SCANNING OPTICAL IMAGING AND STRESS TESTS OF POLYMER LIGHT-EMITTING ELECTROCHEMICAL CELLS

by

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Abstract

Polymer light-emitting electrochemical cells (PLECs) were tested by means of bias stress, luminescent imaging and optical scanning probing. These cells were characterized in terms of the effect of doping on the operational lifetime of the cells, the electronic structure of the p-n junctions formed in the cells and the average doping levels in the cells.

The lifetime performance of sandwich cells was compared in operation with intermediate storage time and in continuous operation. The cells that were stressed intermittently were more prone to black spots degradation than the cells in continuous operation when the total stress time was the same. However, the black spots vanished in the cells’ idle time, which shows that these spots are local highly doped regions. The appearance of the black spots was strongly associated with the storage of the cell in the presence of the aluminum cathode.

The doping in planar PLECs was investigated by optical beam induced current (OBIC) and photoluminescence (PL) scanning using a focused laser beam. Both p-n and p-i-n PLEC junctions were identified and the junction widths were extracted. The widths were as small as 0.21% of the cell size being the smallest width identified for PLECs and light-emitting electrochemical cells (LECs), in general. Exposing the cells to relaxation (de-doping) cycles resulted in shrinkage in the depletion region width, contrary to what is expected. This suggests the presence of submicron structures in the as-activated cells that disappeared after relaxation. In addition, it was observed that relaxation caused a p-i-n junction to emerge from the as-activated p-n junction. The junction doping level was extracted from the OBIC data and was validated via drift diffusion calculations.

The calculations showed PLEC doping levels in the range of $10^{14}$ cm$^{-3}$ – $10^{15}$ cm$^{-3}$ in the junction region.

The average doping level in planar PLECs was measured by stress-discharge tests. The measurement offered validation for the used method to estimate PLEC doping levels by integrating
the activation charge up to the junction formation. The measurement revealed average doping levels of $10^{19}$ cm$^{-3} - 10^{20}$ cm$^{-3}$, which is much higher than doping levels determined for the junction.
Organization of the Dissertation

This dissertation discusses measurements and modelling for PLECs to probe doping related characteristics in these devices. The dissertation is organized as follows: Chapter 1 provides background information important to understand PLEC operation and characteristics; Chapter 2 presents a luminance lifetime study that emphasizes the effect of doping on light emission in sandwich PLECs; and in Chapter 3 OBIC and PL scanning is used to probe the doping profile of frozen planar PLEC homojunctions. A numerical study to extract the actual doping levels in these devices is presented in Chapter 4. Finally, Chapter 5 discusses the average doping levels in planar PLECs by discharge measurements.
Authorship

The content in Chapter 2 to Chapter 5 presents studies that were published in five journal articles:


The text in Chapter 2 and Chapter 5 is the same as in reference (1) and reference (5), respectively with a few changes that were made to maintain the consistency of presentation in this dissertation. Chapter 3 was written based on the results presented in references (2) and (3) while Chapter 4 is based on reference (4). However, the text and the presentation were modified and merged compared to the original references to serve the coherence and clarity of the correlated studies presented in these chapters. All of the necessary permissions for reusing and reprinting the text and illustrations presented in this dissertation were obtained from the publishers.

The experimental work presented in Chapter 2 (reference (1)), was carried out collaboratively by the author of this dissertation, Faleh AlTal, and the research supervisor, Prof. Jun Gao. The experiments and numerical calculations presented in Chapter 3 (references (2) and (3)), Chapter 4 (reference (4)) and Chapter 5 (reference (5)) were implemented by Faleh AlTal. The articles (1)-(5) were collaboratively written by Faleh AlTal and Prof. Jun Gao.
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Finally, I would like to thank the Governments of Ontario and Canada for their great efforts in sponsoring researchers to make contributions to scientific advancement. The government’s financial support through the Ontario Trillium Scholarship and Natural Sciences and Engineering Research Council (NSERC) made this work possible.
Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author. Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

(Faleh AlTal)

(April, 2017)
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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>BHoJ</td>
<td>Bulk HomoJunction</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DUT</td>
<td>Device Under Test</td>
</tr>
<tr>
<td>EBIC</td>
<td>Electron Beam Induced Current</td>
</tr>
<tr>
<td>EHP</td>
<td>Electron-Hole Pair</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>Isc</td>
<td>Short Circuit Current</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>KTF</td>
<td>Potassium Triflate</td>
</tr>
<tr>
<td>LEC</td>
<td>Light-emitting Electrochemical Cell</td>
</tr>
<tr>
<td>LiTf</td>
<td>Lithium Trifluoromethanesulfonate/Triflate</td>
</tr>
<tr>
<td>LPF</td>
<td>Low Pass Filter</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene]</td>
</tr>
<tr>
<td>MSM</td>
<td>Metal-Semiconductor-Metal</td>
</tr>
<tr>
<td>OBIC</td>
<td>Optical Beam Induced Current</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light-emitting Diode</td>
</tr>
<tr>
<td>OW</td>
<td>Optical Window</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly[Ethylene Oxide]</td>
</tr>
<tr>
<td>PFET</td>
<td>Polymer Field Effect Transistors</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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<tr>
<td>PLEC</td>
<td>Polymer Light-emitting Electrochemical Cells</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer Light-emitting Diode</td>
</tr>
<tr>
<td>PLF</td>
<td>Photoluminescence Filter</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>SCR</td>
<td>Space-Charge Region</td>
</tr>
<tr>
<td>SMF</td>
<td>Single Mode Fiber</td>
</tr>
<tr>
<td>VIL</td>
<td>Volt-Current-Luminance</td>
</tr>
<tr>
<td>Voc</td>
<td>Open Circuit Voltage</td>
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Chapter 1

**General Introduction: Conjugated Polymers - Characteristics and Devices**

Despite the ubiquity of conventional semiconductor materials and devices, organic semiconductors have emerged as a low-cost alternative due to their many attractive characteristics such as compatibility with solution processing, mechanical flexibility and chemical tunability.[1] Among functional devices based on organic semiconductors, small-molecule organic light-emitting diodes (OLEDs) have found the greatest commercial success with applications in high performance flat-panel displays and lighting panels.[2]–[8] An OLED is a thin-film device where the active layer or layers are sandwiched between two metal electrodes.[7]–[13] Upon applying a voltage bias above the threshold voltage to the electrodes, electrons and holes are injected into the active layer where they recombine radiatively and emit light. OLEDs typically employ pristine organic semiconductors. Sometimes the emitting layer of an OLED is a host/guest mixture designed to effectively transfer the excitation energy or injected charges to the emitting guest molecules.[14], [15] OLEDs, however, are not chemically doped as in a conventional semiconductor and typically do not contain a homojunction such as a p-n junction. In order to minimize the resistivity of the overall device and to improve charge injection, OLEDs consist of stacks of ultrathin (on the order of nm) organic layers. Currently, commercial OLED devices are not yet solution processed.[16], [17] The active layer stacks are formed by expensive vacuum deposition techniques using multiple shadow masks.

Conjugated polymers are organic semiconducting materials that are able to emit and absorb light similar to small molecules. However, the solubility of polymers in liquid solvents gives the advantage of easy processing such as inkjet or roll to roll printing.[17]–[19] Moreover, the polymer films can be deposited on a plastic substrate for flexible devices applications.[20] These advantages
attract interest in studying and developing polymer based materials and devices. This chapter will give basic background information about this topic.

1.1 Semiconducting Conjugated Polymers

Polymers are materials composed of a large number of identical repeat units, or monomers. The polymers of interest in this text are linear chains of organic monomers. [21] The basic element in any organic molecule is carbon, which is characterized by four valance electrons. Within a single polymer chain, the carbon atoms are strongly attached with covalent bonds. On the other hand, the different polymer chains are held together with weak van der Waals forces. Therefore, these organic solids are flexible, soft and have low melting temperatures.

Polymers are classified into two types, based on the hybridization of the carbon valance orbitals. The first is known as the saturated polymers, in this type, carbon atoms have sp\(^3\) hybridization. All the valance atoms are incorporated in covalent bonds (σ-bonds). This category of polymers is electrically insulating and used for many applications in the plastics industry. The other category is the conjugated polymers in which carbon atoms have sp\(^2\) hybridization and only three σ-bonds are formed. The remaining valance electron resides independently in a p\(_z\) orbital that forms π bonds orthogonal to the sp\(^2\) plane (Figure 1.1).

![Figure 1.1 Binding structure of ethylene where emphasized: (a) three sp\(^2\) orbitals on each carbon atom form σ bonds, and (b) the remaining p\(_z\) electron is incorporated in a π bond.][22]
This free electron is the key feature that gives conjugated polymers their interesting semiconducting characteristics. Conjugated polymers can exhibit metallic conductivity when chemically doped [23], [24]. This has attracted great attention.[25] A first order tight binding solution of a conjugated polymer Hamiltonian shows that the π orbitals of the carbon atoms form π-bands in the long polymer chain. At this approximation level, the π-electrons overlap and uniformly delocalize throughout the polymer chain. The number of the π-bands equals the number of carbon atoms in the polymer unit cell.

Polyacetylene (CH)$_x$ is the simplest and first conjugated polymer that has been studied electronically. Figure 1.2 shows the chain structure of this polymer based on the previously mentioned tight binding model. Each carbon atom contributes one electron to the π-band. Hence the band is half filled, and has an energy level in between the filled bonding σ-band and the empty anti-bonding σ*-band. Based on this model, it is expected that pure polyacetylene acts as a metal. However, experiments suggested that stable forms of polyacetylene are insulators.

![Figure 1.2 Chain and band structure for uniform polyacetylene. The carbon $p_z$ electrons are delocalized along the chain and form a half filled π band. (Adapted from [21])](image)

The instability of uniform polyacetylene can be explained based on Peierl’s principle.[26] It suggests that the energy of a one dimensional system with partially filled electrons can be lowered by dimerization. Su, Schrieffer, and Heeger incorporated lattice vibrations in the formulation of
polyacetylene Hamiltonian (SSH-Hamiltonian).[27] Based on the solution of the updated Hamiltonian, it was found that the delocalized π-electrons do not spread evenly throughout the polymer chain. Instead, these delocalized electrons spread with periodic densities. The result is alternating bond length in the unit cells and the half-filled π-band splits into a filled π-sub-band and an empty π*-sub-band (Figure 1.3). Since the highest energy π-band is full, stable forms of polyacetylene act as insulators. For conjugated polymers, the gap between the π and π* sub-bands range between 0.36 eV to 4.0 eV.[28], [29] Hence, these materials are actually semiconductors.

Electron transitions between the π the π* sub-bands associated with light emission and absorption is important for lighting and photovoltaic (PV) applications. The band gap of semiconducting polymers can be modified by introducing and modifying the side chains of the polymer. Luminescent polymers were realized with emission and absorption spectrum profiles that cover the visible region (Figure 1.4).[21], [30], [31] Moreover the conductivity of the polymers can be tuned by doping, which is also important for developing electronics structures and devices.[32] The concepts of doping and doped semiconducting polymers are discussed in the following sections.

Figure 1.3 Dimerized polyacetylene bonding structure and its corresponding band structure. The alternating π bonds lengths result in π-band splitting into a filled π sub-band and an empty π* sub-band. (Adapted from [21])
Figure 1.4 Luminance and absorption spectrum for a series of semiconducting polymers that cover the visible region.[21]
1.2 Doping in Conventional Semiconductors

The energy band gap in semiconductors is in the range of 1eV to 4 eV; much smaller than that of insulators.[33] Since semiconductors have relatively small band gaps, the charge carriers’ densities are highly dependent on temperature. Electrons can be thermally excited from the valance band to the conduction band and generate free charge carriers. However, the concentration of the thermally generated free carriers in a pure semiconductor is much smaller than the typical values for conductors. Hence, the conductivity of this type of material falls in a region between insulators and conductors.

A very effective way to increase the free charge carriers’ concentration in a semiconductor is by introducing impurities (or dopants). There are two types of doping, categorized based on the type of the free carriers introduced. Excess electrons are introduced with what is called n-doping while excess holes are introduced with p-doping. For example, silicon is a group-IV element with the diamond crystal structure (Figure 1.5). Group V atoms, like phosphorus and arsenic, are n-type dopants or donors. When a donor atom replaces a silicon atom in the crystal lattice, it forms four covalent bonds with four neighboring silicon atoms. The extra valance electron is only loosely bound to the positive ion core and easily excited to become a free electron.

![Figure 1.5 Doping in silicon lattice](image)

Figure 1.5 Doping in silicon lattice where n-doping is realized by replacing one silicon atom by a fifth group atom like phosphorus while p-doping is realized by replacing one silicon atom by a third group atom like boron.[34]
Atoms of group-III elements such as boron are used to p-dope silicon and called acceptors. When a boron atom replaces a silicon atom, an empty state (a hole) is created since boron only has three valence electrons to form covalent bonds with silicon.

In an energy band diagram of a semiconductor, the energies of dopants are represented by discrete impurity levels at low doping concentrations. The donor levels ($E_D$) are below the bottom of the conduction band edge and the acceptor levels ($E_A$) are above to the top of the valence band edge, as shown in Figure 1.6. The energy differences between the impurity levels and the respective band edges are called ionization energies. For “shallow donors” such as phosphorus and arsenic and “shallow acceptors” such as boron, the ionization energies are on the order of thermal energy ($k_B T$). Hence, shallow donors or acceptors easily lose their weakly bound electrons or holes to the conduction band and valence band, respectively. The free charge carrier concentration can increase by a million fold with only 1 ppm of impurity atoms introduced.

Figure 1.6 Energy diagram of a doped lattice showing the valance band edge and the conduction band edge of the host, as well as the energy levels of (a) donors, and (b) acceptors.[35]

1.3 Doping in Conjugated Polymers

In contrast to conventional semiconductors, discussed in the previous section, doping of conjugated polymers involves oxidation or reduction for the $\pi$ sub-band electrons without alternating the atomic components of the polymer chain. Oxidation leads to p-doping while reduction leads to n-doping. These electrons are a main factor in determining the polymer chain structure. Hence,
manipulating the π-electrons distorts the chain structure and leads to chain deformation. There are three types of possible deformations that happen to the polymer chain upon doping, leading to three types of quasi particles: solitons, polarons and bipolarons. These quasi particles can be understood by revisiting the chemical and band structure of polyacetylene.

The chemical structure of polyacetylene in Figure 1.3 suggests that there are two equivalent ways to alternate the bond length along the polymer chain. The resultant structures in both cases are identical and indistinguishable. Consequently, they have the same energy and polyacetylene has doubly degenerate ground states. When polyacetylene is doped, a defect is inserted into its structure. This defect takes the form of an interruption in such a way that the bonding alteration changes around the “kink”. These types of defects are called solitons [27], [36] and symbolized by the blue dot on the polyacetylene chain in Figure 1.7. As shown in the figure, each carbon atom in the non-interrupted segments shares three electrons in σ bonds and one in a π bond. At the kink site, the carbon atom has three σ bonds but no π bond. The fourth p_z state is localized at the interruption location.

In general, solitons take the width that minimizes the soliton energy which is about 14 unit cells in polyacetylene. The modified potential, due to the presence of the kink, results in mid-gap energy states (Figure 1.7). The presence of these mid-gap states were experimentally confirmed by measuring absorption bands at a frequency corresponding to half of the band gap energy.[37] The charge and spin of the soliton is determined by the occupation of these mid-gap energy states as clarified in Figure 1.7. Unlike polyacetylene, most polymers have non-degenerate ground states. In this type of polymer a single soliton is not stable. The soliton defect will be driven to the high energy part to minimize the energy of the polymer chain. Hence, a single soliton in such a system is not stable.
Figure 1.7 Solitons in polyacetylene chains and its energy diagram at the kink site. The distortion results from breaking a π bond at the site and alteration of the π bonding scheme. The localized energy state of the soliton resides at a mid-gap level between the π and the π* bands. The charge and spin of the soliton depends on the occupation of the state as illustrated. q is the soliton charge, e is the elementary charge and s is the spin. (Adapted from [21])

In non-degenerate ground state polymers, the stable form of defects only occurs as charged distortions. There are two types of charged distortions that can occur in polymers with degenerate ground states. The first is called polarons which is formed by a neutral and a charged solitons confining the higher energy phase of the polymer. In this platform, the solitons experience strong interaction. Therefore, the soliton mid-gap states split symmetrically into upper and lower states. Hence, there are two possible forms of polarons, as shown in Figure 1.8:

- Negatively charged polarons formed by two energy states occupied with three electrons,
- Positively charged polarons formed by two energy states occupied by a single electron.

Both of these types have a charge of magnitude e and, since they have an odd number of electrons, they have a spin of one half. The other type of non-degenerate ground state polymer distortions is
called bipolarons. They are similar to polarons but are formed by two same-charge solitons instead of the charged-neutral combination. Hence, bipolarons have a charge of two and spin of zero and, based on the polarity of the charge, they can be classified into:

- Positive bipolarons formed by two empty energy states.
- Negative bipolarons formed by two energy states fully occupied by four electrons.

![Schematic diagram of structure and energy of polarons in non-degenerate ground state polymers](image)

Figure 1.8 Schematic diagrams of structure and energy of polarons in non-degenerate ground state polymers. A charged and a neutral solitons confine the higher energy segment of the polymer chain. The soliton mid-gap states split symmetrically into upper and lower states. The charge and spin of the polaron depends on the occupation of these states as illustrated, where $q$ is the polaron charge, $e$ is the elementary charge and $s$ is the spin. (Adapted from [21])

Doping can be introduced to semiconducting polymers by four mechanisms: interfacial, photo-induced, chemical and electrochemical. [32] Figure 1.9 shows the different applications of these
doping types. Photo-induced and interfacial doping involve charge modification for the polymer chain without introducing redox agents. For instance, interfacial doping happens as a result of charge injection at a metal-polymer interface. Depending on the relative polarity of the voltage bias applied to the metal electrodes, electrons can be added to the $\pi^*$ band or stripped from the $\pi$ band to leave free holes:

\[
\text{Oxidation (p-doping)} \\
(Monomer)_n \Rightarrow [(Monomer)^*]_n + (x \cdot n)e^-
\]

\[
\text{Reduction (n-doping)} \\
(Monomer)_n + (x \cdot n)e^- \Rightarrow [(Monomer)^-]_n
\]

Equation 1-1

where $x$ is the doping level per monomer cell, and $n$ is the number of doped monomer cells. Interfacial doping can be realized in a single polarity manner like in polymer field effect transistors (PFETs) or in balanced injection for electrons and holes in polymer light-emitting diodes (PLEDs) that will be discussed in Section 1.4.1. Photo-induced doping, on the other hand, can only happen in balance between n-doping and p-doping where both parts of Equation 1-1 happen concurrently. Photons are absorbed at the polymer chains where, as a result, electrons are excited from the $\pi$ band to the $\pi^*$ band. This type of doping results in conjugated p- and n- doped monomers at different locations along the excited polymer chain. The Coulomb attraction between the photo-generated p- and n-doped monomers, due to their close proximity, leads to formation of bound states called excitons. These excitons can recombine radiatively or dissociate into free polaron and enhance the photo-conductivity of the photo-excited polymer region or generate electricity when extracted in a PV device. The dissociation of excitons can be enhanced in donor-acceptor systems as demonstrated in polymer heterojunction solar cells (Section 1.4.2).
Chemical doping for semiconducting polymers is achieved by incorporating dopants in between the polymer chains in the presence of an oxidant or a reducing agent. In this type of doping, the oxidant or the reducing agent react with the polymer chains and dope it, while the dopant ions (counter ions) serve to balance the resulting charge and maintain the charge neutrality of the film. Unlike conventional doping in inorganic semiconconductors, the counter ions do not become part of the polymer chains. Since the different chains are held by weak van der Waals forces, the counter ions easily diffuse in between. In other words, the covalent bonds holding the polymer chains together are not broken. An example of chemical doping is doping polyacetylene when exposed to iodine vapor. In this method, iodine serves as the oxidant and the counter ion at the same time and results in p-doping. N-doped polyacetylene can be obtained by dipping into salt solutions like sodium naphthalene where naphthalene serves as the reducing agent and the sodium cation serves as the counter ion.[32] This type of doping is suitable for preparing highly conductive polymers.
where complete doping is needed. P-doped polyacetylene was demonstrated with metallic conductivity comparable to copper.[24] However, for lower levels of doping the chemical approach does not result in uniform doping distribution. Instead, electrochemical doping is used to prepare doped polymers at these levels.[32]

Electrochemical doping is similar to chemical doping in that it involves insertion of counter ions in between the polymer chains.[24], [38], [39] However the activation energy needed to reduce or oxidize the polymer chains is supplied by an external voltage bias instead of using oxidants and reducing agents. This type of doping can be carried out by attaching the polymer material to a working electrode in contact with a polymer electrolyte solution.[40] When a voltage is applied to the electrode, the polymer chains are oxidized or reduced. These reactions break the charge neutrality of the involved chains. Subsequently, counter ions from the electrolyte diffuse into the polymer and are inserted between the polymer chains for charge compensation.[21] The process is depicted in the following formulae:

\[
\text{Oxidation (p-doping)} \quad (\text{Monomer})_n + (xn)\text{Anion}^- \Rightarrow \left[ (\text{Monomer}^{\text{x}^+})(\text{Anion}^-) \right]_n + (xn)e^- \\
\text{Reduction (n-doping)} \quad (\text{Monomer})_n + (xn)e^- + (xn)\text{Cation}^+ \Rightarrow \left[ (\text{Monomer}^{\text{x}^-})(\text{Cation}^+) \right]_n
\]

Figure 1.10 shows that conjugated polymers can exhibit insulating or semiconducting behavior in their pristine state but gain high conductivity, even comparable to metals, upon doping. The ability to control the conductivity of a conjugated polymer is a great feature of these flexible materials. Added to that, as previously mentioned, is the wide spectrum range that these materials can interact with. This has stimulated enormous effort to develop polymer-based electronic and optical devices.[41] The following section reviews the main semiconducting polymer-based devices.
Figure 1.10 Conductivity of doped and un-doped conjugated polymers compared to typical insulators, semiconductors and metals.[42]

1.4 Optoelectronic Devices Based on Semiconducting Polymers

1.4.1 Metal-Semiconductor-Metal (MSM) Polymer Devices

The basic polymer based device can be realized by sandwiching a polymer film in between a low work function metal (cathode) and a high work function metal (anode). Usually, a transparent
indium tin oxide (ITO) film on a glass or plastic substrate is used as the anode while a metal layer, usually aluminum or calcium, on top of the polymer film is used as the cathode (Figure 1.11). Since the luminescent polymer film can both absorb and emit light as well as conduct electricity, such a device can work as a light-emitting device as well as a PV or a photodetector device.

![Figure 1.11 Basic polymer device structure with Metal-Semiconductor-Metal structure.](image)

For visible light-emitting applications, the energy gap of a polymer needs to be between 1.6 eV and 3.1 eV. Due to the large energy gap, pristine polymer films have high resistivity and need to be very thin in order to inject a sufficient amount of current. The film thickness is usually kept under 100 nm. The requirement for ultrathin polymer film make these devices more prone to pinholes and the effect of exciton quenching.[43] The operation of the MSM polymer device is dependent on the bias condition of the electrodes. Figure 1.12 shows the band structure of these devices under different operation conditions. Since the polymer film is very thin, the electric field is uniformly distributed between the electrodes. Hence, the \( \pi \) and \( \pi^* \) bands are linearly tilted under the influence of the field.
Figure 1.12 Single polymer layer device with metal-semiconductor-metal structure at different operation and bias conditions: (a) equilibrium ($V_A - V_C = 0$), (b) flat band ($V_A - V_C = \Phi_A - \Phi_C$), (c) forward bias ($V_A - V_C > \Phi_A - \Phi_C$), (d) reverse bias ($V_A - V_C < \Phi_A - \Phi_C$). (Adapted from [21])
In equilibrium, the Fermi levels of the cathode and the anode are aligned. No electrons or holes are injected or extracted from the device (Figure 1.12 (a)). A minimum voltage bias ($V_A - V_C$), equivalent to the difference between the cathode work function ($\Phi_C$) and the anode work function ($\Phi_A$), is required to set the $\pi$ and $\pi^*$ band edges flat (Figure 1.12 (b)). Hence, it becomes energetically possible for electrons and holes to move through the device. Increasing the bias beyond that level imposes a forward bias operation where it is energetically favorable for the injected electrons and holes to drift into the polymer film to recombine and emit light (Figure 1.12 (c)). The pristine polymer has a small concentration of free carriers, so the electrode-polymer interfaces are not Ohmic. An electron injection barrier is set at the cathode ($\phi_e$) and a hole injection barrier is set at the anode ($\phi_h$). According to the Fowler–Nordheim tunneling theory the injection rate of electrons and holes is exponentially dependent on $\frac{\sqrt{\phi_e^2}}{\sqrt{\phi_h^2}}$.[44] Therefore, it is important to minimize these barriers to achieve efficient injection by selecting the right cathode and anode materials for the polymer film used.

When the MSM polymer device is under light illumination or reverse bias operation, the band edges are set to drive the electrons and holes out of the polymer films towards the cathode and the anode, respectively (Figure 1.12 (d)). Therefore the device under this condition can be used as a solar cell or a photodetector. Photoexcitation in luminescent polymers is generated in the form of excitons which are electron-hole pairs (EHPs) bound by Coulomb force. The dissociation rate of the generated excitons is dependent on the electric field at the generation site.[45], [46] The electric field generated by the work function difference between the cathode and the anode is not sufficient to efficiently disassociate the EHPs. Donor-acceptor hetero-junction structures, such as the well-known P3HT-PCBM system, were introduced to enhance exciton dissociation.

**1.4.2 Donor-Acceptor Polymer Photovoltaic (PV) Devices**

The donor and acceptor components in PV devices are designed (chosen) to have offset energy between their highest occupied molecular orbital (HOMO) or $\pi$ band and lowest unoccupied
molecular orbital (LUMO) or π* band (Figure 1.13 (a)). This offset energy creates potential difference and hence electric field across the donor-acceptor heterojunction. When an exciton is photo-generated in the donor near that interface, the junction field separates the EHPs. Subsequently, the electron drops to the lower energy LUMO or π* level of the acceptor while the hole stays in the higher energy HOMO or π level of the donor. Afterwards, the generated free charge carriers are driven to the cathode and the anode by the electric field generated from the difference between the work-function levels of the electrodes.

The donor-acceptor heterojunction can be realized in planar or bulk configuration. In the planar form, the acceptor and donor films are stacked on top of each other (Figure 1.13 (b)).[47], [48] In that form, the heterojunction extension is in the order of intermolecular spacing.[49] Therefore, the optical overlap with the active area is very small and the conversion efficiency in that platform is very small. In a bulk heterojunction (BHJ) platform (Figure 1.13 (c)) the donor and acceptor material is mixed and form phase separated nano-regions in the deposited film. BHJ structure offers a larger donor-acceptor interface area which increases the efficiency of exciton dissociation.[50]–[52] However, the thickness of the active film set by the optical penetration depth is in the range of 100 nm. Hence, EHPs are photo-generated very close to the electrodes. This can result in electrons being transported to the anode and recombined and holes are transported to the cathode and recombined with electrons, which reduces the efficiency of these BHJ solar cells. Hence, there is a demand to deposit additional layers of a hole transport electrons blocking layer, like Poly(3,4-ethylenedioxythiophene) (PEDOT), at the anode, and an electron transport hole blocking layer at the cathode, like Titanium oxide (TiOx). Multilayer polymer heterojunction solar cells were demonstrated with a power efficiency reaching the 10% that is required for market penetration.[53]–[57]
In addition to light-emitting and PV devices, polymer field effect transistors were demonstrated in metal-insulator-semiconductor structure which is important for incorporating polymer electronics into computing applications.[60] The semiconducting polymer films in these devices are not doped which sets the limitations of low film conductivity. Moreover, the energy mismatch at the metal-semiconductor interface sets a potential injection barrier that elevates the operating voltage of the device. These limitations can be overcome by doping the semiconductor materials.[42] This was firstly implemented in an active optoelectronic device by introducing the polymer light-emitting electrochemical cells (PLECs).[61]
1.4.3 Polymer Light-emitting Electrochemical Cells

PLECs are similar in structure to PLEDs but operate by electrochemical doping for the organic semiconducting materials.[61] They combine the novel electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes. This revolutionary approach for organic light-emitting devices was introduced by Pei and Heeger in 1995.[61], [62] The basic idea was to mix a luminescent polymer and an ion-conducting polymer dissolving an ionic salt. This approach provides a dynamic and reversible way for doping the conjugated polymer. In operation, PLECs gains high doping levels that results in lower resistivity for the polymer film and eliminates the metal-semiconductor injection barriers by forming Ohmic contacts.[42] Moreover, a p-n junction forms in the active polymer film which offers a potential to fabricate devices that surpass the performance of conventional PLEDs and polymer solar cells. PLECs offer more flexibility in the device structure and constituents. Cells with strong light emission have been demonstrated with various metal electrode choices. Operating cells were demonstrated with inter-electrode spacing starting from submicron size in sandwich devices to more than ten millimeters in planar devices.[61], [63]–[65] Moreover, it was shown that the luminescent polymer in the cell can be replaced with other types of luminescent materials like small organic molecules, and ionic metal complexes.[66]–[72] In this text, we use the term “light-emitting electrochemical cells” (LECs) to refer to the more generic family of devices that are made with polymeric or non-polymeric luminescent materials. In general, the operation mechanism and characteristics of polymeric and non-polymeric LECs are very similar but the focus of this text will be on PLECs.

Owing to the fact that PLECs operate with the added benefits of doping, there has been a growing interest in PLECs as a potential candidate for lighting and display applications. Recently, light-emitting fibers and light-emitting papers were demonstrated. In addition, there have been efforts made towards developing PLEC based electrically pumped lasers.[73]–[75] To achieve the minimum requirement for operation and optimized performance for such applications, an understanding of the underlying structure of PLECs is necessary. A great endeavor was invested in
modelling and characterizing the functionality of these devices.[76]–[80] The following text discusses basic concepts and terminology important to understand PLEC basic operations and characteristics.

1.4.3.1 Operation Mechanism of PLEC

The operation mechanism of PLEC is depicted in Figure 1.14 as described by Pei and Heeger.[62] Initially, the PLEC constituents are uniformly mixed and spread between the electrodes. Upon applying a voltage bias, charge starts to accumulate at the electrodes. Since the salt component is dissolved in the ion-conducting polymer, its ionic components are free to move. These ions get attracted to the electrodes, and very thin double layers form at each electrode-polymer interface. The thickness of the formed double layer is extremely small (~0.5 nm) and allows charge tunneling at moderate voltage levels.[81]

Figure 1.14 Operation mechanism of PLEC. (a) Initially, the PLEC constituents are uniformly mixed and spread between the electrodes. (b) Upon applying a voltage bias, a thin double layer forms. (c) p and n doping propagate through the film until they meet and form a light-emitting p-n junction.
Charge carriers are injected into the luminescent polymer through the double layer. The polymer is oxidized at the anode and reduced at the cathode side. The free anions and cations dispersed throughout the cell start to accumulate at the doped polymer regions to compensate for the charge of the reacted polymer molecules. Hence, the doping process for the polymer chains is complete. Subsequently, doping extends through the polymer film until the p- and n-doping fronts approach each other. Upon reaching electrochemical equilibrium, the net ionic current goes to zero and a p-n junction forms. At high doping levels, the polymer becomes highly conductive. Low resistance electrode-polymer Ohmic contacts form, and enable easy charge carrier injection. Therefore, the electronic current does not stop and the charge carriers are constantly injected into the polymer layer. Guided by the bias electric field, the injected electrons and holes drift in opposite directions to finally recombine at the junction region and emit light.

1.4.3.2 PLEC Characteristics

Figure 1.15 shows the volt-current-luminance (VIL) behavior of the first demonstrated PLEC device.[61] Unlike the conventional diode behavior, PLECs can operate for both bias voltage polarities with electroluminescence (EL) intensity symmetric around the zero voltage bias line. The bipolar functionality is attributed to the dynamic doping nature of PLECs and it shows the low sensitivity of PLECs to the electrodes. This is in clear contrast to PLED operation that is highly dependent on the electrode’s material choice. [8], [82]

To facilitate electron injection in PLEDs, a low work function reactive metal cathode is used. The highly reactive cathode material (such as calcium) increases the chance of device failure unless the PLED is carefully encapsulated.[83] Moreover, PEDOT:PSS is usually used on top of the transparent anode (ITO/FTO) as a planarising layer and to enhance holes injection. The acidic nature of this layer causes PLEDs degradation by slowly etching the anode underneath.[84] Doping in PLECs enhances the conductivity of the polymer film which suppresses the potential barrier at the electrode/polymer interface and lowers the operating voltage of the cell. Regardless of the
electrode’s work function, efficient charge injection can occur via quantum mechanical tunnelling between a metal electrode and the heavily doped polymer. Also, since doped polymers are much more conductive than pristine polymers a thick active layer can be used in PLECs. Highly efficient sandwich PLECs have been demonstrated very early on with air-stable cathode materials and without the need to optimize a thin thickness for the active layer.[85]–[87] The high conductivity of the doped PLEC film also ensures a strong and balanced charge injection at the electrode interfaces. It was observed that the quantum efficiency of PLECs was higher compared to PLEDs made with the same polymer material.[61]

At the off state, the fluorescent conjugated polymers in PLECs are in their neutral (undoped) form. Hence, PLECs can be fabricated to be environmentally stable and capable of being stored for long time without degradation. On the other side, for long operation time, self-heating can cause phase-segregation and degradation of PLECs which results in low chemical stability and a short
Moreover, since doping causes luminance quenching, the lifetime of PLECs can suffer from optical self-absorption that affects the luminance lifetime of the device. This will be further discussed in Chapter 2.

1.4.3.3 Frozen PLECs

Despite possessing some very attractive device characteristics, PLECs are not without drawbacks. The very operating mechanism responsible for PLEC insensitivity to the active layer thickness and the electrode work function also brings serious compromises. The turn on or activation of a PLEC typically takes seconds or even minutes as the junction is slowly established by the slow moving ions.[85], [86], [90] Unlike the doping of silicon by chemical diffusion, the in situ electrochemical doping of a PLEC is a room temperature process. The mobile ions, which serve as counter ions to compensate the injected electrons and holes, do not become part of the polymer chain and remain mobile. Once the applied voltage bias is removed, the PLEC junction will eventually disappear as the doped regions relaxes back to the undoped state. Therefore, PLECs are slow to turn on and exhibit strong hysteresis if they are turned on before reaching a fully relaxed state from a previous operation.[91] PLECs also suffer from burn-out if a voltage bias much higher than 4 V (for sandwich cells) is applied due to the limited electrochemical stability window of the electrolyte materials used. This means that PLECs are not suitable for high intensity applications.

It is apparent that a fixed PLEC junction is desirable since it will retain all the advantages of PLECs, while also being fast and stable. In a PLEC, fixing the junction means fixing the counter ions. Realizing that the ion transport mobility in an ion-conducting polymer is strongly temperature dependent, Gao et al. devised a simple method to fix the PLEC junction by cooling the cell after junction formation.[91], [92] When the PLEC temperature is below the glass transition temperature (T_g) of the ion-conducting polymer, the ions, and therefore the PLEC junction, are immobilized. The first demonstration of a frozen PLEC junction was on a sandwich cell. The cell had an active layer of poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV): poly[ethylene...
oxide] (PEO): lithium triflate (LiTf) blend film sandwiched between ITO and aluminium electrodes. The cell was activated at room temperature with a fixed positive (ITO biased positive) or negative voltage bias to emit strongly. Subsequently, the cell was cooled to 100 K. Two key factors contributed to the success of the frozen junction. First, the voltage bias was maintained until the cell temperature had reached the target temperature. Second, the target temperature of 100 K was well below the $T_g$ of PEO (about 208K). This ensured that the PLEC junction was fully stabilized. The resulting “frozen junction” PLEC exhibit much faster response time (μs) than the same cell operated at room temperature. In a frozen junction PLEC, the ions are immobilized and the device response time is no longer limited by the slow doping process. The frozen junction PLECs also exhibit diode-like VIL characteristics, as shown in Figure 1.16.

![Figure 1.16](image.png)

**Figure 1.16** Upper curves: VIL data of a sandwich PLEC measured at 100 K after activation at 300 K and cooling under +4 V bias. The PLEC was then heated to 300 K without external bias, then reactivated at -3 V and cooled to 100 K. Lower curves: the VIL characteristics measured at 100 K after the reactivation. The VIL curves were reversed after reactivation at -3 V compared to the first activation at +4 V bias.[92]
Significant current and EL had only been observed under forward bias, defined here as a bias with the same polarity as the applied activation bias. Varying the polarity of the activation bias can, therefore, change the polarity of the frozen junction. This behaviour is completely different from both regular PLECs, which can conduct and emit under both forward and reverse bias at the same time, or the PLEDs, whose polarity is fixed. The frozen junction also brings new functionality to the PLEC. For the first time, an activated PLEC can operate as a PV cell for power generation.

Figure 1.17 shows the IV traces of a frozen junction cell in dark and under illumination.

![Graph showing IV traces](image)

Figure 1.17 PV response of a frozen sandwich PLEC at 100 K. The upper panel shows the response when the cell was activated using +4 V. The lower panel shows the response after the cell was reheated and activated using -3 V then was frozen again.[93]

The low rectification ratio of the dark I-V curves can be attributed to the high resistance of the film at low temperature. The cell, however, showed a pronounced PV response in either polarity, as
shown by the dashed curves. It is remarkable that the same cell can exhibit either a positive or a negative open circuit voltage ($V_{OC}$) (or short circuit current, $I_{SC}$) depending on the polarity of the activation bias. The PV response of a frozen junction PLEC, just like its EL, is no longer dependent on the electrode work functions. Rather, the PLEC p-n or p-i-n junction determines both the electrical and optical properties of the frozen cell. The large $V_{OC}$ of -1 V or +1.3 V suggests a large built-in potential in the PLEC junction. Adding an electron-accepting polymer to the PLEC blend created a more efficient frozen junction polymer PV cell.[93]

While it is fairly straightforward to cool an activated PLEC to stabilize its junction in a laboratory, eventual application of frozen junction PLECs requires the junctions, once formed, to be frozen at room temperature. Progress toward this goal has been made by using ion-conducting materials with a high $T_g$. [94], [95] The junction is formed at elevated temperatures and the cell is subsequently cooled to room temperature. The PLEC junctions can also be fixed chemically.[96]–[101] One method used ion pair monomers in the PLEC blend.[96] Upon activation, these ions dope the polymer and cause radical-induced polymerization that would significantly reduce the ion mobility and fix the junction. Pei et al. used PEO oligomer capped with methacrylate as the ion-conducting component. It was found that polymerizing the methacrylate group during junction formation results in a stable junction with a lifetime and efficiency comparable to PLEDs.[102] Another approach utilized ionic trapping polymers to establish a permanent junction after junction formation.[99] Also, fixed junctions were formed by incorporating cross-linkable materials that were cured after the junction formation.[103], [104] More recently, Gautier and Gao showed that when the ion solving/transporting material, such as PEO, was removed altogether, the resulting cell, now only containing a luminescent polymer and a lithium salt, can still be activated by applying a relatively higher bias voltage. The activated cells exhibit characteristics of PLECs with strong evidence of doping. More important, the activated state is stable for more than 100 hours
without an applied bias. This was the longest reported shelf-life of a fixed junction at room temperature.[105], [106]

1.4.3.4 Large Planar PLECs

Unlike OLEDs and PLEDs, PLECs can operate in both a sandwich and a planar configuration. In planar configuration, the overall device resistance is dominated by the bulk resistance of the active layer, which can be enormous for an undoped material if the interelectrode spacing is large. The activation potential of PLECs is in the order of the luminescent polymer band gap. This is an advantage of PLECs over conventional PLEDs. For example, a planar PLED with an interelectrode spacing of 30 µm exhibited an EL turn on voltage of 500 V and was only operational at liquid nitrogen temperatures.[107] A planar PLEC of similar dimensions, however, can be turned on to emit light with a mere 4 V bias.[61]

In a PLEC, the presence of mobile ions and the subsequent in situ electrochemical doping render the active film highly conductive. The images of these emitting planar PLECs offered the first visualization of the PLEC junction.[61], [62], [108] The relatively small size (interelectrode gap size) of these early planar PLECs means that they were difficult to fabricate and to study. There had been almost no follow-up studies of planar PLECs in the late 90s and early 2000s. Large planar devices are easy to fabricate using shadow masking compared to photolithographic techniques. Also, this platform gives an access to a cross-sectional view of PLECs. In 2003, Gao and Dane demonstrated planar PLECs with an interelectrode gap size of 1.5 mm.[64] An 800 V bias was applied to turn on two 1.5 mm cells in series at room temperature, as shown in Figure 1.18. The millimetre-sized, extremely-large planar PLECs are easy to fabricate via shadow masking compared to photolithographic patterning. More importantly, the slow turn on process of these planar PLECs is highly advantageous for time-resolved studies of the dynamic doping process and the effects of various operational and material parameters. In situ electrochemical doping of the PLEC film affects not only its electrical conductivity but also its optical properties. Doping
introduces mid-gap impurity states that quench the photoluminescence (PL) of the luminescent polymer (Section 1.3).[109]–[111] The optical effect of doping had been exploited by Gao and Dane to elucidate the doping process of PLECs.[112] Extremely large planar PLECs were imaged under UV light illumination, and for the first time, the dynamic PLEC doping process had been visualized. These visualizations provide indisputable proof that doping did occur in a PLEC, and the formation of a p-n junction was necessary for EL to occur.

Figure 1.18 The photograph of two working 1.5 mm PLECs in series under 800V. Also shown is the device configuration and biasing condition. The green-emitting device is made with the green emitter; and the orange-emitting device is made with MEH-PPV.[64]

From the time-lapse images of planar PLECs, the average doping propagation speed was extracted and shown to be highly sensitive to the operating temperature.[113] By moderately increasing the operating temperature, Gao et al. successfully demonstrated the largest planar PLEC ever with a gap size of over 10 mm.[65] Edman et al., on the other hand, showed that planar PLECs with a gap size of 1 mm could be turned on with only a 5 V bias when heated to 360 K.[114] Figure 1.19
shows an example of the largest planar PLEC under UV illumination during the activation process.[115] In this cell, both p- and n-doping are clearly visible. EL was only observed when the p- and n-doping fronts had made contact to form a p-n junction. Also, the cell current can be observed and associated with the time-lapse pictures. The cell current had increased by several orders of magnitude during the activation process. Subsequently, the cell was cooled to freeze the junction. The large surface area of this cell allowed for contact probing of the cell surface in a micromanipulated cryogenic probe station. With that setup, it was possible to generate a spatially resolved potential profile for an active cell. These measurements, also, confirmed electrochemical doping p-n junction formation in PLECs by demonstrating enhanced conductivity for the activated devices.

Figure 1.19 Time-lapse fluorescence imaging of a 10.4 mm MEH-PPV: PEO: CsClO₄ planar PLEC during turn on and cooling. A fixed DC bias of 400 V was applied to turn on the cell, which was at 335 K and under UV illumination. Time elapsed after the DC bias was applied to the cell: (A) no bias, (B) 2 min, (C) 5 min, (D) 8 min, (E) 19 min, (F) 37 min, (G) 54 min. Panel H shows cell current and temperature as a function of time after the DC bias was applied.[115]
The time-lapse fluorescence imaging of extremely large planar PLECs has proven to be a powerful and versatile technique in the elucidation of PLEC processes. The effect of thermal annealing,[116] electrode work function,[117], [118] electrolyte salt,[119]–[121] and operating voltage[122] had all been studied. The static doping profile of a frozen junction PLEC had been directly observed in a frozen large planar PLEC.[113] Heating the frozen cell briefly, however, led to the partial relaxation of doping and the formation of a p-i-n junction.[123] Under the right conditions, the frozen p-i-n junction is a much more efficient emitter than an as-formed p-n junction due to the former’s less quenched emission zone. A frozen p-i-n junction also exhibits a record open circuit voltage.[124] Moreover, large PLECs allowed for performing spatially resolved probing scans using various optical and cryogenic arrangements. The electric potential distribution across planar PLECs operated at room temperature has been resolved using scanning probe microscopy.[63], [125], [126] Large planar frozen PLECs were used in the work presented in Chapter 3 to Chapter 5 to probe doping characteristics in these devices.

1.4.4 Introduction to p-n Junctions

A p-n junction is an electronic structure that forms at the interface between n-doped and p-doped regions in a semiconducting material. The junction is schematically depicted as two purely doped regions brought into contact. However, the real p-n junction structure is typically formed by compensation doping of a substrate already p- or n-doped. If pure p- and n-doped regions are brought into contact, there will be a large carrier concentration gradient at the interface. This concentration gradient drives diffusion currents between the two regions. Charge carriers from each region diffuse into the opposite region. Consequently, the material loses its charge neutrality in the junction region. Holes migrate to the n region leaving negatively charged acceptors in the p region. On the other hand, electrons migrate to the p region leaving positively charged donors in the n region. Therefore, the junction region is known as the Space-Charge Region (SCR), as shown in Figure 1.20. As a result of the uncompensated ion charges, electric field builds up with a direction
pointing from the n to the p region. This is known as the built-in electric field. The electric field drives a drift current in the counter direction to the diffusion current.

![Diagram of p-n junction and depletion region schematic](image)

**Figure 1.20** The p-n junction and depletion region schematic (up),[127] and its energy diagram (bottom). The black circles denote electrons while the white circles denote holes.

At equilibrium, the net current across the p-n junction is zero. This demands a constant Fermi energy level throughout the p-n junction.[128] The relative distance in energy between the Fermi
level and the band edge is an indicator of the charge carrier concentration and type. In the neutral p-doped region, the Fermi level is closer to the valence band edge due to the region’s majority carriers being holes. In the neutral n-doped region, the Fermi level is closer to the conduction band edge. In the SCR the curvature of the band edges indicates the presence of a built-in field. The SCR is also commonly referred as the transition region or the depletion region. The SCR is largely depleted of free charge carriers. [129]

The functionality of a p-n junction can be fully identified by knowing the doping concentration and the built-in potential in the device. The doping level in the charge neutral region determines the conductivity of the device. The depletion width is important to determining the response time, carrier photogeneration and recombination in the device [130]. The junction width in sandwich PLECxs was determined by junction capacitance measurements. [131]–[137] In these experiments a small AC voltage that is superimposed on a DC bias is used to measure the cell impedance. The geometric capacitance of the cell is dominant at low DC bias. However, once the DC bias exceeds a threshold voltage that depends on the conjugated polymer band gap, doping starts to take place. As a result, a drastic increase in the cell conductance and capacitance is detected due to doping and formation of a forward-biased p-n junction. [136] The values for the junction width that were extracted from these experiments widely varied between 3% and 80% of the active film thickness. This, for once, can be attributed to the variety of materials and operating parameters that were used in these studies. [133], [134] Moreover, the outputs of impedance spectroscopy are susceptible to the circuit model used for parameter extraction. Here, another approach was taken to determine the doping concentration in PLECxs junctions and charge neutral regions. This was done by optical beam induced current (OBIC) and discharge measurements on large planar PLECxs as will be detailed in Chapter 3 through Chapter 5.
Chapter 2

Long-Term Testing of Polymer Light-Emitting Electrochemical Cells: Reversible Doping and Black Spots

Polymer light-emitting electrochemical cells (PLECs) have been tested either continuously or intermittently for a long duration. In situ electrochemical doping of the polymer film causes fluorescence quenching and apparent luminance decay when the effect of quenching outweighs the effect on charge injection. The quenching-induced luminance loss, however, is partly recoverable when the cell is allowed to relax (de-dope) without an applied bias. The long test duration causes the appearance of large black spots in both PL and EL. Two very startling observations shed light on the nature of the black spots. First, black spot growth was completely suppressed when a cell was tested with a freshly deposited top aluminum electrode, even though the polymer film had been stored for up to nine months. Second, the black spots in PL gradually faded when the applied bias voltage was removed. The black spots in these PLECs were therefore sites of heavy doping that were promoted by changes that occurred at the cathode/polymer interface.

2.1 Introduction

Polymer light-emitting electrochemical cells (PLECs) are solid-state devices whose active layer is doped in situ during operation. Doping in PLECs bears similarity to the doping of conventional semiconductors, which requires the presence of counter-ions (i.e., ionized donors and acceptors in conventional semiconductors) to stabilize the additional charge carriers. As a result of doping, both the electrical and optical properties of the luminescent polymer are significantly altered. Injection EL occurs in the vicinity of the junction formed between p- and n-doped regions.

The interest in PLECs is motivated by both a desire to understand their complex device processes and the PLECs’ application potential. Like polymer light-emitting
diodes (LEDs), PLECs possess the same processing and mechanical advantages of polymer devices. A major obstacle preventing the practical application of PLECs is their poor operational stability. Early reports of PLEC lifetime characteristics are scant and the lifetime is typically on the order of tens of hours. By reducing the electrolyte loading and using electrolytes with a wide electrochemical stability window, sandwich PLECs with an operating lifetime on the order of 1000 hours at display brightness have been recently demonstrated. These figures are expected to improve when better materials become available or when the PLEC junction is chemically stabilized.

The operating lifetime of a PLEC is typically studied in the same way as a PLED or OLED. A constant current is applied to the cell and a half-life is determined when the luminance has decayed to 50% of the peak value. The apparent luminance decay in a PLEC, however, is not only caused by irreversible changes to the luminescent polymer and or electrical contacts, but is also the result of fluorescence quenching when the polymer is doped. In the study of large planar cells, the electrochemical doping manifested as fluorescence quenching is observed to be largely reversible when the applied voltage bias is removed or reversed. The reversibility of doping explains why sandwich PLECs, when operated intermittently, display dramatic recovery of loss luminance when the polymer film is allowed to relax when idled. Similar luminance recovery has also been observed in small molecule-based LECs. On the other hand, there is evidence that the doping is not entirely relaxed even after an extended idling period and the cells develop large black spots in their EL images.

In this study, the complex decay mechanisms were elucidated of PLECs by subjecting identical sandwich cells to long-term intermittent and continuous testing. Dominant decay mechanisms during different stages of operation were identify. In addition, results that provide important clue as to the nature of the black spots in these PLECs were presented.
2.2 Materials and Methods

The sandwich PLECs used in this study were nominally identical and similar to the cells used in previous studies by Gao et al.,[156], [157] All cells contained a luminescent polymer MEH-PPV, an ion-solvating polymer, PEO (Mn = 4×10^5 g/mol), and the salt lithium trifluoromethanesulfonate (Li triflate or LiTf). The cyclohexanone solutions of MEH-PPV and PEO:Li triflate were blended to have a solute composition of MEH-PPV:PEO:Li triflate = 24:5:1 by weight. Polymer films were spin cast from this solution and subsequently dried at 50°C for 5 h to remove any excess solvent. The polymer films were then thermally annealed at 130°C for 30 min and quickly cooled to room temperature by placing them on a large copper heat sink.

Using atomic force microscopy, the active layer thickness was measured to be 142 ± 3 nm. Aluminum (ca. 100 nm) was thermally evaporated on top of the PLEC films through a shadow mask to serve as a cathode and define an active emitting area of 0.12 cm^2. The devices were tested in a black box fitted with a calibrated photodiode. All devices were processed and tested inside a glove-box/evaporator system that was filled with dry nitrogen at room temperature. A computer-controlled Keithley source measurement unit (238) was used to bias the cells while simultaneously measuring the operating voltage and luminance. All cells were operated by applying a constant current of 20 mA with the ITO electrode biased positively relative to the aluminum electrode.

The EL and PL images were captured using a Nikon D300s camera through the glove box window. For PL imaging, a handheld UV lamp was positioned below the PLEC with the biasing current removed. Intermittent testing was carried out on the same cell (Cell 2). For each run, the cell was stressed for 23 h. Subsequently, the cell was stored for 7 days in the glove box at 25°C. This ON/OFF cycle was repeated 15 times. The first run (virgin run) commenced after the deposition of the top aluminum electrode without delay.
2.3 Results and Discussion

Figure 2.1 (a) shows the continuous operation of a cell (Cell 1) under a 20 mA constant current (or 167 mA/cm$^2$ in current density). The luminance and operating voltage were monitored as a function of time during the test. There was a brief interruption of the test at around $t = 313$ h when the applied current was removed for less than 30 s. This did not affect the overall test, as both luminance and operating voltage quickly recovered when the test current was re-applied. The brief recovery period (about 60 s) is included in the data for completeness but is not discussed in the following sections.

The total test period was 673 h or 4 weeks, among the longest for a PLEC. The total charge that passed through the cell during the test amounts to $4.04 \times 10^5$ C/cm$^2$, which is the highest to date for a sandwich PLEC. The long test duration brought out features that were not present in shorter tests. The cell luminance degraded sufficiently so that a luminance half-life of approximately 230 h was inferred. The cell luminance displayed a monotonic decay after peaking at about $t = 10$ h. The operating voltage, however, decreased for nearly 100 h before rising slowly. Much information can be deduced by considering the different behaviors of cell luminance and operating voltage in concert.

Figure 2.1 (b) shows the same data in semi-log form. The entire test duration can be divided into three regions based on the dominant decay mechanisms. In stage I, the cell displays ‘‘normal’’ PLEC behaviors when the cell luminance increased while the operating voltage decreased rapidly as the polymer film became doped. Doping led to improved charge injection as the electrode/polymer contacts became Ohmic. Although doping also caused significant fluorescence quenching, the cell luminance increased as the charge injection became more balanced. In stage II, both cell luminance and operating voltage decreased. The operating voltage decreased more slowly than in stage I, but nevertheless indicated a continuation of the doping process. In stage II, the quenching effect of doping became dominant and the luminance decreased. However, much of the
luminance decay during this stage was recoverable. In stage III the luminance decay was accompanied by an increase in driving voltage. This is the normal degradation behavior typically observed in polymer and organic LEDs.[159]

![Graph showing time evolution of luminance and operating voltage](image)

**Figure 2.1** (a) Time evolution of luminance and operating voltage of a ITO/MEH-PPV:PEO:LiTf/Al sandwich PLEC (Cell 1) operated at a constant current density of 167 mA/cm². The cell was operated for the first time after the deposition of the top aluminum electrode. The test commenced after the deposition of the top aluminum electrode without delay. (b) The same data presented in (a) but plotted in a semi-log form with various regions of operation marked.[160]

The increase in operating voltage is an indication of true degradation of the device, possibly due to the decrease of electron mobility or the degradation of the electrical contacts. Beyond stage III, the
cell would eventually fail when the operating voltage increased to a level that caused catastrophic self-heating or field damage, although the device was not run to destruction. It should be emphasized that the above distinction of degradation stages is based on the dominant mechanism that has led to the apparent increase or decrease of luminance or operating voltage. It is entirely possible that the permanent decay began early in the test but was overwhelmed by the effect of doping. In addition, the relative length of various stages depends on the operating current and other device parameters. It has been shown by Gao et al. that the apparent luminance decay was highly reversible when the cell was operated intermittently,[156], [157] it would be interesting to investigate how the operating scheme (continuous vs. intermittent) affects the overall degradation of PLECs.

Figure 2.2(a) shows an identical cell (Cell 2) operated intermittently under the same constant current of 20 mA. The cell was operated for about 23 h then idled for 7 days. This ON/OFF cycle was repeated 15 times. The cell luminance and operating voltage vs. accumulated operating (ON) time are shown in the figure. Luminance recovery was clearly observed each time the cell was turned on again. Unlike in the continuous test, a luminance half-life cannot be determined since the luminance never dipped below 50% of the peak luminance of about 330 cd/m². The last run (run 15), however, brought the cell to near destruction when the operating voltage increased sharply and the luminance decreased to about 100 cd/m², at which point the applied current was removed. The overall light output of Cell 2, calculated by integrating the area below the luminance curves, was about 13% higher than for Cell 1 for the same duration (about 355 h). However, Cell 2 practically failed near the end of run 15 while Cell 1 was still emitting at close to 100 cd/m² after 673 h. It is surprising that the cell that was operated intermittently was less stable than that which was operated continuously.

Figure 2.2(b) displays the Cell 2 luminance and operating voltage at the end of each run (up to run 14) against the Cell 1 luminance and voltage (continuous). The data suggest that the operating
voltage, rather than the apparent luminance decay, was a more reliable indicator of cell stability regardless of how it was operated. The terminal operating voltage increased quickly in Cell 2 right from the start. In addition, the voltage increase in Cell 2 was apparently caused by changes that occurred during the idling (OFF) period. During the first dozen runs the operating voltage actually decreased when Cell 2 was ON.

Figure 2.2 (a) Time evolution of luminance and driving voltage of a ITO/MEH-PPV:PEO:LiTf/Al sandwich PLEC (Cell 2) operated intermittently at a constant current density of 167 mA/cm². The operating time indicates the accumulated run time under bias. For each run, the cell was stressed for 23 h. Subsequently, the cell was stored for 7 days in the glove box at 25°C. The ON/OFF cycle was repeated 15 times. The first run (virgin run) commenced after the deposition of the top aluminum electrode without delay. (b) The operating voltage and luminance at the end of each run in (a) plotted against Cell 1 data in Figure 2.1 for the first 350 h. (c) EL image of Cell 2 at the end of run 14. (d) EL image of Cell 1 after 313 h.[160]
It is noted that a similar cell tested intermittently with an ON/OFF cycle of 68 h/30 days did not suffer from a premature death or rapid voltage increase after a comparable total run time. The cell stability therefore depended on the extent of relaxation. As seen in Figure 2.2(b), the divergence in operating voltage already occurred at the end of run 2. Therefore, black spots, which typically become prominent after several weeks in these PLECs, were unlikely the cause of the rapid voltage increase and instability. On the other hand, black spots can significantly affect the appearance of the cell when they become significant in size. This is apparent in Cell 2 after about 332 h of total run time (at the end of run 14), as seen in Figure 2.2(c). Cell 1, however, was less affected after the same total run time, as shown in Figure 2.2(d). Analysis of the images in Matlab shows that the large black spots in Cell 2 occupied 28% more area than the ones in Cell 1. Therefore, long idling was the primary cause of black spot growth and not the passing of current.

In polymer or organic LEDs, the formation of black or dark spots can be caused by changes at the anode/organic interface,[161], [162] the light-emitting layer itself,[163] or the cathode/organic interface.[164], [165] In the PLECs of this study, however, there is clear evidence that the anode (ITO) interface and the polymer film itself did not change even after a long storage period, as long as the top aluminum electrode was not deposited. Figure 2.3 shows the virgin runs of four identical cells tested months apart. The PLEC films of the four cells were cast at the same time and stored in the glove box. For each cell the virgin run was carried out right after the deposition of the aluminum top electrode without delay on the date shown. It was observed that the four cells displayed nearly identical levels of luminance and operating voltage. More important, there was no black spot growth even though the PLEC film had been stored for up to nine months. This is in stark contrast to PLECs with finished top aluminum electrodes, in which significant performance loss and black spot formation were observed even after weeks of storage.[157] Clearly, the PLEC film and the polymer/ITO electrode interface were stable over the long term and the
cathode/polymer interface was responsible for the growth of black spots and performance deterioration.

Figure 2.3 Virgin runs of four cells with freshly deposited top aluminum electrode at various times. The PLEC films were cast at the same time on August 9, 2013. The date shown in the graphs indicates the date of aluminum electrode deposition and test. The EL images were taken at the end of each test and identical camera settings were applied. A constant current density of 167 mA/cm² was applied to all four cells.[160]

The black spots in these PLECs were not only present in the EL images, as shown in Figure 2.2, but also in the PL images when the cell was imaged under UV illumination. These PL images of the tested cells revealed a surprising fact about the nature of the black spots. Figure 2.4(a) shows
the PL image of a PLEC that had been operated for the second time in 10 months since the deposition of the aluminum electrode, at about 34 min after the removal of the biasing current. The cell was operated for 21 h and the operating voltage was about 3.7 V, higher than for a fresh device. The PL image was populated by many large black spots due to the long storage time in the presence of the top electrode. In less than 24 h, however, the black spots gradually faded, as shown in Figure 2.4(b) and (c). When the biasing current of 20 mA was applied again, the black spots reappeared in the EL images, as shown in Figure 2.4(d).

![PL and EL images of an aged cell that had been stored for 10 months.](image)

Figure 2.4 PL and EL images of an aged cell that had been stored for 10 months. The cell was operated for the second time for 21 h under 167 mA/cm². (a) PL image of the cell 34 min after the removal of the test current. (b) PL image of the cell 6 h after the removal of the test current. (c) PL image of the cell 24 h after the removal of the test current. (d) EL image of the cell 10.5 min after the bias current was reapplied.[160]
A majority of the large black spots in the EL image matched those in the PL image. The surprising fading or disappearance of the black spots in the PL image suggests an origin of doping that heavily quenched the PL of polymer film, but the quenching effect was reversed when the doping relaxes. It is possible that the doping penetrated the entire PLEC film so that a light-emitting p–n junction was not formed. Alternately, the doping was sufficiently heavy so that the p–n junction formed was no longer light-emitting. In either case, the black spots in these PLECs were fundamentally different from those observed in organic and polymer LEDs which are not doped.

The results presented demonstrate the importance of doping in the degradation of PLECs. Doping was responsible for at least three key degradation characteristics of these PLECs. First, doping quenched the fluorescence of the PLEC film and eventually led to the peaking and subsequent drop in EL intensity. Second, the relaxation of doping during the idling period leads to partial recovery of the cell luminance in the subsequent operation. The recovery and overall stability of the cell depended on the extent of doping and its relaxation. Third, doping caused the appearance of large black spots in aged PLECs. The large black spots were absent if the cell had a freshly deposited aluminum electrode.

A last puzzle still remains as to what seeded the initial formation of the black spots and what changes at the cathode interface led to the growth of the black spots. Since idling after the appearance of the large black spots did not prevent them from reappearing in the EL images, the charges at the cathode interfaces appeared to be permanent. Rudmann and Rubner reported that single-layer LECs made with an ionic ruthenium complex and Al cathode suffered from degradation when stored in the off-state in inert atmosphere. They provided strong experimental evidences that the degradation in luminance level was due to the reduction of the Ru(II) complexes in the presence of Al. Devices with silver electrodes, as expected, did not undergo any degradation during storage due to silver’s better electrochemical stability. [166], [167] Vacuum-deposited aluminum, among other metals, is also capable of reacting with conjugated polymers. [168] It is
therefore very probable that the MEH-PPV in this study had been unevenly reduced during storage which led to localized heavy doping. The effect of cathode reactivity can be studied by employing different combinations of cathode and luminescent polymer.
Chapter 3

Optical Beam Induced Current (OBIC) Imaging for Frozen Planar PLEC Junctions

There has been a significant interest and efforts to understand the underlying doping patterns in PLECs. Steady state and dynamic models were proposed to identify the electronic and ionic distribution in the cells.[62], [76], [78]–[80], [122], [169]–[173] Scanning measurements were also carried out to probe the potential profile through planar PLECs. OBIC, micro-manipulated electrodes and Kelvin probe microscopy techniques were used. Many of these measurements were carried out at temperatures higher than the ion-conducting material glass transition point.[63], [108], [125] Therefore, the cells were prone to relaxation when the voltage bias was removed after doping was complete. OBIC scans on fixed PLEC junctions were recently performed by cooling the devices to temperatures lower than 200 K. This freezes the electrolyte and drastically minimizing ions mobility in these devices. Therefore, the distribution of the ions and, consequently, the doping profile was maintained after removing the doping bias. Frozen planar cells with large inter-electrode widths were scanned by various types of optical probes.[92], [112], [115], [174], [175]

OBIC is a scanning imaging technique that is comparable to methods like electron beam induced current (EBIC) and scanning Kelvin microscopy. However, it provides a more cost effective alternative that is easier to handle, non-destructive and eliminates the need for ultra-high vacuum.[176] This technique is well-known as a characterization method for semiconductors. It was invented three decades ago and has been used heavily in industry and research avenues.[129] In this method a light beam is used to probe and characterize semiconductor devices. OBIC has been used to measure parameters like minority carrier diffusion length, impact ionization coefficients and detection of defects in devices.[129], [177]–[182] It can also be used to scan stable
p-n junctions to probe the depletion region electric field.\textsuperscript{[183]}–\textsuperscript{[185]} The following section provides background information about this technique.

3.1 Optical Beam Induced Current Imaging of p-n/p-i-n Junctions

EHPs are generated in semiconducting materials when illuminated with photons having energies greater than the material band gap. When this happens within the SCR in a p-n junction, or at a distance from the SCR within the diffusion length of the charge carriers, the EHPs get separated by the built-in junction field. The excess separated electrons drift to the n region while holes go to the p region. Hence, the photo-generated EHPs can be collected at the electrodes with no external bias.

Figure 3.1 shows a schematic diagram of a p-n junction under optical illumination. The generated EHPs are split and swept by the built-in potential. The holes climb the energy potential step while the electrons take the opposite direction. Since it is energetically unfavorable to counter this energy transition, no counter current is generated. Hence, a non-equilibrium potential step in the Fermi energy is created. This is the difference in the electrons energies between the p and n sides.

![Figure 3.1 A schematic of a p-n junction under light illumination (left) and its energy band diagram (right). Under illumination, a non-equilibrium potential step in the Fermi energy level is created. $E_C$ is the conduction band edge, $E_F$ is the fermi energy level and $E_V$ is the valance band edge.](image)

The electromotive force associated with the energy difference between the junction p and n sides can be used to drive a current in the external circuit. The maximum output current is the short circuit
current using zero output resistance. On the other hand, the open circuit voltage is the maximum non-equilibrium voltage that can be generated. For any other value of the output resistance, the generated current and voltage are bounded by $V_{OC}$ and $I_{SC}$. However, for photovoltage to be measured, the quasi-Fermi levels are deviated from the equilibrium value and cause broadening for the measured OBIC profile. Therefore, a spatially resolved photocurrent profile is more representative for the junction profile than a photovoltage profile. Therefore, the photo-generated current is an indicator of the presence or absence of a SCR in the area illuminated by the beam. This is a very useful observation in characterizing the electric field in p-n junction structures.

In OBIC measurements, a high resolution image can be generated by scanning a focused light beam through the sample and recording the photo-induced current. The depletion width in a planar p-n junction can be measured by observing the contrast peak in the scanned profile across the p-n interface. In charge neutral regions, due to the lack of a built-in electric field, a zero OBIC signal is expected. Reviewing the literature shows that OBIC was used to image p-n junctions in planar devices [185], [186]. As mentioned earlier, electrochemical doping in PLECs creates a light-emitting p-n junction between the oppositely doped regions. The built-in electric field profile is a key parameter in determining the operation characteristics of these devices. Hence, it is important to quantify and understand doping in these structures. Here, OBIC and PL scans data were used to quantify the width of planar frozen PLEC junctions.

### 3.2 OBIC Imaging of Frozen Planar PLECs

Since the discovery of PLECs, only a few optical beam scanning measurements have been reported on these devices. The built-in electrostatic field in a PLEC junction was firstly probed using OBIC scanning by Dick et al.[108] A 20 μm planar cell was activated and cooled then scanned with a focused Argon laser beam. To avoid the possibility of junction relaxation under a short-circuit condition, the photocurrent was not measured. The photovoltage and PL profiles were recorded as the beam was scanned across the p-n junction. A transition in the PL intensity and a voltage peak
was detected at the p-n interface. The width of the photovoltage field was used to extract the width of the depletion region that was identified as two microns, which was 10% of the device width. This initial study established the existence of a built-in field and electrochemical junction at the formed p-n interface. However, the device was cooled and scanned at a temperature of 250 K after it was activated. PEO was used as the ion-conducting material in the device active film which has a glass transition temperature of ~206 K. Therefore, the device was not completely frozen and, at the temperature of 250 K, the junction was prone to relaxation.[178] Also, the open circuit voltage in a p-n junction results from a deviation of the quasi-Fermi levels from the equilibrium state. Hence, it is expected that doing the measurement under an open circuit condition would modify the depletion region. As a result, the photovoltage profile would be different from the built in field in width and shape. This was demonstrated experimentally by Gao et. al.[174] Due to the challenges associated with optically scanning a planar PLEC at a cryogenic temperature and in a vacuum chamber, Dick’s experiment was the only study of its kind for 16 years since the introduction of PLECs. The other measurements were carried out by Gao et. al at Queen’s University.[174], [175] The experiments were performed on frozen planar junctions. The PLEC devices were turned on and cooled to temperatures less than or equal to 200 K to prevent doping relaxation. Therefore, it was possible to measure the short circuit current without affecting the doping profile of the cell. Moreover, a new approach was carried out by scanning large devices with millimeter size to carry out conductivity mapping and OBIC scanning.[115], [174] This offered flexibility in probing the devices by relaxing the limitation requirement on the probe size. Hu et. al. performed photovoltage and OBIC scans on a large cell mounted in a micro-manipulated cryogenic probe station equipped with an optical fiber.[174] The peaks of the photovoltage and OBIC profiles overlapped with the position of the p-n interface. Moreover, a maximum photovoltage signal of about 0.6 V was recorded, indicating a significant junction built-in potential compared to the initial OBIC study that obtained a photovoltage peak of a few tens of μV. However,
the large diameter of the optical fiber (200 μm) used in the scan and the junction jaggedness caused massive broadening to the obtained profiles.

Subsequently, Inayeh et al. utilized a low profile microscopy cryostat and a fluorescence microscope to perform PL and OBIC scans for a large planar frozen junction PLEC. The beam of a mercury lamp that was attached to a fluorescence microscope was focused to ~ 35 um using a 40X objective and scanned through the device in steps of 10 μm. Again, the OBIC signal and the PL coincided with the p-n interface but, due to the large beam profile and step size, the resulted OBIC signal was a replica of the line integration of the scanning beam preventing extraction of the junction built-in field profile.[175]

To get a better resolution for the measurement, smaller beam size is necessary. This can be done by better focusing the laser beam and using a more precise translational stage. Thus, more detailed information about the electric field in the static p–n junction could be obtained. In this chapter, laser sources were utilized to achieve higher resolution PL and OBIC scans. p-i-n and p-n doping structures in large PLECs were resolved.[187], [188] The following text explains the details of the experiment setup and outcomes.

3.3 Scanning OBIC and PL Imaging of a Frozen PLEC p-i-n Junction

The details of the electro-optical setup used for this experiment are shown in Figure 3.2. A Cryo-Industries microscopy cryostat chamber fitted with a hollowed-out copper cold finger is placed on translation stages that provide motion in the two horizontal dimensions. A turbo pump was used to maintain the pressure in the cryostat under ~ 10⁻⁵ torr while testing the devices. A liquid nitrogen cold finger was connected to the cryostat. The temperature of the device under test (DUT) was maintained within ±0.1 K from the target temperature by injecting liquid nitrogen into the cold finger and using an electric heater controlled via a Cryocon 32B temperature controller. The voltage bias was supplied using a Keithely-237 source/measurement unit that simultaneously measured the device current. Two optical windows (OWs) at the top and bottom sides of the cryostat provided
access for light to the DUT. The PL of the device was measured using a silicon photodiode and a low pass filter (LPF) with cut-off wavelength of 500 nm was fixed at the input window of the photodiode to block the excitation light.

Figure 3.2 The experiment setup with the snapshot of the frozen PLEC. The excitation beam appears as a blue dot near the light-emitting region. Note that the PLEC image only shows a small section of the entire device.

The images of the DUT were captured using a CCD camera that was fixed on a Nikon fluorescence microscope. The device was illuminated using a UV lamp with an emission spectrum centered at 365 nm to enable PL imaging for the doping process. The excitation lamp light was filtered using a PL filter (PLF) fixed at a Nikon blue excitation filter block (B-2E/C). A 10X objective lens was used to capture the device images with a field of view of 1.2 mm × 0.9 mm. A blue He-Cd laser (442 nm) was used as the excitation source. The laser beam was guided with mirrors and coupled into the microscope lamp optical path. Since the microscope is quite old, no reference was found about its optics. Different lenses were tried to couple the laser beam into the microscope. A plano-
convex (PCX) lens with 9 cm focal length gave the best focusing for the laser beam. After that, a 6.5/1.1 Galilean telescope was inserted between the mirrors, M2 and M3, to expand the beam and fill the aperture of the PCX lens. A dichroic mirror that is built into the microscope filter block directed the coupled beam into the objective lens.

This resulted in a focused beam out of the 10X objective on the DUT that was captured using the CCD camera on the microscope. The left onset of Figure 3.3 shows the beam intensity profile has a cylindrical TEM00 Gaussian mode shape. The 1-dimensional profile in the scanning direction was obtained by integrating the intensity in the perpendicular direction to the scanning path. The profile had a 1/e² width of 13 µm as shown in Figure 3.3.

![Figure 3.3](image)

**Figure 3.3** The focused scanning beam profile reflected from the polymer film surface. The 2-dimensional profile was captured using the microscope CCD camera (left). The 1-dimensional profile along the scanning direction was fitted to a Gaussian profile (right).[187]

A planar PLEC with 700 µm inter-electrode separation was fabricated inside a nitrogen-filled glove-box/evaporator system. The active film was spin casted on a 15 mm x 15 mm x 1 mm sapphire substrate for enhanced thermal conductivity. The used solution was a mixture of MEH-PPV, PEO and potassium triflate (KTf) dissolved in cyclohexanone. The active material was mixed to have a final weight percentage ratio of 1% (MEH-PPV): 0.5% (PEO): 0.12% (KTf). The casted film was dried on a hot plate set at 50 °C for five hours. This resulted in a final film thickness of 500 nm measured by an optical interferometer. Afterwards, 100 nm thick aluminum electrodes
were deposited through a shadow mask by thermal evaporation at $\sim 1.5 \times 10^{-6}$ torr. The final device was an 8 mm long planar PLEC with 700 µm inter-electrode separation. The device was installed into the cryostat and moved out of the glove box to be scanned. The cryostat was then mounted into the activation and scanning setup.

During the doping process the cell current, as well as the emitted PL intensity and pictures were monitored. In Figure 3.4, the film initially ($t=0$ sec) showed strong orange PL emitted by the luminescent polymer component, MEH-PPV. Subsequently, a DC bias of 150 V was applied to initiate doping and activate the cell. After 15 seconds through the doping process, observable doping fronts appeared at the electrodes edges. Doping causes PL quenching for the doped part of the polymer film.[189], [190] Therefore, the doped regions look darker than the pristine polymer under UV light. Similar to previous studies, the p-doping front forms behind the n front and has a darker color.[112], [115], [175] Subsequently, the doping fronts propagated through the film causing darkening for a larger area of the polymer film. The cell temperature was maintained at the initial temperature for $\sim 250$ seconds. However, the doping current was still at a very low value. This can cause formation of a p-n junction and device degradation before reaching a high film electric conductivity necessary to detect the OBIC signal. Therefore, the temperature was elevated to 330 K to step up the doping rate. Junction formation and EL caused by radiative recombination of the injected carriers was observed at $t=270$ s. As the film gained more doping and higher conductivity, evident by the rapid current increment, significant EL became easily visible. As a result, the photodiode reading started to kick up after reaching a minima due to luminance quenching ($t=850$ s). At this point, the device current reached a high value of $\sim 1.3$ mA. Therefore, cooling was initiated to freeze the formed junction at a rate of $\sim 0.365$ K/s. After the device started to cool down, the injected current continued to increase, as a result of continuing doping, until it reached a maxima of $\sim 5$ mA.
Figure 3.4 Device snapshots (upper panel) and the collected data (lower panel) during the device turn-on and freezing process. The top electrode (anode) was positively biased relative to the lower electrode (cathode). The p-doped region at the top is visibly darker than the n-doped region in the lower part of the film. Only 1100 µm × 700 µm of the entire device active area is shown.[187]

Later on, the current started to decline as the mobility of the charge carriers decreased with cooling. At the same time, the device luminance became more redshifted (Figure 3.4, t=1300 s). As a result, the silicon photodiode registered a higher signal since it has a relatively higher sensitivity at this part of the electromagnetic spectrum. Cooling was continued until the temperature reached the
target freezing point of 200 K, at which point the device current registered ~ 0.8 mA. Previous studies showed that 200 K is sufficient to lower the ionic mobility and fix the junction for a period long enough to scan the frozen cell.[113] Subsequently, the cell bias was set to zero in preparation to carry out the OBIC measurement. The picture of the cell after removing the bias voltage is shown in the last snapshot in Figure 3.4 (t >1300 s). Clearly, a bright line appears between the p and n charge neutral regions showing lower PL quenching in this region. The scanned region was chosen such that the beam passes through a relatively smooth p-n interface (Figure 3.5). The OBIC scan was carried out by moving the cryostat in the direction perpendicular to the p-n junction line with 1 μm steps. The translation stage motion as well as the photo-generated current and luminance were controlled and collected via LabVIEW programs.

![Figure 3.5 The p-n junction region in the scanned 700 μm frozen device (the brightness and contrast were increased by 40 %). The scanning beam is indicated by the blue dot. The white ruler shows the distance from the anode.](image)

The beam profile is needed to be deconvoluted from the measured data. Since the data was collected at discrete points, discrete de-convolution was attempted to get exact measures profiled. Since discrete de-convolution is a division (or derivation) process, it amplifies noise and corrupts the
output. Discrete Fourier transform was also attempted, however, neither worked even after filtering. To get over this problem, the collected data was fitted to Gaussian functions. Thereafter, deconvolution becomes a straightforward process:

\[
G_{\text{Junction}} = A_J e^{-8x^2/W_J^2} \\
G_{\text{Beam}} = A_B e^{-8x^2/W_B^2} \\
G_{\text{OBIC}} = A_0 e^{-8x^2/W_O^2} \\
G_{\text{OBIC}} = G_{\text{Beam}} * G_{\text{Junction}}
\]

\[
\mathcal{F}\{G_{\text{Junction}}\} = \frac{\mathcal{F}\{G_{\text{OBIC}}\}}{\mathcal{F}\{G_{\text{Beam}}\}} = \frac{A_0 W_0 e^{-\pi^2 W_O^2 k_z^2/8}}{A_B W_B e^{-\pi^2 W_B^2 k_z^2/8}} \\
\Rightarrow G_{\text{Junction}} = A_J e^{-8x^2/(W_O^2 - W_B^2)}
\]

Equation 3-1

where \(\mathcal{F}\) is the Fourier transform operator. Hence, from Equation 3-1 the deconvoluted junction width is given by \(\sqrt{W_O^2 - W_B^2}\). Figure 3.6 shows the collected data in the upper panel. Both curves fit well with Gaussian profiles. One Gaussian was enough to give good approximation for the photocurrent. However, fitting the PL peak required a sum of six Gaussians. The measured PL and OBIC profile curves are shown in the upper panel of Figure 3.6. The profiles that were deconvoluted from the measured data are plotted in the lower panel and overlaid onto the scanned device picture. The Gaussian shape resulted from deconvoluting the photocurrent signal peak had a \(1/e^2\) width of \(~18\ \mu\text{m}\). Since the exciton diffusion length in PPVs is on the order of nanometers,[191] the deconvoluted photocurrent width should represent a good approximation to the width of the junction depletion region. Compared to the OBIC peak, a wider PL peak was detected. The peaks of the PL and the photocurrent profiles are displaced by \(~12\ \mu\text{m}\). It appears that in Figure 3.6 the peak of the PL coincides with the relatively bright line at the p-n interface. The peak of the photocurrent occurs exactly at the interface between that line and the p region. This can happen only if a lightly doped region forms next to the depletion region, which results in a p-
i-n junction structure. Such a doping profile has rarely been observed although it was early predicted in a theoretical study by Manzanares et al.[80] Such information was not possible to be extracted if the OBIC and PL scans were not performed simultaneously which shows the importance of combining these measurements in a single setup. It is expected that this type of doping structure formed since cooling the device was started at an early stage of the junction formation. As a result, the ionic mobility was reduced drastically before the doping fronts penetrated the quasi-intrinsic region and caused significant PL quenching.

According to the conventional semiconductors theory, the field strength increases with doping concentration gradient. The detected photocurrent peak occurs between the quasi-intrinsic region and the p region. This suggests that the detected quasi-intrinsic region is a lightly n-doped region. This is consistent with the detected stronger PL in this region compared to the darker n region.

Figure 3.6 The spatially resolved photocurrent and PL profiles obtained for the scanned cell. The upper panel shows the measured data. The lower panel shows the profiles resulting from deconvoluting the beam profile from the measured peaks. The background in the lower panel shows the frozen device pictured at zero bias.[187]
Hence, the doping pattern that is revealed from the scans has n/n-/p structure. The absence of a significant photocurrent in the vicinity of the n region suggests that the doping gradient between the n and n- regions is relatively small.

3.4 High Resolution Scanning OBIC and PL Imaging of a Frozen PLEC p-n Junction

The setup in Figure 3.6 was updated to achieve higher resolution and more flexible alignment as shown in Figure 3.7. The He-Cd laser failed after performing the first set of OBIC scans and was replaced with a blue diode laser (473 nm).

![Figure 3.7 Updated experiment setup for high resolution OBIC and PL scans.][188]

The beam was guided and coupled into a single mode fiber (SMF) using mirrors (M1, M2) and a coupler lens. The output beam of the fiber was collimated, 2X expanded and directed into an objective via a beam splitter cube to be focused onto the DUT. The aforementioned components were attached via a cage system to the microscope. In the scanning measurements, the beam was focused onto the device to ~1.9 µm $1/e^2$ width using a 50X objective. This configuration enabled
reattaching the microscope mercury lamp. The lamp light was filtered using the blue excitation filter on the Nikon cube (B-2E/C) to provide the excitation light for PL imaging.

The spatial structure of the formed junction at the p-n interface can convolute into the profile obtained from the OBIC scan. To rule out the effect of such an interference, the p-n junction formed in the cells should be smooth and straight along the cell. To achieve this, multiple cells were fabricated and activated to optimize the active film mixture, the electrode materials, as well as the activation bias and temperature. Two film recipes were tried with MEH-PPV:PEO:KTf weight ratios of 1:0.5:0.12 and 1:1:0.25. Figure 3.8 shows a sample of the activated cells with the fabrication and activation parameters labeled on each cell figure, in the following order: electrodes material, MEH-PPV:PEO:KTf weight ratio, activation voltage or current (for constant current the initial voltage is quoted in parenthesis), and activation temperature.

It was noticed that the cells with a MEH-PPV:PEO:KTf ratio of 1:0.5:0.12 resulted in a non-straight light-emitting area line and the junction was not smooth enough to be scanned as shown in the first column in Figure 3.8. For a PPV:PEO:KTf ratio of 1:1:0.25 the cells with aluminum electrodes did not form smooth junctions when activated using a constant voltage bias as shown in the second column. Constant current bias resulted in smoother junctions when the cell was activated at elevated temperature as shown in the third column. On the other hand, devices with gold electrodes showed much better smoothness in general, due to the better work function alignment with the HOMO level of MEH-PPV. The last two rows in the second column show examples of gold electrode cells (k and n). For the scans done here, a cell was fabricated with a MEH-PPV:PEO:KTf ratio of 1:1:0.25 with gold electrodes and 700 µm inter-electrode spacing by a similar method to what was explained in Section 3.3.
Figure 3.8 Formed junctions for different PLEC fabrication and activation parameters. The parameters are labeled as the following: electrodes material, MEH-PPV:PEO:KTf ratio, activation voltage or current (for constant current, the initial voltage is quoted in parenthesis), activation temperature.
The cell was activated by applying a 20 V DC bias at a temperature of 360 K. Subsequently, it was cooled at a rate of 0.19 K/sec to 170 K (Figure 3.9). The lower freezing temperature of 170 K compared to 200 K in Section 3.3 fixed the junction for a long time. This allowed performing multiple scans with no relaxation happening in between as observed by the non-varying IV behavior over the course of the experiment.

Figure 3.9 Activation process of the 700 µm PLEC under 20 V DC bias. Top: time evolution of the cell current and temperature during the activation process. The inset shows a schematic of the planar PLEC. Bottom: time-lapse fluorescence images of the planar PLEC during the activation process. Only a section of the entire cell is shown. The bright line formed after t=9 s is due to the EL of the cell.[188]
The lower panel of Figure 3.9 depicts the time evolution of the doping fronts and junction formation before cooling. There is clear interaction between the p- and n-doped regions that shifted the position of the p-n junction after it was initially formed. At the start, p-doping penetrated into the n-doped region as shown in the snapshots that cover the time frame between t= 9s to t=36s. However, as the last snapshots reveal, the n region showed a slightly slower expansion in the last 15 seconds before the junction position settled. The dark p-doping in MEH-PPV has been known to be partially irreversible even when the cell bias polarity is reversed.[65] Consequently, the p-doped region that was reversed by the propagating n-doping front appeared relatively darker.

After the device was activated, a PL image was taken for the frozen cell under UV illumination as shown in Figure 3.10. Clearly, the used activation conditions resulted in a smoother junction compared to the device in Section 3.3 and exhibited strong and uniform EL under bias indicating a high-quality junction for scanning purposes. The light-emitting region appears as a bright line between the darker n region that was p-doping-compensated and the dark p-doped region on the other side of the junction. This PL structure seems to be similar to the one observed in Section 3.3 and suggests a p-i-n junction. Nevertheless, the spatially resolved beam-generated PL data does not back this possibility and reveals a p-n junction for the activated frozen cell. Moreover, it will be shown that the as-activated p-n junction can be relaxed into a p-i-n junction when subjected to warming-cooling cycles.

A total of 18 scans for spatially resolved OBIC and PL were performed at seven locations along the formed junction. These locations are labelled by the letters shown in Figure 3.10. On the same figure, there are arrows that specify the direction of the OBIC scans across the p-n junction at each location. The scanned regions did not suffer from any observable jaggedness that could interfere into the scanned profiles.
Figure 3.10 PL images of the planar PLEC at 170 K after activation. The upper panel shows the portion of the cell through which the optical scans were performed. The letters and arrows indicate the location of and direction of the scans. The lower panel shows the same region of the frozen planar PLEC with an applied voltage bias of 20 V. Uniform EL along the horizontal p-n junction can be seen.[188]

The profile of a simultaneous OBIC and PL scan going through position E is presented in the top panel of Figure 3.11. The scan was performed to cover the full length of the cell between the electrodes. A large slope in the PL profile is observed near the electrodes which reveals a corresponding doping gradient in these regions. The doping level is the highest next to the edges of the electrodes and gradually decreases toward the charge neutral regions. This confirms a previous observation in a contact probing measurement where the film in an active PLEC was found to have the highest conductivity near the electrode edges.[115]
Figure 3.11 OBIC and PL profiles of the frozen planar PLEC along position E. (a) full OBIC and PL scans of the planar PLEC across the entire planar PLEC along position E. The cathode is located at -230 µm and the anode is located at 470 µm as indicated by the vertical blue dashed lines. (b) OBIC scan data of four scans along position E and Gaussian fit to the data near the OBIC peak.[188]

Since multiple scans were performed at each location, the OBIC signal peak was used as a reference point and was assigned the center of the spatial profile (zero µm). To the left of the OBIC peak, the n-doped region registered higher PL compared to the p-doped region PL to the right. The PL intensity drop from -45 µm to 0 corresponds to the above-mentioned dark p-doping residuals in the
n region. The slight local PL peak next to the OBIC peak matches with the thin bright line, which is also the light-emitting region, observed in Figure 3.10. The PL intensity at this peak is \( \sim 10\% \) lower than the PL intensity of the neighboring n-doped region. This is clearly different than the p-i-n PL profile that was seen in Figure 3.6 and discussed in Section 3.3. Despite its dark appearance in the UV PL image, the PL intensity of the scanned p-doped PL still registered a significant level in evidence for the sensitivity of the PL scan. A “transition zone” appears between 0 and \(+30\,\mu m\) in which the PL intensity drops from the level on the n-side to the constant level of the p-side. The narrow OBIC peak is magnified in the lower panel of Figure 3.11. A total of four scans across the junction at location E were incorporated in the shown profile. The data from these different scans were combined by fitting each to a Gaussian function and then shifting the fitting profile peak to the spatial reference point (X=0). The resultant Gaussian from the total data points has a \(1/e^2\) width of \(3.1\,\mu m\). Taking into account the width of the scanning beam of \(1.9\,\mu m\), the inferred junction width was \(\sim 2.4\,\mu m\). The metallurgical p-n junction, marked by the OBIC peak, is located six microns to the right of the local PL peak at the n-doped side. On the other side of the junction, a sharp PL gradient is observed. The electric field that causes the OBIC signal is maximum at the p-n interface. Therefore, the observed PL gradient must be inferring a drop in doping level at the p-doped side. It might also be a result of a graded junction structure.

Similar processing was done for the rest of the OBIC scans at the other locations as listed in Table 3-1. The measured OBIC profiles show different widths at the different scanned locations and all of them were larger than the excitation beam width of \(1.9\,\mu m\). The aforementioned profile at location E was the widest while the narrowest width of \(2.1\,\mu m\) was measured at location F. The arithmetic mean of the measured OBIC widths was \(\sim 2.53\,\mu m\) and the standard deviation was \(\sim 0.45\,\mu m\). Knowing that the effect of the exciton diffusion is ignorable, this average OBIC signal corresponds to an average junction width of \(1.5\,\mu m\). The OBIC signals had peak values of \(292 \pm 40\,pA\) resulting from the scanning beam power of \(2\,\mu W\).
Table 3-1 OBIC scans data in all seven locations (A-G). The OBIC peak widths were determined from Gaussian fits. The average OBIC peak widths were calculated by fitting all data together for each location. The junction widths were determined by quadratic subtracting the beam width of 1.9 µm from the average OBIC width.[188]

<table>
<thead>
<tr>
<th>Position</th>
<th>Number of Scans</th>
<th>$1/e^2$ OBIC Width (µm)</th>
<th>Peak Current (pA)</th>
<th>Average OBIC width (µm)</th>
<th>Average junction width (µm)</th>
<th>Average Peak Current (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>2.7</td>
<td>300</td>
<td>2.6</td>
<td>1.8</td>
<td>315</td>
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<td></td>
<td></td>
<td>2.5</td>
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<td></td>
<td></td>
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<tr>
<td>B</td>
<td>2</td>
<td>2.1</td>
<td>335</td>
<td>2.1</td>
<td>0.9</td>
<td>343</td>
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<td>2.2</td>
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<tr>
<td>C</td>
<td>2</td>
<td>2.3</td>
<td>305</td>
<td>2.6</td>
<td>1.8</td>
<td>294</td>
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<td></td>
<td>2.9</td>
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<tr>
<td>D</td>
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<td>336</td>
<td>2.5</td>
<td>1.6</td>
<td>313</td>
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<td>E</td>
<td>4</td>
<td>3.1</td>
<td>252</td>
<td>3.1</td>
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<tr>
<td>F</td>
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The 1.5 µm average junction width obtained is the smallest ever reported for a planar PLEC. It is also worth mentioning that this width is only 0.21% of the inter-electrode gap, which is smaller than the reported values for planar and sandwich devices. This number takes into account the broadening caused by the scanning beam by deconvolution. Hence, this measurement has, for the first time, directly resolved the depletion width of a frozen PLEC p-n junction. Compared to this resolved width, the widths of the visible EL zone and the PL gradient zones are ~ 7 times and ~ 20
times larger respectively. Evidently, the distinction between these three different regions shows the importance of the high resolution scans for PLECs.

The doping gradient inferred from the PL drop at the p-n interface can be a uniform gradual concentration change in the p- and n-doping. Having the jaggedness of the initially formed junction leaves a strong possibility that the seemingly uniform doping along the junction still had sub-micrometer scale roughness features. Similar sharp features were observed on a larger scale in another study where the p-n junction suffered from severe jaggedness.[124] The presence of these structural elements was attributed to cause a tunneling leakage current that causes the non-ideal diode linear I-V curves often observed for frozen planar PLECs. Also, it was found that exposing the device to a heating cycle causes doping relaxation and eliminates these features. This was observed visually in the PL images and by the enhanced open-circuit photo voltage of the relaxed junction attributed to the relatively suppressed leakage current. When these features are on a submicron scale they cannot be resolved by the diffraction limited optical means such as PL imaging or focused beam PL scans. Higher resolution is required to probe features at that scale which can be achieved using a focused electron beam or an optical near field probe. The spatially resolved junction widths obtained from the measurements here account for a small portion of the total cell size. For PV and light-emitting applications, the depletion region is the only active area where free carrier generation and recombination occur. Therefore, the cell performance can be enhanced by expanding this area relative to the device size. A powerful approach to achieve that in large planar PLECs is to form more junctions by the introducing metallic nano-particles to the active film.[192], [193] This approach has not yet been applied to sandwich devices. However, there is great potential that using this method can lead to high efficiency sandwich PLECs.

3.5 PLEC p-n Junction Relaxation
To understand the effect of protrusions on the measured PLEC junctions’ widths, OBIC scans were carried out on relaxed PLECs. The planar cell presented here was fabricated as explained in
Section 3.3 with a MEH-PPV:PEO:KTF weight ratio of 1:1:0.25 in the active film. Aluminum electrodes were deposited with 560 µm spacing since it was learned that PLECs with aluminum electrodes resulted in a wider junction profile compared to cells with gold electrodes, as was seen in Section 3.4. Hence, it is expected that the effect of doping protrusions on the PLEC junction would be more pronounced with aluminum electrodes. The cell was activated at 340 K using a constant current bias of 5 mA. This is the same as the maximum doping current value reached for the device described in Section 3.4. In Figure 3.12, the voltage curve showed an initial drop as the conductivity was enhanced due to doping. The device was doped at the initial temperature until the voltage reached ~22V.

Figure 3.12 Time evolution of cell voltage and cell temperature during the activation process. A DC bias current of 5 mA was applied. The inset shows time-lapse fluorescence images of doping evolution in the planar PLEC. Only a section of the entire cell is shown. The planar PLEC was under illumination of blue light (450 nm-490 nm) filtered from a Mercury lamp.
As cooling started, the device conductivity started to drop and the voltage increased to maintain the required 5 mA current value. As the activation snapshots show, the junction of this device formed much faster than for the device described in Section 3.4 since the initial voltage bias was relatively high (500 V). Hence, the initial drop in luminance was not captured within the time frame of the first data point in the PL curve. The device showed more doping and luminance quenching after the formation of the junction. Similar to Section 3.4, the junction was jagged as formed but smoothed out afterwards. Cooling was started after the junction smoothness was suitable for scanning as shown in the last snapshot. The bias was removed after the temperature reached 180 K. The PL picture of the frozen device is shown in Figure 3.13.

![Figure 3.13](image)

**Figure 3.13** Scanning regions on device-2 shown on a snapshot for the cell under zero bias (upper panel) and 125 V bias (lower panel). The images were captured under blue light illumination and higher camera exposure compared to the exposure used during the activation process.[194]

OBIC and PL scans were done along the frozen junction at two locations labeled on Figure 3.13. A beam power of 50 µW was used since higher power, compared to the 2 µW power used in
Section 3.4, is needed to detect the OBIC signal after relaxing the device. Three scans were done at each location and the measured data was fitted to Gaussian profiles, similar to what was done in Sections 3.3 and 3.4. The average measured $1/e^2$ OBIC width for the device was ~ 4.85 µm as summarized in Table 3-2. This was a wider profile compared to the one measured in Section 3.4.

<table>
<thead>
<tr>
<th>Position</th>
<th>Number of Scans</th>
<th>OBIC $1/e^2$ Width (µm)</th>
<th>Peak Current (nA)</th>
<th>Average width (µm)</th>
<th>Average Peak Current (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3</td>
<td>4.7</td>
<td>17.1</td>
<td>5.0</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.7</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>4.7</td>
<td>13.1</td>
<td>4.7</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>13.1</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>17.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.7</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In an attempt to smooth out the junction and eliminate submicron protrusions, the frozen cell was partially relaxed after the scans for the as-frozen cell. The relaxation was carried out by exposing the cell to warming/cooling cycles by elevating the temperature to 270 K and then lowering it back to 180 K. During these cycles, the cell was kept at open-circuit condition to avoid quick relaxation and loss of the active junction. After each cycle, the IV trace of the frozen cell was recorded. Figure 3.14 shows the time dependent cell temperature profile during the relaxation cycles and the IV curves of the cell before and after each relaxation cycle. The IV curves were measured at the freezing cell temperature of 180 K. Three relaxation cycles were carried out with a total relaxation time of 5060 seconds. Comparing the IV curves of the relaxed cell to the as-activated cell IV curve shows a clear drop in conductivity due to de-doping after each relaxation. Moreover, the linearity and symmetry of the as-activated I-V curve were lost after relaxation.
Figure 3.14 Relaxation temperature and duration with the relaxation duration time at 270 K is marked at the top of the curve (up). IV curves of the device before and after three consecutive relaxation cycles (bottom). The IV curves were measured at the freezing temperature of 180 K.

The frozen junction resulted from the relaxation cycles was scanned at position A, as pointed out in Figure 3.13. Figure 3.15 shows the profiles of the PL scans for the device before and after doping.
relaxation. The line X=0 was taken as the reference that indicates the measured OBIC peak in each scan. A noticeable difference between the as-activated cell and the relaxed cell is the PL peak at the reference point that emerged after the second relaxation cycle. In this region, the PL level is higher than the rest of the cell in a clear contrast to the device before relaxation. This new PL profile is similar to the one observed in Section 3.3, which shows that a sharp quasi-intrinsic region opened after relaxing the device and a p-i-n junction was formed.

Figure 3.15 Measured PL profiles of the relaxed p-n junction at location A before and after the relaxation cycles. The reference line X=0 indicates the measured OBIC peak.

The normalized OBIC profiles at location A before and after relaxation are plotted in Figure 3.16. After relaxation, the OBIC peak width reduced from 4.8 μm to ~ 3.9 μm. This implies a depletion
width of 3.4 μm compared to 4.4 μm for the as-activated cell. The same pattern was consistently observed in other relaxation experiments.

![Normalized OBIC scanning profiles at location A before and after relaxations. The excitation laser power used was 50 µW.](image)

In contrast to the obtained results, it was expected that junction broadening would take place after relaxation due to doping reduction and the development of a quasi-intrinsic region between the p and n regions, as discussed before. Evidently, this supports the aforementioned proposal for submicron features along the as-activated junction. These protrusions presumably formed when the p- and n-doping fronts came into contact by penetrating the junction region. The PL transition between the p and n regions after relaxation is much sharper compared to the p-n junction before relaxation. The relatively abrupt doping transition in the relaxed junction can explain the narrower OBIC profile as a result of reduced depletion region width after relaxation.
The PL profile level in the charge neutral regions did not show a noticeable change. This shows that, within the initial time of relaxation, de-doping mainly happens in the junction region and causes an intrinsic region to emerge. The PL profile before relaxation shows a smooth gradient around the OBIC peak, X=0 in Figure 3.15, suggesting that the depletion region is situated in a transient region with mixed p- and n- doping. On the other hand, after three relaxation cycles, the OBIC maximum occurs exactly at a newly formed PL peak. Around this peak, a more separated doping profile emerges with a sharp transition in between. This more defined p- and n-doping separation is consistent with the observation that doping relaxation in PLECs happens in a reverse pattern to doping propagation.[65] Removing the applied voltage at high temperature allowed the doping ions to move freely and recombine, minimizing doping in the junction region. As a result, the p and n fronts start to retard back away from the junction region, which leads to more well-defined and separated p- and n-doped regions and a lower doped junction forms. Indeed the regions in the vicinity of the junction show less PL quenching compared to the as-formed junction, suggesting that the doping level in this region decreased. A lightly n-doped region formed to the left of the OBIC peak and a lightly p-doped region formed to the right. These lightly doped p and n regions still showed a gradient toward the outer charge neutral regions which did not seem to be significantly affected by relaxation. In spite of the small change in PL quenching in the charge neutral regions after relaxation, the measured OBIC showed significant reduction in the measured current of ~20 folds. This confirms that the resistivity of the device increased significantly, attributed to the mobility reduction even with a small doping change. This was also observed in a previous study on planar PLECs discharging, and will be presented in Chapter 5.[195] Although the PL suggests that doping around the depletion region was reduced, the measured OBIC width after relaxation was smaller than the as-formed junction. This supports that the mixed doped region, formed in the as-frozen region, is populated with submicron protrusions emerging from the doping fronts into the junction region.
It is worth mentioning at the end of this chapter that some factors, related to the experiment setup, could interfere with the measured signal. Especially for the high resolution OBIC measurement, it is important to estimate and mitigate the effects of these factors on the measured data and the extracted parameters. All the scans reported here were done in dark and the excitation beam was the only source of illumination. The background thermal noise in the measure current and PL was estimated by measuring these values in dark, and found to be not measureable. The calculated error in the measured OBIC data points is 0.3 %, based on the source-measurement unit specification sheet. The error in the measured PL is estimated based on the photodiode amplifier output noise, the temperature drift and the voltage drift ratings. This was found to be less than 0.1% at a measured PL equal to 10 % of the peak PL value. The laser power was stable within less than ± 2 % over 2.5 hours. This is longer than a single scan time. The laser was restarted and left to cool down between lengthy scans. Moreover, the laser power was measured before and after each scan to insure the stability of the output power during the scan. The error in determining the width of the scanning beam fitting profile was within 1% considering a confidence coefficient of 95%.

Divergence causes broadening of the laser beam in the scanned film. The used beam of 1.9 um width has a depth of field, given by the Rayleigh range, of 23 µm. Therefore, even that the beam profile was captured from the reflection at the polymer film surface; the beam will not suffer from any significant divergence-related broadening as it is penetrating the film (~ 0.5 µm thick). The beam that was used for the high resolution scans was characterized with M² factor of 1.05. Hence, at the bottom part of the film, the excitation beam width will only expand by ~ 0.38 %. It should be noted that the beam is attenuated significantly as it penetrates the active film, as will be explained shortly, which reduces the divergence effect on the measured OBIC profiles. Nevertheless, since we are interested in setting an upper bound for the error, this value is included in the error estimate for the beam width to be ~ 1.38 %.
The vertical excitation of the beam eliminates the possibility of the beam coupling into the film-guided modes. Any significant coupling requires phase matching between the beam and the guided modes. Since the beam wave vector is perpendicular to the guided modes propagation direction, the coupling is expected to be zero. Moreover, if any coupling happens, due to a possible small tilt in the scanned device, it should be observable in the PL image of the device under the beam excitation. However, and no measurable PL was observed beyond the beam area in these images.

MEH-PPV is characterized by a high absorption coefficient of $\sim 5 \times 10^4$ cm$^{-1}$ in the blue spectrum region. Considering the film thickness of 0.5 µm, only 8.2% of the beam reaches the polymer/sapphire substrate interface. The reflection at the polymer/sapphire interface is very small and characterized by a power reflection coefficient of $(1.77-1.6)^2/(1.77+1.6)^2 = 0.25\%$. Hence, the net excitation power reflected from this interface is about four orders of magnitudes less than the incident power and can be ignored. The power reflection coefficient at the bottom surface of the sapphire substrate is $(1.77-1)^2/(1.77+1.6)^2 = 7.7\%$. Hence, a total of $8.2\% \times 7.7\% = 0.63\%$ of the original beam will be reflected back to the active film. However, the beam will be diverging as it is travelling through the 1 mm thick substrate. Therefore, this reflected beam diverges to 400 times the incident beam waist at the Sapphir/polymer interface. So, the intensity of the excitation light reflected back from the bottom surface of the sapphire substrate is about six orders of magnitude lower than the incident beam light intensity and can be ignored.

From the discussion above, the laser power fluctuations is the main source of error in the measured data. It is assumed that the relationship between the laser power, and the PL and OBIC signals is linear. Hence, the expected error in the measured data is within 2.1% for the PL signal and 2.3% for the OBIC signal. This error value in the OBIC signal results in a corresponding error upper bound of 4.5% in the measured OBIC width. Considering this value of error, the minimum measured OBIC width of 2.1 µm is still beyond the error margins of the scanning beam width. Therefore, the conclusion of resolved junction is valid. In addition, the estimated errors in the above
discussion are upper bound values for individual data points. In the performed scans, the error values are expected to be further minimized because of error averaging when the multiple scanned curves are fitted to the data points.
Chapter 4

Junction Depletion Width Estimation from OBIC Profiles: A Numerical Study

Charge transport occurs due to a potential gradient that can be chemical or electrical. The resulting currents and charge concentrations are modelled via the drift-diffusion, continuity and Poisson’s equations. In steady state, the transport equations are given, respectively, by: [196]

\[ J_n = k_B T \mu_n \nabla n - q \mu_n n \nabla u \]

\[ J_p = -k_B T \mu_p \nabla p - q \mu_p p \nabla u \]

Equation 4-1

\[ \nabla J_n + (G - Q(np - n_i^2)) = 0 \]

\[ -\nabla J_p + (G - Q(np - n_i^2)) = 0 \]

Equation 4-2

\[ \nabla^2 V = \frac{-\rho}{\varepsilon_0} \]

Equation 4-3

where \( J \) is the current density, \( k_B \) is the Boltzmann constant, \( T \) is temperature, \( n \) is the electron concentration, \( p \) is the hole concentration, \( \mu \) is the mobility coefficient, \( q \) is the elementary charge, \( u \) is the electrostatic potential, \( G \) is the generation rate, \( Q \) is the recombination coefficient, \( V \) is the electric potential and \( \rho \) is the charge density. The subscripts \( n, p, \) and \( i \) stand for electrons, holes, and intrinsic respectively. The Einstein relation was assumed valid.

The basic question that should be answered about OBIC scans is where to expect a significant signal to be generated? In the absence of an external electric field or potential gradient, the second part of Equation 4-1, the drift part, vanishes. The first part of Equation 4-1 represents the diffusion part of the current, which is driven by the gradient of electrons and holes. The electron and hole components of this part counter each other due to the opposite electronic charges for electrons and holes. These parts vanish when the diffusion coefficients and spatial gradients of electrons and
holes are equal. Considering balanced electron-hole generation and recombination, if the electrons and holes have different diffusion coefficients, the higher mobility component will be more depleted from the generation zone and will minimize the net diffusion current. Thus, the electron and hole diffusion currents tend to cancel each other out. Considering the charge neutral regions with uniform doping levels throughout, no drift current is expected in the absence of an external electric field. Having an axisymmetric excitation source leads to an axisymmetric generation and recombination rate for electrons and holes. Hence, the spatial integral of the diffusion currents vanishes under these conditions. Therefore, it is not expected to detect OBIC signal in uniformly doped charge neutral regions when the exciton’s diffusion length is very small. A significant OBIC signal is only expected at semiconducting interfaces with a large potential gradient, which leads to a built-in electric field. In such regions, the electron and hole drift currents add up proportional to the electrostatic potential gradient to maximize the net drift current. Moreover, according to the Onsager-Braun model, the free carrier generation rate in organic semiconductors is strongly enhanced by the presence of an electric field.[45], [46] Thus, OBIC peaks detected at PLEC p-n junctions represent the built in electric field in this region and are largely attributed to the drift photo-induced current.

4.1 Drift Current in a Space-Charge Region
The electric field in the depletion region drives the photo-generated EHPs to the charge neutral regions. The drift current value given by the second part of Equation 4-1 corresponds to the terminal velocity of the charge carriers being accelerated by the electric field under the influence of scattering. However, this value does not carry information about the electric field level where the charge carrier was generated. It turns out that the question that is needed to be answered is: could a charge carrier leave the depletion region with a velocity less than its terminal velocity under practical conditions? This can be examined by quasi-classical treatment. The equation of motion for the electronic charge carriers in one dimension is given by:
\[
\frac{d^2x}{dt^2} + \frac{m}{\tau} \left( \frac{dx}{dt} \right) = \pm qE, \quad \tau = \frac{m\mu}{q}
\]  
Equation 4-4

where \( x \) is the spatial coordinate and \( t \) is the temporal coordinate, \( m \) is the effective mass of the charge carrier and \( \tau \) is a phenomenological constant to account for the scattering lifetime of the charge carrier.

It is assumed that a photon is absorbed in a p-n junction at point \( x_0 \) to generate an EHP and the photo-generated EHPs have a negligible effect on the junction field. Also, it is assumed that the electric field is slowly varying over the junction so that the equation can be solved within segments of constant field values. Under these assumptions, Equation 4-4 can be solved analytically and results in:

\[
x(t) = \pm E\mu \left[ t + \frac{m\mu}{q} e^{-\left( \frac{q}{m\mu} \right)} + \frac{m\mu}{q} \right] + x_0,
\]

\[
\frac{dx}{dt} = \pm E\mu \left[ 1 - e^{-\left( \frac{q}{m\mu} \right)} \right]
\]

Equation 4-5

As expected, the velocity of the charge carrier takes a damping function form. The velocity of the particle reaches 99% of the terminal velocity at time: 

\[
t_{0.99} = \left[ 4.6 \frac{m\mu}{q} \right].
\]

By that time the particle would move a distance: 

\[
|x_{0.99} - x_0| = \left[ 5.61E \frac{m\mu^2}{q} \right].
\]

The effective mass can be approximated by the free electron mass. Mobility values are known for a wide range of materials. Thus, an estimate for the average field in the junction is necessary. A reasonable estimate of the average junction field can be obtained with the following reasoning. For OBIC scans, light sources are used; hence, the resolution of these measurements is in the order of the source focus spot. The best focus spots can be achieved with single mode laser sources. These are mostly available in the visible and near infrared region. Hence, the resolution should be in the range of microns. Therefore, a diffraction
limited OBIC setup can only resolve structures that span micron extensions, such as the junctions presented in Chapter 3. The potential drop in the junction is usually less than the band gap of the material. Band gaps of semiconductors are in the range of a few electron volts. Hence, a $\sim 10^{-4}$ V/cm is a very reasonable estimate for the average electric field in the junction. Therefore, $|x_{0.99} - x_0| = 20 \times \mu^2 \text{um}$. The mobility range lies between $\sim 10^{-3} \text{ cm}^2/\text{V.s}$ for conventional semiconductors like silicon and $\sim 10^{-2} \text{ cm}^2/\text{V.s}$ for semiconducting polymers. [122], [170], [197]–[199] Thus, the charge carrier accelerates to the terminal velocity within submicron distance in the junction. Therefore, the photo-generated charge carriers will most likely leave the depletion region at the terminal velocity. This information, however, is not useful in interpreting the generated OBIC current.

If the drift by the local electric field was not the cause for the observed variation in the OBIC profile what could be the reason? It is most likely due to the variation in the density of the photo-generated EHPs. It is well-known that, due to the presence of the p-n junction, bands bend under the influence of the built in electric field (Figure 1.20). This results in the depletion of electrons and holes from the junction region and causes variations in the occupation probability along this region, and thus the concentration of the generated EHPs vary as well. Therefore, to find the relation between the photo-generated OBIC current and the local potential at the point of excitation, the drift-diffusion equation should be solved along with the continuity equation.

The problem of extracting the built-in electrostatic field profile from OBIC scan traces was treated by Fang and Ito.[200]–[202] They developed an algorithm based on linearizing the drift-diffusion and the continuity equations using the Maxwell-Boltzmann distribution function. The exponential Maxwell-Boltzmann functions were approximated to first order, and therefore the outcome of implementing the algorithm was not accurate. Figure 4.1 shows the results calculated using a code based on this algorithm. On the top panel a test case study presented in [202] was reproduced to ensure the accuracy of the written code.
Figure 4.1 Top: OBIC signal and electrostatic potential reproduced for a case study presented in [202]. Bottom: Gaussian OBIC signal of $1/e^2$ width of 4.7 $\mu$m and the associated electrostatic potential and built-in electric field using the same code developed based on the algorithm presented in [200]–[202].
The bottom panel of Figure 4.1 shows the potential and built-in electric field calculated using the same code for an example Gaussian OBIC profile. The calculated electric field was exponentially proportional to the OBIC profile considered, which is not expected based on the discussion provided in the introduction of this chapter. The OBIC signal can only be generated at areas with significant electric field level. Hence, to find the doping profile in the junction, another approach based on a forward solver will be explained in the following section.

4.2 Junction Potential Correlation to OBIC Signal Using a Forward Solver

Here, an educated initial guess for the doping profile of the cell was made based on the measurements presented in Chapter 3. A one-dimensional steady-state solution for Equation 4-1 to Equation 4-3 was found numerically based on the OBIC scan conditions and the initial guess for doping. Then, the doping profile was refined in an iterative procedure until the calculation results matched the measured OBIC signal and the measured OBIC signal was correlated to the doping profile of the p-n junction.

4.2.1 Scharfetter-Gummel Algorithm

Comparing the drift-diffusion equation (Equation 4-1) and the continuity equation (Equation 4-2) shows that the evaluation of these equations is carried out on different grid points. Since the evaluation of these equations involves the correlated currents and concentration gradients, any numerical error rising in an iteration process would amplify and causes instability in the numerical calculation. The Scharfetter-Gummel algorithm is used to optimize the stability when solving these equations in steady state or transient domain.[203] The algorithm is based on imposing the assumption that, between adjacent grid points the electric field, current density and mobility are constant. Then considering Equation 4-1 for holes in one dimension:
\[
\frac{d}{dx} p = -\frac{1}{k_B T \mu_p} J_p - \frac{q}{k_B T} p E; \quad E = \nabla u
\]

\[
\int \frac{d}{dx} p \left( \frac{J_p}{\mu_p E} + q p \right) dx = \int -\frac{E}{k_B T} dx
\]

\[
q p + \frac{J_p}{\mu_p E} = \pm e^{\frac{E}{k_BT} x+c}, \quad c \text{ is constant}
\]

Considering grid points \(i\) and \(i+1\)

\[
\left( q \rho_{i+1} + \frac{J_{p,i+1/2}}{\mu_p E} \right) \left( q \rho_i + \frac{J_{p,i+1/2}}{\mu_p E} \right) = e^{\frac{E}{k_BT}(x_{i+1}-x_i)}
\]

\[
\Rightarrow J_{p,i+1/2} = q \mu_p E \left( \frac{p_i}{e^{\frac{E}{k_BT}(x_{i+1}-x_i)}} - \frac{p_{i+1}}{1 - e^{-\frac{E}{k_BT}(x_{i+1}-x_i)}} \right)
\]

Equation 4-6

Using this derived formula in Equation 4-6 to calculate the current density results in a more stable solution compared to conventional differentiation. In this study, the semiconductor module was used in COMSOL that implements the Scharfetter-Gummel algorithm to solve the drift-diffusion and continuity equations.[204]

4.2.2 Model Parameters

In the calculations, Fermi-Dirac statistics were used to calculate the charge carriers’ densities, which are given by:

\[
n = N_c \left( \frac{2}{\sqrt{\pi}} \right) F_{1/2} \left( \frac{E_f - E_c}{k_B T} \right) \quad , \quad N_c = 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2}
\]

\[
p = N_v \left( \frac{2}{\sqrt{\pi}} \right) F_{1/2} \left( \frac{E_v - E_f}{k_B T} \right) \quad , \quad N_v = 2 \left( \frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2}
\]

Equation 4-7

where \(N_{e/v}\) is the effective density of state for the conduction and the valance bands, \(F_{1/2}\) is the Fermi integral of order 1/2, \(m_{e/h}\) is the effective mass of electrons/holes, \(k_B\) is the Boltzmann constant,
$E_{c(v/f)}$ is the energy level of the conduction ($\pi^*$) band edge, the valance ($\pi$) band edge and the Fermi level respectively, $T$ is the temperature, and $\hbar$ is the modified Planck’s constant.

Under the influence of optical pumping, electrons are excited from the $\pi$ band to the $\pi^*$ band and form excitons on the polymer chains. Subsequently, excitons dissolve into negative and positive polaron pairs localized on different monomer blocks but bound with Coulomb attraction force. These polarons escape into free charge carries or they recombine and decay into the ground state.[45], [205] Knowing that, the free EHPs generation rate can be calculated, realizing the balance between the absorbed photons and the photo-generated pairs. The light beam used in the scan is Gaussian, hence the spatial profile for generation is given by:

$$\frac{dN_{np}}{dt} = G_0 e^{-\left(\frac{x-x_0}{w}\right)^2} \left(1 - \frac{P+n}{N_v}\right)^{\frac{1}{N_v}}$$

Equation 4-8

$G_0 = \xi \sigma \frac{8P}{h\omega \pi w^2} N_v$

where $N_{np}$ is the free EHP’s concentration, $\xi$ is the exciton dissociation probability into free EHPs, $\sigma$ is the absorption or emission cross section, $P$ is the beam power, $\hbar\omega$ is the photon energy, $w$ is the $1/e^2$ beam width, and $N_v$ the effective density of states in the valance band. The spatially independent prefactor were lumped into the constant $G_0$.

The recombination rate of free charge carriers in polymers and low mobility materials is calculated using the Langevin model.[206] The model uses the drift current driven by the Coulomb force between electrons and holes. Taking a single EHP, the recombination rate is depicted in the following formula:

$$Q = \frac{e\mu E_c A_r}{e} = \frac{e\mu}{4\pi \varepsilon r^2} 4\pi r^2 = \frac{e}{\varepsilon \mu}$$

Equation 4-9

where $E_c$ is the Coulomb point charge electric field induced by a charge carrier, $A_r$ is the recombination sphere area, $\varepsilon$ is the dielectric coefficient of the material, and $r$ is the recombination radius. The mobility coefficient ($\mu$) in this equation is usually taken as the arithmetic average of
the electron and hole mobility values. The Poole–Frenkel formula was used to calculate the mobility values of electrons and holes which is given by:[207], [208]

\[
\mu_{e/h}^* = e^\gamma_{e/h} \sqrt{E} E_{e/h}^{A} / (k_B T)
\]

\[
\gamma_{e/h} = \left( \frac{1}{k_B T} - \frac{1}{k_B T^0_{e/h}} \right) \cdot B_{e/h}
\]

Equation 4-10

where \( \mu^* \) is the mobility prefactor, \( \gamma \) is the electric field mobility enhancement factor, \( E \) is the electric field, \( E^A \) is the thermal activation energy, \( T^0 \) is a thermal threshold constant, \( B \) is a proportionality constant, and \( e,h \) subscripts stand for electrons and holes respectively.

The material parameter constants were obtained from literature and are summarized in Table 4-1. The dependence of mobility on temperature and electric field were calculated.[207], [209]–[212]

Absorption and mobility in doped polymers are dependent on the doping level.[62], [109], [213]–[218] Also, the mobility values in literature are reported for sandwich devices.[207], [211], [212]

Therefore, the value of \( \mu^* \) in Table 4-1 as well as the generation rate were adjusted to match the OBIC signal that was obtained from the scans.

Table 4-1 Material parameters for electronic conduction in MEH-PPV. [207], [211], [212], [219]–[221]

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice temperature (T)</td>
<td>180 K</td>
</tr>
<tr>
<td>( \mu_e^* )</td>
<td>5.1493 \times 10^{11} \text{ cm}^2/(V.s)</td>
</tr>
<tr>
<td>( \mu_h^* )</td>
<td>2.4195 \times 10^{13} \text{ cm}^2/(V.s)</td>
</tr>
<tr>
<td>Activation Energy ( E_{e/h}^A )</td>
<td>( E_e^A = 0.34 \text{ eV}; \ E_h^A = 0.38 \text{ eV} )</td>
</tr>
<tr>
<td>Density of states ( N_{V/e} )</td>
<td>( 2.4 \times 10^{19} \times \left( \frac{T}{300} \right)^{3/2} \text{ cm}^{-3} )</td>
</tr>
<tr>
<td>( T^0_{e/h} )</td>
<td>( T_e^0 = 800 \text{ K}; \ T_h^0 = 600 \text{ K} )</td>
</tr>
<tr>
<td>( B_{e/h} )</td>
<td>( B_e = 2.5 \times 10^{-5}; \ B_h = 2.3 \times 10^{-5} \text{ V. m} )</td>
</tr>
<tr>
<td>Relative permittivity (( \varepsilon_r ))</td>
<td>3</td>
</tr>
<tr>
<td>Band Gap ( E_g )</td>
<td>2.2 eV</td>
</tr>
<tr>
<td>Beam width (w)</td>
<td>1.9 \mu m</td>
</tr>
</tbody>
</table>
4.3 Results and Discussion

The PL and the OBIC data were used to make an initial guess for doping, using the device in Section 3.5 as an example. Before relaxation, the resulted OBIC signal had a minimum measured $1/e^2$ width of 4.3 $\mu$m as summarized in Table 3-2. The smallest width was considered to minimize the possibility of jaggedness broadening for the OBIC signal. The transition of the measured PL across the junction suggests a gradual doping level at the p-n interface. Moreover, deconvolution of the beam width out of the measured OBIC signal results in a Gaussian peak of $\sim 3.9$ $\mu$m width.

A linearly graded junction is characterized with a doping concentration gradient ($a$) and width of the depletion region ($W_d$) that are given by: [196]

$$N_A - N_D = -ax, \quad a = \frac{12\varepsilon_0\varepsilon_r V_j}{e(W_d)^3}$$

Equation 4-11

where $N_A$ is the acceptor ion concentration, $N_D$ is the donor ion concentration, and $x$ is the spatial coordinate. Using $\varepsilon_r = 3$ [219] and a built in voltage of 1 V results in a doping gradient of $\sim 3.4 \times 10^{-13}$ cm$^{-3}$ um$^{-1}$. The doping snapshots in Figure 3.12 show that the n region width is half of the p region width. Due to balanced injection, the device p-doping level should be half the n-doping concentration. Using this estimation the doping concentration was tuned to get the OBIC width observed in the experiment. Doping gradient factors of $a_D=13.33 \times 10^{-13}$ cm$^{-3}$ um$^{-1}$ and $a_A= 6.67 \times 10^{-13}$ cm$^{-3}$ um$^{-1}$ at the n side and p side, respectively, produced the measured OBIC width of 4.3 $\mu$m. This doping gradient is less than an order of magnitude within the initial guess.

Figure 4.2 shows the OBIC signal that was calculated for this graded doping profile for a range of generation rates. The normalized profile for generation rate peaks ($G_0$) between $10^{27}$ cm$^{-3}$/s to $10^{30}$ cm$^{-3}$/s match a Gaussian profile of $\sim 4.3 \mu$m $1/e^2$ width. The calculated OBIC profile deviates from Gaussian shapes as $G_0$ increases beyond that level as shown for peak rates of $10^{31}$ cm$^{-3}$/s and $10^{32}$ cm$^{-3}$/s. This suggests that the scanning beam across the junction causes broadening to the built-in electric field compared to the equilibrium junction field.
Figure 4.2 OBIC signals calculated for a linearly graded junction with doping gradient factors of $a_0=13.33 \times 10^{13}$ cm$^{-3}$/um, $a_a= 6.67 \times 10^{13}$ cm$^{-3}$/um at generation rate peak values of $10^{27}$ cm$^{-3}\cdot$s$^{-1}$ to $10^{32}$ cm$^{-3}\cdot$s$^{-1}$.

Figure 4.3 shows the built-in field distribution as the beam approaches the junction area. Within the vicinity of the junction area, the generation of extrinsic carriers causes the electric field to expand in the charge neutral region due to excess electron and hole accumulations. Therefore, a significant OBIC signal is generated outside the depletion region. A peak generation factor value ($G_0$) beyond $10^{29}$ cm$^{-3}\cdot$s$^{-1}$, as shown with the $10^{30}$ cm$^{-3}\cdot$s$^{-1}$ case, causes more expansion for the normalized electric field as shown by the wider and non-Gaussian OBIC profile as shown in Figure 4.2.

It can be concluded from the previous discussion that the $G_0$ value used should be less than $10^{30}$ cm$^{-3}\cdot$s$^{-1}$ to result in a Gaussian OBIC beam. Having that, the beam width is ~ 2 um and the film thickness is 0.5 um and, based on the calculated photo-generated current density current, a $G_0$ value of $10^{29}$ cm$^{-3}$ s$^{-1}$ satisfies the measured value of the OBIC photocurrent in Table 3-2 (~13 nA). At this point, all the parameters needed to duplicate the OBIC profiles observed experimentally were obtained. However, the generation rate and mobility coefficients that were adjusted to reach these results need to be justified before going farther in this discussion.
Figure 4.3  Built-in electric field for a graded junction with doping gradient factors of $a_D=13.33 \times 10^{13} \text{ cm}^{-3} \text{ um}^{-1}$, $a_A=6.67 \times 10^{13} \text{ cm}^{-3} \text{ um}^{-1}$ at peak generation rate ($G_0$) of $10^{28} \text{ cm}^{-3} \cdot \text{s}^{-1}$ and $10^{30} \text{ cm}^{-3} \cdot \text{s}^{-1}$ and beam positions of -1 µm, 0, 1 µm, compared to the electric field at equilibrium ($G_0=0$).

The values that were used for zero-field electron and hole mobility were $\mu_0^e=160 \text{ cm}^2/(\text{V.s})$ and $\mu_0^h=600 \text{ cm}^2/(\text{V.s})$, respectively. Smaller values resulted in a small photocurrent value, which does not account for the measured signal shown in Table 3-2. This is thirteen orders of magnitude compared to the values calculated from a model reported in literature.[207] However, this model is based on undoped sandwich cell measurements, which suggests that MEH-PPV has higher mobility in the planar platform where the polymer chains are aligned along the plane of charge motion. In contrast, in sandwich configuration the chains are aligned in the direction perpendicular to charge carrier motion. Also, this is consistent with orders of magnitude mobility factor enhancement by doping as reported in many studies.[211], [218], [222], [223]

The scanning beam power of 50 µW used in Section 3.5 results in a peak photon injection rate of $10^{32} \text{ cm}^{-3} / \text{s}$, assuming a uniform photon distribution across the thickness of the film. This shows that only 0.1% of the optical power was converted into free EHPs. This also shows that the majority of photons did not end up converting into free EHPs. A portion of the beam power is reflected at
the film surface, which, in air, is given by \( R = \left[ (n-1)/(n+1) \right]^2 \), where \( n \) is the film refractive index. Using \( n = \sqrt{3} \), reflection still accounts for only 7% of the light loss. The mechanism that is responsible for significantly lowering the EHPs generation rate is the polaron pairs decay.\([45], [46]\) A dissociation rate value of 1% was measured in MEH-PPV at electric field levels comparable to the value calculated for the device junction field. Moreover, blue light absorption in MEH-PPV decreases upon doping which results in a lower generation rate for polaron pairs.\([62], [109]\) Hence, 0.1% is a reasonable estimate for a photon to free EHP generation rate given the findings from the previous discussions.\([224]\) This explains that the generation rate value of \( 10^{29} \text{ cm}^{-3}/\text{s} \) resulted in a calculated OBIC signal that matches the measured OBIC scan.

The calculated equilibrium junction space-charge density for the doping profile under study is shown in Figure 4.4. Considering \( 1/e^2 \) drop at the depletion region outer edges leads to a p- and n-depletion (penetration) widths of 2.15 \( \mu \text{m} \) and 1.56 \( \mu \text{m} \), respectively. The total depletion width is therefore \( \approx 3.7 \mu \text{m} \), very close to the deconvoluted OBIC width. The doping concentrations at the p and n boundaries of the depletion region are \( 1.43 \times 10^{14} \text{ cm}^{-3} \) and \( 2.08 \times 10^{14} \text{ cm}^{-3} \), respectively. Taking into account the broadening effect of possible protrusion structures, the calculated junction space-charge density in Figure 4.4 can be over estimating the depletion region width.\([36]\) However, the reduction after relaxation was relatively small, and the doping estimation is still within a threefold range of the actual value (assuming \( \text{WaN}^{-2} \)). Despite the discrepancies, the doping concentration estimate presented here is, for the first time, calculated from static junction properties and from the PLEC (or LEC) junction itself.
Figure 4.4 Equilibrium space-charge density for a linearly graded junction with doping gradient factors of $n_0=13.33 \times 10^{13}$ cm$^{-3}$ cm$^{-1}$, $n_\lambda= 6.67 \times 10^{13}$ cm$^{-3}$ cm$^{-1}$. The depletion region outer edges leads to a p- and n- depletion widths of 2.15 $\mu$m and 1.56 $\mu$m, respectively. [194]

In Figure 4.5, the width of the junction extracted from the calculated OBIC profiles is plotted against the actual calculated equilibrium junction field width for a range of doping gradient values. It can be seen that the estimated junction width based on OBIC scanning overestimates the actual junction width in general. This is attributed to the aforementioned junction built-in field expansion caused by electronic charge accumulation due to photoexcitation (Figure 4.3).
Figure 4.5 Depletion region width extracted from calculated OBIC signals as a function of the calculated actual built-in field width for a graded junction with varying doping gradient from $a_0$ to $20a_0$, where $a_{0D}=10 \times 10^{13} \text{ cm}^{-3} \text{ um}^{-1}$, $a_{0A}=5 \times 10^{13} \text{ cm}^{-3} \text{ um}^{-1}$.

Therefore, it is important to extract junction information using drift-diffusion solutions if accurate interpretation for OBIC measurements is needed. Otherwise, deconvolution of the beam profile from the OBIC signal gives a good estimate for the junction properties.
Planar PLECs are typically turned on, or activated, by applying a fixed voltage bias. It has been observed that the p- and n-doping of the luminescent polymer originates from the electrode interfaces, and the doping fronts propagate, leaving behind a doped region until they meet to form a p-n junction. The cell current changes accordingly. Initially, it increases slowly as the doping fronts propagate. Since the doped regions are still separate, the cell current is limited by the ionic conduction of the undoped region. After junction formation, the cell current begins to increase rapidly as the PLEC becomes a forward-biased p-n junction and an electronic current begins to flow. In the last stage the cell current reaches a plateau before decreasing as a result of degradation. While these activation characteristics have been widely documented, the discharging of the planar cell, when the voltage bias is removed, has rarely been reported. The most significant observation so far has been that the de-doping of an activated cell is approximately equal to the time reversal of the doping process. The doping fronts recede towards the electrode interfaces, leaving behind a widening quasi-intrinsic region between the still doped regions. This phenomenon has been exploited to realize a frozen p-i-n junction that displays a very high open circuit voltage.

The de-doping current of a planar PLEC (or LEC), however, has never been measured. It is particularly difficult to measure the de-doping current of an extremely large planar PLEC, which discharges slowly and at a very minute current. This requires a highly sensitive ampere-meter to monitor the de-doping current over a long period of time. The de-doping current will, however, allow for straightforward determination of the amount of doping charge injected and the doping level of the cell. Currently the doping level of a large planar cell is estimated by integrating the turn
on (charging) current up to the moment of junction formation.[118], [121], [228] This approach, however, relies on the assumption that additional doping does not occur after junction formation. Since the PLEC current can increase by several orders of magnitude after the initial formation of a junction, this approach must be justified for its validity.

In this study, several large planar cells were discharged after they were turned on to reach different terminal current values. In each run, the de-doping current was recorded for an extended period and down to pA level. It was discovered that the amount of de-doping charge was approximately equal to the amount of injected charge up to the moment when a p-n junction is fully formed. However, there was also evidence that some additional doping had occurred after junction formation. At low to medium injection levels, the total de-doping charge increased logarithmically with the amount of total injected charges. At high injection levels, the total de-doping charge is independent of the amount of the injected charge. Overall, the total de-doping charge varied by less than threefold when the terminal current and the amount of total injected charge increased by two orders of magnitude.

5.1 Experimental Information
The planar PLECs were fabricated as explained in Section 3.3. A cyclohexanone solution of MEH-PPV, PEO, and KTF was prepared to have a weight ratio of 1:1:0.24. The PLEC solution was spin cast onto a 15 mm x 15 mm x 1mm sapphire substrate and subsequently dried for five hours at 50 °C on a hot plate. On top of the PLEC film, 75 nm of gold was thermally evaporated through a shadow mask with a BOC Edwards AUTO306 evaporator built into one of the gloveboxes. The finished cells had an active area of 7 mm by 670 μm (Cells 1 and 2). Two other cells with a size of 7 mm by 495 μm were also fabricated. The size of the cells was defined by the evaporated gold electrodes. The thickness of the gold electrodes was measured in situ with a quartz microbalance. All fabrication steps were carried out in a nitrogen-filled glove-box/evaporator system. The PLEC film thickness was measured at about 700 nm with a stylus profiler.
The planar PLEC was mounted into the Cryo-Industries microscopy cryostat with a hollowed-out copper cold finger (similar to what was presented in Chapter 3). The device mounting was done inside the glove box. The cryostat was sealed before it was taken out so that the cell was never exposed to air during the transfer process. The cryostat was then placed under the Nikon fluorescence microscope (Figure 3.7) on an optical table and evacuated with the turbomolecular pump to maintain a vacuum of ~ $10^{-5}$ torrs. The device images were captured using the CCD camera attached to the microscope at a frame rate of 4 seconds/image. Underneath the cryostat, the amplified silicon photodiode captured the PL and EL of the cell during the activation process. The device was illuminated with UV light during the activation process. The unabsorbed UV excitation light was removed by a long-pass filter with a cut-off wavelength of 500 nm placed above the photodiode. A Keithley-237 source measurement unit was used to supply the voltage bias and simultaneously measure the PLEC current. All PLECs in this study were turned on by applying a fixed voltage bias of 20 V. Discharging was carried out by activating a switch from the front panel of the Labview control software. The device temperature was maintained at 340±0.1 K during the activation and discharging processes via a Cryo-con 32B temperature controller. The operating temperature of 340 K was chosen so that the doping propagation speed was neither too fast nor too slow. A schematic representation of the experimental set-up is shown in Figure 5.1.

5.2 Results

The 20 V bias was applied to Cell 1 for about 80 seconds to establish doping and a continuous light-emitting p-n junction. Selected time-lapse fluorescence images of the cell are shown at the top of Figure 5.1. *In situ* electrochemical doping of the PLEC film can be seen as darkened regions propagating away from the positive and negative electrodes, as shown in the images at $t=4$, 8 and 12 s. After 12 s, the propagation of the doped regions had stopped, indicating the formation of a p-n junction when the propagating p- and n-doping fronts met, but EL was not yet visible against the still strong background PL. Faint EL was visible at $t=28$ s at some parts of the junction. With time,
the EL grew much stronger. The last image, taken at t=72 s, showed continuous EL along the long p-n junction. During this process, the PL of the PLEC film became heavily quenched in the p-doped region and partly quenched in the n-doped region. PL quenching is the direct result of doping which creates defect states within the energy gap of the luminescent polymer.[109]

Figure 5.1 Top: time-lapse fluorescence images of Cell 1 under activation at 340 K. The cell was biased at 20 V. The images were cropped to show the same region of the cell. Bottom left: schematic of the experimental set-up. Note that the cell was mounted inside a cryostat with two transparent quartz windows. Bottom right: light intensity as a function of time since the application of the voltage bias.[195]
Figure 5.1 also displays the light intensity measured by the photodiode, which corroborates the observations taken away from the time-lapse images. The light intensity began to decrease as soon as the 20 V bias was applied. The sharp decrease of intensity in the first 10 s or so was mainly caused by the expansion of the dark, propagating, p-doped region. The intensity continued to decrease after the initial junction formation, but at a slower rate. Eventually the light intensity slowly increased after reaching a minimum at t~30 s. This increase was caused by the onset and subsequent increase of EL. At t=73 s the UV illumination was turned off, and the total light intensity dropped from about 7.9, which included contributions from both EL and PL, to the EL-only value of about 3.5. The activated Cell 1 in Figure 5.1 was discharged in the dark by switching the applied bias from 20 V to 0 V. The switching was done in Labview by the push of a button on the front panel.

Figure 5.2 (top) shows both the charging and de-doping currents of the cell as a function of time in a log-log plot. The charging process lasted about 80 s. The sharp change in the slope of the charging curve at t~10 s marks the initial formation of the p-n junction when the tips of the doping fronts meet. The terminal charging current reached was 0.114 mA. The terminal charging current is the instantaneous cell current just before the applied voltage bias was removed. The cell was allowed to discharge for 89,200 s (~24.8 hours) when the de-doping current decreased to 31 pA from the initial 0.56 µA. Figure 5.2 (bottom) shows the integrated charging and de-doping currents on the same time scale. Each point of the curve depicts the amount of injected charge or de-doping charge, up to that particular moment. It is noted that the injected charge increased rapidly at the end of the charging process. The de-doping charge, however, barely changed beyond t~10^5 s. The end points of the curves give the total injected charge and the total de-doping charge at 2.6 x 10^{-3} C and 1.83 x 10^{-5} C, respectively. The latter amount was entirely due to the de-doping of the PLEC film and can be used to calculate the doping level of the film. This will be discussed later.
Figure 5.2 Top: time evolution of Cell 1 current during activation and discharge. Bottom: injected charge and de-doping charge of Cell 1 as a function of time. This plot was obtained by integrating the top plot with respect to time. The end points denote the total injected charge during activation and the total de-doping charge at the end of discharge. [195]

The PL image of Cell-1 after discharging is shown in the inset of Figure 5.3. The UV illumination applied for this image was stronger than that applied during the charging process. Also observed some faint remnants of both p- and n-doping, along with a bright and broad de-doped region in-between. The same cell was subsequently re-activated and discharged for three additional cycles. All four sets of the charging and discharging curves are shown in Figure 5.3. The applied voltage bias was nulled at different times, resulting in different terminal currents and total amounts of injected charge. It was observed that the charging curves were highly reproducible. The discharging curves, however, did not overlap. The table in Figure 5.3 shows the total amounts of injected charge...
and de-doping charge for all four runs. The de-doping charge amounts were obtained for a period of 80,000 s, although some runs lasted much longer than others. In Run 3, for example, the cell was discharged for 2.50 \times 10^5 s (69 hours), but the amount of de-doping charge beyond 80,000 s accounted for only 7% of the total. The tabulated data show an increasing trend in the de-doping charge as the amount of injected charge increased. This increase, however, is not proportional. When the injected charge more than tripled from 0.0026 C to 0.0083 C, the amount of de-doping charge only increased by 72%.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Total injected charge (C)</th>
<th>Total dedoping charge (x10^{-5} C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0026</td>
<td>1.82</td>
</tr>
<tr>
<td>2</td>
<td>0.0050</td>
<td>2.49</td>
</tr>
<tr>
<td>3</td>
<td>0.0056</td>
<td>2.73</td>
</tr>
<tr>
<td>4</td>
<td>0.0083</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Figure 5.3 Time evolution of the activation and discharging current of Cell 1 in four runs.

The inset table shows the total injected charge vs. the total de-doping charge for each of the four runs. The de-doping charge amounts were calculated and determined for a period of 22.2 hours. The photograph shows the PL of Cell 1 after it had been discharged for 24.9 hours in Run 1.[195]
In Figure 5.4 a second, nominally identical cell (Cell 2) was also charged and discharged four times, with very different results. In Cell 2, the terminal charging current was allowed to reach a maximum before discharging commenced. Consequently, the terminal current was reached and the amounts of injected charge were much higher. It was observed that the charging curves dropped lower each time the cell was re-activated. In the four activation/discharging cycles, the amount of injected charges varied by as much as twenty-fold, but the total de-doping charge barely changed.

![Graph showing current vs. time for Cell 2 across four runs.]

**Figure 5.4** Time evolution of the activation and discharging current of Cell 2 in four runs. The inset table shows total injected charge vs. the total de-doping charge for each of the four runs. The de-doping charge amounts were calculated for a period of 22.2 hours. The photographs shows the PL of Cell 1 after it had been discharged for 25.9 hours in Run 1. Compared to Cell 1, Cell 2 has been allowed to reach a much higher terminal current before discharging is commenced.[195]
The decreasing charging current indicates irreversibility, which apparently did not affect the overall level of de-doping charge and doping levels. It was also noted that for Run 1, the total injected charge of 0.45 C was 173 times that of Run 1 of Cell 1, but the de-doping charge of the two cells differed by only three fold. The PL image in Figure 5.4 shows the cell just after the first discharging run, which lasted 93,300 s. The dark remnant of p-doping is highly visible, which persisted after an additional storage period of 46 hours under the open-circuit condition, before the 2nd Run. Despite this dark appearance, however, the discharge of Cell 2 in Run 1 was quite complete relative to the fully charged state. Figure 5.5 shows the time-lapse fluorescence images of Cell 2 undergoing re-activation in Run 2.

Figure 5.5 Time-lapse fluorescence imaging of Cell 2 during activation in Run 2. The cell was discharged for 25.9 hours after Run 1 and stored for an additional 46 hours before Run 2. The contrast and brightness of the composite image has been enhanced in Photoshop.[195]
It is noted that the old, still-visible p-doping front did not propagate. Instead, fresh p- and n-doping appeared from the electrode edges and propagated rapidly (t=4 s, 8 s and 12 s). The new, columnar doping fronts led to the formation of a very jagged p-n junction (t=16 s, 24 s, and 32 s). The old, relatively smooth p-doping front appeared to have been pierced by the sharp p-doping and n-doping tips. Closer examination reveals that sharp p-doping tips evolved from the tips of the old p-doping fronts, while the new n-doping tips preferentially penetrated the areas with a negative curvature. This indicates that the residual p-doped region has elevated conductivity relative to that of the undoped film. The effect is akin to that caused by an uneven electrode, which is visible in the bottom electrode of Cell 1, as seen in the images of Figure 5.1. Eventually the EL along the jugged p-n junction became stronger and continuous, as shown in the images at t=44 s, 56 s and 84 s. By comparing the images at t=4 s and t=84 s, it can be concluded that re-activation had led to a much heavier doping than did the relaxed state. Accordingly, the relaxation was considered to be fairly complete, despite the observation of the visible dark p-doping remnant.

5.3 Discussion
Here, a few key features of the data presented above that are important to the determination of the doping concentration are discussed. First, it is noted that the initial discharging current, on the order of μA, is much lower than the terminal charging current, which ranged from 0.11 mA (Cell 1, Run 1) to 2.14 mA (Cell 2, Run 1). When the PLEC was activated to emit light, it was a forward-biased p-n or p-i-n junction. The PLEC therefore possesses stored excess electronic charges and a corresponding storage capacitance. The discharge of the stored electronic charges, however, was not captured due to the time delay (0.23 ±0.05 s) involved in switching the bias voltage. Nor should the stored charges be included in calculating the doping concentration. The stored electronic charges are excess minority carriers uncompensated by the electrolyte ions and therefore do not contribute to doping. Since the initial discharging current was largely independent of the vastly varying terminal charging current, it can be concluded that the entire discharging current was a de-
doping current associated with the slow moving ions. Similar significant differences between terminal charging current and initial discharging current were also observed when discharging a sandwich PLEC.[62]

For each activation/discharging cycle, the amount of injected charge and the amount of de-doping charge also differed significantly. In Run 1 of Cell 2, for example, a total of 0.45 C was injected, this being 6,800 times that of the amount of de-doping charge measured. This enormous difference can be understood when considering that vast majority of the injected charges are annihilated by radiative and non-radiative recombination. In other words, a large recombination current accounts for many of the injected charges, which is absent when the PLEC is being discharged under zero bias. The recombination current is responsible for the strong EL observed, but does not contribute to doping. The doping concentration, therefore, should be extracted from the amount of de-doping charge extracted from the discharging curve. The average doping concentration $c_{ave}$ of the PLEC can be calculated as:

$$c_{ave} = \frac{Q_{disch}}{ev} = \frac{\int I_{disch} \, dt}{ev}$$  

where $Q_{disch}$ is the total amount of de-doping charge, $e$ is elementary charge, $v$ is the volume of the PLEC film, $t$ is time and $I_{disch}$ is the time-dependent discharging current. For Cell 2 in Run 1, an average doping concentration of $1.25 \times 10^{20}$ cm$^{-3}$ is obtained. For Cell 1 in Run 1, the average doping concentration is $3.46 \times 10^{19}$ cm$^{-3}$. It should be mentioned that both the p- and n-doped regions are electrically neutral. In addition, the total amounts of p- and n-doping charges are equal due to the charge balance requirement.[122] Since the volume ratio of the p- and n-doped regions of the p-n junction formed from the time-lapse images can be extracted, the doping concentrations of the individual regions can be easily calculated. This results in p- and n-doping concentrations of $0.83 \times 10^{20}$ and $2.5 \times 10^{20}$ cm$^{-3}$, respectively, for Cell 2. For Cell 1, the p- and n-doping concentrations
are $2.60 \times 10^{19}$ cm$^{-3}$ and $5.19 \times 10^{19}$ cm$^{-3}$, respectively. The doping concentration as a percentage of the polymer (MEH-PPV) repeat unit can also be calculated according to the following equation:

\[
N_{\text{mono}} = \frac{c_{\text{ave}}}{c_{\text{mono}}} = \frac{2.2 \cdot c_{\text{ave}}}{(p_{\text{mono}}/W_{\text{mono}}) \cdot N_{\text{Ava}}} \times 100\%
\]

Equation 5-2

where, $c_{\text{ave}}$ is the average doping concentration as determined from Figure 5.1, $c_{\text{mono}}$ is the volumetric concentration of MEH-PPV monomers, $W_{\text{mono}}$ is the formula weight of MEH-PPV, and $N_{\text{Ava}}$ is the Avogadro constant. Assuming a density of 1 g/cm$^3$ for the polymer film and knowing the formula weight of MEH-PPV to be 276 g/mol, we obtain a p- and n-doping concentration of 7.6% and 23%, respectively for Cell 2 and 2.4% and 4.8% for Cell 1. Note that a factor of 2.2 in the above equation was added to account for the fact that the polymer film also contains PEO and KTF, but only MEH-PPV is doped. The salt molecule to monomer segment ratio is given by the salt to luminescent polymer weight ratio normalized to the formula weight of these components. This gives 13.55% salt molecules per monomer segment on average. Based on the p and n charge neutral regions size ratio in Cell 2 (3:1), the upper pounds for the p and n doping levels are 18% and 54.2% respectively. Thus, for Cell 2, which was fully doped, only 40% of the salt available in the cell got involved in doping. Hence, the doping level in the cell was not hindered by the salt availability and the doping level in the cell was dictated by the doping propagation process.

If the total amount of injected charge far exceeds the doping charge, can the time-dependent activation current still be used to estimate the level of doping? The answer is yes if the amount of charge that is consumed by recombination is excluded. Since recombination only occurs after junction formation, the amount of injected charge up to the point of junction formation should be used. Figure 5.6 plots the injected charge of Cell 2 in Run 1 as a function of time during the activation process. Also included in the graph is the light intensity (PL+EL) of the cell as a function of time. From the time-lapse images and the change of slope in the injected charge curve, point a is identified as the moment of initial junction formation. Due to the highly uneven doping
propagation, however, the p-n junction was not fully formed until the total light intensity reached a minimum, after which the onset of strong EL indicated that recombination had dominated the device process. Remarkably, when we mark the total de-doping charge of 6.6 x 10^{-5} C on the activation curve, the resulting point b coincides with the minimum light intensity. It is expected that the light intensity minimum will shift to the left if we lower the excitation intensity. Nevertheless, the amount of charge injected in the vicinity of light intensity minimum represents a very good approximation of the amount of de-doping charge, and therefore the amount of doping charge. It is noted again that the total amount of injected charge (0.45 C) is more than three orders of magnitude higher. Similar plots for other devices tested in this study confirmed the above observation, where point b (de-doping charge amount) had been observed to fall between point a and the point of minimum light intensity.

The results therefore validate the current practice of using the amount of injected charge, up to the moment of junction formation to estimate the doping concentration of a planar PLEC.[118], [121] Not surprisingly, the doping concentrations determined in this study based on the amounts of de-doping charge are highly comparable to those determined with the previous method for MEH-PPV:PEO:KTf planar cells of similar sizes.[121], [228] As expected, the doping level of these planar cells is much higher than that of a sandwich cell on account of the heavy PL quenching observed in planar cells.[62]

While the doping concentration inferred from both the de-doping charge and the injected charge up to junction formation are consistent, the fact that the cell current continues to increase after the p-n junction has been fully formed cannot be ignored. The increase in cell current can approach three orders of magnitude, as seen in Figure 5.4. In addition, fluorescence images of the cell revealed significant darkening of the doped regions after junction formation, as seen in Figure 5.5. These observations seem to suggest that additional, heavy doping had occurred, long after the junction had been fully formed.
Figure 5.6 Time evolution of the light intensity and injected charge of Cell 2 in Run 1. The light intensity was initially PL only. When the p-n junction began to form, EL also contributed and eventually dominated the total light intensity measured. The injected charge was obtained by integrating the activation current with respect to time. On the injected charge curve, point (a) marks the initial formation of the p-n junction; point (b) represents the amount of injected charge that corresponds to the amount of de-doping charge measured in the subsequent discharging portion of Run 1; and point (c) denotes the total amount of injected charge at the end of Run 1.[195]

If the cell current were proportional to the level of doping, then the bulk of doping would have occurred long after junction formation. This scenario, however, is very unlikely. As mentioned earlier, the cell current after junction formation is mainly composed of an electronic junction current that does not contribute to doping. In addition, the conductivity of a doped semiconductor can be expressed as $\sigma = en\mu$, where $e$ is electron charge, $n$ is charge carrier concentration and $\mu$ is
charge carrier mobility. Therefore, the conductivity increase can also be caused by an increase in mobility. Hole mobility in conjugated polymers such as polythiophenes and PPVs have indeed been observed to increase by several orders of magnitude when the level of doping only increased modestly.\[222], [229], [230] The doping-induced mobility charge has been attributed to the shift of the Fermi level, relative to the energy-dependent density of state function.

It is believed that some additional doping did occur after junction formation. This explains the dependence of total de-doping charge on the total amount of charge injected. But this dependence is fairly weak, as shown in Figure 5.3. When the cell was activated to reach a maximum current, this dependence had all but disappeared, as shown in Figure 5.4. The tabulated data in Figure 5.3 and Figure 5.4 are plotted in Figure 5.7 in semi-log form.

The trend in the data suggests that the level of doping had a logarithmic dependence on the amount of injected charge, up to about 0.1 C. After this, the level of doping remained constant. This graph again shows that the amount of de-doping charge varied by a mere three fold when the amount of injected charges varied by more than two orders of magnitude. It is noted that other authors also suggested the presence of additional doping based on the observed current change after junction formation.\[225] Here, an additional evidence of this occurrence by measuring the amount of de-doping charge has been provided. The solid green squares in Figure 5.7 represent the data from two additional planar cells, each charged and discharged twice. Their smaller interelectrode spacing of 495 \( \mu \)m consistently led to a de-doping charge amount about 10-50% lower than observed in Cells 1 and 2 for the same amount of injected charge.
In a sense, PLECs are like a rechargeable battery. The discharged amount is proportional to the capacity of the battery, which should depend on the physical size (volume) of the cell. Therefore, a lower amount of de-doping charge from a smaller planar cell is expected. The ability to determine the de-doping charge and its dependence on various operational and device parameters provides additional tools with which to understand the complex doping and de-doping processes in PLECs.

Figure 5.7 Plot of the amount of discharge vs. the total injected charge for Cells 1 and 2, which had an inter-electrode gap size of 670 µm (solid red dots). Also shown are data obtained from two additional cells with an inter-electrode gap size of 495 µm (solid green squares).[195]
Chapter 6

Conclusions and Future Work

The ability to mix organic semiconducting materials with ionic conductors and dopants creates versatility for devices and applications. PLECs, and LECs in general, are remarkable devices that have operational characteristics that are not be offered by other undoped organic devices. Electrochemical doping in PLECs drastically enhances the conductivity and lowers the injection barriers in these devices. Nevertheless, these benefits come at a cost that is still hindering PLECs from commercial competency. Doping the active material in PLECs results in luminance quenching and lowers the device lifetime. Moreover, the mixed ionic and electronic mechanisms create complexity in the device functionality and electronic structure. In this work, luminance lifetime, OBIC and discharge measurements were performed to tackle these issues.

In Chapter 2, sandwich PLECs were monitored under continuous and intermittent operation conditions. The cell’s luminance and voltage characteristics were recorded while stressed under a constant current density of 167 mA/cm². It was concluded that luminance decay over time is mainly attributed to doping luminance quenching. This type of decay was reversible after the bias was removed and the cell was relaxed. The cells under continuous operation showed EL levels lower than identical cells that were operated by intermittent ON/OFF cycles, adding up to the same total operation time. Moreover, EL imaging revealed the appearance of dark spots on the cell exposed to long operation. The appearance of such dark spots was associated with the storage time for the cell after depositing the aluminum electrodes. The spot growth was suppressed when a cell was operated with a freshly deposited top aluminum electrode, despite the polymer film being stored for nine months. The black spots that appeared in the EL images were also observed in the PL images, but recovered when the voltage bias was removed. Therefore, it was concluded that the
appearance of the spots in these PLECs was caused by heavy doping and was stimulated by chemical changes at the cathode/polymer interface.

It is still not established with certainty what causes these heavily doped regions to appear and how the cathode contributes to the growth of these regions. It can be the uniformity of the electrode/polymer interface or the cathode material reacting with or diffusing into the active film. Lifetime studies using different cathode materials and surface scan measurement using stylus profiler or atomic force microscopy can reveal the correlation of these parameters to black spot formation. Also, PEDOT/PEDOT:PSS can be used to smooth out the interface between the electrodes and the active PLEC film to minimize the effect of metal diffusion from the electrodes into the active film.

In Chapter 3 p-i-n and p-n junctions of frozen planar PLECs were spatially resolved by scanning PL and OBIC measurements. The profiles of these junctions indicated depletion region widths in the micrometer range which is a small fraction of the cell width. For the first time, the junction depletion widths of a planar p-i-n junction and a planar p-n junction were resolved. The resolved depletion widths accounted for a portion of the total cell width as small as 0.2%. Since the junction is the active portion of the device, the narrow width of the junction contributes to the device deficiency. A possible solution for that problem is to form multiple junctions over the cell area, as was demonstrated in planar bulk homojunction (BHoJ) PLECs.[192], [193] However, these devices have not been implemented in sandwich configuration and frozen at room temperature which represents an opportunity in PLEC (and LEC) research to demonstrate more efficient cells. The PL profile of the relaxed device showed more abrupt transition between the p and n regions compared to the as-frozen device. Moreover, the profile showed reduced PL quenching in the junction region after relaxation, which proposes reduction in the doping ion concentrations in the junction region. Therefore, it is possible that the junction doping profile changed from a graded p-n junction in the as-frozen device to a p-i-n junction structure with more abrupt transition between
the p and n regions. Also, relaxing the devices resulted in OBIC peak narrowing. This suggests the possibility for submicron features. However, detecting features at that scale is beyond the OBIC experiment in this dissertation. A near field OBIC probe can offer the resolution required to resolve features at this scale. Also, electron beam induced current measurement has the resolution capability required, however, such a measurement will be extremely challenging having the requirement to activated the device by applying a voltage bias inside a tool like an electron microscope and then cooling the device to a cryogenic temperature.

In Chapter 4, numerical calculations were performed to extract the doping level in the p-n junction using the measured OBIC signals. It was found that the doping level at the tested planar junctions’ boundaries is about $10^{14}-10^{15}$ cm$^{-3}$. Also, the calculation showed that the electronic mobility in the doped device should be 13 orders of magnitude larger than the values reported for pristine MEH-PPV in sandwich devices. Possible reasons for this are the preferred alignment of the polymer chains in planar configuration as well as the mobility enhancement by doping. Moreover, the suitability of using OBIC scans to extract the depletion region width by deconvolution was also examined. It was found that the method gives a good order of magnitude estimate for that value. However, a full drift-diffusion calculation is needed to extract the exact profile for the junction. On that end, the calculations presented here were sufficient to interpret the measured OBIC data. However, it does not allow prediction for the formed junction parameters. A full time dependent drift diffusion calculation that considers the ion redistribution under external electric field bias can give the capability to predict the formed junction properties and their sensitivity to the uniformity and smoothness at the electrode/polymer interface. Such a study is still lacking in literature.

Planar PLEC charging/discharging measurements were presented in Chapter 5. The startling observation in these measurements was the high average doping concentration of $10^{19}-10^{20}$ cm$^{-3}$ for the cells compared to $10^{14}-10^{15}$ cm$^{-3}$ in the junction region as revealed from the OBIC measurements. The contrast between the obtained numbers can be attributed to a lower doping level
in the junction region as a result of doping compensation at the p-n interface. Another possibility is that the depletion region is smaller than the micrometer range and the OBIC profiles are broadened by fine structures that could not be resolved optically. As mentioned earlier a higher resolution scanning imaging technique can shed more light on this area. Also, it was found that the average doping level in PLECs can be estimated by integrating the charging current up to the junction formation point. Afterwards, the recombination current dominates and minimal doping takes place. This finding is consistent with the currently adapted method to estimate doping in planar PLECs and offers validation for this method.

In conclusion, PLECs have been and will continue to attract interest in research avenues. Both the physics and the operational characteristics of these devices form the main motivational drive to research and optimize these devices in hopes to achieve market penetration with efficient, cost effective, and environmentally friendly technology.
Bibliography


