the interface with air ($x = 0$) and ending at the interface with the gate dielectric ($x = t$).

In the first step we derive the differential equation that determines $\phi(x)$, and its relation to the DOS of the semiconductor. Changes in the vacuum level are always attributed to the build-up of space charge ρ in the semiconductor as defined by the Poisson equation:

$$\frac{d^2\phi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0} \quad (3.6)$$

The space charge results directly from the Fermi–Dirac integral

$$\rho(E_F) = q_0 \left[N_D - \int_{-\infty}^{+\infty} g(E) f(E, E_F) dE \right] \quad (3.7)$$

where $g(E) = N_t \exp\left(\frac{E}{E_t}\right)$ is the assumed density of states of the conduction band tail, $f(E, E_F)$ is the Fermi–Dirac distribution and N_D the oxygen vacancies doping density, which quantifies the number of positively charged dopant sites present in the band tail. We note that here the signs in the derivation are adapted for an n -doped semiconductor with exponential tail of the conduction band.

To solve the Fermi–Dirac integral, we introduce the following simplifications: first, far from the interfaces, inside the bulk, there cannot be any space charge, thus $\rho(E_F) = 0$. Second, we set $T = 0$. We note that this assumption is less restrictive than it appears at first sight since for finite temperature the offset can be calculated and results only in a shifting factor on the flat band voltage. We obtain

$$N_t = \frac{N_D}{E_t} \exp\left(-\frac{E_{F,\text{FB}}}{E_t}\right) \quad (3.8)$$

and then

$$\rho(E_F) = q_0 N_D \left[1 - \exp\left(\frac{E_{F,\text{FB}} - E_F(x)}{E_t}\right) \right] \quad (3.9)$$

Equation (3.9) explains how local variations in the Fermi level are related to accumulation

of space charge in the semiconductor. The variations in Fermi level are directly tied to the shift in vacuum level; indeed the surface potential is defined as

$$\phi(x) = E_{F,FB} - E_F(x), \quad (3.10)$$

Substituting (3.9) and (3.10) in (3.6) we obtain the full non-linear Poisson equation that contains DOS parameters E_t , N_D and indirectly N_t :

$$\frac{d^2\phi(x)}{dx^2} = \frac{q_0 N_D}{\varepsilon \varepsilon_0} \left[1 - \exp\left(\frac{\phi}{E_t}\right) \right] \quad (3.11)$$

Equation (3.11) is a non-linear, second-order differential equation which is not solvable analytically in the general case. A determined function $\phi(x)$ solves the differential equation if appropriate boundary conditions are defined. For the case of the KPFM experiment Cauchy boundary conditions are defined:

$$\phi(x=0) = \phi_0, \quad \left. \frac{d\phi}{dx} \right|_{x=0} = 0 \quad (3.12)$$

The first condition in (3.12) accounts for the finiteness of the semiconducting layer. Hence an electric field applied by the gate is not completely screened in the semiconductor, but leaves a residual causing an offset potential ϕ_0 at the semiconductor interface exposed to the AFM tip. It is this residual potential that is related to the KPFM voltage as discussed below. The second boundary condition implies the absence of an electric field. This condition is justified by the KPFM experiment: the tip DC voltage is adjusted until no electrostatic forces are acting. In other words, the electric field is zero in the space between tip and semiconductor surface.

To solve equation (3.11) numerically with a Runge–Kutta algorithm, we rewrite it as two coupled first-order differential equations:

$$\frac{d\phi}{dx} = \eta, \quad \frac{d\eta}{dx} = \frac{q_0 N_D}{\varepsilon \varepsilon_0} \left[1 - \exp\left(\frac{\phi}{E_t}\right) \right] \quad (3.13)$$

We use a 4th order Runge–Kutta method with automatic adjustment of the step-size, to propagate the solution from the initial point $y_0 = (\phi_0, 0)$. Step size adjustment is crucial since the more ϕ_0 increases the more the steepness of the solution at $x = t$ is high and the more the step-size must be reduced to correctly propagate the solution.

It is also possible to obtain analytical solutions for equation (3.11) for two limiting conditions. The first regards accumulation and is valid for $\phi(x=0) > E_t$. In this condition the exponential term is predominant in the differential equation. By substituting $\alpha = \frac{q_0 N_D}{\varepsilon \varepsilon_0}$

equation (3.11) simplifies to:

$$\frac{d^2\phi}{dx^2} = -\alpha \exp\left(\frac{\phi}{E_t}\right) \quad (3.14)$$

The final solution is then

$$\phi(x) = E_t \ln \left(\exp\left(\frac{\phi_0}{E_t}\right) \left[\tan^2 \left(\frac{1}{\sqrt{2}} \exp\left(\frac{\phi_0}{2E_t}\right) \frac{x}{\lambda} \right) + 1 \right] \right) \quad (3.15)$$

where boundary conditions (3.12) are already included and $\lambda = \sqrt{\frac{E_t \varepsilon \varepsilon_0}{q_0^2 N_D}}$ is a characteristic length of the semiconductor. Equation (3.15) describes the surface potential as a function of the position inside the semiconducting layer. It depends on ϕ_0 , N_D and E_t (through λ). As shown in Figure 3.5, the solution has several singularities due to the presence of the tangent function. The physically meaningful interval regards ϕ_0 values that range from $\phi_0 > E_t$ up to the first singularity. The singularity occurs as a thin layer of charge accumulation appears at the gate–dielectric/semiconductor interface, that screens any further increase in gate field.

The second limiting analytical solution for the non-linear Poisson equation (3.11) is obtained in depletion condition ($\phi_0 \ll E_t$):

$$\phi(x) = -\frac{\alpha}{2} x^2 + \phi_0 \quad (3.16)$$

The predicted relation between $\phi_t = \phi(x = t)$ and ϕ_0 is linear once the thickness of the layers is fixed, as expected for depletion regime.

3.6.2 Relation of band bending to experimental parameters

In KPFM experiments we measure the relation between the gate voltage V_G and the variation in KPFM tip voltage, namely V_{KPFM} . The latter is directly related to ϕ_0 through the relation

$$\phi_0 = q_0 V_{\text{KPFM}} - \phi_{\text{ds}} \quad (3.17)$$

as it can be deduced directly from Figure 3.1(b). ϕ_{ds} denotes additional offsets that originate from (i) possible dipole layer forming at the semiconductor interface exposed to the AFM tip, (ii) work function of the AFM tip and (iii) amplifier offsets. The direct relation between ϕ_0 and V_{KPFM} is supported by the CPD interpretation of KPFM experiments. The measured potential in a KPFM experiment can be seen as an approximation of the difference between the work functions of tip and sample. In semiconducting materials, the presence of an external electric field influences the internal charge distribution. It induces the formation of a region with non-zero net charge, the so-called space charge density. In general, the CPD interpretation of KPFM measures is valid for materials with a fixed charge distribution, thus with a charge per

unit area that can be expressed as $\sigma = C(V - V_{\text{offset}})$.

In order to relate the gate voltage V_G to band bending, we consider again the energy level diagram in Figure 3.1(b) and write down two equations: one for flat band condition and one for depletion:

$$\begin{aligned} q_0 V_{G,\text{FB}} &= \Phi_g - \Phi_s + \phi_{\text{ds}} + \phi_{dg} \\ q_0 V_G &= \Phi_g - \Phi_s + \phi_{\text{ds}} + \phi_t + q_0 V_{\text{ox}} + \phi_{dg} \end{aligned} \quad (3.18)$$

where $\phi_t \equiv \phi(x = t)$. If we subtract the second equation from the first and divide by the electron charge, we obtain an equation that relates the gate voltage to ϕ_0 :

$$V_G = V_{G,\text{FB}} + \frac{\sigma(\phi_0)}{c_{\text{ox}}} + \frac{\phi_t(\phi_0)}{q_0} \quad (3.19)$$

Here σ is the value of accumulated charge in the semiconductor and determines the potential drop across the dielectric V_{ox} determined by c_{ox} , the capacitance per unit area of the dielectric. $V_{G,\text{FB}}$ is the flat band potential and contains different physical contributions such as the gate metal work function or interfacial dipole layers causing a shift in vacuum level. Moreover, flat band potential does depend on other DOS parameters, namely N_D , E_t , N_t and the experimental offsets, as explained below.

To obtain the full relation to the experimental parameters, we have to express σ as a function of ϕ_0 using the calculated band bending, with either numerical or approximated analytical scheme. Starting directly from Poisson's equation (3.11) we can write

$$\frac{d^2 \phi}{dx^2} = \alpha \left[1 - \exp \left(\frac{\phi}{E_t} \right) \right] \quad \alpha \equiv \frac{q_0 N_D}{\varepsilon \varepsilon_0} \quad (3.20)$$

Multiply both terms by $\frac{d\phi}{dx}$ and integrate. The result is

$$\left(\frac{d\phi}{dx} \right)^2 = 2\alpha \left[\phi - E_t \exp \left(\frac{\phi}{E_t} \right) \right] + c \quad (3.21)$$

which is a solution for the first derivative of the surface potential. We can again impose boundary conditions (3.12) to find the correct value of the constant c , yielding

$$\frac{d\phi}{dx} = \sqrt{2\alpha \left[\phi - \phi_0 - E_t \left(\exp \left(\frac{\phi}{E_t} \right) - \exp \left(\frac{\phi_0}{E_t} \right) \right) \right]} \quad (3.22)$$

From Poisson's equation it is also known that the amount of accumulated charge in the

semiconductor can be expressed in function of the first derivative, thus

$$\sigma = \epsilon\epsilon_0 \left[\left(\frac{d\phi}{dx} \right)_{x=t} - \left(\frac{d\phi}{dx} \right)_{x=0} \right] \quad (3.23)$$

$$= \epsilon\epsilon_0 \sqrt{2\alpha \left[\phi_t - \phi_0 - E_t \left[\exp \left(\frac{\phi_t}{E_t} \right) - \exp \left(\frac{\phi_0}{E_t} \right) \right] \right]} \quad (3.24)$$

The last required parameter to completely explicit equation (3.19) is $V_{G,FB}$. Flat band potential is not a material-related parameter, but it is important when dealing with semiconductor-based devices since it indicates, in transistors, the switching point between depletion and accumulation condition. Consider that $q_0 V_{G,FB} + \Phi_s + q_0 \phi_{dg} = \phi_{ds} + \Phi_g$ and at flat band it is also true that $\phi_{ds} + \Phi_g = E_{F,FB}$. Recalling equation (3.8) it is possible to express $E_{F,FB}$ as

$$E_{F,FB} = -E_t \ln \left(\frac{N_D}{N_t E_t} \right) \quad (3.25)$$

Combining all the previous equations we obtain

$$q_0 V_{FB} = \Phi_g + \phi_{dg} - E_t \ln \left(\frac{N_D}{N_0 E_t} \right) \quad (3.26)$$

Combining equations (3.15), (3.19), (3.24) and (3.26) we obtain an expression that relates gate voltage and ϕ_0 , that is the KPFM potential. For the approximate analytical model we obtain:

$$V_G = \phi_t + \epsilon\epsilon_0 \sqrt{2\alpha \left[\phi_t - \phi_0 - E_t \left[\exp \left(\frac{\phi_t}{E_t} \right) - \exp \left(\frac{\phi_0}{E_t} \right) \right] \right]} + \frac{\Phi_g}{q_0} + \frac{\phi_{dg}}{q_0} - \frac{E_t}{q_0} \ln \left(\frac{N_D}{N_0 E_t} \right) \quad (3.27)$$

Figure 3.6 compares results calculated with the numerical and the approximate analytical scheme. One can note that the value of σ found with the analytical relation corresponds to the one found with the numerical approach. Only when the semiconductor approaches the flat band situation, small differences become notable as the condition $\phi(x=0) \gg E_t$ is no longer valid and the analytical solution starts to fail. However, this discrepancy is negligible when dealing with the full experimental V_{KPFM} vs V_G curve (its only effect is to produce an incorrect slope in depletion region). Therefore, as expected, the approximated solution is not reliable in depletion condition, where the correct behavior is provided by solution (3.16).

Looking at the band diagram in Figure 3.1(b) one can detect the existence of two offsets: ϕ_{dg} and ϕ_{ds} which enter directly in equation (3.27). These are strictly related to the experimental

measure, and it is necessary to clarify their relation with the numerical solution. The first offset ϕ_{dg} is related to the formation of a dipole between the gate and the dielectric whose presence produces a shift in gate voltage values. The second offset ϕ_{ds} can be due either to the formation of a dipole at the air–semiconductor interface or the non-perfect alignment of source and semiconductor. It produces an unknown shift in KPFM potential. The interaction with air can be deleted by performing the measure in Argon atmosphere, while the second one cannot be cancelled since it's dependent on the fabrication process of the device.

In order to fit equation (3.27) to experimental results one has to consider the different fitting parameters: E_t , N_D , ϕ_{ds} , ϕ_{dg} and their interdependency. Oxide capacitance c_{ox} , ε and thickness t are typically known for a measured structure. The presence of interdependencies between parameters is the cause of the indeterminacy of the system; indeed it is not possible to find a unique set of DOS parameters only by fitting the experimental V_{KPFM} vs V_G curve as many combinations are possible. Because of that, the determination of the two unknown offsets cited above is important as they provide an uncertainty directly on the estimation of some parameters, such as trap doping density N_D . Two cases are useful in practice: if flat band voltage is known, then it is enough to adjust the KPFM curve knowing that $q_0\Delta V_{KPFM}(V_G = V_{G,FB}) = \phi_{ds}$. Second, if one can assume that the dipole ϕ_{ds} is zero, the flat band potential is the voltage that satisfies the condition $q_0\Delta V_{KPFM}(V_G = V_{G,FB}) = 0$. If we suppose to have an error of $2k_B T \simeq 50, \text{ meV}$ on the measure due to the uncertainty on ϕ_{ds} , it is possible to propagate it to the fitting parameters. One obtains an error of ~ 0.6 percent on the estimate of E_t and a wider range for N_D . Specifically, for $N_D = 2.01 \times 10^{12} \text{ cm}^{-3}$ a maximum possible value $N_{D,\text{max}} = 4.02 \times 10^{12} \text{ cm}^{-3}$ and a minimum $N_{D,\text{min}} = 1.04 \times 10^{12} \text{ cm}^{-3}$. As expected, the value of E_t is not influenced by ϕ_{ds} , which plays a role only in the correct determination of trap states doping density.

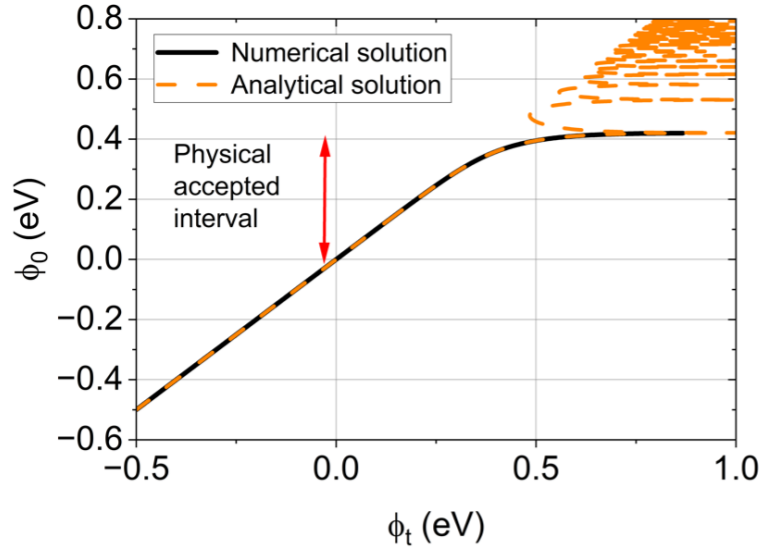


Figure 3.5: Approximated analytical solution for accumulation regime and comparison with numerical solution. Parameters of the simulation are $N_D = 10^{12} \text{ cm}^{-3}$, $E_t = 50 \text{ meV}$, $t = 60 \text{ nm}$. With the red arrow it is depicted the range of validity of the analytical solution: it is valid only for $\phi_0 \gtrsim E_t$ and up to the first tangent singularity.

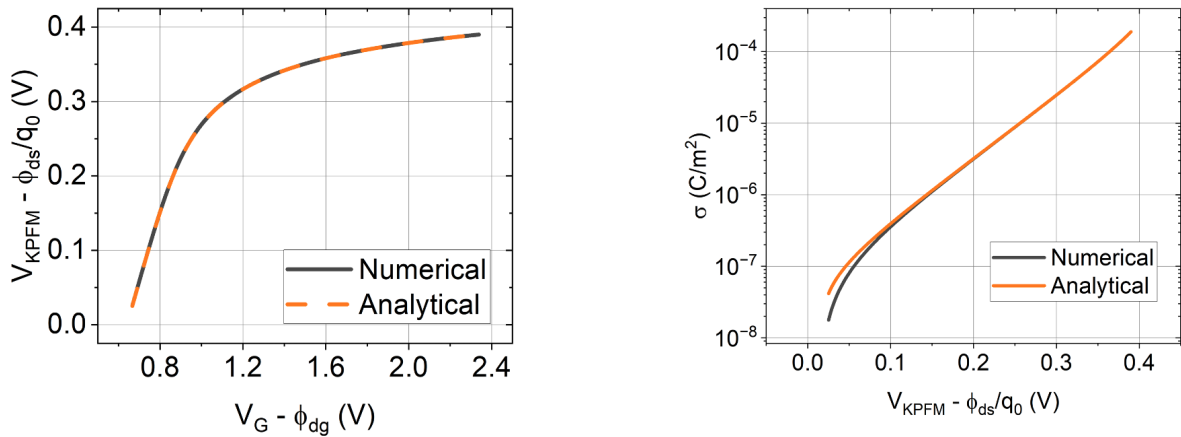


Figure 3.6: (Left) Plot of accumulated charge density in the semiconductor calculated with both numerical and analytical model. (Right) Plot of ϕ_t as a function of gate voltage. Both simulations were done only in accumulation regime with the following parameters: $N_D = 10^{12} \text{ cm}^{-3}$, $E_t = 60 \text{ meV}$, $t = 50 \text{ nm}$.

4 How to Achieve High Spatial Resolution in Organic Optobioelectronic Devices?

4.1 Introduction

Microelectrode arrays have been established as a powerful tool to stimulate and record single electroactive cells in in-vitro and in vivo experiments and are the main working horse for bioelectronic experiments with single cell resolution [115, 116]. Recent research in materials science has further improved and optimized the biocompatibility, stability, selectivity, and sensitivity of microelectrodes for different bioelectronic experiments [117–120]. Despite such advances, two fundamental problems of microelectrode arrays remain to be solved. First, each electrode requires a connecting wire causing complex routing and connection problems for large arrays. Integrated circuits have been developed to simplify this problem, but a general solution is still outstanding [121, 122]. Second, once placed in contact with the biological tissue, the position of the microelectrodes is fixed and cannot be adapted to achieve spatial proximity to cells of interest or to follow changes in the biological tissue as caused by cell migration or tissue restructuration. To overcome these issues, novel bioelectronic interfaces based on light activated materials are being explored [123–125].

A promising solution to these problems leverages on the optoelectronic properties of semiconductors as used in solar cells where light absorption causes the generation of electronic charges and subsequent photoconductivity and polarization of the solar cell [23, 24, 123, 126]. Following this principle, semiconductor based photoelectrodes have been realized that are stable in aqueous biological environments and that show polarization upon illumination with light pulses. Cells in close vicinity to such photoelectrodes are subjected to a transient electric field or photoelectrochemical reactions when illuminated [127]. Optimized photoelectrodes and sufficiently strong light pulses enable the stimulation of neuronal tissue by light without the need for electrical wires. The effect opens immense opportunities for novel bioelectronic

interfaces with reduced invasiveness. An example regards the development of retinal prosthesis to restore visual capability when the retina loses functionality due to disease.[13,16] For this purpose, different semiconductor-based arrays have been developed and were demonstrated to stimulate selectively retinal neurons upon light activation and without any invasive wired connection [23, 24, 128]. Other applications of semiconductor optobioelectronic devices regard the optical stimulation of peripheral nerves [129], the optical control of cell-differentiation in in-vitro experiments [130, 131] and the development of novel microscopy methods [132].

The crucial factor in the development of optobioelectronic technology is the semiconductor's materials science, merging biocompatibility with optoelectronic capabilities. Device operation in the biological media requires high (electro)chemical stability in aqueous, saline environments as well as soft and flexible mechanical properties to adapt to the curved shapes and the continuous motion of living tissue. At the same time, a high photoelectric activity is needed to achieve efficient charge generation and polarization, activated by the reduced amounts of light that penetrate biological tissue. Organic semiconductors are an emerging material platform that potentially complies to such needs [19–21]. Recent articles report small molecules or polymeric semiconductors as active layers in light activated stimulation devices [23, 24, 133]. Strong light-activated polarization for cell stimulation was observed in heterojunctions made with organic semiconductors [22]. The energy level alignment at the interface between p-type (donor) and n-type (acceptor) semiconductors enables efficient separation of optical excitations into free holes and electronic charges causing surface polarization of the device and the generation of transient electric fields on the photoelectrode surface. The resulting photocapacitive effect was explored in in-vitro experiments to stimulate neurons with light using organic heterojunctions originally developed for organic solar cells such as P3HT (poly(3-hexylthiophene)) and PCBM (phenyl-C61-butyric-acid-methylester) or H₂Pc (Phthalocyanine) and PTCDI (3,4,9,10-Perylenetetracarboxylic diimide)[23, 24]. An alternative transduction mechanism relies on photoelectrochemistry, where excited electrons or holes are transferred from the semiconductor into the biological medium to generate biological messenger molecules such as hydrogen peroxide or protons [131, 134]. In this photofaradic mechanism, the photocurrent controls the release of the active messenger molecules and impact locally on cell phenotype and differentiation with applications for example in regenerative medicine. P-type organic semiconducting polymers have been demonstrated to be particularly suited for such a transduction pathway [135]. Recent in-vitro experiments show how p-type semiconducting polymers enable to control cardiovascular tissue formation with light pulses [131, 136–138].

In addition to the efficiency of the wireless optical stimulation, also the spatial resolution is a critical aspect to consider [123]. Light pulses can be focussed on small spatial areas potentially enabling precise local stimulation of a single biological cell. Furthermore, the light

spot can be moved and adapted in real time allowing to follow dynamic biological processes and overcoming the limitations of microelectrode arrays. To achieve this vision, high requirements on the spatial resolution of the optoelectronic transduction process must be fulfilled. Basic reasoning clarifies that the spatial resolution in optobioelectronic interfaces is defined at three different levels. First, the size of the light spot that activates the semiconductor matters. Theoretically, here only limitations due to the diffraction limit occur and sub-cellular resolution can be achieved. Second, excitons and separated charge carriers generated in the semiconducting layer are subjected to diffusion and hence cause a broadening of the excitation that reduces the spatial resolution. In crystalline inorganic semiconductors the diffusion length extends over several tens of micrometers and spatial resolution can only be obtained by structuring the semiconductor into physically separated pixels to limit the dispersion of the local excitation [139–141]. Such photopixel arrays still allow wireless excitation but limit the resolution and adaptation of the stimulation area to the size of the patterned pixels. Third, once the optical excitation is transduced into a physico-chemical stimulus (i.e., an electric field or a released chemical), further broadening occurs in the biological medium before the signal reaches its target. The smallest resolution of the transduction process is determined by all three contributions. Materials research can optimize organic semiconductor properties to minimize resolution losses. To guide this optimization and to reach the intrinsic resolution limit of organic optobioelectronic interfaces, a detailed understanding of the processes that impact on resolution in organic optobioelectronic devices are necessary.

In this work, we investigate the spatial resolution limits in organic optobioelectronic devices with a p-n heterojunction fabricated with the organic semiconductors H2PC and PTCDI. Such photo-capacitor devices have been developed as phototransducers in in-vitro and in-vivo experiments. Furthermore, exceptional long-term stability in biological environment was demonstrated [23, 127]. Upon illumination, charge separation generates strong enough electric fields to depolarize neuronal cells in close vicinity to the illuminated spot [24, 142]. To investigate the spatial and temporal properties of the excitation profile generated in the planar heterojunction we exploit Kelvin Probe Force Microscopy (KPFM) and transient photovoltage measurements. The findings are analyzed with a carrier diffusion and recombination model. Our results show how carrier mobility and lifetime control the broadening of the excitation in the semiconducting layer. We apply our findings to demonstrate spatial resolution in the range of cellular length scales in devices with unpatterned pn heterojunction layers in photocurrent mapping experiments. From our findings we deduce design principles for future organic semiconductor junctions combining high efficiency and high spatial resolution.

Organic bioelectronic devices have gained increasing attention due to their biocompatibility, flexibility, and capability to transduce optical stimuli into electrical signals [143–145]. Light-addressable organic interfaces are especially appealing, as they enable remote stimula-

tion and readout without the need for direct wiring, thereby opening opportunities for neural interfaces, biosensing, and implantable systems [146, 147].

A central challenge for these applications is the achievable spatial resolution. In inorganic semiconductors such as silicon, the high carrier mobility and long diffusion lengths lead to broadening of the optical excitation and poor localization. Organic semiconductors, on the other hand, offer intrinsically shorter diffusion lengths, which in principle should allow for more confined photoresponses [148, 149]. However, the effective resolution is still strongly influenced by factors such as carrier lifetime, heterojunction morphology, the presence of additional conducting layers, and the interaction with the aqueous electrolyte [150, 151].

The present study addresses these issues by directly probing the spatial resolution of organic heterojunctions using Kelvin probe force microscopy and electrochemical photocurrent imaging. By quantifying how photovoltage and photocurrent profiles evolve under different experimental conditions, we identify the physical mechanisms that limit localization in organic systems. This knowledge provides a framework for the design of organic bioelectronic interfaces capable of operating at the single-cell length scale, thus advancing the potential of light-controlled organic devices in biomedical applications.

4.2 Diffusion model for planar heterojunctions

4.2.1 Kelvin Probe Force Microscopy experiments

Figure 4.1 introduces the KPFM experiments performed on the planar H2PC/PTCDI heterojunction to measure the broadening of the local optical excitation. Illumination is done through the transparent substrate with a laser diode of wavelength 520 nm at which both p and n semiconducting layers exhibit strong absorption [143, 144]. The laser is focused through a 2 μm pinhole and optical lenses to yield a spot on the semiconductor with a gaussian profile of $\sigma_{\text{SPOT}} = (2.59 \pm 0.03) \mu\text{m}$ (see below). With KPFM, we measure the surface morphology and the local surface photovoltage defined as $\phi(x) = V_{\text{CPD,light}} - V_{\text{CPD,dark}}$ where V_{CPD} denotes the contact potential measured at the exposed surface of the heterojunction in darkness ($V_{\text{CPD,dark}}$) and during illumination ($V_{\text{CPD,light}}$). To improve the signal to noise ratio in the photovoltage measurement, we modulate the light source with a frequency of 720 Hz and measure directly the modulation of the off-resonance electrostatic force microscopy signal (see methods section for details). Typical KPFM images of the investigated samples are shown in Figure 4.1b,c. We compare the pure p-n junction to a junction covered with a 200 nm thin film of PEDOT:PSS (poly[3,4-ethylenedioxythiophene]:poly[styrene sulfonate]). Such PEDOT:PSS films have been demonstrated to increase photovoltage and photocurrent generation in heterojunctions [145–147]. The sample without PEDOT:PSS exhibits a morphology with evenly

distributed nanometric structures corresponding to nanocrystals formed during the thermal deposition process [22]. Instead the PEDOT:PSS layer displays a different morphology where the roughness of the underlying nanocrystalline film disappears and instead some larger accumulations of polymeric material emerge. The corresponding photovoltage maps are shown in Figure 4.1d,e. In both images, the center of the light spot is clearly visible and corresponds to the region with the maximum intensity. In the pure H2PC/PTCDI sample, the photovoltage remains localized and in some parts the diffraction pattern due to the circular aperture emerges. Instead on the PEDOT:PSS covered surface, the photovoltage signal is more delocalized. This impression is confirmed in Figure 4.1f that provides profiles of the photovoltage maps as indicated (blue dashed lines). In addition to the broadening, also a strong reduction in maximum photovoltage value is observed in the presence of PEDOT:PSS.

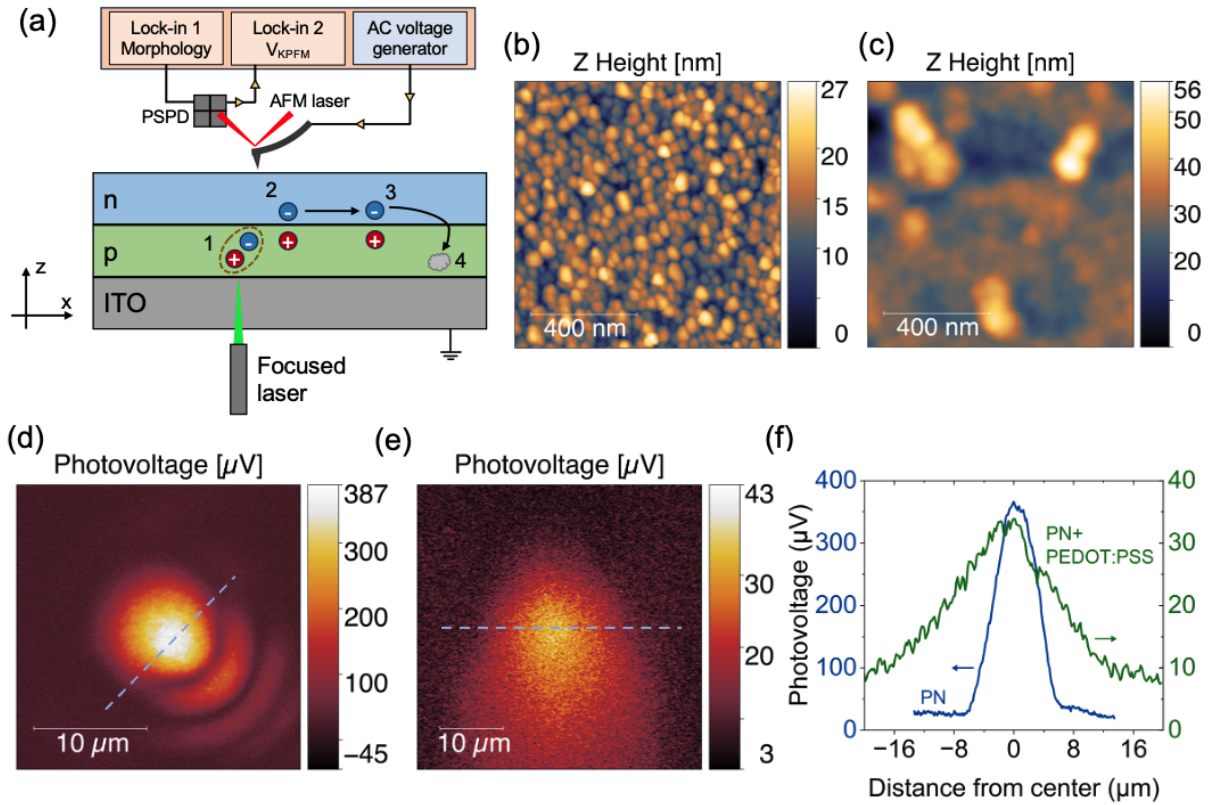


Figure 4.1: (a) Schematic of the experimental setup and the physical mechanism causing resolution losses in the semiconductor. (b,c) AFM morphology images of the investigated samples consisting of the organic p-n heterojunction without (b) and with (c) a top layer of PEDOT:PSS. (d,e) Photovoltage image of the sample without (d) and with (e) the layer of PEDOT:PSS. (f) Comparison of photovoltage profiles of H2PC/PTCDI heterojunction (blue curve) and H2PC/PTCDI + PEDOT:PSS (green curve) for a common light power of 126 nW.

To analyze our findings, we consider the basic physical processes determining the spatial resolution for optoelectronic excitations in organic p-n heterojunctions as depicted in Fig-

ure 4.1a. Excitons are generated in the semiconducting layer in the focused light spot (1) and dissociate at the p-n interface into charge separated states (2). As positive and negative charges accumulate in the respective p and n layer, a shift in the vacuum level happens and the photovoltage is built-up. Photogenerated charges are subjected to diffusive motion along the heterojunction and charge spreads out of the illuminated area (3) causing a reduction in spatial confinement of the optoelectronic excitation. Finally, recombination (4) reduces the local concentration of photogenerated carriers. Combining these processes, the local variation of charge carrier density $n(x, t)$ is given by:

$$\frac{\partial n(x, t)}{\partial t} = G(x, t) + D\nabla^2 n(x, t) - \frac{n(x, t)}{\tau(n)} \quad (4.1)$$

Here $G(x, t)$ is the generation rate due to the incident light, D is an effective charge carrier diffusion constant and $\tau(n)$ is the lifetime of charge carriers whose dependence on carrier concentration is governed by the type of recombination mechanism. As usual, we introduce the carrier diffusion length as $\lambda_d = \sqrt{D\tau(n)}$. In general, the charge carrier concentration $n(x, t)$ is a function of the three spatial coordinates. For the case of a planar heterojunction made with organic semiconductors with low doping concentrations, the motion along the z -direction is faster than the planar one. This allows to consider the two components separately and study the x - y diffusion once the charges already moved away from the junction. Further, we neglect drift motion caused by electric fields because at the planar heterojunction the field is perpendicular to the interface. Only at the border of the illuminated spot, stray fields with components in the direction of the junction cause slightly accelerated drift, but it is expected to be small compared to the impact of thermal diffusive motion in disordered organic semiconductors. Equation (4.1) contains all the fundamental contributions determining the intrinsic spatial resolution limit for an optically excited semiconductor transducer device. In such a device, locally generated charge carriers initiate the biological sensing or stimulation process. But they can also diffuse out of the illuminated area before triggering the transduction event, reducing in this way the spatial resolution.

In order to achieve a quantitative analysis of the KPFM surface photovoltage maps, we assume that the local photovoltage $\phi(x)$ is directly proportional to the local concentration of photogenerated charge $n(x)$ at the heterojunction. This assumption is justified considering that each generated charge is paired to a counterbalancing charge across the p-n interface to form a dipole. Such a dipole is characterized by an average distance l between the centers of charge which does not depend on carrier concentration or light intensity. Accordingly, we can simplify by approximating that the dipoles in the p-n junction form a plane capacitor for which the distance between the two plates is l . Then the photovoltage can be written as $V_p = \sigma/c = \sum q_i \times l/\epsilon\epsilon_0 A = nq_0l/\epsilon\epsilon_0$ demonstrating the proportionality between photovoltage

V_p and the carrier concentration n .

We can further simplify Equation (4.1) due to the radial symmetry of the system and the isotropic diffusion of the photogenerated charges in the direction parallel to the heterojunction. The only coordinate that needs to be considered is r describing the distance from the center of the illumination spot. Further, for the KPFM experiment with continuous illumination, we have to consider the steady state solution of Equation (4.1) with $\partial n(r, t)/\partial t = 0$ so that the carrier concentration $n(r)$ is only a function of the radial coordinate r . In our experiment we are mostly interested in understanding the diffusion processes outside of the illuminated region causing the reduction in resolution. In this region no charge carrier generation occurs and we can set $G = 0$. The resulting differential equation that determines the tail of photovoltage profile then reads

$$\frac{d^2 V_p(r)}{dr^2} + \frac{1}{r} \frac{dV_p(r)}{dr} - \frac{1}{D\tau(V_p)} V_p(r) = 0 \quad (4.2)$$

We substitute the charge carrier lifetime with the expression $\tau(V_p) = a^{-2} K_{bi}^{-1} V_p^{-1}$ based on a bimolecular recombination mechanism as determined with transient photovoltage measurements (see below). Equation (4.2) has no simple analytical solution, and we use a numerical Runge–Kutta scheme to fit the equation to the experimental data. Boundary conditions are given by the experimental photovoltage and its first derivative at the border of the light spot (r_{spot}), i.e., $V_p(r_{spot}) = V_0$ and $V_p'(r_{spot}) = V_0'$ as obtained from the experimental data.

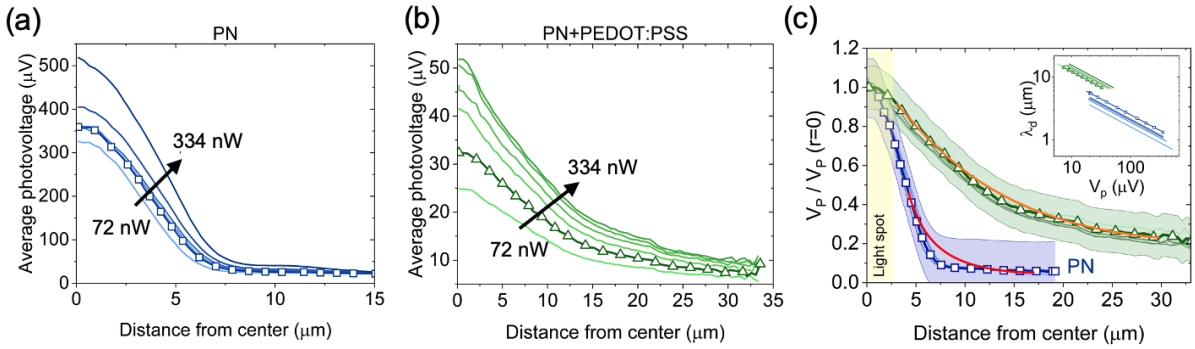


Figure 4.2: (a) Photovoltage as a function of distance r from the light spot center as measured on the H2PC/PTCDI heterojunction. (b) Same as (a) but for a sample with PEDOT:PSS deposited on top of the p-n junction. In both (a) and (b) the photovoltage is reported for different light powers ranging from 72 nW (lighter curve) to 334 nW (solid curve). (c) Normalized photovoltage profiles of H2PC/PTCDI and H2PC/PTCDI+PEDOT:PSS samples for light power of 126 nW, with numerical fit to diffusion equation. Due to the normalization, curves obtained with different light power overlap into a single curve. The inset shows the diffusion length as a function of the local photovoltage V_p .

To compare the model to our KPFM data, we determine averaged radial photovoltage pro-

files from the images taken at different light intensities. They are shown in Figure 4.2a,b for the pure p-n heterojunction (blue squares) and for the one with the top PEDOT:PSS layer (green triangles). Profiles were obtained with different laser powers ranging from 72 to 334 nW. In both devices, the photovoltage increases with increasing laser power while the shape of the curves is not affected. In Figure 4.2c, we present the normalized KPFM photovoltage profiles for both the p-n and p-n+PEDOT:PSS samples as obtained at a power of 126 nW, along with their respective numerical fits using Equation (4.2). The fitting range is determined by the size of the light spot, exclusively considering the region where carrier generation is not present. The boundary conditions are directly calculated from experimental data at the left border of the fitting range. The thinner curves correspond to the other profiles reported in Figure 4.2a,b, confirming that the average photovoltage shape remains consistent across various power values. From our fitting procedure with the diffusion equation we obtain the combined parameter $p^2 = a^2 K_{bi} D^{-1}$ from which we can compute the diffusion length by $\lambda_d = \sqrt{1/(p V_p)}$. The resulting values are shown in the inset of Figure 4.2c. Values of diffusion length at the border of the illumination spot are $\lambda_d(\text{PN}) = (1.5 \pm 0.1) \mu\text{m}$ and $\lambda_d(\text{PN} + \text{PEDOT} : \text{PSS}) = (7.0 \pm 0.3) \mu\text{m}$. The full profile takes the shape of a gaussian bell curve with $V_p \approx \exp(-z^2/(2\sigma_e^2))$ with $\sigma_e^2 = \sigma_{hv}^2 + \lambda_d^2$ where the σ_{hv} describes the gaussian profile of the focused light spot. For the standard deviation σ_e describing the profile of the excitation we find $\sigma_e(\text{PN}) = (3.11 \pm 0.01) \mu\text{m}$ for the p-n junction and $\sigma_e(\text{PN} + \text{PEDOT} : \text{PSS}) = (7.78 \pm 0.08) \mu\text{m}$ for the p-n+PEDOT:PSS sample.

Our findings demonstrate that the carrier diffusion length in the p-n sample is much shorter than in the pn-PEDOT:PSS sample. Accordingly the PEDOT:PSS layer causes a broader, more diffuse photovoltage signal. The increased diffusion length is also associated to the lower photovoltage magnitude in the center of the light spot of the PEDOT:PSS functionalized sample. Still, the causes for the extended diffusion length observed in the p-n+PEDOT:PSS sample cannot be clarified from these data: an increased diffusion length could be attributed to enhanced charge carrier diffusion but also to extended carrier lifetime.

4.2.2 Transient photovoltage measurements

To answer this question, we perform transient photovoltage measurements that provide access to the carrier lifetime. In such experiments the spatial resolution is not relevant, as we are interested in measuring the time-dependent photovoltage build-up and decay. To perform macroscopic time-resolved photovoltage measurements we use a setup as introduced in Figure 4.3a. The p-n photoelectrode sample is mounted on a holder and a thin dielectric spacer is used to position an ITO covered glass slide above the photoelectrode. This structure functions as a capacitor, with the p-n junction of the photoelectrode serving as one plate and the

ITO electrode as the other. Importantly the dielectric spacer avoids any direct contact between the p-n junction and the ITO electrode to avoid direct current generation. An LED ($\lambda = 530 \text{ nm}$) produces light pulses of $50 \mu\text{s}$ duration illuminating uniformly the heterojunction. The photovoltage that builds up over the capacitor is measured with a high impedance amplifier and visualized on an oscilloscope screen. In Figure 4.3b,c, we present the recorded photovoltage transients for both the p-n and p-n+PEDOT:PSS samples obtained at different light power densities ranging from 108 to 531 mW cm^{-2} , comparable to the values used in the KPFM experiment. The yellow region in the plots indicates the duration of light illumination. In both samples, we observe a consistent increase in the maximum photovoltage values as power density increases, ranging from approximately 4 to 10 mV. Notably, in this experiment the p-n+PEDOT:PSS sample exhibits a higher photovoltage response than the pure p-n heterojunction sample.

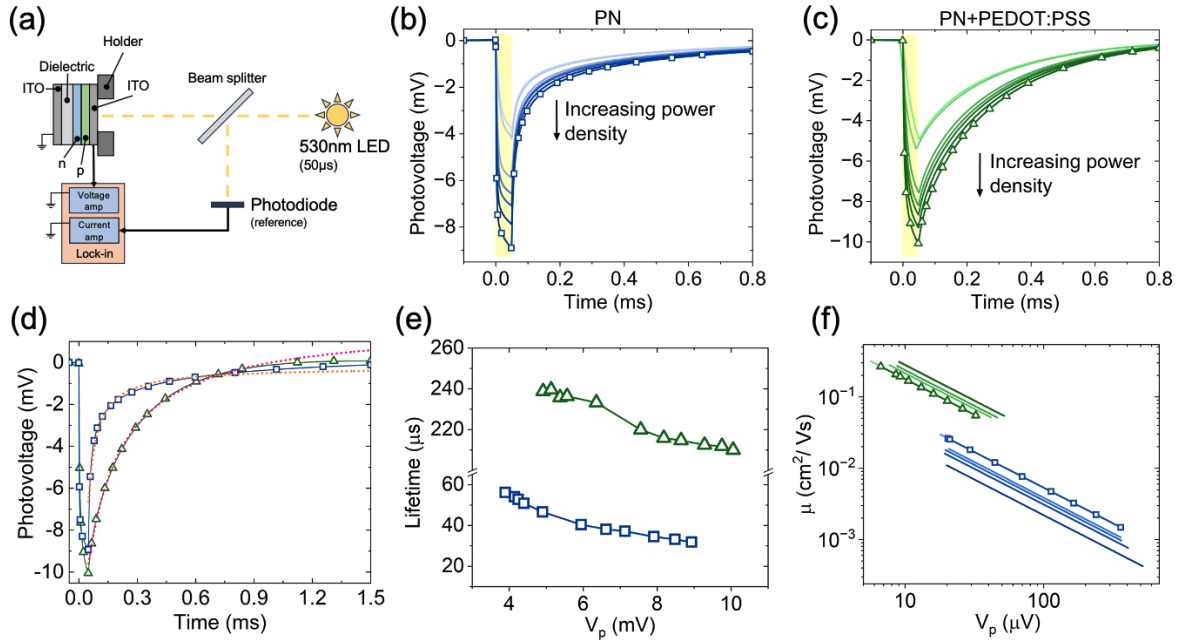


Figure 4.3: Photovoltage transient analysis during illumination with $50 \mu\text{s}$ duration pulses. (a) Schematic of the experimental setup. (b) Photovoltage transients recorded at different power densities for the p-n sample and (c) for the p-n junction with the top PEDOT:PSS layer. (d) Transients of both samples obtained at a power density $P = 531 \text{ mW cm}^{-2}$ with fit to the model. (e) Average charge carrier lifetime as a function of local photovoltage V_p . (f) Mobility of the two samples as a function of laser power (color scale) and local photovoltage.

In order to analyze the data quantitatively, we consider Equation (4.1) describing generation and recombination processes causing photovoltage transients. In the experiment, we illuminate the whole p-n junction area, therefore the photovoltage is no longer a function of position x and we can neglect diffusion processes. Furthermore, we consider only the photo-

voltage decay when the light source is switched off. Removing the diffusion and generation terms we obtain the differential equation that describes the photovoltage decay:

$$\frac{dn(t)}{dt} = -\frac{n(t)}{\tau(n)} \quad (4.3)$$

By substituting the characteristic time τ with the expression for bimolecular recombination and the concentration with photovoltage, we can obtain an analytical solution for Equation (4.3):

$$V_p(t) = \frac{V_{p0}}{1 + V_{p0} b K_{bi} t} \quad (4.4)$$

where $V_{p0} = V_p(t = 0)$ and b is the constant that relates the transient photovoltage to the charge carrier concentration in the p-n junction. In Figure 4.3d, we present the photovoltage transients for both samples measured at a power density of 531 mW cm^{-2} , along with their corresponding fits to Equation (4.4). Figure 4.3e shows the carriers lifetime as function of photovoltage (and thus as function of laser power density) for the two samples. In both cases the lifetime increases when the local photovoltage decreases. Comparing the lifetimes averaged over the photovoltage, we find that in the p-n+PEDOT:PSS sample the lifetime is approximately ten times larger than in the p-n sample. With the knowledge of the carrier lifetimes, we can also calculate the local effective diffusivity $D = \lambda_d^2 \tau^{-1}$ from the diffusion length obtained in the KPFM experiment. Using the Einstein relation, we further compute the effective carrier mobility $\mu = D k_B^{-1} T^{-1}$. The dependence of mobility on total photovoltage and light intensity is reported in Figure 4.3f where the strong difference between the two samples is clearly appreciable. The average values for the two samples at the border of the light spot are $\mu(\text{PN}) = (0.02 \pm 0.01) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-2}$ and $\mu(\text{PN} + \text{PEDOT} : \text{PSS}) = (0.58 \pm 0.02) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-2}$ showing that p-n+PEDOT:PSS sample entails a mobility that is approximately thirty times the one of the pure p-n junction.

4.2.3 Discussion

Our findings explain the effect of the outer PEDOT:PSS layer on the charge separation, photovoltage, and photocurrent generation in photoelectrodes. We find that PEDOT:PSS increases significantly the lifetime of carriers or in other words, it slows down recombination processes. As a consequence the PEDOT:PSS coating improves the charge generation. Most notably this causes increased photocurrents. For example when illuminating the photoelectrodes immersed in electrolyte with a focussed laser spot (see below) a photocurrent of $320 \text{ } \mu\text{A}$ is observed. In the pure p-n junction with faster recombination a value of $140 \text{ } \mu\text{A}$ is measured. The disadvantage of the PEDOT:PSS coated photoelectrode is instead the increased carrier mobil-

ity. As a consequence, carriers diffuse faster and transfer energy out of the illuminated region. The latter effect reduces strongly the resolution of optobioelectronic interfaces as observed in the photovoltage microscopy experiment. Knowing the electronic properties of PEDOT:PSS, we try to rationalize why the outer layer of PEDOT:PSS increases the lifetime and effective carrier mobility. Upon illumination negative carriers are accumulated in the outer PTCDI layer of the heterojunction. If these carriers remain close to the interface, they can rapidly recombine with the positive charges in the H2PC layer. In the presence of a PEDOT:PSS layer bound to PTCDI layer, negative carriers can be stabilized due to image charges in the highly doped (metallic) PEDOT:PSS layer. Such an image charge effect pulls the generated carriers away from the junction. Additionally, the high doping of PEDOT:PSS enables that some negative charges are transferred into PEDOT:PSS where they fill the mobile hole states. The consequence is that generated carriers are more distant from the junction and hence less likely to recombine with positive carriers in the H2PC layer. Furthermore, space charge present in PEDOT:PSS is expected to have a much higher effective mobility. Values from transport measurements in PEDOT:PSS demonstrate mobilities of up to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [25] exceeding by more than an order of magnitude mobilities associated to PTCDI or H2PC.

Our measurements demonstrate that the organic p-n junction without PEDOT:PSS coating is advantageous for interfaces where a high spatial resolution is important. Due to the small diffusion length in the organic heterojunction, the optoelectronic excitation remains localized and a spatial resolution of below $3 \mu\text{m}$ is feasible following the results from the KPFM photovoltage measurements. However, when photocapacitors are operated in electrolyte, the spatial resolution is further altered due to additional mechanisms. For example, water is a strongly polarizable medium and impacts on optoelectronic processes in the semiconductor [152]. In addition, the electric field diverges in the semi-infinite space of the electrolyte and high resolution requires that transduction processes occur in close vicinity to the semiconductor/electrolyte interface. To investigate such issues and to demonstrate the potential to achieve high resolution we perform a model imaging experiment with the semiconductor in contact with an aqueous electrolyte.

4.3 Photoelectrochemical microscopy

Figure 4.4a illustrates the experimental setup for the photoelectrochemical current imaging. The system consists of a motorized micrometric x-y stage that enables precise scanning movement of the focussed laser spot over the sample surface. The sample is fixed in position with a dedicated holder that avoids any movement of the electrolyte and acts as a Faraday cage. The distance between the sample and the laser is controlled by a micrometric screw to focus the

the laser spot on the p-n junction. The electrolyte is connected to the electrical ground with an Ag/AgCl wire. The photoelectrode is connected to a current amplifier. Upon switching on and off the light source the p-n junction gets polarized and an ionic displacement current is generated in the electrolyte. Due to the small size of the illuminated spot (ca. $2\text{ }\mu\text{m}$), the photocurrent signal is small ($< 1\text{ nA}$). To obtain a stable signal we modulate the light source intensity at $f = 4.4\text{ kHz}$ and use a lock-in amplifier to measure amplitude and phase of the AC current signal. Images of photocurrent amplitude and phase are generated by scanning the light spot over the photoelectrode and collecting for each pixel amplitude and phase values with a data acquisition board. Similar electrochemical photocurrent microscopy setups have been used to monitor local electrochemical currents at inorganic semiconductor/electrolyte interfaces [148, 149].

The electrochemical photocurrent image of the p-n junction electrode with a diameter of $500\text{ }\mu\text{m}$ is presented in Figure 4.4b and compared to the optical microscopy image. One clearly notices the shape of the circular p-n junction corresponding to the region where photocurrent is generated. A part of the circular electrode is covered by an isolating layer of polydimethylsiloxane (PDMS). Even though the p-n junction is present below the PDMS, no photocurrent is generated in this area. Figure 4.4d shows a profile of the photocurrent amplitude taken across the border of the PDMS layer along with the corresponding fit to the cumulative error function. The profile shows a clear transition from the covered to the uncovered regions, revealing a gaussian shaped excitation profile described by $\sigma_{e,\text{PDMS}} = (6.5 \pm 0.9)\text{ }\mu\text{m}$ as extracted from the error function fit. The finding demonstrates that a micrometric resolution can be obtained with the p-n junction in realistic aqueous operation conditions. The resolution value is similar to the size of single cells ($\approx 10\text{ }\mu\text{m}$ diameter) and shows that single cell transduction is feasible in optically activated organic bioelectronic devices. It is interesting to compare our resolution with other inorganic semiconductors used in optoelectronic transduction experiments as reported in the literature [150, 151].

4.3.1 Discussion

Compared to the KPFM experiment, the size of the excitation profile doubled under the electrochemical conditions. This loss in resolution can be attributed to different effects. First, the presence of water at the p-n junction interface can impact on carrier lifetime and diffusion. Due to water polarization charge carriers are attracted toward the solid/liquid interface, reducing the probability for recombination and increasing the carrier diffusion length. For the p-n junction, the solid/liquid interface is distant 30 nm from the solid liquid interface, and using a simple image charge model a stabilization of up to 0.1 eV can be estimated [152]. Other reasons for the reduced resolution could be undercuts or structural inhomogeneities at the

PDMS border and related current dispersion.

Combining these arguments on resolution, our finding demonstrates that the overall extension of the excitation at such semiconductor/electrolyte interfaces is determined by three contributions

$$\sigma_e = \sqrt{\sigma_{h\nu}^2 + \lambda_d^2 + \sigma_{ec}^2}$$

in which $\sigma_{h\nu}$ denotes the extension of the focused light spot, λ_d the effective diffusion length in the semiconducting layer and σ_{ec} additional losses in the semiinfinite half space of the electrolyte. From these findings we can propose different options to improve resolution in optobi-electronic experiments: i) optical engineering allows to minimize $\sigma_{h\nu}$ to the diffraction limit. ii) Having the biological system close to the photoelectrode is fundamental to keep σ_{ec} small. iii) Mini- mization of λ_d regards tuning of the semiconductor properties. For Silicon reduced diffusion length was achieved by making ultra-thin layers[151] or by introducing mesoporous structuring [150]. In both cases carrier scattering is increased so that carrier mobility drops. For organic semiconductors further strategies are feasible. One possibility could regard the anisotropic transport properties that can be realized in π -conjugated organic molecules. By controlling molecular alignment at the heterojunction, one could orient the fast mobility axis vertical to the junction to facilitate carrier separation. Instead small mobility would be advantageous in the direction parallel to the heterojunction to suppress carrier diffusion.

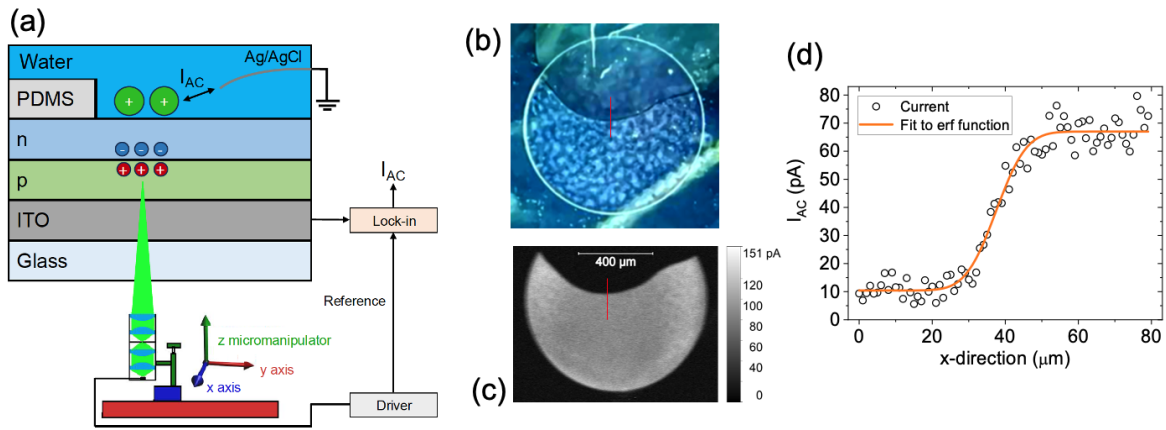


Figure 4.4: Photoelectrochemical current microscopy with organic planar p-n junction to determine the spatial resolution. (a) Scheme of the experiment in which a part of the p-n junction is covered by a dielectric PDMS layer. (b) Optical micrograph of the p-n-junction electrode covered partially with PDMS. (c) AC photoelectrochemical current image of the electrode. (d) Profile of the current map and fit to error function. The red lines in (b,c) show the location of the profile.

Materials	Resolution [μm]	Refs.
Nanoporous silicon	≈ 106	Li et al. (2024)
BiFeO ₃ thin film	≈ 2.6	Meng et al. (2024)
Ultra-thin silicon on sapphire	≈ 2.0	Wang et al. (2015)
H2PC/PTCDI thin film	≈ 6.5	This work

Table 4.1: Comparison of estimated resolutions obtained in photocurrent scanning measurements. The resolution is estimated from reported photocurrent profiles or images and describes the radius at which the photocurrent presents a 40% drop from its maximum assuming a point-like light source.

4.4 Conclusions

In this work we provide insight into the physical mechanisms that determine the spatial resolution in organic optobioelectronic devices. As a model system we investigate organic photocapacitor devices that consist in a planar organic p-n junction made of the small molecule semiconductors H₂PC and PTCDI. Local photovoltage measurements with Kelvin Probe Force Microscopy show how a focussed optoelectronic excitation of a laser spot broadens due to carrier diffusion. By modeling the diffusion and recombination processes we show that the resolution losses due to the broadening are directly related to the effective diffusion length λ_d of carriers in the organic semiconductor. In our experiments we determine a diffusion length of $\lambda_d = (1.5 \pm 0.1) \mu\text{m}$ for the p-n junction and of $\lambda_d = (7.0 \pm 0.3) \mu\text{m}$ for the p-n junction with a top coating of PEDOT:PSS. Further insight into the differences between these two layers is provided with time-resolved photovoltage measurements. The PEDOT:PSS coating increases the carrier lifetime and makes the photocapacitor more effective in terms of charge carrier generation. However, the PEDOT:PSS coating also significantly increases the carrier mobility ($\mu_{\text{PN}} = (0.02 \pm 0.01) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ versus $\mu_{\text{PN+PEDOT:PSS}} = (0.58 \pm 0.02) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), explaining the increased diffusion length and associated losses in resolution.

To demonstrate the strongly localized excitation and the high resolution predicted for the pure H₂PC/PTCDI photocapacitor also under electrochemical conditions, we developed a microscopy experiment in which we map the alternating ionic current generated locally when the p-n junction is immersed in the electrolyte and illuminated by a focussed laser spot with modulated light intensity. The localization of the photoactivated current source is quantified by measuring how the current is blocked at the border of a dielectric obstacle deposited onto the semiconductor surface. From these measurements we determine an effective spatial resolution of $\sigma_e = (2.4 \pm 0.2) \mu\text{m}$.

In conclusion, our experiments reveal the different contributions to spatial resolution in or-

ganic optobioelectronic devices. The resolution in the planar organic heterojunction is mainly determined by the diffusion length of the carriers in the semiconductor. At the same time, the resolution is affected by the ionic environment in which the devices operate, as the electrochemical transduction process is strongly localized at the semiconductor/electrolyte interface. These results provide guidelines for the design of organic optoelectronic devices with improved spatial resolution, which is crucial for the development of bioelectronic interfaces that operate at cellular and subcellular length scales.

4.5 Supplementary material

4.5.1 Microscopic measurement of photovoltage spatial decay

Figure 4.5(a) shows the AFM setup used to measure the spatial decay of photovoltage. The tip is operated directly above the exposed device's surface where it measures the morphology and the electrical potential coming from the heterojunction. The light source is a laser diode of wavelength $\lambda=520\text{nm}$ which is focused by a collimating optical tube to obtain a spot size of $2.6\mu\text{m}$. The light beam passes through a prism and is directed onto the sample, which is positioned on top of a holed sample holder. We used two different samples to demonstrate our technique and characterize the photovoltage decay. A schematic of the first type is reported in figure 4.5(b) and it is composed of three layers: the ITO serves as bottom contact for the grounding while on top we deposited two organic semiconducting layers. The p-type semiconductor is H_2PC while the n-type one is PTCDI. The other type of sample is reported in figure 4.5(c) and it is completely equivalent to the previous one, except for an additional layer of PEDOT:PSS deposited on top. In our experiment we drive the laser diode with a 720Hz square wave to induce the production of a modulated photovoltage in the PN junction. Subsequently, we demodulate the measured EFM signal with a lock-in amplifier. The photovoltage can be calculated from EFM data through the relation

$$V_{\text{contact},RMS} = \frac{V_{EFM}}{V_{tip}} \times V_{EFM,RMS} \quad (4.5)$$

where $V_{EFM,RMS}$ is the signal measured with the lock-in. 1 With this technique we were able to produce the photovoltage maps shown in figure 4.1.

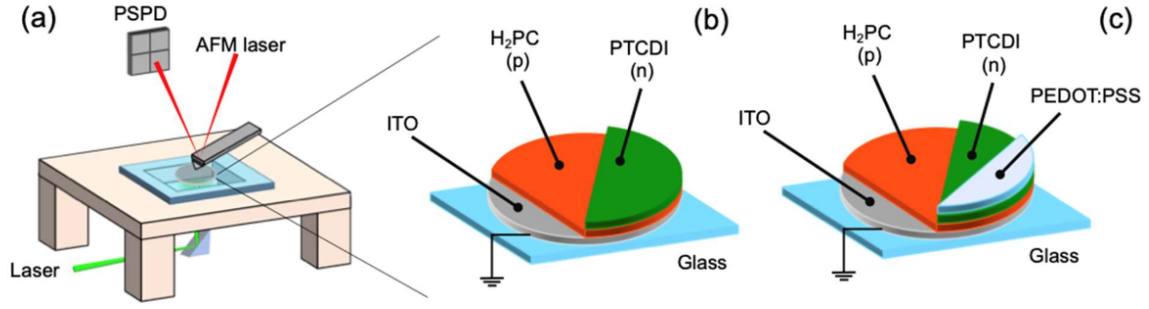


Figure 4.5: (a) AFM setup used to measure the photovoltage spatial decay in the organic PN heterojunctions. (b) Sample composed of only ITO and p-n layers. (c) Sample with the layer of PEDOT:PSS on top.

4.5.2 Full derivation of photo-generated dipole diffusion equation for an organic PN heterojunction in the steady state condition

The motion of excitons at the p–n interface can be described by a drift–diffusion scheme. We can assume to have a light source that impinges on the sample and triggers the production of electron–hole pairs. The exciton motion is bidimensional and thus we expect to obtain a smeared photovoltage with radial symmetry, as they will diffuse in all directions starting from the generation point. We can describe the process with the general diffusion equation:

$$\frac{\partial n(\vec{r}, t)}{\partial t} = \nabla \cdot [D(n, \vec{r}) \nabla n(\vec{r}, t)] \quad (4.6)$$

where D is the diffusivity and n the function that describes the concentration. In general, the vector $\vec{r} = (x, y, z)$ spans three spatial coordinates. However, in the case of a planar heterojunction we neglect the diffusion motion in the z direction. Since the material is expected to be homogeneous, we assume a constant diffusivity D , which does not depend on position or concentration.

In addition, we introduce radial symmetry of the system and consider the steady–state solution ($\partial n / \partial t = 0$), integrated over the angle θ . The remaining coordinate r is the distance from the center of the light spot. Equation 4.6 thus reduces to:

$$D \left(\frac{1}{r} \frac{dn}{dr} + \frac{d^2 n}{dr^2} \right) = 0 \quad (4.7)$$

Equation 4.7 only describes the diffusion of excitons in two dimensions, and we must include the generation (G) and recombination (R) terms. The former can be modeled as a step function, null outside of the light spot, while the latter depends on the type of recombination occurring in the p–n junction. The predominant mechanism in organic heterojunctions is bi-

molecular recombination [153]. This process is described by a recombination rate proportional to the square of the concentration:

$$R = K_{bi} n^2(r, t) \quad (4.8)$$

where K_{bi} is a constant that depends on the lifetime of charge carriers and can be determined with photovoltage transient measurements. The complete diffusion equation in the steady state condition is then:

$$\frac{d^2 n}{dr^2} + \frac{1}{r} \frac{dn}{dr} - \frac{K_{bi}}{D} n^2 = 0 \quad (4.9)$$

where the constant $K_{bi}/D = \alpha$. Equation 4.9 does not allow an analytical solution; thus we provide a numerical solution using mixed boundary conditions:

$$n(r = r_{spot}) = n_0 \quad \left. \frac{dn}{dr} \right|_{r=r_{spot}} = N \quad (4.10)$$

where r_{spot} corresponds to the position in space where the light–dark transition is located.

The numerical solution to Eq. 4.9 is reported in Figure 4.6 for different values of α , and shows the normalized concentration, calculated as $n(r)/n(0)$, as a function of radius. The solution is obtained using a 4th order Runge–Kutta scheme with automatic step-size adjustment. In this example, the boundary conditions are $n(r = 3\mu m) = 0.83$ and $n'(r = 3\mu m) = -0.07$, assuming the light–dark transition takes place at $r = 3\mu m$. The solution is highly sensitive to the α parameter, so even a small change leads to significant variations in the simulated curve. However, this sensitivity is beneficial since it ensures strong convergence of the fit and makes the parameter determination more reliable.

To obtain α from experimental data we first integrate the KPFM potential map over the angular coordinate. This is done with a numerical procedure that provides $V_{KPFM}(r)$ as a function of distance from the spot center. The algorithm requires the estimated position of the spot center and two angles to identify the correct region of the image to integrate, excluding parts that could affect the final profile (e.g., laser diffraction pattern). Subsequently, we fit the integrated profile with the numerical solution of Eq. 4.9. The boundary conditions are taken directly from the experimental data: n_0 is the photovoltage at the first fitting point, while the slope N is obtained from a linear fit of the initial part of the curve.

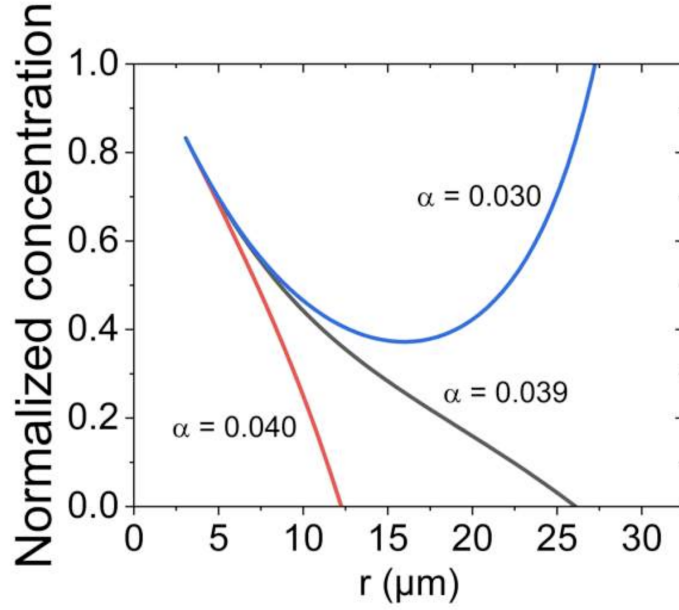


Figure 4.6: Simulated numerical solution of the diffusion equation with boundary conditions $n_0 = 0.83$ and $N = -0.07$ for different values of parameter α .

4.5.3 Determination of photogenerated dipoles diffusion length from photovoltage average profiles

Differently from monomolecular recombination, the bimolecular decay time constant depends on light intensity, resulting in a distribution of decay times rather than a single value. Therefore, if we consider the steady-state solution in Eq. 4.9, we can obtain a unique value for the diffusion length

$$\lambda_d = \sqrt{D/V_p \alpha K_{bi}} = \sqrt{D \times \tau} \quad (4.11)$$

only for a specific photovoltage. Figure 4.7 shows the photovoltage profiles for p-n and p-n+PEDOT:PSS samples mirrored with respect to the axis $x = 0$ to obtain the complete Gaussian shape.

The fits demonstrate that the photovoltage decay is well described by a normal distribution. Therefore, we choose to use the standard deviation σ as representative value for the resolution in the p-n junction. The standard deviation of the light spot can be measured directly with the knife-edge method, and it is shown together with photovoltage profiles in Fig. 4.7. We report $\sigma_{spot} = (2.59 \pm 0.03) \mu\text{m}$.

From the fitting procedure we obtained:

$$\sigma(PN) = (3.11 \pm 0.01) \mu\text{m}, \quad \sigma(PN + PEDOT : PSS) = (7.78 \pm 0.08) \mu\text{m}$$

To calculate the value of the diffusion length we use $V_p(\sigma)$ as multiplication factor in the expression for λ_d to remove the constant α . We report:

$$\lambda_d(PN) = (1.5 \pm 0.1) \mu\text{m}, \quad \lambda_d(PN + PEDOT : PSS) = (7.0 \pm 0.3) \mu\text{m}$$

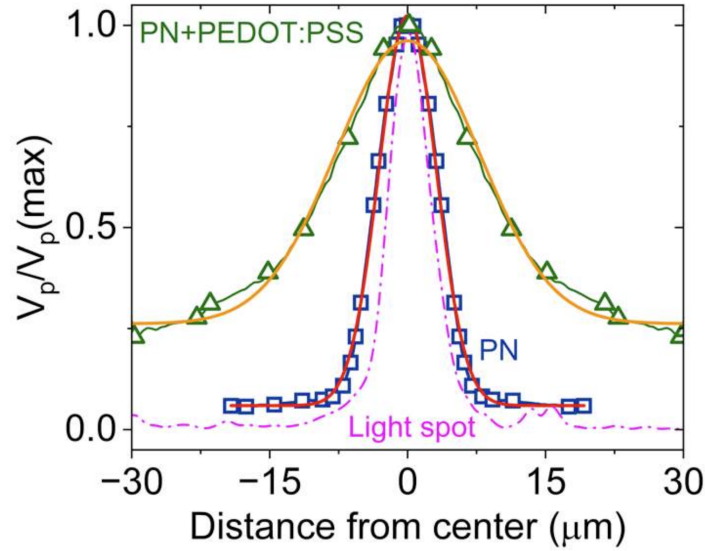


Figure 4.7: Mirrored average photovoltage profile around the axis $x = 0$ to obtain the complete Gaussian shape. The symbols represent experimental data, while the solid lines are Gaussian fits. The dashed line indicates the Gaussian profile of the spot measured with the knife-edge method.

4.5.4 Measurement of photo-generated dipole's decay time constant

By looking at equation 4.9 it is clear that the value of K_{bi} is required to find the dipoles diffusion constant, since from steady state photovoltage fits only the combined value K_{bi}/D can be determined. We evaluated the photovoltage buildup with a macroscopic experiment (see above). The effect of the p-n junction can be modeled as a capacitance which charges or discharges when photovoltage is generated inside the device. When the first layer charges up due to the photovoltage, the others also accumulate charge, producing a potential proportional to the actual photovoltage. Experimentally, the sample was illuminated with the same power density values used in the EFM experiment, and the light was pulsed to produce the rise and fall photovoltage transients.

The value of the decay time constant can be determined through the solution of equation 4.6 under different boundary conditions. In the experiment we illuminate the whole p-n junction area, therefore the photovoltage is no longer a function of position. Removing

diffusion-dependent terms and the generation term, we obtain from equation 4.6:

$$\frac{dn}{dt}(t) = -K_{bi}n^2(t) \quad (4.12)$$

which can be solved analytically once the initial concentration $n_0 = n(t = 0)$ is defined. The full solution of equation 4.12 yields:

$$n(t) = \frac{n_0}{1 + n_0 K_{bi} t} \quad (4.13)$$

Equation 4.13 describes the decay of photovoltage at a fixed point as a function of time, assuming that the only recombination mechanism is bimolecular.

4.5.5 Relation between model and experimental quantities

The whole model described in the previous paragraphs uses the concentration u as main variable. However, we measure a voltage in both the AFM and the macroscopic experiments. We can consider the concentration of photogenerated dipoles to be proportional to the photovoltage in both cases. We can then write

$$u = a \times V_{KPFM} = b \times V_{TR}$$

where V_{KPFM} is the potential extracted with equation 4.9 and V_{TR} is the photovoltage measured in the transient experiment. The substitution is straightforward, and the two new equations are

$$\begin{cases} \frac{d^2 V_{KPFM}}{dr^2} + \frac{1}{r} \frac{dV_{KPFM}}{dr} - \frac{aK_{bi}}{D} V_{KPFM}^2 = 0 \\ V_{TR}(t) = \frac{V_{TR}(0)}{1 + V_{TR}(0) b K_{bi} t} \end{cases} \quad (4.14)$$

The new solutions depend, through the parameters a and b , on an effective recombination rate aK_{bi} or bK_{bi} which is different in the two processes. However, it is possible to obtain the relation that links the recombination constant K_{bi} to the diffusivity. Let us call $\frac{aK_{bi}}{D} = p_1$ and $bK_{bi} = p_2$ the values of parameters extracted from the experimental fitting procedures. It follows

$$K_{bi} = \frac{p_1 D}{a} = \frac{p_2}{b}$$

from which we can obtain the value of diffusivity

$$D = \frac{p_2}{p_1} \frac{a}{b}$$

The ratio a/b can be derived from the definition of parameters a and b :

$$\frac{a}{b} = \frac{V_{TR}}{V_{KPFM}}$$

The values of V_{KPFM} and V_{TR} are measured at the point of maximum light intensity to ensure the same power density. In the case of V_{TR} , the power density is uniform as the sample is completely illuminated, while for V_{KPFM} we chose the center of the light spot. The diffusivity constant is thus given by

$$D = \frac{p_2}{p_1} \frac{V_{TR}(P = P_{MAX})}{V_{KPFM}(P = P_{MAX})} \quad (4.15)$$

4.5.6 Alternative method for the estimation of diffusion length

Instead of considering the photovoltage at the distance σ from the spot center, one could consider the flex point of the Gaussian, as the differential equation simplifies considerably. Indeed, at the flex point we have that the second derivative of photovoltage must vanish, and we can write the approximated steady-state diffusion equation as

$$\frac{1}{r} \frac{dV_p}{dr} - \frac{V_p}{\lambda_d^2} = 0 \quad (4.16)$$

This differential equation cannot be directly solved, as the analytical dependence of diffusion length on photovoltage $\lambda_d(V_p)$ is not known. However, we can calculate the derivative from experimental data and obtain the value $\frac{dV_p}{dr}(r = r_0)$, where r_0 is the point where the second derivative is null. The diffusion length can be expressed as

$$\lambda_d = \sqrt{\frac{V_p(r_0) r_0}{\left(\frac{dV_p}{dr}\right)_{r=r_0}}} \quad (4.17)$$

This calculation for our data is reported in Figure 4.8, where the two photovoltage profiles are shown with their first derivative in the point $r = r_0$. In the inset we also report the value of the first derivative for the PN sample, as an example. Note that the value r_0 is equivalently determined by the point of maximum absolute value of the first derivative of photovoltage.

We obtained

$$\lambda_d(PN) = (3.3 \pm 0.3) \mu\text{m}, \quad \lambda_d(PN + PEDOT : PSS) = (8.7 \pm 0.2) \mu\text{m}$$

for the bare p-n and p-n+PEDOT:PSS samples, respectively.

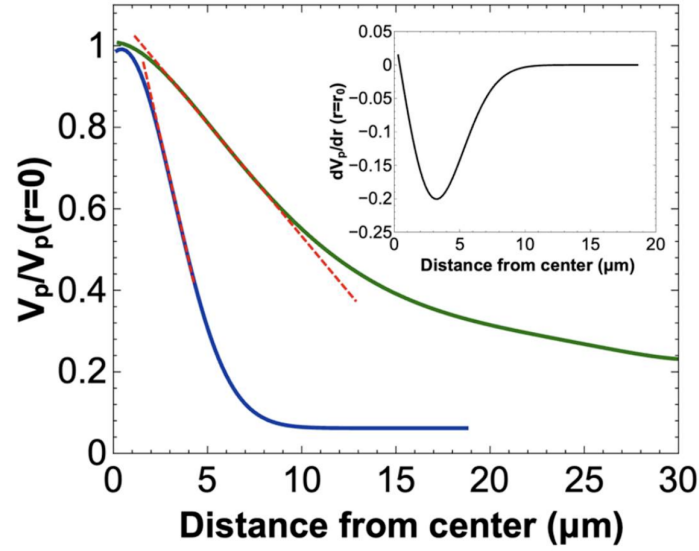


Figure 4.8: Normalized photovoltage profiles for p-n (blue) and p-n+PEDOT:PSS (green). The red dashed lines represent the first derivative of the curve at the point of null second derivative. In the inset we report the value of the first derivative of the p-n photovoltage as a function of radius.

5 Lateral electrostatic force microscopy for quantitative electric field mapping

5.1 Introduction

The quantitative mapping of local electric fields represents a central challenge for the microscopic characterization of semiconductor devices and functional materials. Electric fields govern fundamental processes such as charge injection, drift, recombination, and carrier trapping, which ultimately determine efficiency and stability of semiconductor-based devices. The study of internal electrical fields is particularly critical in disordered materials—such as amorphous oxides, organic heterostructures, and low-dimensional semiconductors—where structural inhomogeneity, localized defect states, and electrostatic disorder can strongly affect device behavior. In amorphous oxide transistors, threshold-voltage drifts and stability issues are due to charge trapping at border states in the oxide layer [154]. Moreover, electric fields can dynamically modify defect distributions, transforming localized gap states into conduction-band-edge states and viceversa [155]. In organic semiconductors, electrostatic disorder arising from randomly oriented dipoles and quadrupoles strongly influences field-dependent mobility and transport [156]. Trap states further degrade carrier mobility and increase recombination rates, reducing lifetime and device performance [157]. Notably, higher carrier mobility shortens transit times and reduces recombination losses, thus mitigating field-induced degradation [158]. These examples underline that local electric fields directly control transport and stability in many material systems, making their quantitative investigation a key step to understand device operation.

Kelvin Probe Force Microscopy (KPFM) is among the most used techniques to study electrostatic properties at the nanoscale, since it measures directly the surface potential with high spatial resolution [69]. The signal comes from the contact potential difference between tip and sample, which can be mapped to obtain quantitative information on work function variations, local charge accumulation, and internal fields oriented normal to the surface. This ability has been exploited in different material systems and device structures. In amorphous oxide

semiconductors, KPFM spectroscopy has been applied to extract density-of-states parameters and band-tail widths with nanometric accuracy [159]. In thin-film transistors, mapping the potential along the channel allowed to identify voltage drops, charge trapping, and threshold-voltage shifts under bias [160]. In abrupt junctions and organic heterostructures, the technique revealed sharp potential steps due to built-in electric fields, directly evidencing charge separation. Similar approaches have been used in low-dimensional semiconductors, where defects and interfaces dominate charge transport, and in supramolecular or hybrid organic–inorganic systems, where KPFM correlates the local electronic structure with self-assembled morphology [161]. Through these examples, KPFM has established itself as the reference method to link microscopic potential distributions with the macroscopic behavior of devices.

Despite its widespread use, KPFM presents intrinsic limitations that restrict its applicability. The technique requires a certain degree of conductivity to maintain a stable feedback loop; purely insulating materials cannot be investigated, as surface charges cannot dissipate and the measured potential becomes unstable [69]. Furthermore, while KPFM provides quantitative maps of the surface potential from which the electric field distribution can, in principle, be obtained by numerical differentiation, this procedure amplifies noise and is constrained by the finite spatial resolution of the potential data. As a result, the vertical field component—directly linked to the measured contact potential difference—remains the most robust, whereas in-plane components are less reliable [162]. Several variants have been developed to address these issues. Frequency-modulation KPFM (FM-KPFM) achieves higher sensitivity and spatial resolution than amplitude-modulation schemes, but remains affected by stray capacitance and feedback artifacts. Open-loop KPFM avoids feedback altogether, inferring the potential from the electrostatic force signal, typically detected at the second harmonic of the tip oscillation [163]. While this approach mitigates closed-loop instabilities, it essentially operates as electrostatic force microscopy (EFM) and is dominated by the out-of-plane force component. Time-resolved KPFM implementations, such as G-mode KPFM, acquire the full cantilever response and reconstruct the potential with improved temporal resolution, but highlight the sensitivity of field retrieval to raw-signal handling and deconvolution procedures [164]. Finally, sideband and heterodyne KPFM couple electrostatic forces to higher-order cantilever resonances, enabling enhanced resolution, but remain intrinsically sensitive to the gradient of the force rather than to the field itself, which in simple geometries (e.g. parallel-plate capacitors) vanishes [165]. Taken together, these developments confirm the versatility of KPFM for nanoscale electrostatics, but also underline its fundamental constraints: the technique is not applicable to insulating systems, and lateral electric fields can only be inferred indirectly with reduced accuracy. A direct and quantitative approach to probe the in-plane component of the electric field is still missing.

In the following, lateral Electrostatic Force Microscopy (lateral EFM) is presented as a

methodology to achieve direct sensitivity to the in-plane component of the electric field. The technique exploits the torsional response of the cantilever, which couples selectively to lateral forces, thereby enabling the quantitative mapping of electric fields parallel to the sample surface. A calibration strategy based on reference capacitor structures provides a direct link between the measured torsional signal and the absolute field strength. After introducing the working principle and calibration procedure, we will demonstrate the application of lateral EFM to different case studies, showing how the method allows to disentangle vertical and lateral contributions and to obtain quantitative maps of in-plane electric fields with nanometric resolution.

5.2 Theoretical model for lateral electrostatic force

The interpretation of lateral EFM measurements requires a clear description of how the biased AFM tip interacts with the sample. In this section we introduce a model that explains the origin of the lateral force and its dependence on the applied voltages. We start from the simplest case of two electrodes at opposite potential and then extend the discussion to the more general situation where the tip is coupled to several regions through different capacitances. This provides the basis for understanding the frequency components of the measured signal and clarifies which physical quantities lateral EFM is actually probing.

5.2.1 Two-capacitance model for tip-sample interaction

In Fig. 5.1(a) we show the simplified geometry used to model the lateral amplitude-modulation EFM configuration. Two electrodes on the sample surface are biased at opposite potentials, thus forming an in-plane dipole that generates a lateral electric field. A conductive AFM tip is positioned above the surface at a finite height and is immersed in this field. To describe the geometry quantitatively, we define the distances between the tip and the two electrodes as d_1 and d_2 . The imbalance between d_1 and d_2 determines the net field experienced by the tip: when $d_1 = d_2$ the lateral force cancels by symmetry, while for $d_1 \neq d_2$ a finite lateral component arises. The metallic tip polarizes in response to the local potential difference, and the electrostatic interaction produces a measurable force along the surface plane (x -direction), which constitutes the lateral EFM signal.

The electrostatic interaction between the tip and the biased electrodes can be expressed starting from the general expression for the force associated with a capacitance C and a potential difference ΔV :

$$F_x(t) = \frac{1}{2} \frac{\partial C}{\partial x} \Delta V^2(t) \quad (5.1)$$

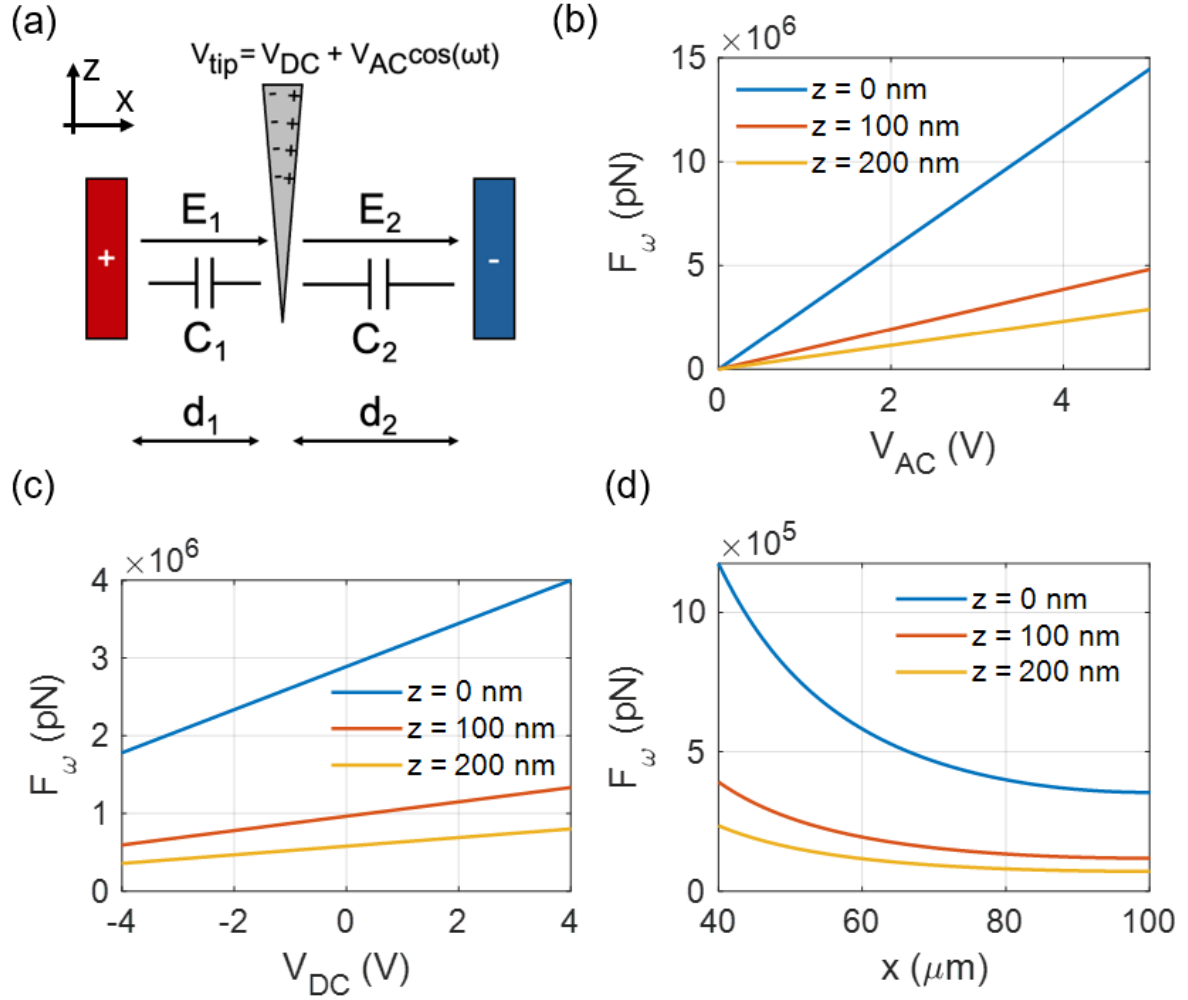


Figure 5.1: (a) Scheme of the dipole model with the AFM tip placed between two biased electrodes at distances d_1 and d_2 . The tip potential is expressed as $V_{\text{tip}} = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$, and the interaction is described through the capacitances C_1 and C_2 . (b) Calculated lateral force at the modulation frequency, F_ω , as a function of the AC bias amplitude for different tip-sample separations z . (c) F_ω as a function of the applied DC bias for the same values of z . (d) F_ω as a function of the lateral tip position x across the capacitor gap, reported for three tip-sample separations.

In the lateral configuration, however, the tip couples capacitively to both electrodes, with capacitances C_1 and C_2 defined by their respective geometrical distances d_1 and d_2 . As a consequence, the net force results from the sum of the two contributions:

$$F(t) = \frac{1}{2} \left[\frac{dC_1}{dx} (V_{\text{tip}} - V_1)^2 + \frac{dC_2}{dx} (V_2 - V_{\text{tip}})^2 \right] \quad (5.2)$$

Here $V_{\text{tip}} = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$ is the applied tip potential, while V_1 and V_2 denote the potentials of the two electrodes. The net lateral force therefore vanishes in the symmetric case ($C_1 = C_2$, $V_1 = -V_2$ and $d_1 = d_2$), and becomes finite as soon as the tip is displaced laterally from the center of the dipole.

Equation (5.2) can be expanded by substituting the applied tip bias $V_{\text{tip}} = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$. The quadratic terms in V_{tip} generate different frequency components in the force: a static contribution (DC), a term oscillating at the drive frequency ω , and a second harmonic at 2ω . The resulting expression reads

$$F(t) = F_0 + \left[\frac{dC_1}{dx} (V_{\text{DC}} - V_1) + \frac{dC_2}{dx} (V_{\text{DC}} - V_2) \right] V_{\text{AC}} \cos(\omega t) + \frac{1}{4} V_{\text{AC}}^2 \left(\frac{dC_1}{dx} + \frac{dC_2}{dx} \right) \cos(2\omega t) \quad (5.3)$$

Here F_0 collects the static (time-independent) terms, the second contribution represents the force component at frequency ω , and the last term corresponds to the higher harmonic at 2ω . The amplitude at ω is therefore directly proportional to the applied AC voltage V_{AC} , to the DC offset with respect to the local electrode potentials, and to the difference of the two capacitance gradients. In contrast, the second harmonic depends on the sum of the two gradients $\frac{dC_1}{dx} + \frac{dC_2}{dx}$, which is the net capacitance gradient acting on the tip. As a result, while the ω component provides sensitivity to the lateral asymmetry of the system, the 2ω component is related to the overall capacitive coupling acting on the tip.

It is important to note that, unlike in conventional (vertical) EFM and KPFM, in this lateral geometry the ω -component of the force cannot be nullified by adjusting the applied DC bias. In KPFM, the condition $V_{\text{DC}} = V_{\text{CPD}}$ suppresses the ω -term, enabling the direct measurement of the contact potential difference. Here, instead, the force at frequency ω arises from the imbalance of the two capacitance gradients $\frac{dC_1}{dx}$ and $\frac{dC_2}{dx}$, which have opposite sign. As a consequence, even if the DC bias compensates the local surface potential, the ω contribution cannot be completely cancelled. This prevents the use of the standard KPFM feedback scheme in the lateral EFM configuration.

To evaluate the expected response of the system we performed numerical calculations of

the lateral force according to Eq. (5.3). In these calculations the two electrodes are biased at +10 V and −10 V and separated by a total distance of 200 μm . The electrodes are treated as point-like charges, so that the plane $z = 0$ coincides with the line connecting the two sources, while larger z values correspond to lifting the tip vertically above this line. The AFM tip is modeled by an effective interaction area of 10^{-12} m^2 , and the dielectric constant of air is used for the capacitance calculation. The following parts of Fig. 5.1 report the dependence of the force component at frequency ω , F_ω , on the applied voltages and on the tip position.

Figure 5.1(b) shows the calculated dependence of the lateral force component at frequency ω on the applied AC bias V_{AC} . The simulations are performed with the tip located at $x = 25 \mu\text{m}$ from the left electrode. As expected from Eq. (5.3), the force increases linearly with V_{AC} . The three curves correspond to tip–sample separations of $z = 0, 100$, and 200 nm . When the tip is placed directly in the dipole plane ($z = 0$), the capacitive coupling is strongest and the force reaches the largest values. Increasing z progressively reduces the amplitude of F_ω , while the linear scaling with V_{AC} is preserved. The reduction of the slope with tip height arises because the capacitance gradients $\frac{dC_1}{dx}$ and $\frac{dC_2}{dx}$ decrease as the tip moves away from the electrodes, leading to a weaker lateral coupling. These results confirm that the sensitivity of lateral EFM is maximized at small tip–sample distances, where the capacitive interaction with the lateral field is strongest.

Figure 5.1(c) reports the simulated dependence of the lateral force amplitude F_ω on the applied DC bias V_{DC} , again with the tip fixed at $x = 25 \mu\text{m}$. The results show a clear linear trend, in agreement with Eq. (5.3), where the ω component is proportional to $(V_{\text{DC}} - V_s)V_{\text{AC}}$. The slope of the linear dependence is set by the capacitance gradients, and therefore decreases with increasing tip–sample distance. As a consequence, when the tip is lifted further from the surface the overall force amplitude is reduced, but the linear relation with V_{DC} remains unchanged. These simulations confirm that lateral EFM provides a direct readout of the local potential difference between the tip and the sample electrodes, with the sensitivity controlled by the strength of the capacitive coupling.

Figure 5.1(d) shows the simulated lateral force profile $F_\omega(x)$ as the AFM tip is scanned across the dipole axis. The electrodes are located at $x = 0$ and $x = 200 \mu\text{m}$ and biased at $\pm 10 \text{ V}$, while the tip position x is varied laterally at different heights z above the surface. The force profile exhibits a broad minimum in the central region ($x = L/2$), where the contributions from the two electrodes partially compensate each other. As the tip approaches one of the electrodes, the imbalance between the two capacitance gradients $\frac{dC_1}{dx}$ and $\frac{dC_2}{dx}$ increases, and the force amplitude grows rapidly.

The dependence on x is clearly non-linear: the capacitance gradients scale as

$$\frac{dC_i}{dx} \propto \frac{x - x_i}{[(x - x_i)^2 + z^2]^{3/2}}$$

so that the central region shows a relatively flat plateau around the minimum, while the curves steepen when the tip is close to the electrode edges. Increasing the vertical tip-sample separation z reduces the overall magnitude of the force and broadens the plateau, since the lateral field appears smoother when probed at larger distances.

These results demonstrate that the lateral EFM signal is directly linked to the spatial distribution of the dipole field: the central minimum reflects the partial cancellation of the two electrode contributions, while the steep rise near the electrodes originates from the strong local gradients of the capacitive coupling.

5.2.2 Extension to multiple-capacitance systems

The discussion so far has been focused on the case of two electrodes, which represent the minimal dipole configuration. In practice, however, the AFM tip never interacts with a single capacitance only. The apex, the cone, and even the cantilever body contribute to the total tip-sample coupling, and additional sample regions may also be at different potentials. For this reason, the lateral force in a realistic geometry must be regarded as the superposition of several independent capacitive interactions.

In the general case, the electrostatic energy of the tip-sample junction can be expressed as the sum of the contributions from all capacitive channels C_i , each interacting with a sample region at potential V_i :

$$U(t) = \frac{1}{2} \sum_i C_i(\mathbf{r}) (V_{\text{tip}}(t) - V_i)^2 \quad (5.4)$$

The corresponding lateral force is obtained by differentiating the total energy with respect to the lateral coordinate x , leading to

$$F_x(t) = \frac{1}{2} \sum_i \frac{\partial C_i}{\partial x} (V_{\text{tip}}(t) - V_i)^2 \quad (5.5)$$

This expression emphasizes that the measured force is simply the sum of all independent interactions between the tip and the underlying regions of the sample, each weighted by the lateral gradient of its capacitance.

By substituting the applied tip bias

$$V_{\text{tip}}(t) = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$$

into Eq. (5.5), each term in the summation generates three distinct frequency components. The total lateral force can thus be written as

$$F_x(t) = F_0 + \left[\sum_i \frac{\partial C_i}{\partial x} (V_{\text{DC}} - V_i) \right] V_{\text{AC}} \cos(\omega t) + \frac{1}{4} V_{\text{AC}}^2 \left[\sum_i \frac{\partial C_i}{\partial x} \right] \cos(2\omega t) \quad (5.6)$$

where F_0 collects all static (DC) contributions. The second term represents the fundamental component at the drive frequency ω , and the last term corresponds to the higher harmonic at 2ω . Equation (5.6) shows that the ω signal directly reflects the weighted sum of all potential differences $(V_{\text{DC}} - V_i)$ multiplied by the corresponding capacitance gradients, whereas the 2ω component depends only on the total capacitance gradient acting on the tip. Equation (5.6) confirms, as already noted for the dipole case, that the ω component cannot be suppressed by tuning V_{DC} , in contrast to conventional KPFM.

In practical AM-EFM operation, both vertical and lateral electric forces modulate the cantilever at the same drive frequency. This superposition makes it intrinsically difficult to decouple the two contributions. A more rigorous approach would be to employ frequency-modulated EFM, where the vertical and lateral force components couple selectively to the flexural and torsional resonances of the cantilever, thus separating the signals. However, side-band detection in FM-EFM is sensitive to the force gradient, which vanishes for the case of a constant electric field. For this reason, a quantitative calibration of the lateral response cannot be obtained with FM-EFM. In the following, we will show that, using dedicated samples and exploiting additional control strategies, it is still possible to suppress the vertical contribution and isolate the lateral signal.

5.3 Experimental implementation and calibration procedure

To establish a quantitative calibration of the lateral response, we exploit a well-defined reference system: the parallel-plate capacitor, where the applied potential and geometry provide a controlled and determined electric field distribution.

Figure 5.2(a) shows the experimental implementation of lateral EFM on a parallel-plate capacitor. A combined bias $V_{\text{tip}}(t) = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$ is applied to the AFM tip, which drives the cantilever both in vertical oscillation and in torsion at the excitation frequency $\omega = 17\text{kHz}$. The optical beam deflection system allows one to separate these two responses: the difference signal A–B of the four-quadrant photodiode provides the conventional vertical EFM channel, while the difference LFM (Lateral Force Microscopy, C–D) corresponds to the torsional deflection that defines the lateral EFM signal. In the parallel-plate capacitor geometry, and

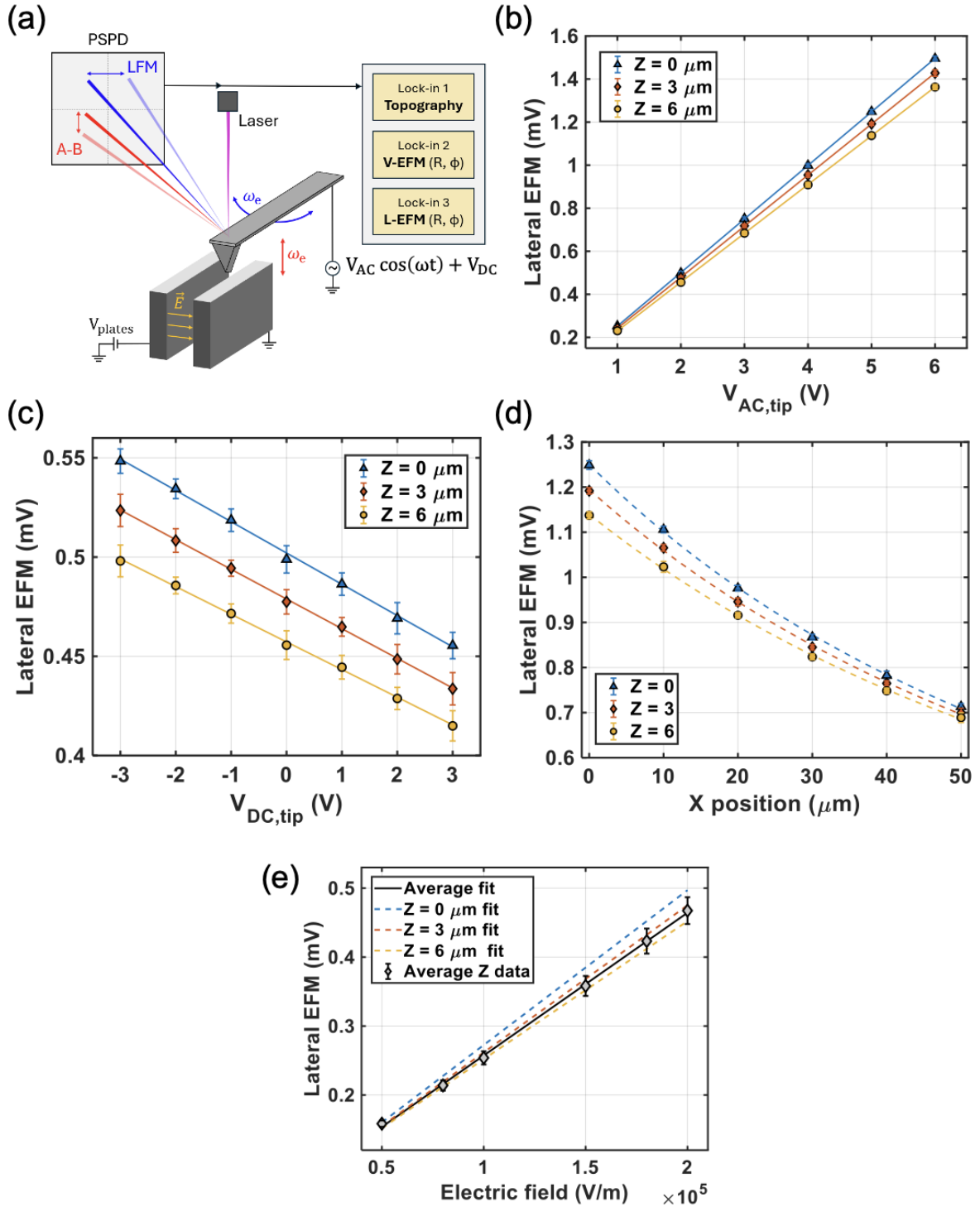


Figure 5.2: (a) Experimental scheme of the lateral EFM measurement. The torsional motion of the cantilever is detected with a position sensitive photodiode (PSPD) that separates the vertical (A-B) and lateral (LFM) signals. The tip potential is applied as $V_{\text{tip}} = V_{\text{DC}} + V_{\text{AC}} \cos(\omega t)$. (b) Lateral EFM signal as a function of V_{AC} for different tip-sample separations z . (c) Lateral EFM signal as a function of V_{DC} for the same z values. (d) Lateral EFM signal as a function of lateral tip position x across the capacitor gap. (e) Calibration curve of the lateral EFM signal as a function of the electric field, with fits obtained at different z and the global fit.

away from the fringing fields at the edges, the electric field between the electrodes is purely lateral, so the detected torsional response directly probes the lateral force component predicted by the model. The strength of the applied field can be tuned by varying the potential difference across the two plates, providing a controlled reference system to test the sensitivity and scaling of the lateral EFM signal.

Figure 5.2(b) shows the dependence of the lateral EFM signal on the applied AC bias. In these measurements the DC tip bias was set to $V_{DC} = 0$ and the capacitor plates were biased at ± 20 V, corresponding to a total potential difference of $\Delta V_{\text{plates}} = 40$ V. The detected amplitude increases linearly with V_{AC} , as predicted by the expression of the ω component of the force. Amplitude–distance spectroscopies recorded at different tip–sample separations show that the signal decreases in magnitude as the tip is retracted, while the linear dependence on V_{AC} remains unchanged. This reduction reflects the weaker capacitive coupling at larger z , which lowers the overall force without affecting its proportionality to the AC drive.

Figure 5.2(c) shows the dependence of the lateral EFM signal on the applied DC tip bias. In this case the AC drive was kept constant at $V_{AC} = 2$ V, while the capacitor plates were biased at ± 20 V ($\Delta V_{\text{plates}} = 40$ V). The detected amplitude scales linearly with V_{DC} , in agreement with the model where the ω component is proportional to $(V_{DC} - V_i)V_{AC}$. The slope of the curves decreases as the tip–sample distance z increases, reflecting the reduction of the capacitance gradients with vertical separation. Unlike in conventional KPFM, there is no value of V_{DC} that cancels the signal, since the response originates from the imbalance of the two capacitive couplings.

Figure 5.2(d) reports the lateral EFM signal as a function of the tip position across the capacitor gap, starting from ~ 30 μm away from the left electrode and extending up to the middle of the gap. In these measurements the tip bias was set to $V_{DC} = 0$ and $V_{AC} = 5$ V, while the plates were biased at ± 20 V ($\Delta V_{\text{plates}} = 40$ V). The profile shows a monotonic decrease of the signal when moving away from the electrode, eventually reaching a nearly constant value in the central region of the gap. The strong maximum expected directly at the electrode edge is not accessible here, since the lateral field was too strong and led to unstable tip–sample interaction. The observed behavior is nevertheless consistent with the simulated profiles, which predict an enhanced response at the electrode boundary followed by a gradual reduction toward a flat plateau in the middle of the capacitor. The experimental profiles are well reproduced by an empirical decay of the form

$$A(x) = A_{\infty} + \frac{A_0}{(x + x_0)^2}$$

which captures both the rapid variation close to the electrode and the gradual approach to a plateau in the middle of the gap. While this expression provides an excellent description of the

data, the fitted parameters A_0 and x_0 should be regarded as effective quantities, since their microscopic meaning is not straightforward and depends on several geometric and electrostatic factors (tip shape, tip-sample separation, finite plate size).

Finally, figure 5.2(e) reports the calibration curve that relates the lock-in amplitude of the torsional oscillation to the electric field inside the parallel-plate capacitor. The electric field values are not measured but calculated from the applied potential and the known electrode geometry, providing a controlled quantitative reference. To assess the role of the tip-sample separation, the calibration was repeated at three different heights z ; the corresponding fits are shown as colored curves, each describing the response at its specific distance. Although the absolute amplitude varies with z , the scaling is consistent across the set, which allows extracting a robust averaged calibration. The black line in panel (e) is this averaged fit and constitutes the conversion function used to map the raw lateral EFM lock-in signal into absolute values of the lateral electric field acting on the AFM tip.

For each dataset, we fit the linear relation

$$A_{\text{LI}}(E) = \alpha E + \beta$$

where A_{LI} is the measured lock-in amplitude (mV) and E is the electric field (V/m). The resulting slopes and intercepts at different tip-sample distances are very similar, demonstrating the reproducibility of the calibration procedure and indicating that the estimated electric field varies only marginally with z . The quantitative fit parameters are summarized in Table 5.1. In the following analyses we will use the global calibration (black line), with

$$\alpha_{\text{global}} = 2.071 \times 10^{-6} \text{ mV}/(\text{V/m}), \quad \beta_{\text{global}} = 0.05032 \text{ mV}$$

$Z \text{ (}\mu\text{m)}$	$\alpha \text{ [mV}/(\text{V/m})]$	$\beta \text{ [mV]}$
0.0	2.246×10^{-6}	0.04795
3.0	2.133×10^{-6}	0.04846
6.0	2.002×10^{-6}	0.05183
Global	2.071×10^{-6}	0.05032

Table 5.1: Linear calibration parameters α (slope) and β (intercept) linking the lock-in amplitude to the electric field.

In summary, the capacitor structure with a defined lateral field allowed us to calibrate the lateral EFM response in a quantitative way. Knowing the electrode geometry and the applied bias, we calculate the electric field in the gap and compare it with the measured torsional deflection of the cantilever. This procedure provides the conversion factor that links the raw

lateral-EFM signal to the actual electric field acting on the tip; the global parameters α_{global} and β_{global} above are used throughout the next section to analyze measurements on a real doped semiconductor sample.

5.4 Application to doped semiconductor junctions

In the following, we move from the ideal capacitor geometry to a doped semiconductor surface. To this end, we investigate an Infineon dopant calibration sample, which provides well-defined implantation profiles across a wide range of concentrations. By applying the calibration factor obtained in the previous section, we can now convert the lateral EFM signal into absolute electric field values and verify how the technique performs under realistic device conditions. This section therefore bridges the controlled calibration experiment with the analysis of patterned doped regions, allowing us to test the applicability of the model beyond simplified geometries.

The calibration sample consists of a p-type silicon substrate with a nominal background doping concentration of about $1 \times 10^{15} \text{ cm}^{-3}$, covered by a thin oxide layer of approximately 3 nm. On this substrate, a set of well-defined implant regions were fabricated, including both n-type (phosphorus) and p-type (boron) areas. The implanted regions span over ten different concentrations, ranging from 4×10^{15} up to $1 \times 10^{20} \text{ cm}^{-3}$, thereby covering more than four orders of magnitude in doping density. The sample layout is divided into different zones for complementary characterization: large rectangular fields for SIMS reference measurements, arrays of parallel implant stripes with widths down to $0.5 \mu\text{m}$ and pitch of $2.5 \mu\text{m}$, horizontal mesa structures crossing the implant lines, and cross-shaped junctions with alternating p- and n-type doping.

For the lateral EFM measurements we focused on the part of the calibration sample containing the $1 \mu\text{m}$ wide implant stripes. We placed the AFM tip at the boundary between the heavily doped $1 \times 10^{20} \text{ cm}^{-3}$ p-type and $1 \times 10^{20} \text{ cm}^{-3}$ n-type regions, where the lateral electric field is expected to be strongest. The imaging was performed directly on the implanted area, which is essentially flat and free of surface morphology. This was important to make sure that the torsional response originates purely from the lateral field and not from any mixing with topography or vertical signals. To avoid such cross-talk even further, we kept the KPFM feedback loop active during the scans. In this way the vertical component of the electrostatic force was continuously compensated, so that the measured deflection reflects only the lateral forces across the p-n junction. This setup provided clean experimental conditions to test our calibration on a real semiconductor structure with well-defined doping profiles.

Figure 5.3(a) shows the KPFM potential image of the $1 \mu\text{m}$ stripes at the interface between the $1 \times 10^{20} \text{ cm}^{-3}$ p- and n-type regions. According to standard CPD theory, two silicon

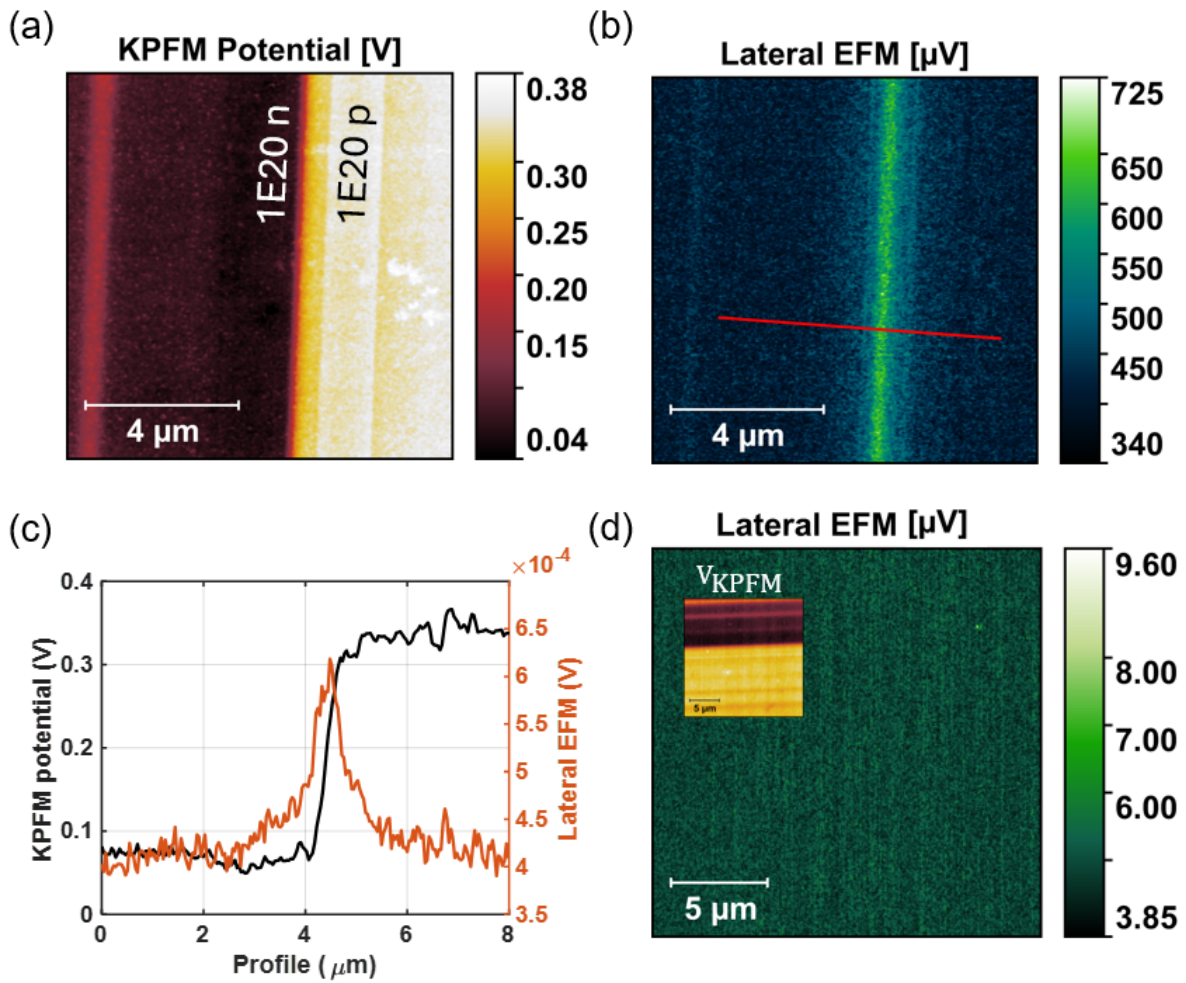


Figure 5.3: (a) KPFM potential map acquired across a highly doped n - p junction. (b) Lateral EFM map of the same region; the red line indicates the profile plotted in (c). (c) Line profile reporting the KPFM potential (black) and the lateral EFM signal (orange) across the junction. (d) Lateral EFM map acquired with the sample rotated by 90° with respect to panels (a-c); inset: corresponding KPFM potential map.

regions with opposite doping should exhibit a surface potential difference equal to the silicon band gap. In contrast, the measured contrast between the p- and n-type stripes is about 250 mV. This reduced value can be explained by the extremely high doping levels, which make the implanted regions degenerate and shift their Fermi levels deep into the bands, resulting in a metallic-like behavior. The pronounced potential step at the junction further indicates the presence of a strong internal electric field, consistent with the abrupt transition between highly doped regions. KPFM studies on doped III-V semiconductors confirm that variations in local surface potential are directly linked to doping concentration and space charge regions[166]. For these measurements, the KPFM feedback loop was operated with an AC bias of $2 V_{\text{rms}}$ applied to the tip, no DC offset, and a lock-in time constant of 1 ms, ensuring stable and reproducible signal acquisition.

Figure 5.3(b) shows the lateral EFM image acquired simultaneously with the KPFM measurement. The torsional signal is negligible across the uniformly doped p- and n-type stripes, while a sharp feature emerges at the p/n interface, i.e. where the lateral electric field is expected to be strongest. This correspondence is confirmed by the line profiles reported in Figure 5.3(c): the KPFM curve displays an abrupt potential step, and the lateral EFM signal exhibits a peak at the same position. The observed behavior reflects the electrostatic relation between potential and electric field,

$$E_x(x) = -\frac{dV_{\text{KPFM}}}{dx} \quad (5.7)$$

From the KPFM profile we determine a potential variation of $\Delta V_{\text{KPFM}} = 255$ mV across $1 \mu\text{m}$, which corresponds to a lateral electric field of (255 ± 13) V/mm. The peak amplitude of the lateral EFM signal, $A_{\text{LI}} = 0.60$ mV, converted through the global calibration, yields (265 ± 20) V/mm.

A direct comparison of the two independent determinations is reported in Table 5.2, showing an excellent agreement within the experimental uncertainty.

Method	Electric field [V/mm]
KPFM	255 ± 13
Lateral EFM	265 ± 20

Table 5.2: Comparison between electric fields extracted from KPFM and lateral EFM.

Figure 5.3(d) shows the lateral EFM signal acquired after rotating the sample by 90° . In this configuration, the in-plane electric field at the p/n junction is oriented perpendicular to the lateral oscillation direction of the cantilever. Under these conditions no electrostatic torque can be induced, and the lateral EFM response is completely suppressed. This control experiment is essential, as it demonstrates that the contrast observed in the previous figures arises only from

the lateral component of the electric field. The inset reports the corresponding KPFM potential image recorded on the same region. The potential step at the junction remains clearly visible, confirming the presence of the lateral field.

5.5 Probing in-plane fields on floating electrodes with lateral EFM

Measuring the surface potential with KPFM already provides full access to the electric field distribution, since the in-plane component can be obtained by taking the spatial derivative of the potential map. However, the use of KPFM feedback is not possible on insulating substrates or on floating metallic structures, where the compensation of the contact potential difference cannot be established. In such cases, lateral EFM offers a direct way to probe the in-plane electric field, providing information that would otherwise remain inaccessible with conventional vertical EFM. To demonstrate this capability, we designed an experiment on a gold interdigitated electrode sample that can be operated both in grounded and floating configurations. Figure 5.4(a) shows an optical microscope image of the sample, consisting of two interdigitated electrode sets deposited on a glass substrate. This geometry enables applying a lateral bias between adjacent fingers or, alternatively, isolating the structure from ground to simulate a floating condition. The following measurements demonstrate that lateral EFM reliably detects the lateral field even when KPFM feedback is not active.

Figure 5.4(b) shows the AFM topography of the gold interdigitated electrode structure fabricated on a glass substrate. The device consists of two independent electrode circuits that can be selectively biased, with a lateral spacing of $3.5\ \mu\text{m}$ between adjacent fingers.

In the lateral EFM measurement, the two electrode sets were biased to establish a potential difference of $\Delta V_{\text{fingers}} = 6\ \text{V}$ between adjacent fingers. The resulting torsional response is reported in Figure 5.4(c). A clear lateral signal is detected within the electrode gaps, while the response vanishes on the metallic regions. The intensity of the torsional oscillation follows the expected distribution of the lateral electric field.

The quantitative comparison between KPFM and lateral EFM is shown in Figure 5.4(d). The line profiles of potential and torsional amplitude were extracted across the center of the gap. Within the $3.5\ \mu\text{m}$ spacing, the lateral EFM amplitude sharply rises near the electrode edges and reaches a plateau in the middle of the gap, consistent with the field distribution between parallel biased electrodes. From the slope of the KPFM potential, an average lateral field of $E_{\text{KPFM}} = (171 \pm 4)\ \text{V/mm}$ is obtained. Applying the previous calibration to the torsional amplitude yields a consistent value of $E_{\text{lat-EFM}} = (169 \pm 6)\ \text{V/mm}$. The close agreement between these two independent measurements confirms that lateral EFM provides a correct

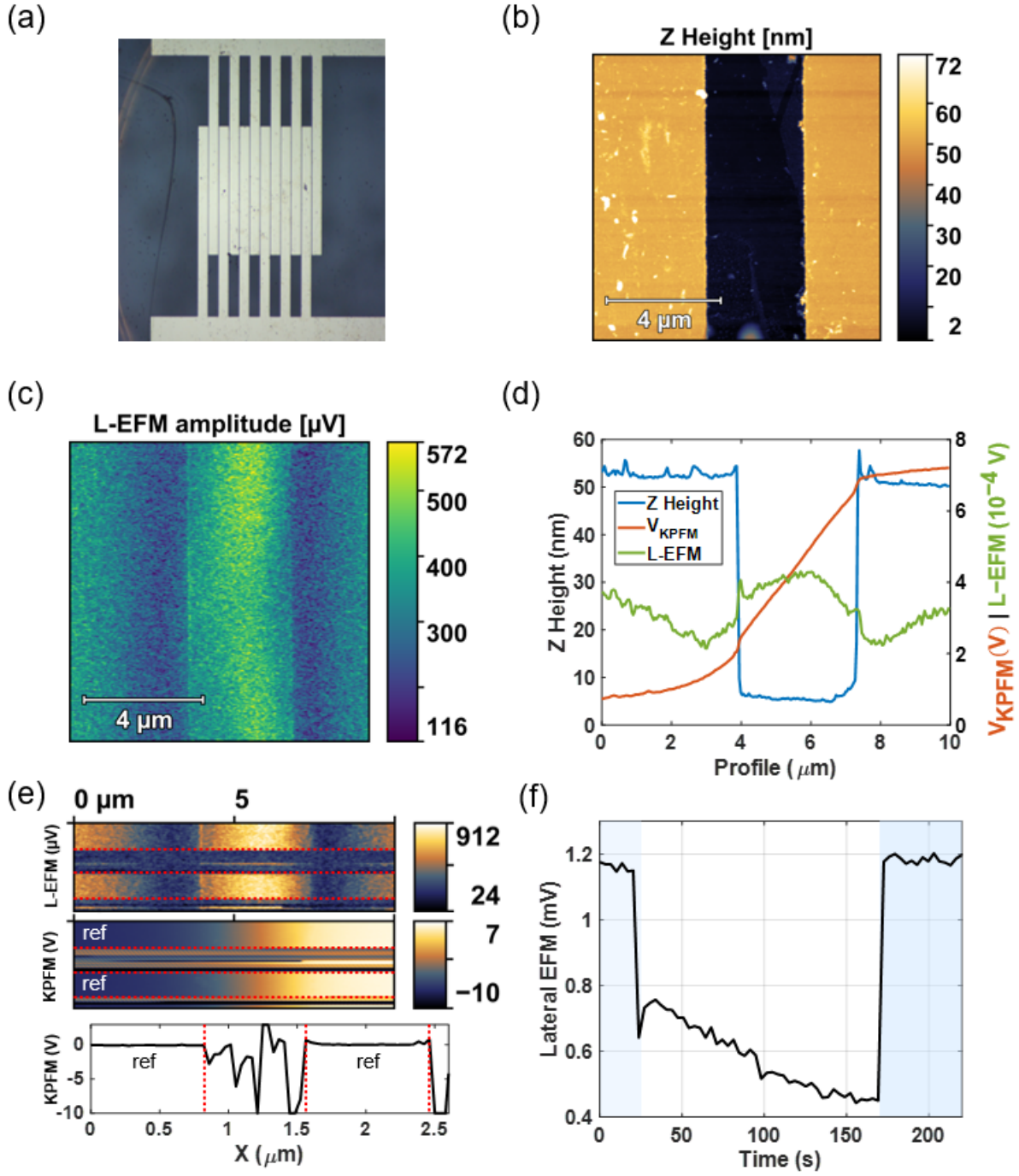


Figure 5.4: Lateral EFM on gold interdigitated electrodes. (a) Optical image of the structure on glass. (b) AFM topography of one electrode gap. (c) Lateral EFM amplitude map under $\Delta V = 6$ V bias. (d) Line profiles of height, KPFM potential, and L-EFM amplitude across the 3.5 μm spacing. (e) Comparison between grounded and floating configurations: (top) L-EFM signal, (center) KPFM potential, and (bottom) potential profile; red lines mark connection transitions and ref indicates stable reference regions. (f) Time evolution of L-EFM amplitude with KPFM feedback disabled, showing signal decay and recovery upon reconnection.

and quantitative measure of the in-plane electric field in this geometry.

Figure 5.4(e) summarizes the measurements performed on the interdigitated device operated in alternating grounded and floating configurations. The top panel reports the lateral EFM response when the two electrodes are connected with a potential difference $\Delta V_{\text{fingers}} = 12V$. A clear torsional contrast appears across the $3.5 \mu\text{m}$ gap, consistent with the presence of a strong in-plane electric field between adjacent fingers. When the electrodes are disconnected from the external circuit and the structure is left floating, the L-EFM signal apparently collapses. The red dashed lines indicate the time intervals in which the sample is connected or disconnected from ground, while the label *ref* marks the regions where the system is referenced and the signals are reliable. The apparent suppression of the lateral response does not correspond to the physical disappearance of the field: under floating conditions the KPFM feedback continues to operate without a defined reference potential, inducing spurious oscillations of the cantilever and cross-talk between the vertical and lateral detection channels. As a result, the measured L-EFM amplitude in the floating interval cannot be considered representative of the actual in-plane field.

The center panel of Figure 5.4(e) shows the corresponding KPFM potential maps recorded under the same sequence. When the electrodes are referenced (*ref* regions), the potential drop across the gap reproduces the applied bias with a stable difference of about 12 V. In the floating interval, the lack of a fixed reference makes the KPFM feedback unstable, resulting in random potential oscillations and loss of spatial contrast.

The bottom panel reports the potential profile extracted along the center of the gap. The red vertical markers again delimit the connection and disconnection phases, while the *ref* labels identify the portions of the scan acquired with a stable reference. During the floating segment, the measured potential fluctuates unpredictably and its slope loses physical meaning; once the electrodes are reconnected, the expected potential drop is immediately recovered. This sequence confirms that the KPFM feedback, when operating without reference, generates artefacts that affect both potential and torsional signals. In the following measurements, the feedback is therefore disabled to directly probe the in-plane field under true floating conditions.

Figure 5.4(f) shows the time evolution of the lateral EFM amplitude when the KPFM feedback is disabled and the sample is operated in floating configuration. In this condition, the tip potential is fixed and the cantilever response directly reflects the in-plane electrostatic field between the gold electrodes. The measurement starts with the device connected to ground, where the lateral signal reaches its maximum amplitude. As soon as the electrodes are disconnected, the signal exhibits a sharp drop, indicating the rapid discharge of the biased structure through residual leakage paths and surface conduction on the glass substrate. During the floating interval, the lateral EFM amplitude remains nearly constant at a lower value, showing

that a weak residual field persists due to slow redistribution of surface charges. When the electrodes are reconnected, the initial signal is immediately recovered.

This experiment demonstrates that, also when the KPFM feedback is disabled, lateral EFM can reliably measure the in-plane electric field even under floating conditions. The transient response observed upon disconnection and reconnection reflects the charge dissipation dynamics of an isolated metallic structure on an insulating substrate. Altogether, these results confirm that lateral EFM provides a robust and quantitative method to probe lateral fields in systems where conventional KPFM operation fails.

5.6 Uncertainty analysis and systematic effects

The quantitative accuracy of the lateral EFM calibration is ultimately limited by a combination of experimental uncertainties and systematic effects related to the cantilever mechanics and sample geometry. Among the dominant contributions is the uncertainty on the torsional spring constant of the cantilever, which directly affects the conversion between the measured lock-in amplitude and the applied lateral force. Manufacturer specifications typically report variations of the torsional constant on the order of 20–30%, which translates into a comparable uncertainty on the absolute electric field values. In the present work this contribution is partially mitigated by the empirical calibration against a reference capacitor, which effectively absorbs the cantilever-dependent prefactor into the slope α of the calibration curve.

A second relevant source of systematic error is related to deviations from ideal parallelism between the cantilever axis and the capacitor plates. A residual tilt angle introduces a mixing between vertical and lateral force components, leading to a systematic offset in the measured torsional response. Based on the optical alignment accuracy of the AFM setup and on the flatness of the reference capacitor, this contribution is estimated to remain below 5% and does not affect the linear scaling of the lateral signal with the applied electric field.

Additional uncertainties arise from the definition of the effective tip–sample distance z and from the finite lateral extension of the capacitor plates. While these factors influence the absolute magnitude of the capacitive gradients, their effect is inherently included in the distance-dependent calibration curves reported in Fig. 5.2(e). The consistency of the fitted slopes obtained at different z values indicates that geometrical uncertainties do not introduce significant systematic distortions in the extracted electric field.

Overall, the agreement between lateral EFM and independent electric field estimates obtained from KPFM differentiation, within the combined experimental uncertainty, confirms that the dominant sources of error are well controlled. Under the present experimental conditions, the absolute accuracy of the calibrated lateral EFM measurements is estimated to be

within 10–15%.

5.7 Conclusions

In this chapter we developed and validated a new methodology for the quantitative mapping of in-plane electric fields using lateral EFM. We first introduced the principle of the technique and established a calibration protocol based on well-defined capacitor structures, where the electric field distribution can be calculated analytically. This allowed us to correlate the torsional response of the cantilever with absolute field values, providing the basis for quantitative measurements.

We then applied this calibration to more complex device geometries. Measurements on interdigitated electrodes showed that the lateral EFM signal reproduces the expected field distribution, with good agreement between the torsional response and the derivative of the KPFM potential maps. Quantitative comparison confirmed the accuracy of the calibration beyond the ideal capacitor structure. Finally, by disconnecting the electrodes and operating the system in floating configuration, we demonstrated that lateral EFM continues to provide a reliable measure of the in-plane electric field under conditions where KPFM feedback cannot operate. The observed charging and discharging dynamics further confirmed the sensitivity of the technique to transient electrostatic phenomena.

Taken together, these results establish lateral EFM as a robust tool for probing in-plane fields in device structures, including situations that are inaccessible to conventional KPFM. Future improvements could focus on refining the calibration procedure by extending it to different cantilever geometries and oscillation modes, as well as on enhancing the spatial resolution by optimizing the detection of the torsional response. Moreover, the combination of lateral EFM with time-resolved or frequency-modulated schemes may allow access to dynamic processes and field gradients with higher sensitivity.

Overall, this chapter demonstrates that lateral EFM extends the scope of scanning probe techniques towards the quantitative and versatile study of lateral fields in semiconductors, insulators, and complex device architectures.

6 Conclusions

In this thesis I addressed the study of electronic processes in disordered semiconductors, focusing on both amorphous oxides and organic materials. The work was motivated by the need to understand how microscopic disorder affects charge transport and device stability, and how advanced scanning probe techniques can be used not only for imaging but also for the quantitative extraction of key material parameters. By combining concepts from semiconductor physics with tailored experimental approaches, the thesis aimed to provide new insights into the link between local electronic states and macroscopic device functionality.

The thesis was organized in three main parts. The first part focused on amorphous oxide semiconductors, where an analytical model for Kelvin Probe Force Microscopy was developed and applied to IGZO thin-film transistors, enabling the quantitative extraction of band-tail parameters and clarifying their role in device stability. The second part was devoted to organic semiconductors, using photovoltage and photocurrent microscopies to investigate how carrier diffusion and recombination set the intrinsic limits of spatial resolution in optobioelectronic interfaces. The third part introduced and validated lateral Electrostatic Force Microscopy, establishing its calibration on model capacitor structures and applying it to interdigitated electrodes, with the aim of quantifying in-plane electric fields and potentials in thin-film devices.

In the first part of the thesis, I addressed the case of amorphous oxide semiconductors, focusing on indium–gallium–zinc oxide (IGZO) thin-film transistors. By developing an analytical solution of the Poisson equation for finite-thickness MIS structures, I demonstrated that Kelvin Probe Force Microscopy spectroscopy can be turned into a quantitative tool for extracting density-of-states parameters at the local scale. The method provided values for the conduction band-tail width of $E_t = (44.4 \pm 0.1) \text{ meV}$ and a doping density of $N_D = (1.4 \pm 0.6) \times 10^{12} \text{ cm}^{-3}$, in excellent agreement with photocurrent spectroscopy. The same methodology was then applied to analyze device stability under ionizing radiation: the measurements revealed that threshold voltage shifts of about $\Delta V_{\text{th}} = -1.1 \text{ V}$ originate from static charge accumulation in the gate dielectric, while the density-of-states parameters of the semiconductor remain unaffected. This demonstrates how local probe techniques can provide direct insight into the microscopic origin of macroscopic instabilities in amorphous thin-film

devices.

In the second part of the thesis, I focused on organic semiconductors and their application in optically driven bioelectronic interfaces. Using photovoltage and photocurrent microscopies, I investigated how carrier diffusion and recombination govern the spatial resolution of optoelectronic transduction. Experiments on planar H₂Pc/PTCDI heterojunctions revealed that the effective diffusion length of photogenerated carriers is $\lambda_d = (1.5 \pm 0.1) \mu\text{m}$ in the bare junction and increases to $\lambda_d = (7.0 \pm 0.3) \mu\text{m}$ when the structure is coated with PEDOT:PSS. This improvement in charge generation efficiency comes at the expense of reduced spatial confinement, as the higher carrier lifetime and mobility enhance lateral spreading. Photoelectrochemical current microscopy in aqueous electrolyte confirmed that the excitation remains localized at the micrometer scale, with a gaussian profile of $\sigma_e = (6.5 \pm 0.9) \mu\text{m}$, comparable to the size of individual cells. These results demonstrate that organic heterojunctions can sustain optical stimulation with single-cell resolution, while highlighting the trade-off between efficiency and spatial precision introduced by transport properties.

In the third part, I developed and validated Lateral Electrostatic Force Microscopy (L-EFM), a new approach to quantify in-plane electric fields in thin-film devices. Starting from a multi-capacitor description of the tip-sample interaction, I derived a model linking the first-harmonic lateral force to the local potential difference along the surface, establishing the quantitative basis of the technique. Experiments on planar capacitor structures confirmed the predicted dependence on bias and lift height, demonstrating accurate field calibration. When applied to interdigitated electrodes and semiconductor thin films, L-EFM resolved lateral potential gradients and distortions inaccessible to conventional EFM, providing a direct means to map local electric fields and assess charge redistribution in complex device geometries.

An important aspect underlying all the results presented in this thesis concerns the reproducibility and interpretation of quantitative data obtained with local probe techniques. At the instrumental level, the measurements reported here show a high degree of repeatability: repeated acquisitions performed on the same structure under identical experimental conditions yield consistent signal amplitudes, spatial profiles, and extracted parameters. This applies both to Kelvin Probe Force Microscopy spectroscopy and to lateral Electrostatic Force Microscopy, once the corresponding calibration procedures are established. These observations confirm that the experimental methodologies employed in this work provide stable and internally consistent results at the single-device level.

Variations observed between nominally identical samples, or between different regions of the same sample, are instead primarily associated with intrinsic material inhomogeneities and fabrication-related variability. Local differences in doping concentration, defect density, interface quality, electrode morphology, or surface charging directly affect the electronic landscape and therefore the measured electrostatic or transport-related quantities. Since scanning probe

techniques access local physical observables rather than spatially averaged properties, such variations are faithfully captured by the measurements and should be regarded as physically meaningful rather than as a lack of experimental reproducibility.

Within this framework, the results presented throughout the thesis demonstrate that local probe techniques offer reproducible access to quantitative electronic parameters while simultaneously revealing genuine device-to-device and spatial variability. This dual capability represents a strength rather than a limitation, as it enables the identification of non-idealities and microscopic processes that are often hidden in macroscopic characterization approaches.

Taken together, the three parts of this thesis provide a unified view of how microscopic disorder and interfacial processes shape the electronic behavior of amorphous and organic semiconductors. By combining advanced scanning probe methods with analytical modeling, the work demonstrates how local measurements can be turned into quantitative probes of material parameters and device operation. Beyond the specific systems investigated, including IGZO thin films, molecular heterojunctions and planar capacitors, the approaches developed here establish general strategies for correlating nanoscale electrostatics with macroscopic functionality. The results highlight the importance of integrating local and global perspectives to understand transport, stability and photoresponse in emerging semiconductor technologies. The methods introduced, in particular quantitative KPFM and L-EFM, open new routes for the microscopic diagnosis of electronic processes in disordered materials, paving the way toward more stable, efficient and predictable thin-film devices.

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